SHORT FIBRE- REINFORCED ELASTOMERIC COMPOSITES

*fundamental routes towards improvement of the
interfacial interaction of short-cut aramid fibres in a SBR
compound, to improve friction and wear properties.*

Nadia Vleugels

Short fibre-reinforced elastomeric composites,
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interfacial interaction of short-cut aramid fibres in a SBR
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SHORT FIBRE-REINFORCED ELASTOMERIC
COMPOSITES, FUNDAMENTAL ROUTES
TOWARDS IMPROVEMENT OF THE INTERFACIAL
INTERACTION OF SHORT-CUT ARAMID FIBRES IN
A SBR COMPOUND, TO IMPROVE FRICTION AND
WEAR PROPERTIES.

THESIS

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Summary

Short-cut fibre-reinforced rubber composites represent a class of materials which are extremely complicated. There are many factors involved in establishing their properties, ranging from the constituents, mixing and dispersion, orientation of the fibres, the degree of vulcanization, the degree of fibre-matrix interaction and the way in which the final articles are loaded. After reviewing pertinent literature in **Chapter 2** – not exhaustive, because that was impossible owing to the excessive amount – none of the authors had addressed and compared all factors involved in their studies. A ‘holistic’ approach is therefore considered necessary to include all possible factors and their interactions. Otherwise, no significant progress in understanding can be expected.

As far as the approach and rubber formulation components are concerned, an agreement was made with the steering committee for the present project to try to avoid, as much as possible, disturbing factors which were thought not to be of importance to the friction and wear study. In particular, this pertains to the following: the choice of the type of elastomer, the fibres, use of silane coupling agents in combination with epoxy-amine pretreated fibres, sulphur vulcanization and omission of reinforcing and/or non-reinforcing fillers like carbon black or silica. The choice of silane coupling agents was made based on the literature survey in **Chapter 2** as - possibly - the most promising candidates for epoxy-amine pretreated aramid fibre-elastomer interaction. A second reason was the extensive basis of know-how belonging to the Elastomer Technology and Engineering Department, where this research was to be carried out, about the silane-coupling technology between silica and rubber.

In **Chapter 3** and from the aforementioned perspective, an initial screening is done on the influence of controllable and non-controllable (resulting from the choice of the first) factors on a short-cut aramid fibre-reinforced Styrene-Butadiene Rubber compound. Two types of 3 mm short-cut aramid fibres are investigated: an untreated, virgin fibre (VF) and a fibre treated with an adhesion-active epoxy-amine coating (EF). The fibres are added at a concentration of 5 parts per hundred of rubber (phr). The coupling agents selected are: *Bis*-(triethoxysilylpropyl)-disulphide (TESPD), *S*-3-(triethoxysilylpropyl)-octanethioate (NXT), *Bis*-(triethoxysilylpropyl)-tetrasulphide (TESPT) and a mercapto silane (Si 363). They are compared on an equimolar basis with regard to the amount of reactive ethoxy groups of TESP. The Mooney viscosity, vulcanization performance, tensile properties and hardness tests are used to assess the behaviour of the coupling agents in the rubber and to characterize the processability of the compounds. Apart from the unexpected but clearly reproducible result, that 5 phr non-oriented fibres give higher Young's moduli than after orientation of the fibres either parallel or perpendicular to the drawing direction, the other results show that too many factors are influencing the properties of short-cut aramid reinforced elastomers, which makes it impossible to draw clear conclusions. The friction coefficients of the formulations in **Chapter 4** show much lower values than those for formulations without fibres. The deformation component of the total friction coefficient has a dominant contribution over the adhesion component for the epoxy-coated fibres, which is quite opposite to the virgin fibres. The interaction between fibres and matrix, achieved by adding coupling agents, consequently lowers the total friction and the adhesion component in particular. The wear rate for the fibre-reinforced compounds is 25-30 times lower than for unreinforced, but there are no clear differences observed between the various fibres containing compounds: VF vs. EF with

coupling agents. Therefore, a more systematic investigation is needed, to separate the interfacial interaction factor between the matrix and fibres from other influencing factors, which is the basis for the following chapters. Hence, a more systematic investigation is proposed based on a Design of Experiments approach.

The Design of Experiments in **Chapters 5, 6 and 7** gives an overview of the relative importance of controllable factors on the processability and mechanical properties of short-cut aramid fibre-reinforced elastomers, for the four different coupling agents mentioned above. The results show that various factor effects, and in particular the effect of fibre-matrix interaction, are grossly overshadowed by other factors: fibre concentration and orientation, respectively, are effects of the vulcanization system. The effect of the coupling agents is related to the interaction with adhesion active fibres, which in turn affects either the molecular integrity of the reinforced elastomer or enhances elastomer cross-linking. For each mechanical properties response an optimization prediction is calculated and confirmed with a confirmation run, showing for example a 330% potential improvement in the Young's modulus.

Based on the results from the optimization in the Design of Experiments, the compounds are further optimized in **Chapter 8** for optimal performance, by increasing the coupling agent NXT concentration to 7.5 phr. Tensile tests show the interaction of the fibres with the rubber matrix, with emphasis on low strain properties. Epoxy-amine treated fibre-filled compounds oriented in the milling direction give a significant increase in tensile moduli and hysteresis relative to untreated fibres. A clear optimum is observed in tensile moduli at 6 phr of coupling agent NXT. The results show that all moduli at low strain and the tensile curve itself need to be considered in detail to determine the relevance of the different factors involved in fibres-silane elastomer interaction. An extra check for the ability of the EF-fibres and NXT to react in a simplified curing test confirms the reactivity of this system vs. the other two fibre systems: VF and fibres with Standard Finish (SF).

The study presented in this thesis was hampered by the lack of an easily accessible method to measure and quantify the orientation of the short-cut fibres in the rubber compounds. Therefore, a cooperation was embarked on with the company PANalytical B.V. in Almelo, the Netherlands, to develop such a method based on X-ray diffraction, making use of the crystalline nature of aramid, as presented in **Chapter 9**. The characterization of the mesoscopic orientation of short-cut aramid fibre-reinforced elastomeric compounds with X-ray diffraction shows that the rubber and the fibre signals are situated in the same crystal structure plane, where the latter becomes visible when the fibre concentration is sufficiently high. Disturbances by other compounding ingredients remain limited to not disturb the signals from rubber and fibres. Volume-surface reconstruction of the composite material and subsequent analyses reveal that the aramid fibres look as though macroscopically arranged in bundles in the Y-X plane of the sample, where fibre bundles are oriented in the Y-direction. The aligned fibre bundles have a mean thickness of 65 μm because of the lower resolution limit of the technique, so that individual fibres are not visible. However, even with this limitation it is, after all, a good quantification method of fibre orientation at much lower costs and scanning times, which would have been needed to see the individual fibres. DiPhenyl Guanidine (DPG), as secondary accelerator, shows a large orientation preference in bloom, towards the direction of the fibres. The explanation is that an excess amount of DPG forms crystals on the surface of the compound, which orient themselves just in the same direction as the fibres. The method as developed does work well to characterize and quantify the fibre orientation, but – unfortunately – came too late to be included in the holistic approach as presented above. It

may very well be used for future studies.

The advantage of fibre-reinforced elastomers to withstand deformation forces plays a significant role in their friction behaviour. The existence of an adhesion-active coating on aramid fibres for a silane coupling agent to act as intermediate between the fibres and the elastomer matrix has not been investigated before; nor has the importance thereof on the friction performance of elastomers. The role of the coupling agent in the fibre-elastomer matrix interaction and how it influences the specific macroscopic wear of the corresponding rubber samples is studied in **Chapter 10**, based on the optimized compound formulation derived from the Design of Experiments in the previous chapters. The wear is compared for two types of fibres: one with (EF) and fibres with Standard Finish (SF) but without an adhesion-active coating, measured in two different directions: transversely and longitudinally aligned along the sliding direction. Pin-on-disk friction tests show that the friction coefficient is approximately 15% lower for samples reinforced with adhesion-active epoxy-amine coated fibres in combination with a coupling agent, compared to fibres without coating. Samples with transversely oriented fibres give higher friction than for longitudinal orientation. The hysteretic contribution to the overall friction plays only a minor role, while the adhesion contribution is dominant in the present tribo-system. Further investigations of the contact area show that it is largely influenced by the material properties, i.e. the Young's modulus. The specific wear rate of the rubber samples with epoxy-coated fibres is lower than for the non-reactive fibre-containing samples. The specific wear rate of rubber samples with transversely oriented fibres is much higher than for longitudinally oriented fibres. SEM pictures show a higher interaction effect with the elastomer for epoxy-amine coated fibres vs. non-reactive in the presence of the silane coupling agent NXT.

To investigate the influence of extra reinforcing fillers like carbon black or silica, a more realistic practical tyre tread compound formulation was investigated in **Chapter 11**. The results show that the reinforcement caused by the short-cut aramid fibres in the elastomeric matrix depends on four main factors: 1) fibre volume fraction, 2) fibre orientation, 3) the properties of the components (elastomers / type of fibre) and 4) fibre-matrix interfacial strength (type and amount of coupling agent). The properties of the highly silica-reinforced elastomeric compounds in combination with short-cut aramid fibres differ enormously in comparison with those for non-silica reinforced compounds. The strength at break and strain at break are greatly increased. Above 5 phr of fibres a yield point in the tensile curves appears, which is a new indicator of fibre reinforcement. Compounds based on interaction-enhanced epoxy-amine coated EF-fibres show an increase in Young's modulus and a shift of the yield point towards higher stresses compared to virgin fibres. As tensile strength and elongation at break decrease with increasing Young's modulus and yield point, these two tensile characteristics don't lend themselves to quantify fibre reinforcement any further. Longitudinal orientation of the fibres increases their effect on the tensile strength, yield point and Young's modulus, compared to transverse and random orientations. The dynamic-mechanical $\tan \delta$ values in the 60°C temperature range, as indicative for Rolling Resistance of tyre treads based on compounds made thereof, are not affected by VF-concentrations in the presence of 7 phr TESPT, while the Skid Resistance, as indicated by the $\tan \delta$ in the 0°C region, is lower compared to the reference compound without any fibres, which needs to be valued negatively.

The final **Chapter 12** discusses scaling-up of the results in previous chapters to a 1.5 litre internal mixer at Teijin aramid company, in order to check whether the large positive effects found for epoxy-amine coated fibres in combination with coupling agent NXT could be

reproduced in the larger mixer. Similar to the results for the smaller mixer, a sufficiently long period at elevated temperature must be created during the mixing stage in order for the silane coupling agent to be able to properly react with the epoxy-amine coating. The results further show that the fibre-filled compounds oriented longitudinally with the mill direction give a significant increase in tensile moduli, closely followed by the randomly oriented fibres, independent of the process: large vs. small mixer. A clear difference in the tensile results is observed between the types of fibre-coating. The fibres longitudinally oriented with an epoxy coating in combination with a coupling agent give the highest reinforcement in moduli again, compared to non-reacting fibres, confirming the positive effect of fibre-elastomer interaction as observed before for the small mixer.

Samenvatting

Korte vezel versterkte rubbercomposieten vertegenwoordigen een klasse van materialen die zeer ingewikkeld zijn. Dit komt omdat er met veel factoren rekening moet worden gehouden die hun eigenschappen bepalen, zoals de ingrediënten, mate van menging en verdeling, de oriëntatie van de vezels, de vulkanisatie-graad, de vezel-matrix interactie en de wijze waarop het uiteindelijke materiaal wordt gebruikt. Na het bekijken van relevante literatuur in **hoofdstuk 2** - niet uitputtend, want dat bleek onmogelijk door de overmatige hoeveelheid – laat geen van de auteurs zien welke factoren en in welke mate deze belangrijk zijn in hun studies. Om deze reden wordt een 'holistische' benadering noodzakelijk geacht waarbij alle mogelijke factoren en hun interacties in ogenschouw moeten worden genomen. Anders is het niet mogelijk significante vooruitgang te boeken en een beter begrip te krijgen.

In overeenstemming met de stuurgroep van het huidige project is besloten om te proberen zoveel mogelijk storende factoren m.b.t de aanpak en het rubber recept, waarvan gedacht werd dat deze niet van belang zouden zijn voor de wrijving en slijtage studie, te vermijden. In het bijzonder betreft dit de keuze van het type rubber, de vezels, gebruik van silaan koppelingsmiddelen in combinatie met epoxy-amine voorbehandelde vezels, zwavelvulkanisatieversnellers en bewust weglaten van versterkende en / of niet-versterkende vulstoffen, zoals roet of silica. De keuze voor de silaan koppelingsmiddelen werd gemaakt op basis van het literatuuroverzicht in **hoofdstuk 2**, die werden beschouwd als meest veelbelovende kandidaten voor de epoxy-amine voorbehandelde aramide vezel-rubber interactie. Een tweede reden was de uitgebreide basiskennis van het silaan-koppelingsmechanisme tussen silica en rubber, aanwezig bij de leerstoel Elastomer Technology and Engineering waar dit onderzoek werd uitgevoerd.

In **hoofdstuk 3** wordt een eerste screening gepresenteerd van de invloed van controleerbare en niet-controleerbare (op basis van de keuze van de eerste) factoren op een korte aramide vezel-versterkte styreen-butadieen rubber composiet. Twee types van 3 mm korte aramide vezels zijn onderzocht: een onbehandelde, maagdelijke vezel (VF) en een vezel behandeld met een adhesie-actieve epoxy-amine coating (EF). De vezels worden toegevoegd in concentraties van 5 delen per honderd rubber (phr). De volgende koppelingsmiddelen zijn gekozen: bis(triethoxy silylpropyl) disulfide (TESPD), 3-octanoylthio-1-propyltriethoxysilane (NXT), (bis(triethoxysilylpropyl) tetrasulfide) (TESPT) en een mercaptosilaan, 3-mercaptopropyl-di(tridecan-1- oxy-13-penta(ethyleneoxide)) ethoxysilane) (Si 363). Ze worden met elkaar vergeleken op equimolaire basis t.o.v. de hoeveelheid reactieve ethoxy groepen van TESPd. De Mooney viscositeit, de vulkanisatie eigenschappen, trek-rek eigenschappen en hardheid testen worden gebruikt om het gedrag van de koppelingsmiddelen in het rubber te evalueren en daarnaast wordt er ook gekeken naar de verwerkbaarheid van het materiaal. Naast het onverwachte, maar duidelijk reproduceerbare resultaat dat 5 phr niet-georiënteerde vezels hogere Young's moduli geven dan na oriëntatie van de vezels (hetzij evenwijdig of loodrecht op de trekrichting), zijn er veel andere factoren die ook van invloed zijn op de eigenschappen van korte aramide vezel-versterkte elastomeren, die het onmogelijk maken om duidelijke conclusies te trekken.

De met pin-on-disk gemeten wrijvingscoëfficiënten van de formuleringen zijn weergegeven in **hoofdstuk 4** en laten een veel lagere waarde zien dan die van de formuleringen zonder vezels. De deformatie component van de totale wrijvingscoëfficiënt laat

een dominantere bijdrage zien dan de hechtings component voor de epoxy-behandelde vezels, dit in tegenstelling tot de maagdelijke vezels. De interactie tussen vezels en matrix wordt versterkt door toevoeging van koppelingsmiddelen, waardoor de totale wrijving en in het bijzonder de hechting component worden verlaagd. De slijtagesnelheid van de vezel-versterkte verbindingen is 25-30 keer lager dan bij niet versterkte, maar er zijn geen duidelijke verschillen te zien tussen de verschillende vezelhoudende composieten: VF vs. EF met koppelingsmiddelen. Daarom is er meer systematisch onderzoek nodig om de factor wisselwerking op het grensvlak van matrix en vezels te scheiden van andere factoren, die van invloed zijn. De volgende hoofdstukken worden hierop gebaseerd. Vandaar wordt een meer systematisch onderzoek voorgesteld op basis van Design of Experiments.

Design of Experiments uitgevoerd in **hoofdstukken 5, 6 en 7** voor de vier verschillende koppelingsmiddelen geven inzicht in het relatieve belang van de controleerbare factoren op de verwerkbaarheid en de mechanische eigenschappen van aramide vezel-versterkte elastomeren. De resultaten tonen aan dat verschillende factor effecten, m.n. het effect van vezel-matrix interactie, grotendeels worden overschaduwd door andere factoren: vezel-concentratie en -oriëntatie en effecten van het vulkanisatiesysteem. Het effect van de koppelingsmiddelen is gerelateerd aan de interactie met de adhesie-actieve coating op de vezels, waardoor die ofwel de moleculaire integriteit van het versterkte elastomeer beïnvloedt ofwel de elastomeerverknoping bevordert. Voor alle gemeten mechanische eigenschappen is een optimalisatie voorspelling berekend en bevestigd met een bevestigings meting, waarin bijvoorbeeld te zien is dat een verbetering in de Young's modulus van 330% mogelijk is.

Op basis van de resultaten van het optimaliseren van Design of Experiments, worden de composieten verder geoptimaliseerd in **hoofdstuk 8**, door de concentratie van het koppelingsmiddel NXT te verhogen oplopend naar 7,5 phr. Trekproeven tonen duidelijk de wisselwerking van de vezels met de rubbermatrix aan. In de wals richting georiënteerde epoxy-amine behandelde vezels geven een aanzienlijke toename in lage-rek moduli en hysteresis in vergelijking met onbehandelde vezels. Een duidelijk optimum wordt waargenomen in lage-rek moduli bij 6 phr koppelingsmiddel NXT. De resultaten laten zien dat alle moduli bij lage belasting en de trek-rek curve zelf in detail bekeken moeten worden om de juiste vezel-silaan-elastomeer interactie te kunnen bepalen. Een extra controle op het vermogen van de EF-vezels en NXT bij een vereenvoudigde uithardings-test te reageren, bevestigt dat de reactiviteit van dit systeem ten opzichte van de andere twee vezelsystemen (VF en SF), toch echt verschilt.

Het onderzoek in dit proefschrift werd gehinderd door het gebrek aan een gemakkelijk toegankelijke methode voor het meten en kwantificeren van de oriëntatie van de korte vezels-rubber composieten. Daarom werd samenwerking gezocht met de firma PANalytical B.V. in Almelo, Nederland, om een dergelijke methode op basis van röntgendiffractie te ontwikkelen. Zoals weergegeven in **hoofdstuk 9** werd hierbij gebruik gemaakt van het kristallijne karakter van aramide. De karakterisering van de mesoscopische oriëntatie van korte aramide vezel-versterkte elastomeren met röntgendiffractie laat zien dat de rubber- en vezel-signalen in hetzelfde kristalstructuurvlak liggen, waarbij de laatste zichtbaar worden wanneer de vezel-concentratie voldoende hoog is. Verstoringen van andere ingrediënten blijven beperkt, waarbij de signalen van rubber en vezels niet verstoord worden. Volume-oppervlakte reconstructie van het composietmateriaal en de daaropvolgende analyses laten duidelijk zien dat de aramide vezels macroscopisch gerangschikt zijn, waarbij vezelbundels zijn georiënteerd in de Y-richting in het X-Y vlak. De uitlijnde vezelbundels hebben een gemiddelde dikte van 65

micrometer. Door de lage resolutie van de techniek, zijn afzonderlijke vezels niet zichtbaar. Zelfs met deze beperking is dit toch een goede werkwijze om kwantitatief de vezeloriëntatie te bepalen tegen veel lagere kosten en scan tijden. Difenylguanidine (DPG), een secundaire versneller, vertoont een grote oriëntatie voorkeur bij blooming, in de richting van de vezels. De verklaring is dat zich een overmaat DPG kristallen vormt, die zich oriënteren in precies dezelfde richting als de vezels. De ontwikkelde methode werkt goed om de vezeloriëntatie van het materiaal te karakteriseren en te kwantificeren, maar - helaas - kwam hij te laat om te worden opgenomen in de holistische benadering als hiervoor gepresenteerd. Het kan goed worden gebruikt voor toekomstige studies.

Het voordeel van vezel-versterkte elastomeren is dat ze vervorming kunnen weerstaan. Deze eigenschap speelt een belangrijke rol in hun wrijvingsgedrag. Het bestaan van een adhesie-actieve coating op aramide vezels voor een silaan koppelingsmiddel om als intermediair te fungeren tussen de vezels en de elastomeermatrix, resp. het belang ervan op de wrijvingseigenschappen van de elastomeren, zijn niet eerder onderzocht. De rol van het koppelingsmiddel in de vezel-elastomeermatrix interactie en hoe deze de specifieke macroscopische slijtage van de overeenkomstige rubber monsters beïnvloedt, wordt in **hoofdstuk 10** beschreven, op basis van het geoptimaliseerde composiet recept verkregen uit de Design of Experiments, reeds gepresenteerd in de voorgaande hoofdstukken.

De slijtage wordt vergeleken voor twee soorten vezels: een met EF en vezels met standaard finish (SF), maar zonder adhesie-actieve coating, gemeten in twee verschillende richtingen, transversaal op en longitudinaal in de richting van de schuifrichting. Uit de pin-on-disk wrijvingstesten blijkt dat de wrijvingscoëfficiënt ongeveer 15% lager is voor monsters versterkt met adhesie-actieve epoxy-amine gecoate vezels in combinatie met een koppelingsmiddel, in vergelijking met vezels zonder coating. Composieten met transversaal georiënteerde vezels geven een hogere wrijving dan longitudinaal georiënteerde vezels. De bijdrage van de hysteresis aan de totale wrijving speelt slechts een kleine rol, terwijl de hechtingsbijdrage dominant is in het huidige tribo-systeem. Verder onderzoek van het contactoppervlak laat zien dat het grotendeels wordt beïnvloed door de materiaaleigenschappen, zoals de Young's modulus. De specifieke slijtagesnelheid van de rubbermonsters met epoxy behandelde vezels is minder dan van het niet-reactieve vezels-bevattende monsters. De specifieke slijtagesnelheid van rubbermonsters met transversaal georiënteerde vezels is veel hoger dan voor longitudinaal georiënteerde vezels. Scanning elektronen microscopische opnamen laten een hoger interactie-effect zien tussen de elastomeer en epoxy-amine beklede vezels dan voor niet-behandelde vezels in aanwezigheid van het silaan koppelingsmiddel NXT. Het frictie- en slijtageonderzoek zal verder worden voortgezet door de leerstoel Surface Technology and Tribology.

Om de invloed van extra versterkende vulmiddelen zoals roet of silica te onderzoeken, werd een meer realistische, in de praktijk gebruikte autoband loopvlak-formulering onderzocht in **hoofdstuk 11**. De resultaten tonen aan dat de versterking als gevolg van de korte aramide vezels in de rubber matrix afhankelijk is van m.n. vier factoren: 1) vezelvolumefractie, 2) vezeloriëntatie, 3) de eigenschappen van de componenten (elastomeren, soort vezel) en 4) vezel-matrix grensvlaksterkte (type en hoeveelheid koppelingsmiddel). De eigenschappen van de zeer actieve silica-versterkte rubber composieten in combinatie met korte aramide vezels, verschillen enorm in vergelijking met die van niet-silica-versterkte mengsels. De sterkte en rek bij breuk zijn sterk toegenomen. Boven 5 phr vezels is een yield point in de trek-rek curven te zien, wat een nieuwe aanwijzing is voor vezelversterking. Mengsels op basis

van epoxy-amine gecoate EF-vezels die de interactie versterken, laten een toename zien van de Young's modulus en een verschuiving van het yield point naar hogere spanningen in vergelijking met maagdelijke vezels. Omdat de treksterkte en rek bij breuk afnemen bij toenemende Young's modulus en yield point, zijn deze twee treksterkte kenmerken niet geschikt meer om vezelversterking te kwantificeren. Longitudinale oriëntatie van de vezels verhoogt hun effect op de treksterkte, yield point en Young's modulus in vergelijking met transversale en willekeurige oriëntaties. De dynamisch mechanische $\tan \delta$ waarden in het 60°C temperatuurbereik als indicatie voor de rolweerstand van banden loopvlakken gebaseerd op deze mengsels, worden niet beïnvloed door VF-concentraties in aanwezigheid van 7 phr TESPT, terwijl de slipweerstand, zoals geïndiceerd door de $\tan \delta$ in het 0°C bereik, lager is in vergelijking met het referentiemengsel zonder vezels, hetgeen als negatief moet worden aangemerkt.

In het laatste **hoofdstuk 12** staat de opschaling van de resultaten in voorgaande hoofdstukken centraal. Hierbij is een 1,6 liter interne menger bij Teijin Aramid B.V. gebruikt, om te controleren of dezelfde grote positieve effecten, gevonden voor epoxy-amine gecoate vezels samen met koppelingsmiddel NXT, kunnen worden gereproduceerd. Net als bij de resultaten voor de kleinere 0,39 L menger moet een voldoende lange periode bij verhoogde temperatuur tijdens de mengstap worden gewaarborgd, zodat het silaan koppelingsmiddel goed kan reageren met de epoxy-amine coating. De resultaten tonen verder aan dat de longitudinaal georiënteerde (d.w.z. in de walsrichting) vezel-gevulde composieten een aanzienlijke toename in de trek-rek modulus geven, op de voet gevolgd door de willekeurig georiënteerde vezel-gevulde composieten, ongeacht welke mixer is gebruikt. Een duidelijk verschil in de treksterkte resultaten wordt waargenomen tussen de vezels met en zonder coating in samenspel met het koppelingsmiddel. De vezels longitudinaal georiënteerd, met een epoxy-amine coating en met koppelingsmiddel geven de hoogste versterking in moduli in vergelijking met de maagdelijke vezels en dit bevestigt andermaal het positieve effect van vezel-elastomeer interactie zoals eerder waargenomen voor de kleine mixer.

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Glossary

Symbols

A	Real contact area
$A, B, C, \dots, K$	Control factors
$a_{k,i}$	Individual measurement value of sample i of run k
E'	Storage modulus
E''	Loss modulus
f	Factor
F_{adh}	Adhesion/shear component
F_{def}	Deformation component
F_n	Normal force
F_{total}	Overall Force
$i=1,2,3,4$	Running numbers with 1 and 2, resp. 3 and 4 based on separately mixed and processed formulations/runs
$k = 1,2,3,\dots,12$	Experimental runs
k_{wear}	Specific wear rate
L_{12}	12 Arrays of experimental runs, each corresponds to one compound and processing combination
l_c	Critical fibre length
<i>Level 1, Level 2</i>	Level settings of control factors
l_w	Initial fibre length
M_h	Maximum torque
M_h-M_l	Highest-lowest torques in the vulcanization curve
M_k	Average of $a_{k,i}$ for run k
M_k , level 1 or 2	Highest average value of M_k for level 1 or level 2 for run k
M_{total}	Grand average of M_k over all runs k
M	Predefined tensile stress at $x\%$ strain
O_f	Orientation factor
s	Sliding difference
s_k	Standard deviation of $a_{k,i}$ for run k
$(S/N)_f$	Mean Signal to Noise ratio for certain control factor
$(S/N)_k$	Signal to Noise ratio for run k
T	Temperature
t_{90}	Time till 90% of the curing curve
t_{s1}	Scorch time
V	Wear volume
$v\%$	Volume percentage
$w\%$	Weight percentage
X	Random orientation
0°	Longitudinal orientation
90°	Transverse orientation
α	Average angle relative to the main orientation direction
δ	Phase angle
τ	Shear stress

μ	Friction coefficient
ε	Optimization factor for Design of Experiments
Δ	Difference

Abbreviations (in alphabetical order)

AFM	Atomic force microscopy
BR	Butadiene rubber
CBS	N-Cyclohexyl-2-Benzothiazole Sulphenamide
DoE	Design of Experiments
DMA	Dynamic mechanical analysis
DPG	Diphenyl Guanidine
DPI	Dutch Polymer Institute
EF	Epoxy-amine coated short-cut aramid fibres, with finish
EPDM	Ethylene propylene diene rubber
DSC	Differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatograph
LCMS	Liquid chromatography mass spectrometry
NR	Natural rubber
NXT	S-(3-(triethoxysilyl)propyl)-octanethioate
MV	Mooney viscosity
phr	Parts per hundred rubber
PET	Poly(ethylene terephthalate)
Ref.	Reference
RFL	Resorcinol formaldehyde latex
RPA	Rubber process analyser
SEM	Scanning electron microscopy
S-SBR	Solution polymerized styrene-butadiene elastomer
SF	Standard short-cut aramid fibres, with finish
Si 263	3-(triethoxysilyl)-propane-thiol
Si 363	mercapto silane
St. dev.	Standard deviation
tan	tangent
TESPD	<i>Bis</i> -(triethoxysilylpropyl)-disulphide
TESPT	<i>Bis</i> -(triethoxysilylpropyl)-tetrasulphide
TGA	Thermogravimetric analysis
TM	Tangent modulus at ?% strain in MPa
VF	Short-cut aramid fibre without finish
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
YM	Young's modulus

Rubber types (in alphabetical order)

ACM	Copolymer of ethyl acrylate or other acrylates and a small amount of a monomer that facilitates vulcanization
AEM	Ethylene-acrylate copolymer
AU	Polyester urethane
BR	Butadiene rubber
CM	Chlorinated polyethylene
CR	Chloroprene rubber
CSM	Chlorosulphonated polyethylene
ECO	Ethylene oxide and epichlorohydrin copolymer
EPDM	Ethylene propylene diene rubber
EVM	Ethylene-vinyl acetate copolymer
FMVQ	Silicone rubber having fluorine, methyl, and vinyl substituents on the polymer chain.
FPM	Rubber with fluoro, fluoroalkyl, or fluoroalkoxy substituents on the saturated carbon chain
FZ	Polyphosphazene rubber having fluoroalkyl or fluoroalkoxy substituents on the polymer chain.
HNBR	Hydrogenated acrylonitrile-butadiene rubber
IIR	Isobutylene-isoprene copolymers
NBR	Acrylonitrile-butadiene rubber
NR	Natural rubber
(S-)SBR	(Solution) polymerized styrene-butadiene rubber
VMQ	Silicone rubber having both methyl-vinyl and vinyl substituents on the polymer chain

1 Introduction

The number of applications of elastomeric and thermoplastic materials in which tribological properties play a prominent role is very high and strongly expanding. Apart from the wish to control the tribological properties purely for the purpose of performance, they also determine to a large extent the wear and consequent lifetime of articles. By dispersing short-cut fibres in elastomers the tribological properties can be significantly improved. The combined fibre/elastomer composites can be considered new, high-tech materials in which, to reach optimum performance, the different constituents have to collaborate with each other. Fibre-reinforced polymer matrix composites exhibit the potential to equally fulfil structural-mechanical and functional requirements. High-performance structures in terms of stiffness, strength and damage tolerance and a wide variety of products with specific multifunctional properties may be designed and manufactured for engineering applications. While metallic materials may reveal high modulus and isotropic behaviour, polymer matrix composites exhibit high stiffness and various degrees of anisotropic behaviour.¹ Although a lot of knowledge about the 'separate' constituents of such composites is available, the understanding about how they interact and cooperate is still limited. The project funded by the Dutch Polymer Institute (DPI), Sustfibre project #664, has recently uncovered the tip of the iceberg, but the scientific and technological challenges to turn this into feasible applications still need a great amount of research and development.²⁻⁴ More understanding will lead to the development of improved materials, with e.g. longer lifetime, contributing to a more sustainable world.

1.1 Background of the investigation

Short fibres, also known as discontinuous fibres, with commonly an aspect ratio between 20 and 500, have been embedded into many types of materials for two principal reasons.⁵ First, to reduce costs and second, to modify the mechanical and tribological properties. Structured materials with fibres embedded are considered composites. The mechanical properties of the matrix will improve by embedding the fibres, called the reinforcing phase. The use of composite materials started because of the lack of a single material that has all the properties required for a particular task. Fibres of all sorts have historically been used in construction, a historical example is the adobe brick. These bricks were made of clay, water and an organic material such as straw or bamboo shoots. The latter allowed the clay to bind and dry evenly. Many constructions were made with this reinforced material, for example Egyptian constructions from 1500 B.C. Examples of modern composites are glass-fibre-reinforced resins used in aeronautical constructions. However, in elastomeric applications they have had only limited use because of difficulties in achieving uniform dispersion and fibre breakage during processing.¹⁻³

There is ongoing interest in short "high performance" fibres being applied in elastomers. Research into the design of short fibre-reinforced composites and into the fundamental mechanisms that govern their behaviour in various matrices is crucial for further development and exploitation. In order to obtain optimal performance of such short fibres in polymers, there are claimed to be two main governing factors involved:

- Strong interfacial interaction/coupling of the fibre to the matrix polymer, in order to withstand shearing forces exerted on the fibre-matrix interface during deformation of the composite material;

– Orientation of the short fibres in the matrix, in order to prevent or just provoke anisotropy in properties.

In the Sustfibre project #664 a concerted effort has been made to generate basic understanding of the elements mentioned above.²⁻⁴ Great progress has been made, which can be summarized as follows.

An analogy with the work of Wennekes in DPI project #459: 'Characterization of the interfacial bonding layer between treated reinforcing cords and vulcanized elastomers', proved not to exist.⁶ Adhesion/interaction between short-cut aramid fibres and vulcanized rubber has been shown to be of a totally different nature than for continuous cords. First, the reinforcing effect of the short-cut fibres was claimed to be mainly mechanical in nature, due to various reasons.⁷ Surface irregularities on the fibre surface caused by bending of the highly crystalline material. The possibility to raise the surface irregularities by laser treatment was submitted as an invention disclosure for DPI⁸. Dog-bone shaped fibre ends created by the fibre cutting, which need to be pulled out of the matrix. Surface irregularities on coated fibres due to dip-coating with Resorcinol Formaldehyde Latex (RFL)-adhesive layers. RFL can be claimed to be the most successful method so far and a lot of industrial examples of RFL-coated fibres can be found to reinforce elastomers.⁶ Fibrillation of the fibres leading to anchoring of the fibres in the matrix. All these factors play no role in continuous cords reinforcement. Second, the rubber matrices that were investigated in the Sustfibre project¹⁻³: Natural Rubber (NR) and Ethylene Propylene Diene Rubber (EPDM), either one vulcanized with a sulphur- and/or peroxide-based curing system, turned out to give totally unexpected results. Sulphur-cured NR did practically not achieve chemical adhesion, neither with the virgin short-cut fibres nor with the RFL-treated fibres, although this is daily practice in tyre construction, but peroxide-cured rubbers did adhere to the RFL-treated fibres, in particular in EPDM. Where RFL is the most common coating on all sorts of cords and therefore has a very broad bearing in cord- and fibre-technology, this led to a search for chemical modification systems for fibres, which would give adhesion to sulphur-cured as well as peroxide-cured rubbers of all sorts. Such systems have been discovered for peroxide-cured systems, patent application by DPI⁸ and similar patent by DuPont⁹. Third, this previous work has shown that the type of rubber matrix in combination with its most appropriate vulcanization system is a major factor. In that respect it was concluded that the two rubber polymers selected for the study, NR and EPDM, were too far apart to characterize the matrix influences on the fibre-rubber adhesion in depth. In particular, the natural origin of NR vs. the synthetic basis of EPDM turned out to be a major disturbing factor. NR may contain up to 10% of proteins, phospholipids and other impurities of all sorts, which hamper the scientific elucidation of fundamental factors influencing interfacial interaction. These impurities happen to settle in particular at the interface between the fibres and the matrix. The fourth main factor is fibre orientation by the shear field created in the processing equipment: the fibres tend to align themselves parallel to the direction of the flow. The effect of controlled orientation of short fibre reinforcement on anisotropic properties was investigated by Clarke and Harris¹⁰. They indicated that the hysteresis, friction and wear reduction were strongly related to the orientation of the short fibres, being maximum under an orientation perpendicular to the contact surface. This element of the technology has been studied in depth by the Leibniz-Institute in Dresden in cooperation with the two groups involved in the previous Sustfibre project #664.²⁻⁴ Anisotropic or orthotropic fibre orientation has been shown to have a strong influence on the mechanical and tribological properties of the composites. However, the main problem left was to quantify the fibre orientation in carbon

black filled rubber systems, where the black disturbed practically all optical techniques. Model systems without carbon black were quantitatively characterized, but the remaining question was whether the orientation in a black-free system is the same or similar to a carbon black filled rubber. This part of the previous project is developed well enough now, so that this can be considered as being solved.²⁻⁴

All in all, the application of short-cut fibres in elastomers (and thermoplastics) has turned out to be 'another world', where mechanisms known from long cord reinforcement of rubbers do not apply. Often even opposite effects are found with respect to expectations. The overall results obtained in DPI the Sustfibre project #664 are highly interesting and challenging, but are only the tip of the iceberg.

1.2 Objective

The scope of the present project is to study the fundamental hysteric, friction and wear mechanisms that occur in reinforced elastomers, how they depend on the material properties and the operating properties and the interaction between the fibres and matrix. In the course of the study it became necessary to provide solutions for the improvement of the mixing process of fibre compounds based on existing technology. The commonly used mixing equipment shall be adjusted in order to increase the mixing capacity by a more efficient dispersion and interfacial interaction of the fibre-matrix. All this is to grasp the many difficult challenges involved due to:

- Agglomeration of the fibres by strong inter-fibre forces resulting in a poor dispersion;
- Poor interaction between the fibres and the polymer, to employ a coupling agent together with an adhesion-activating coating on the fibres;
- High initial viscosity of the fibre-polymer blend and strong decrease of viscosity during mixing;
- Reaction of the coupling agent with the fibre during the mixing cycle in the mixer, which is not specially designed for a chemical reaction;
- Increased scorch sensitivity due to the commonly used sulphur containing coupling agents;
- Narrow operational temperature window limited by the decrease of the silanization rate at low temperatures and the scorch risk at higher temperatures;
- Fibre orientation, during mixing and moulding;
- In order to exclude eventual disturbing effects of reinforcing fillers like carbon black or silica, resp. non-reinforcing mineral fillers, the decision was made by the Project Steering Committee of DPI to begin with excluding those from the rubber formulations, even though this would mean that the practical value of these formulations was not realistic. Later, also, a series with silica-reinforcement was done.

This thesis reflects one part of the project, with emphasis on the compounding and shaping background of short fibre elastomer interfacial interaction and a focus on the basic tribology properties. This research was performed in the Elastomer Technology and Engineering group, chaired by Prof. A. Blume at the University of Twente. A second thesis elaborated within this project will focus on the detailed tribology of the reinforced elastomers and is being performed in the Surface Technology and Tribology group, chaired by Prof. D. Schipper at the University of Twente.

1.3 Structure of the thesis

The structure of the thesis is as follows: **Chapter 1** gives an introduction to the project and its historical background. **Chapter 2** gives an overview of the fundamentals of short fibre-reinforcement and rubber mixing from a theoretical as well as a practical point of view, including how to measure the interfacial interaction in a short-cut aramid fibre-reinforced elastomer system. **Chapter 3** presents an initial screening of the influence of the controllable and non-controllable factors on a short-cut aramid fibre-reinforced elastomeric compound. **Chapter 4** presents an initial tribological screening. **Chapters 5, 6 and 7** give an overview of the relative importance of controllable factors on the processability and mechanical properties of short-cut aramid fibre-reinforced elastomers, for four different coupling agents, based on Design of Experiments. **Chapter 8** deals with the influence of the coupling agent concentration and investigates the compound effects based on stress-strain properties and hysteresis. One coupling agent was chosen for this investigation based on the results in Chapters 5, 6 and 7. In **Chapter 9** a new X-Ray Diffraction method and Computed Tomography are introduced in order to characterize the fibre orientation. **Chapter 10** covers the tribological properties for the most optimal compounds from Chapter 8. All the compounds described above are non-silica or carbon black reinforced. **Chapter 11** shows the results for short-cut aramid fibre-reinforcement of highly silica-reinforced compounds. The effects of coupling agent concentration, fibre concentration and fibre orientation are discussed. The optimal formulation from Chapter 8 is up-scaled at Teijin Aramid BV, as described in **Chapter 12**. And finally, **Chapter 13** contains an outlook.

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2 A literature survey on short fibre-reinforced elastomers

2.1 Abstract

Discontinuous fibres in an elastomeric compound are referred to as a short fibre-reinforced elastomeric composite. The term 'short fibre' means that the fibres in the composites have a critical length which is neither too high nor too low to allow individual fibres to entangle with each other, nor too low for the fibres to lose their fibrous characteristics. The term 'composite' signifies that the two main constituents, i.e. the short fibres and the rubber compound remain recognizable in the designed material. When used properly, a degree of reinforcement can be generated from short fibres, which is sufficient for many applications. Proper use includes: maintaining a high aspect ratio of the fibre, control of fibre orientation, creation of strong interfaces through physicochemical bonding, establishment of a high state of dispersion, and optimum formulation of the rubber compound itself to accommodate processing and facilitate stress transfer, while as much flexibility as possible is maintained to preserve dynamic properties. Moreover, short fibres provide dimensional stability during fabrication and in extreme service environments (i.e. high temperatures and solvent contact) by restricting the matrix distortion. A particular benefit is improved creep resistance. Other benefits include improved tear, friction and wear.

Because short fibres can be incorporated directly into the rubber matrix along with other additives, the resulting compounds are compatible with the standard rubber-processing steps of extrusion, calendaring, and the various types of moulding operations. Economical high-volume outputs are thus feasible. This is in contrast to the slower processing required for incorporating and placing continuous fibres. The penalty is a sacrifice in reinforcing strength with discontinuous fibres, although they give better strength and moduli compared to particulate fillers, like carbon black and silica.

The mechanisms of how such fibres affect the mechanical and tribological properties of such composites are still poorly understood. A better understanding of the fundamental principles in tension, friction and wear of such compounds will lead to the design of more sustainable materials because of a prolonged lifetime. This chapter gives an overview of the known literature, to later explain the improvement in mechanical properties reached with short fibre reinforcement, particularly a better elastic stiffness, friction and wear performance of the materials.

2.2 Introduction

A composite material is defined as a microscopic combination of two or more distinct materials, having a recognizable interface between them.¹ The materials act together to produce characteristics not obtainable by either constituent acting alone. Composites are commonly used for their structural properties and typically have a fibre or particle phase that is stiffer and stronger than the continuous matrix phase. In order to provide sufficient reinforcement, there generally must be substantial volume fraction of the fibre or particle phase.

Almost all high-stiffness and high-strength materials fail because of the propagation of flaws. A fibre of such a material is inherently stronger than the bulk form because the size of the flaw is limited by the small diameter of the fibre. In addition, if equal volumes of fibrous

and matrix material are compared, it is found that even if a flaw does produce failure in a fibre, it will not propagate to fail the entire assembly of fibres as would happen in the bulk material.² Furthermore, preferred orientation, such as shown in Figure 2.1, may be used to increase the lengthwise modulus and perhaps strength, well above isotropic values.³ Since the material is also lightweight, there is a huge potential advantage in strength/weight and/or stiffness/weight ratios over conventional materials. The desirable fibre properties can be translated into application when the fibres are embedded in a matrix that binds (mechanical, chemical etc.) them together, transfers load to and between the fibres, and protects them from environments and handling.

Figure 2.1 — Microscopic image of a vulcanized 3 mm long aramid fibre-reinforced styrene-butadiene rubber compound.

High-performance composites and compounds made from glass, carbon, aramid, cellulose etc. in polymers have been studied extensively because of their application in aerospace and other demanding applications.⁴ The reinforcement of rubbers using particulates filler such as carbon black or precipitated silica has also been studied at length.⁵ However, complete studies on composites based on fibre and rubber compounds need to be strengthened.⁷ The fibre-reinforced rubber compounds are characterized by the extremely low stiffness of the rubber compound compared to that of the reinforcing cords.⁸ Both continuous and discontinuous fibres are used to reinforce rubber compounds; the most significant example for the former is the use of continuous fibres/cords-reinforced rubber in pneumatic tyres.

Discontinuous fibre-reinforced rubber composites are usually referred to as short fibre-rubber composites. The final balance of properties exhibited by moulded short fibre-reinforced elastomers have been the subject of much debate and are determined to a large degree by the properties of the components, fibre volume fraction, fibre orientation distribution, fibre length distribution, and the interface strength between the fibres and rubber compound: see Figure 2.2. De and White⁹ reviewed short fibre-polymer composites covering thermoplastics, thermoset and thermoplastic elastomers, and rubber matrices. Goettler and Cole¹⁰ also reviewed the various aspects of short fibre-reinforcement of rubber. The mechanics of short fibre-reinforcement of rubbers based on constitutive equations and transformation laws were reviewed by Abrate¹¹. The Ullmann's Encyclopedia of Industrial Chemistry prepared already a full survey about fibres.¹² This chapter explains short fibre-reinforced rubber composites with special emphasis on their characterization, properties and applications.

2.3 Constituents of short fibre-rubber composites

2.3.1 Rubber compounds

Fillers find applications in all conventional rubber compounds. Table 2.1 shows an overview of some selected carbon black-reinforced vulcanizates with a comparative rating. The functions of the rubber compound are generally based on the best balance between low-temperature flexibility, mechanical properties, ozone resistance and price. In the case of short fibre-reinforcement the matrix is used to support and protect the fibres, to act as a principal load-carrying agent, and to provide a means of distributing the load among and transmitting it between the fibres without itself being fractured.² When a short fibre breaks, the load from one side of the broken fibre is first transmitted to the matrix and subsequently to the other side of the broken fibre and to the adjacent fibre.^{1, 2} In short fibre-reinforced compounds, the shearing stress in the matrix contributes to load transfer. Typically, the matrix has a considerably lower density, stiffness (modulus), and strength than those of the reinforcing fibres material, but the combination of the two main components (matrix and fibres) produces high strength and stiffness, while still possessing a relatively low density.

Figure 2.2 — Factors influencing the mechanical, tribological and physical properties of short fibre-reinforced elastomeric compounds.

According to market shares and prices, three different categories are usually distinguished, see the dotted lines in Tables 2.1a and b.¹³ Natural rubber (NR), Styrene-Butadiene Rubber (SBR) and Butadiene Rubber (BR) are general purpose rubbers. The second group are specialty rubbers. They are superior to general purpose rubbers in at least one property. The representatives of the last group are distinguished by at least two major properties. It must be recognized that the values in the table are highly influenced by the compounding ingredients and the vulcanization systems used.¹⁴ Examples of typical ingredients are curatives like sulphur or peroxide, activators, accelerators, inhibitors, zinc oxide, stearic acid, fillers like carbon black and silica (see later) and processing aids oils. Typically the proportion of ingredients in an elastomer compound is given in parts per hundred parts of rubber (phr).

In the present work a clean general purpose rubber, synthetic SBR, is used, see Figure 2.3. SBR has the highest market value of all synthetic rubbers, and has the second highest

performance indicator in Table 2.1. The mechanical properties of Natural Rubber are better because SBR lacks the possibility to crystallize under high strain. Compounds based on SBR in combination with fillers are especially suitable for hard-wearing applications, like in tyres and conveyor belts.

Active fillers with high specific surface area like carbon black and silica tend to agglomerate to particle networks and are binding the rubber matrix at their surface in layers of highly reduced mobility.^{15, 16} For higher filler volume fractions exceeding a certain threshold they create percolation networks. These networks lead to an effect described by Payne¹⁷ in 1962. He described the dramatic decrease of the storage modulus with increasing amplitude of dynamic strain at a constant frequency, as is shown in Figure 2.4a. The origin of this effect is the break-up of the filler-filler interactions in the three-dimensional filler network. Another effect originating from the same was described by Mullins¹⁸ for cyclic tensile testing of the same rubber specimen. It is a softening effect of the stress-strain curve which occurs if a lower resulting stress for the same applied strain appears after the first loading. This effect is shown in Figure 2.4b. The hysteresis of the unfilled NR gum is caused by the strain-induced crystallization, a unique property, of this material.

Table 2.1a — Comparative rating of properties of filled vulcanizates (1 poor and 10 outstanding performance).¹³

Rubber	Low temp. performance		Maximum service temp.		Mechanical performance	
	T_g , °C	Rating	T_{max} , °C	Rating	Tensile strength, MPa	Rating
NR	-72	8	80	1	25	10
SBR	-70/+10	6	95	3	22	7
BR	-120/-70	10	85	2	20	6
EPDM	-60/-45	5	145	6	24	8
IIR	-60	6	135	5	15	3
NBR	-70/+10	5	125	5	22	7
CR	-39/-35	4	115	4	22	7
CM	-25	3	140	6	15	4
CSM	-25	3	135	5	16	4
EVM	-35/+10	4	170	8	14	3
AEM	-35	4	170	8	15	4
ECO	-50	5	130	5	15	4
AU	-30	4	80	1	25	10
VMQ	-120	8	250	10	10	1
ACM	-45/-10	4	170	8	14	3
NHNB	-26/ - 34	3	150	6	25	10
FPM	-20	2	250	10	14	3
FMVQ	-70	8	215	9	10	1
FZ	-65	8	180	8	16	4

Figure 2.3 — SBR elastomer.

Table 2.1b — Comparative rating of properties of filled vulcanizates.¹³

Rubber	Oil swell* vol % (T, °C)	Rating	Ozone resistance Rating	Overall perform. Index	Price, \$/kg	Perform. /price ratio
NR	>140 (70)	1	1	21	1.3	16.2
SBR	130 (70)	2	1	19	1.1	17.3
BR	>140 (70)	1	1	20	1.1	18.2
EPDM	>140 (70)	1	8	28	1.8	15.6
IIR	140 (70)	1	6	21	2.3	9.1
NBR	5 – 60 (100)	7	2	26	1.8	14.4
CR	80 (100)	3	6	24	2.7	8.8
CM	80 (150)	4	5	22	2.6	8.5
CSM	80 (150)	4	9	25	4.0	6.3
EVM	20–100 (150)	6	9	30	3.3	9.1
AEM	50 (150)	5	9	30	7.3	4.1
ECO	30 (150)	6	8	28	7.8	3.6
AU	3–25 (100)	7	9	31	6.9	4.5
VMQ	30–50 (150)	6	10	35	9.9	3.5
ACM	20–40 (150)	7	9	31	7.7	4.0
HNBR	15–40 (150)	8	9	36	25.0	1.4
FPM	5 (150)	9	10	34	36.0	0.9
FMVQ	10 (150)	9	10	37	36.0	1.0
FZ	10 (150)	9	10	39	500.0	0.1

Figure 2.4 — a) Payne¹⁷ and b) Mullins¹⁸ effect of NR vulcanizates with 0, 20 and 80 phr carbon black.

2.3.2 Fibre reinforcement

The degree of short fibre reinforcement is determined largely by the following characteristic properties of the fibres: aspect ratio and orientation, interfacial interaction with the compound, dispersion in the compound, and processability to ensure minimum fibre breakage.² Due to the high viscosity of the rubber compounds, the short fibres are buckled and/or broken by the high shear stresses experienced during mixing. According to Ashida¹⁹ the length distributions of short poly(ethylene terephthalate) (PET), poly(vinyl alcohol), nylon 6, aramid, rayon, carbon and glass fibres after mixing with polychloroprene are very different. Short PET and poly(vinyl alcohol) fibres maintain their original length of 6 mm without breakage while nylon, aramid and rayon are buckled or broken and give rise to a broad distribution in a range of shorter lengths. Carbon and glass fibres are broken into much smaller pieces and their lengths are reduced to about 150 μm . Depending on the compound and type of fibres used, as long as the aspect ratio stays above the critical aspect ratio, the stress will be transferred and the reinforcement will be sufficient and will not be influenced too much.

As far as the length of the initial fibre is considered, short fibres fall into one of the following categories, shown in order of descending length, staple (kinked short fibres), short-cut (0.25-6 mm) fibres, pulp, whiskers, fibrils and nano. There is no well-defined demarcation line where one category ends and the other begins. Staples are usually more than 5 mm long and fibrils are microscopic. Rigid straight inorganic fibres, usually with relatively low aspect ratio are called whiskers. Fibrils are diminutive staples with random length and cross-section distribution and are usually the by-product of some mechanical abrasive force. Pulp material is usually produced by grinding regular fibre material which will cause randomization, reduction of the average length and a large increase in the specific surface area. The common fibres used for the reinforcement of rubber can be divided into two categories: natural fibres, and high-performance synthetic fibres.

The most commonly used reinforcements are stiff glass fibres. However, to meet various demands from industry on compound strength and modulus, various fibres are applied. A survey of the mechanical and physical properties of some selected reinforcing fibres are summarized in Table 2.2, in which the properties of high carbon steel are also provided for comparison. These data show that carbon, boron, silicon carbide and aramid fibres have a much higher Young's modulus than glass fibres. The fibres can be subdivided into two groups: flexible and rigid short fibres. A detailed description of the most important is given by Fu et al.² and Ullmann's Encyclopedia of Industrial Chemistry¹². Sometimes hybridization of two or more different types of fibres is used to reinforce polymers to achieve a balance of properties and costs. A detailed discussion on these fibres has been given by Jang²⁰ and Weeton et al.²¹. More information about how these high performance fibres are produced and characterized can be found in the Ullmann's Encyclopedia of Industrial Chemistry⁷. Table 2.2 does not include natural fibres like cellulose, sisal, jute, silk, coir and oil palm based fibres, which are also mostly rigid in nature. Natural fibres have the advantage that they are renewable and sometimes show a better bonding to rubber. Their complicated fabrication and fluctuating reinforcement levels are their disadvantages. Compared to the natural fibres, the synthetic fibres like, for example, nylon, polyester, glass, carbon and aramid have continuous fabrication and therefore narrower tolerances in shape and uniformity. Rigid fibres like carbon and glass are not so common for reinforcing elastomers, because of dramatic fibre breakage during processing.

In the present study aramid fibres are used. Aramid is the generic term for aromatic poly(amide) fibres. Three main types which are commercially available are m-aramid poly(m-phenylene isophthalamide), p-aramid poly(p-phenylene terephthalamide), like is shown in Figure 2.5 and co-poly-(paraphenylene/3,4'-oxydiphenylene terephthalamide). These fibres have a high modulus and are often used in composite structures. Some typical physical and mechanical properties of representative classes of aramid fibres are listed in Table 2.2. Although aramid fibres contain superior properties, the mixing with an elastomer matrix is quite difficult due to the differences in surface polarity between the aramid fibres and rubber.²² As a result, modification of the aramid surfaces is performed via various techniques to improve fibre dispersion and polymer-filler interaction.

Table 2.2 — Typical physical and mechanical properties of some selected fibres.²

	Fibre materials	Density (g/cm ³)	Fibre diameter (μm)	Young's modulus (GPa)	Tensile strength (GPa)
Rigid	Carbon (PAN HM)	1.8	7-10	400	2.0-2.8
	Carbon (PAN A)	1.9	7-10	220	3.2
	Boron	2.6	130	400	3.4
	SiC (whisker)	3.2	1-50	480	Up to 7.0
	E-glass	2.50-2.54	10-14	70-72.4	1.5-3.5
	S-glass	2.48-2.60	10-14	85.5-90	4.6
	Polyethylene	0.97	12	117	2.6
	High carbon steel	7.8	250	210	2.8
Flexible	Polyester ²⁰	1.38	25	3.0-8.5	1.1
	Nylon 6.6 ²⁰	1.14	25	1.0-3.0	1.0
	Para-aramid	1.44	12	60-130*	2.8-3.6*

*depends on level of crystallinity

2.4 Fibre-rubber interfacial interaction

The mechanical properties of short fibre-reinforced elastomeric compounds, like strength and toughness, depend critically on the properties of the interface or interphase between the fibres and matrix. An 'interface' is a boundary layer demarcating distinct phases such as fibre, matrix, and coating layer. An 'interphase' may be a diffuse zone, a nucleation zone, a chemical reaction zone, a thin layer of fibre coating or any combination of the above. The coating material of the fibre could fulfil different purposes: a film-forming agent for protection against mechanical damage, or as a lubricant for reduction of wear during handling or for fixation in the matrix or to increase the fibre-matrix interfacial interaction, chemical or physical. For glass reinforcement used in short fibre-reinforced elastomeric compounds, the coating usually contains an interfacial interaction-active promoter to bridge the fibre surface with the polymer resin matrix used in the short fibre-reinforced composites. The coating of the fibres leads to an interlayer between the two components.

The interface plays an important role in stress transfer from polymer matrix to short fibres and controls the mechanical properties, thus sufficient high stress transfer must be guaranteed to achieve high strength of the compound. Therefore, investigations into the effect of surface treatments on the interfacial interaction of fibres are often used to improve the quality of bonding between the fibres and the polymer matrix.

Figure 2.5 — Para-aramid: poly(p-phenylene terephthalamide).

The research on aramid fibres started in the mid-seventies.²³ Since then a lot of different methods have been developed. Kalantar and Drzal²⁴ give a broad review about bonding mechanisms of aramid fibres to epoxy matrices. Roughly speaking, these methods can be divided into three groups: use of coupling agents, surface roughening and introduction of functional groups. Most attempts at elucidating the relation between molecular structures and interfacial interaction/adhesion have followed either one of two approaches. One approach deals with the microstructural aspects of bond formation and focusses on the chemistry and physics of the interphase. The other approach deals with the macrostructural aspects and mechanical analysis of the interphase. The following sections review some of the literature relevant to the aramid bonding systems.

2.4.1 Coupling agents

The resorcinol/formaldehyde resin/latex (RFL) dip, like shown in Figure 2.6, has been a common industrial standard for rubber-cord adhesion for about 80 years²⁵, based on an aqueous dip system. The resin, which is formed by resorcinol and formaldehyde, provides bonding to the fibre. The latex component bonds to the rubber compound due to co-vulcanization.

Figure 2.6 — Proposed RFL morphology by Wennekes²⁵.

The standard RFL-dip system is a two-stage process. The first stage is a maturation of resorcinol and formaldehyde resin. This process takes place at room temperature for several hours in the presence of a strong base, usually sodium hydroxide. In the second RFL-dip stage, a mixture of resorcinol and formaldehyde resin is added to a mixture of latex and water.

The most commonly used latex is a ter-polymer of styrene, butadiene and vinyl-pyridine also known as VP-latex. The structure of the RFL forms a continuous branched-network with dispersed latex²⁴ as shown in Figure 2.6. However, as a result of the chemically inert surface of aramid fibres which comes from the high crystallinity and the lack of polar functional groups - the amide groups are hidden between the bulkier aromatic groups - it is necessary to increase the reactivity of aramid fibres prior to the RFL-dip treatment.²⁵ Therefore, a sub-coating process is usually applied by the use of an epoxy or isocyanate. The possible reaction of epoxy with aramid fibres according to Ishihara et al.²⁶ is shown in Figure 2.7.

Figure 2.7 — Possible reaction of epoxy and aramid fibres.²⁵

Another chemical sub-coating is an isocyanate. The two types of reaction products between isocyanate and aramid fibres according to Aziz²⁷ are shown in Figure 2.8. The remaining isocyanate functionality can react further with the next layer of the RFL-dip. The RFL-coated aramid fibres with epoxy or isocyanate sub-coating interact well with the rubber matrix. For a sulphur-cured system, it is suggested that sulphur and accelerators diffuse from the rubber matrix into the RFL film and form sulphur cross-links during the vulcanization of rubber. While for a peroxide-cured system, the bonding happens not only between the rubber and the latex but also with the resin part of the RFL.²⁵

Figure 2.8 — Reaction of aramid fibres with methylenebis (4-phenyl-isocyanate) (MDI).²⁵

O'Connor²⁸ studied the effect of three different bonding agents on natural rubber and nitrile rubber composites containing various fibres including short aramid fibres. The bonding agents studied were a hexamethylene-resorcinol-hydrated silica (HRH) system, a resorcinol-hexamethylene (RH) system which omitted the silica and a hexamethoxymethyl melamine (HMMM) coupling agent. Based on his research higher properties, especially Young's modulus and tear strength of short aramid fibres, were obtained with the HMMM resin of which the typical structure of HMMM is shown in Figure 2.9.

Figure 2.9 — Structure of HMMM coupling agent.²⁸

Martin et al.²⁹ synthesized block copolymers consisting of a rigid poly(benzamide) block and flexible co-polyamide 6/6.6 block which improved the interfacial interaction to polar thermoplastic resins. A drawback of the proposed method, however, is that the sulphuric acid used to apply the block copolymer attacks and partially dissolves the surface of the aramid filaments. Although this ensures a strong interfacial interaction between the block copolymer and the aramid, it has a detrimental effect on the tensile strength of continuous fibre/cord-reinforced compounds.

Vaughan et al.³⁰ experimented most extensively with coupling agents, as others did as well.³¹⁻³⁶ Preferentially, low molecular weight organic compounds were applied. Generally these compounds proved to be of limited use and increased the interfacial interaction only marginally. This was attributed to the fact that although immobilized on the surface, most of these compounds do not penetrate or react with aramid fibre. Positive effects were only noted for highly reactive coupling agents. Examples include poly-functional aziridines which more than double the inter-laminar shear strength (tested with long fibres) of polyester composites, and the addition of di-isocyanates in the case of aramid reinforced rubber.

Li and Michiels³⁷ patented in 2000 two potential silane species for the modification of polyamides including aramids, as additives that can be added to rubber compounds during the mixing process. The silanes contain at least two different silane functional groups in which one silane was selected as an amine-containing functional group and another group contained a radical selected from the group consisting of a mercapto, a sulphide, an isocyanate, an epoxy, a pyridine, a hydrophobic saturated alkyl group, or a group having at least one unsaturated carbon-carbon bond as shown in Figure 2.10.

Sulphur-containing silanes are widely used in tyre applications, where silica and silanes are used to reduce the rolling resistance. The silane reacts first with the silanol group of the silica during rubber compounding. The rubber-active group of the silane (tetrasulphide, disulphide, thiocyanato or mercapto group) has a strong tendency to form rubber-to-filler bonds

during curing of the rubber compound.³⁸ However, in the patent of Li and Michiels³⁷ there are no examples given of improved mechanical properties, nor are all other governing factors, (see Figure 2.2) included in the arguments. As such, the patent is not very convincing, but worth a revisit including the other factors. The work of Borup and Weissenbach³⁹ gives a comprehensive overview of silane coupling agents from which a selection could be made.

Figure 2.10 — Two examples of silane coupling agents patented by Li et al.³⁷.

2.4.2 Introduction of functional groups

A Mix of chemical and physical treatment

Plasma treatment is carried out by treating aramid fibres with inert gases such as argon, nitrogen, carbon dioxide, etc. The treatment can be used for cleaning or etching the surface of the fibres, introducing functional groups on the surface of the fibres by using more reactive gases, and adding an extra component (polymer coating).

Sharma⁴⁰ patented inert cold plasma treated aramid fibres in the form of continuous filaments or cords as an alternative for the pre-dip step of the standard RFL-dip system. Morin et al.⁴¹ patented a plasma treated textile including aramids using a vinyl compound to replace the sub-coating system, followed by a standard RFL-dip after the plasma treatment.

De Lange and Akker⁴² explored plasma treatment with atmospheric plasma to replace the epoxy-amine coating.

Shuttleworth et al.⁴³ patented a two-stage plasma treatment as an alternative, to entirely replace the standard RFL-dip system. The first stage is a plasma treatment of polyester fibres using oxygen or tetrafluoromethane to clean the surface of the fibres, followed by a second plasma treatment using gases selected from the groups consisting of sulphides, thiols or isocyanates. The reinforcing fibres then could be added directly into the rubber compound without the need of RFL-treatment.

Brown et al.⁴⁴ showed that aramid fibres which have been treated in an ammonia and oxygen plasma show enhanced interfacial interaction with phenolic resins. The plasma treatments resulted in significant improvements in inter-laminar shear strength and flexural strength of composites made from these materials. Composites containing aramid fibres with epoxide groups reacted onto the ammonia plasma-treated fibre surface also showed further improvements in the inter-laminar shear strength and flexural strength.

Chemical treatments

Some were developed to replace the RFL-treatment either partially or entirely. The current trend in short fibre-reinforced rubber compounds is to omit the coating and replace it with direct bonding by adding fibres and adhesion promoters into the rubber compound directly during mixing. Interfacial interaction between aramid fibres and rubber matrix is then achieved during the vulcanization process. For example, work done by Aziz²⁷ using a phenol-

blocked di-isocyanate in combination with a di-urethane cross-linker to bond short aramid fibres and an NR matrix. An example of phenol blocked di-isocyanate is diphenol-4,4'-methylenebis (phenyl carbamate); the chemical structure is shown in Figure 2.11.

Recently Jaycox from DuPont⁴⁵ filed a patent comprising multifunctional isocyanate-oligomers and multifunctional epoxy-oligomers to successfully increase the rubber-fibre bond strength. The H pull-out test performed for the treated fibres showed an increase of more than 300%.

Figure 2.11 — Structure of diphenol-4,4'-methylenebis (phenyl carbamate).²⁷

Another work proposed by Burlett et al.⁴⁶ is treating aramid cords with an aramid-poly(diene) copolymer. The copolymer has aramid functionalities included to enhance the interaction with the aramid surface as well as allylic hydrogens to achieve interaction with the rubber. However, the interfacial interaction values obtained by this method were far below the standard RFL-dip system.

The work done by Shirazi⁴⁷ showed a promising way to enhance the interfacial interaction between short aramid fibres and rubber by functionalizing the surface of epoxy-treated short aramid fibres with allyl-isocyanate and allyl-chloroformate. Nevertheless, treating epoxy-treated short aramid fibres with those chemicals results in fibre bundles (fibres stick to one another). The proposed reaction mechanism between those above-mentioned molecules with hydroxyl groups from the epoxy-treated short aramid fibres is shown in Figure 2.12. An effective way to apply this technique is by treating aramid fibres in the form of yarn or cord to avoid fibre sticking. After the treatment the aramid yarn can be cut into short fibres.

DuPont filed in 2000 a patent⁴⁸ where they grafted the polyamide with nitro-benzyl- and nitro-stilbene-groups to increase interfacial interaction. The tests were done on long cords with H pull-out tests; the results showed a 900% increase and, compared with the RFL standard, a 20% increase.

Figure 2.12 — Proposed reaction mechanism of (above) allyl isocyanate and (below) allyl chloroformate with epoxy-treated aramid fibres.⁴⁷

A Mix of fibre and rubber functionalization

Another chemical treatment for improving the interfacial interaction of short aramid fibres with styrene-ethylene-butylene-styrene (SEBS) block copolymers was obtained by slightly hydrolysing the fibre with a sodium hydroxide solution to increase the number of reactive amino $-CH_2$ and $-COOH$ end groups, as shown in Figure 2.13.⁴⁹ The hydrolysed-aramid fibres were then mixed with a matrix of maleic anhydride grafted SEBS (MA-g-SEBS). The use of a reactive compatibilizer like maleic anhydride grafted polymer with a non-polar part having a structure similar to the polymer matrix was also used to promote fibre-matrix interactions in aramid fibre-reinforced composites. The tensile strength of the compatibilized composite was found to increase for a compatibilizer concentration up to 5% weight.

Ahmad et al.⁵⁰ used graft co-poly(ethylene/maleic anhydride) (PE-g-MA) as compatibilizer to improve the mechanical properties of thermoplastic compounds of high density polyethylene (HDPE) and natural rubber that were reinforced with RFL-coated short aramid fibres. The incorporation of PE-g-MA as compatibilizer significantly improved the tensile modulus of composites with an optimum corresponding to 20% fibres loading.

Wu and Cheng⁵¹ showed the results of a so called rare-earth modifier (RES) and the epoxy chloropropane grafting modification method. The surface treatment was done on aramid fibres. It was shown that the RES surface treatment was superior to the epoxy chloropropane grafting treatment in promoting the interfacial interaction between aramid fibres and the epoxy matrix. However, the tensile strength of single fibres is almost unaffected by the RES treatment. The optimum inter-laminar shear strength was obtained at a 0.5 wt% content of rare-earth elements.

Figure 2.13 — Hydrolysis of aramid fibres surface.⁴⁹

Metalation reaction followed by grafting

One chemical method used to modify the surface of aramid fibres is the metalation reaction of the fibre surface to form anions, which is then followed by reaction with some functional groups or the grafting of suitable polymer segments.⁵² M. Nillawong⁵³ in his thesis studied the effect of surface modification of aramid pulp on the properties of hydrogenated nitrile rubber (HNBR) compound using this method followed by chemical grafting of a silane coupling agent, in this case 3-chloropropyl triethoxysilane. Dimethyl sulphoxide and sodium hydride were used for surface metalation before grafting aramid fibres with the chlorosilane coupling agent. The reaction is shown in Figure 2.14.

However, after treating the aramid pulp with DMSO and NaH, the fibres stuck to one another resulting in poor aramid fibres dispersion into the HNBR rubber compound. Chantaratcharoen et al.⁵⁴ also did a metalation reaction to modify the surface of aramid short fibres for reinforced SEBS and instead of using excessive NaH they only used 0.025 mol of NaH to prevent fibres from becoming hard and sticking together. The metalation reaction was followed by an N-alkylation reaction with heptyl- or decyl-bromide. Some increase in tensile strength was noted with the addition of the alkylated fibres vs. non-treated fibres, which incidentally also could be due to surface roughening of the fibres by the metalation reaction.

Figure 2.14 – Grafting reaction of chlorosilane on p-aramid fibre surface.⁵²

Friedel-Crafts Reaction.

Conventional chemical modification approaches are mainly carried out by introducing active functional groups onto the fibre surface via the graft reaction onto the active hydrogen atoms of imide groups of the aramid. However, this method produces a very poor interfacial interaction effect, because the hydrogen atoms in the imide groups are strongly inactivated by the conjugation effect among imide groups, carbonyl groups as well as by the steric hindrance effect of phenyl rings.⁴⁹

A new chemical graft reaction based on a Friedel-Crafts reaction was carried out by Liu et al.⁴⁹ to break out of the shielding and steric hindrance effects of the phenyl ring by an electrophilic substitution reaction on the phenyl ring. Epoxy-chloropropane was used for the surface modification of aramid fibres under the addition of an aluminium tri-chloride catalyst and heating. The possible reaction mechanism is shown in Figure 2.15.

Figure 2.15 — Possible reaction mechanism of aramid fibres and epoxy chloropropane.⁴⁹

In reaction 1, an epoxy lateral chain is grafted onto the phenyl rings of the aramid molecular chain, while in reaction 2, a lateral chain of halogenated alcohol is grafted onto the

phenyl rings of the aramid molecular chain. Based on the experiment it is worth mentioning that no matter which kind of possible mechanism takes place, the aramid fibre surface wettability can be enhanced remarkably via the introduction of oxygen containing functional groups. Once wetting occurs, there will be adhesive-substrate interaction and dispersion forces that occur will be sufficient to give strong bonds. However, the work done by Liu et al.⁴⁹ needs further investigation to be applied in short aramid fibres-rubber interfacial interaction, because the Friedel-Crafts reaction which was used by Liu et al.⁴⁹ was for improving interfacial bonding strength of long aramid fibres with epoxy resin and not for short aramid fibres.

2.4.3 Surface roughening

The roughening of a fibre surface acts as mechanical anchoring, and high bond strengths can be obtained even when chemical interactions may be weak. The mechanism has a profound influence on the interfacial interaction of polymers with porous materials such as wood, textiles, and metal oxides, but for the microscopically smooth surfaces of aramid fibres, mechanical interlocking is not expected to be very significant.

Knittel et al.⁵⁵ showed that for polyamides and aramids irradiated with argon-fluoride and krypton-fluoride lasers, the originally smooth surfaces of these fibres change their morphology into a rather regular roll-like structure perpendicular to the fibre axis after this treatment. No compounding was done.

Shirazi⁴⁷ treated aramid fibres with laser pulses to roughen the fibre surface. The results showed that the surface of aramid fibres was successfully roughened without severe damage. The depth of the treated area could be estimated to be between 1 to 2 microns, while the diameter of the fibres was around 12 μm . No further testing was done with this method. The effect of surface roughening of the fibres via the metalation approach was implicitly covered in the previous paragraph.

2.5 Determination of interfacial interaction level and optimization

The main problem in studying the interfacial interaction in the case of short fibre reinforcement is that it cannot be measured directly. An indirect way is to determine the reinforcement of the fibre and compound separately. The reactivity of the fibres could be assessed with techniques like FTIR, XPS, LCMS or GC. Another indirect method to quantify interfacial interaction for composites is with the help of rheometer cure data. The work of Hinze²² shows a slight increase for the maximum torque (M_h) values for the interfacial interaction active compounds in an EPDM hose compound.

Dynamic mechanical analysis is also used to evaluate fibre-rubber interfacial interaction in short fibre-reinforced composites. Figure 2.16 shows the effect of the addition of 5 phr of two pretreatments of short fibres vs. standard finish fibres, the reference, in an EPDM-based hose compound.²² All were measured in longitudinal direction after a fibre orientation step. The role of the pretreatments in improving the fibre-matrix interfacial interaction is evidenced in raising the E' and E'' in the rubber plateau, in comparison with the standard fibres; as well as lowering the $\tan \delta$ peak of the EPDM around -50°C . It can also be noted that when fibres are present in the matrix, with or without pretreatment, there is a slight shift in the $\tan \delta$ peak towards lower temperature, but too little to use this as a strong quantifiable indicator. In EPDM rubber-melamine fibre composite also a lower $\tan \delta$ height peak was observed by the composite containing the pretreatments owing to better fibre-matrix interfacial interaction, though no shift was observed in the glass transition temperature of the rubber.

Figure 2.16 — E' and E'' versus temperature T (left), $\tan \delta$ versus T (right) for different fibre types and treatments in an EPDM hose compound.²²

Swelling characteristics were also used to determine interfacial interaction.⁵⁶ Varghese and co-workers⁵⁷ used equilibrium swelling as a probe for investigating the interfacial interaction between short sisal fibre and natural rubber. The swelling decreased with an increase of fibre content and also with the addition of bonding agents. However, this method is erroneous since the restriction in swelling due to the presence of fibres and that due to interfacial interaction cannot be separated.

The interfacial interaction level was also assessed by studying the fracture surfaces using the SEM technique. This method was extensively used by several authors to assess the interfacial interaction between various short fibres and rubber compounds.^{22, 51, 53, 58, 59-66} The SEM images a) and b) in Figure 2.17 show the fracture surface morphology of aramid fibres in an EPDM and NR compound including a bonding system.⁴⁹ The smooth fracture surface and de-bonding of the fibres from the matrix show weak interfacial interaction between the fibres and the matrix. However, when the pretreatment system with RFL is present, the morphology of the fracture surface is changed with fracture occurring in more than one plane between the fibres.²² Figure 2.17 c) is taken by the author as an indication of strong interfacial interaction between the fibre and the matrix and d) even fibre breakage.^{22, 59} In the latter stage the bonding system is considered to be perfect.⁴⁹

Stress-relaxation studies were also used as an indirect method to assess interfacial interaction between short fibres and rubber compounds. O'Connor²⁸ suggested that, in order to understand the effect of an interfacial interaction promoter, the stress-strain curve of the composites needs to be observed closely, as shown in Figure 2.18 left and right, as already discussed in the previous paragraph. It can be seen that with the addition of 9 v% fibres in combination with an interfacial interaction promoter the stress in the low strain region is significantly increased, as it shows in the form of a yield strength. However, this is primarily seen for rigid short fibres: carbon, glass and cellulose, but practically not for the flexible aramid and nylon fibres. The strain at break greatly reduces with adhesion promoter added, again for the rigid short carbon or cellulose fibres, not so for the glass fibres. But for aramid and nylon there is no clear trend seen in the strain at break. The question is justified, whether the interaction promoter selected by O'Connor did work for aramid and nylon in the first place. From these results O'Connor concluded that the interaction promoter settled preferentially at

the matrix-fibre interface.²⁸ Amornsakchai et al.⁴⁹ claimed the opposite, namely that if a composite failed at higher strain, this would suggest that the interfacial bonding between matrix and fibres was improved. The two opposite interpretations may either be due to the specific systems investigated, or due to effects of the other factors influencing tensile properties, as explained in the beginning of this chapter: fibre orientation, fibre dispersion, etc.

Figure 2.17 — SEM images for fibre-elastic interaction a) and b) aramid fibre with RFL²², c) strong interfacial interaction between fibre and the matrix⁵⁹ and d) fibre breakage.⁴⁹

In the work by Rajeev et al.⁶⁰ aging properties are related to the hysteresis. Atomic force microscopy (AFM) measurements were used to do surface analyses, and to show that, depending on the system, the surface roughness is reduced when the samples are aged. The measurements were taken on a relatively flat surface structure in order to avoid damaging the AFM-tip. The specimens need to be below their T_g , using liquid nitrogen, and then prepared by using cryo-microtoming using special glass knives.

2.6 Processing aspects of short fibre-rubber composites

Short fibre incorporated rubber compounds can be processed in a way similar to that of conventional rubber compounds. Proper dispersion of the fibres in the rubber compound is the primary objective.^{61, 62} The problem of unravelling and obtaining proper dispersion of the flexible short fibres is an enormous challenge. The problem is practically identical to the dispersion problems with modern carbon nanotubes, which up to the present day are a large obstacle to commercial acceptance. The consequences of various processing steps on fibre breakage, fibre distribution and fibre orientation in an internal mixer as well as on a two-roll mill are described in detail in the recent work of Hintze²². An alternative method, and suitable for short carbon fibres, which is also often used for carbon nanotubes, was employed by Jana et al.⁶³ already in 1992, where the rubber was first dissolved in a solvent, to form a paste.

Figure 2.18 — Typical stress-strain curves for short fibre-reinforced nitrile rubber without (left) and with (right) bonding agent, 9 v% fibre and tested in longitudinal direction.²⁸

The fibres were then incorporated by stirring. Later on the paste was dried to constant weight and afterwards passed through a two-roll mill to get a uniform dispersion of the fibres. They found that this method of fibre-rubber mixing caused less fibre breakage than the conventional method and produced rubber composites with higher hardness and modulus. First Moghe³ and later (in more detail) Goettler and Cole¹⁰ suggested a similar method where a better stage of mixing was achieved if the fibres were first wetted by forming a highly concentrated mixture with a coating containing a resinous or polymeric binder. They found that fibre dispersion and the tendency of fibre breakage depend critically on the rheology of the formulation. This means that factors like mixing protocol, mixing time and rubber matrix viscosity are of great importance. For internal mixers, the fill factor and mixing conditions can affect the stage of fibre dispersion as well as the degree of fibre damage, which will influence the mechanical properties of the vulcanized composites. The mixing shows improvement when the internal mixer is less full, as long as there is sufficient pressure against the ram. Multiple stages including a two-roll mill step, gave improved dispersion. The research also showed that mixing without pre-mastication of the rubber and adding the fibres in multiple small charges are recommended for improved mixing. A longer mixing time and generation of more energy through increasing mixing speed or the viscosity of the rubber are favourable for improved fibre dispersion. Increasing viscosity raises the power input, which has two beneficial effects on the mixing process: total energy input builds faster with time, and higher stresses are generated to disperse the fibres more easily from their highly concentrated initial state into the final compound. Goettler and Cole¹⁰ suggested that the above standards are applicable to many discontinuous fibres like rayon, nylon or acrylic fibres. Hintze²² showed for aramid fibres that the length of the fibre is progressively decreased when more mixing steps are involved. The longer the fibres to start with, the greater the damage. Figure 2.19 is taken from his work and shows the influence of the initial fibre length l_w on the resulting average length after six minutes mixing for a highly carbon black-reinforced EPDM model system in an internal mixer. The dotted diagonal line represents the optimum line where no fibre breakage occurs and l_w after mixing is equal to the initial l_w . The shearing action between the rotors or rolls in the case of milling causes the damage, which may differ depending on the mechanical work involved in the mixing process.

Figure 2.19 — Influence of the initial fibre length on the resultant fibre length after one mixing step of an EPDM model system in an internal mixer.²²

With respect to fibre orientation, research from Moghe³ showed that only with milling the mill nip width influences the orientation of the fibres and so also the mechanical properties of the resulting elastomeric compounds. A large shear flow during milling forces the fibres to orient along the mill direction, and is already achieved during the first pass, which makes additional milling unnecessary. Other orientations are also feasible by changing the geometrical configuration. In calendering the fibre orientation occurs preferentially in the machine direction.^{2, 66}

Compression moulding is one of the oldest manufacturing techniques that places compounds between two matched steel dies. This process basically involves the pressing of a deformable elastomeric compound charged between two heated mould sides, and its transformation into a viscoelastic form stable under the effect of an elevated mould temperature. After placing the laminate to be cured, the cavity is closed. The moulds are heated to a high temperature which causes the charge viscosity to be reduced. With increasing mould pressure, the charge flows towards the cavity extremities, forcing air out of the cavity. High pressure helps to eliminate the problem of development of voids. The primary advantage of compression moulding is its ability to produce a large number of parts with few dimensional variations. Various shapes, sizes and complexity can be achieved by compression moulding. Depending on the product shape, this process has high tooling costs and is not practical for low volume production. By compression moulding an amount of orientation may be generated. The orientation is dependent on the place in the mould. Figure 2.20 shows an example generated by Hintze²², where for 5 tensile bars punched out of a vulcanized sheet, the average orientation of fibres was characterized with confocal laser scanning microscopy. The orientation was quantified with a proprietary algorithm developed for carbon nanotubes in polycarbonate. For the moment it suffices to show the orientation factor α_f (where 1 signifies full orientation and 0 random), resp. the average angle α relative to the main orientation direction, as given in Figure 2.20. The figure shows that orientation of the fibres in the centre of the mould differs from the sides, so that care should be taken as regards where and how to cut samples out of vulcanized sheets.

Figure 2.20 — α and α versus position in the mould for aramid fibre incorporated in internal mixer or two-roll mill.²²

2.7 Properties of short fibre-rubber composites

In the rubber world, the Mooney viscosity is the most commonly measured quantifier to characterize the flow behaviour of elastomers. Unfortunately, it must be recognized that its low shear rate is not the most adequate tool to predict rubber flow behaviour during typical production. Ibarra⁶⁵ and Rajeev⁶⁶ showed that the Mooney viscosity can be related to the fraction of short-cut fibres in combination with the particular rubber polymer used. Hintze²² showed that the Mooney viscosity only slightly increased in an EPDM hose compound and NR tread compound, varying only the interfacial interaction active coating on the fibres: virgin fibres versus epoxy- and RFL-treated.

Determination of mechanical properties like tensile strength, moduli and strain at break are the most common methods to determine the cured properties of short fibre-rubber composites. De and White⁹ and Fu et al.² discussed in detail the properties of short fibre-rubber composites and reviewed the mechanism of short fibre reinforcement. The fibre concentration in the compound plays an important role in the optimization of the required properties. When fibres are added to an elastomeric compound, as with any polymer, the tensile strength first drops due to a dilution effect, even when fibres are strongly bonding to the matrix. Depending upon the nature of the fibres, the elastomer, interaction level and state of dispersion of the fibres, the strength of the resulting vulcanizates significantly increases at fibre concentrations higher than around 10-15% loading. Lopez et al.⁶⁷ show that the fibre loading, where the effect on tensile strength becomes visible for aramid fibre-reinforced rubber composites, varied with the gum strength of the rubber. Hintze²² showed that less than 10 w% fibre loading was sufficient in short aramid fibre-reinforced EPDM and NR to achieve significant improvement in mechanical properties, see Figure 2.21. In many cases, the fibre seems to have no effect on the strain at break, as it is mainly matrix or elastomer dependent, see again Figure 2.21.²² Rajeev et al.⁶⁰ added up to 60 phr melamine fibre in an EPDM rubber compound and found that 40 phr is the optimum fibre loading for the best mechanical properties including tensile strength. They also found that the best fibre concentration for optimum tensile strength depends on factors like the type of rubber (polar or non-polar), the amount of filler and cross-linking system used. Shirazi and Noordermeer found that when a short aramid fibre-reinforced EPDM compound was cured by using a sulphur cross-linking system compared to a peroxide curing system, there was no clear difference in tensile

strength, but a decrease in elongation at break with 5 phr of fibre loading, for the peroxide cure.⁶⁸

Figure 2.21 — Stress-strain curve comparison of EPDM model and EPDM hose (with 105 phr carbon black) compound filled with increasing 3 mm short aramid fibre concentration.²²

It is generally found that the incorporation of short fibres at low loadings can elevate the tear strength of composites above that of its unreinforced rubber matrix.⁶⁹ At very high loadings, the strain amplification between the fibres can promote tearing of the rubber matrix parallel to the fibre direction thus reducing the tear strength.

The work of Rajeev⁶⁰ proved that fibres and constituents of the RFL bonding system hinder the formation of ionic cross-links in short fibre-rubber composites cured by using ionic or mixed cross-linking systems, which involve both sulphur/accelerator and ionic cross-linking (involving zinc oxide and stearic acid) in the same compounds. The difference can be observed in dynamic mechanical analysis data. In this work the increase in the $\tan \delta$ peak height at the ionic transition can be used to assess the degree of reinforcement due to ionic aggregates, while lowering the $\tan \delta$ peak height is ascribed to plasticization of the ionic aggregates.

The behaviour of composites under tension can be explained based on the stress-transfer theory by Cox.⁷⁰ The analysis of mechanics of short fibre-reinforced composites is difficult, compared to continuous fibre-rubber composites, because perfect orientation of continuous fibres is straightforward, while in the case of short fibres there is always more or less a spread in orientation. In short-fibre composites, the efficiency of fibre reinforcement depends on the maximum tensile stress that can be transferred to the fibre by the shearing mechanism between the fibre and the matrix. Since the matrix/compound has a lower modulus, the longitudinal strain in the matrix is higher than that in adjacent fibres: strain amplification. Assuming a perfect bond between the fibre and the matrix, the difference in longitudinal strains creates a shear stress distribution across the fibre-matrix interface. In this condition, maximum reinforcement would be achieved when the fibres are long enough so that maximum stress transfer occurs. The corresponding critical fibre length can be calculated with the equation proposed by Rosen and Dow⁷¹. The values of the critical fibre length in Table 2.3, calculated by Hintze²² for two EPDM and NR compounds, decrease with increasing volume fraction of fibres. The calculated values for volume fractions of 5 phr fibres are all

larger than the 3 mm fibres used for that study (and later on in this thesis). At higher fibre loadings, the critical fibre length decreases to values below 3 mm, which may be one of the reasons why short-cut fibres begin to show their reinforcing effect only at higher loadings. When very high fibre loadings are employed, the elastomer matrix cannot effectively wet all the fibres anymore and the strength decreases.

Table 2.3 — Calculated l_c values for investigated compounds in mm.²²

l_c		Content, phr		
		1	3	5
EPDM: Model		8	6	5
	Hose	8	6	5
NR: Model		10	8	7
	Tread	3	4	3

The modulus of the composites can theoretically be calculated using the Halpin-Tsai theory⁷². The Young's moduli values calculated using the Halpin-Tsai equation compared with observed values of an aramid fibre-reinforced EPDM compound are shown in Figure 2.22, in dependence of fibre orientation: random, transverse and longitudinal.²² The observed moduli for the transversely oriented fibres lie close to the calculated values. The observed values in the longitudinal direction are greatly overestimated by Halpin-Tsai. The random orientations lie somewhere in between. The author believed that in the case of the longitudinally oriented fibres, a portion of the fibres remained transversely oriented, or had no perfect orientation, causing a negative deviation in the experiment versus the theory. Another explanation might be fibre breakage of the fibres during mixing. However, this theory applies primarily to rigid particles. The question may be raised in how far rigid bodies represent the behaviour of flexible fibres. Of course, the overall shape of the fibres embedded in the matrix can be approximated by a tube-like ellipsoid; however, upon deformation of the ensemble the ellipsoid does not deform as the fibre does. So, after all, this Halpin-Tsai theory, however important, is of limited use for the present purpose.

Figure 2.22 — Young's modulus and Shore A hardness versus aramid fibre content for EPDM model compound mixed in an internal mixer.²²

2.8 Morphological characterization

Microscopic techniques are extensively used to study the morphology of reinforcing fibres. The characterization of the microstructure of polymer-fibre composites gives valuable insight into the structure-property relationships. Microscopic techniques have been employed for the characterization of polymeric fibres to study features such as fibre shape, diameter, crystal size, voids, and molecular orientation. In order to understand the relation between the structure and properties of any polymeric material including fibres, their morphology should be clearly understood. XRD, optical microscopy and TEM, along with a range of other analytical tools, are commonly used to determine the structure of such composites. The surface and bulk analyses of aramid fibres using different analytical techniques are already commonly used.^{52, 75} Optical microscopy is not feasible to detect fibre morphology in compounds filled with carbon black or silica. SEM is the most widely used imaging technique for the study of both short- and continuous-fibre composites. See for example Figure 2.23 where different types of coating are shown on the aramid fibre.

Figure 2.23 — SEM images of initial aramid fibre with a): standard, b): epoxy- and c): RFL-pretreatment.²²

A relatively new technique is high resolution X-Ray Computed Tomography, a technique with submicron resolution and able to visualize the morphology in 3D even for highly filled elastomeric samples. Figure 2.24 shows the resulting virtual cut and the reconstruction of an EPDM hose sample filled with 5 phr aramid fibres. The geometry was $1 \times 1 \times 1 \text{ mm}^3$ and a step-size of $1.5 \text{ }\mu\text{m}$ was used with scanning time of 3 hours.

Figure 2.24 — High-resolution computed tomography for EPDM hose compound with 5 phr aramid fibre: virtual cut (left) and cubic reconstruction (right).²²

With this high resolution X-Ray technique it was possible to distinguish the fibres and their orientation and length even in a carbon black filled EPDM compound. Further studies with this technique were too difficult to execute due to lack of the appropriate equipment, and the high costs involved in hiring of external measurement facilities, next to the long scanning times involved. This approach was not pursued further, but will be revisited in Chapter 9 of this thesis.

2.9 Applications of short aramid fibre-rubber composites

Typically, short fibre-reinforced rubber compounds may be found in applications like hoses, seals, belts, tyres, and other automotive parts.^{9, 19, 21, 54, 61, 76} The main performance characteristics aimed for are: improved strength/weight balance of the composites, wear/abrasion resistance e.g. in seals, vibration damping and therefore noise reduction for example in V-belts. There is a continuous drive to further develop this technology in high-performance applications.

When aramid was being developed, the original expectation of DuPont and Akzo was that it would be used mostly for tyre cords. After all, there is a much broader application range of interest. In most cases the applications are driven by the unique combination of mechanical and thermal properties combined with low density. At this point, applications for high strength fibres are very diverse and development of new uses frequently requires different fibre forms beyond the continuous cords envisaged in the original tyre cord application. It should be remembered that these new materials frequently require the development of a sophisticated understanding of the way they work in the final structures. Consequently, design of structures needs to be optimized specifically for these materials. One critical difference versus traditional materials like steel and concrete is the anisotropy of the properties of high-performance fibres. A more complete (but still brief) review of applications can be found elsewhere^{77, 78}.

2.10 Concluding remarks

It has become clear in this chapter that short fibre-reinforced composites represent a class of materials which are extremely complicated. There are a great many factors involved in establishing their properties, ranging from the constituents, mixing and dispersion, orientation of the fibres, the degree of vulcanization, the degree of fibre-matrix interaction and the way in which the articles are loaded. After reviewing all this literature – not exhaustive because that was impossible – none of the authors had addressed and compared all factors involved in their studies. A **holistic** approach is necessary to include all possible factors and their interactions. Otherwise, no significant progress in understanding may be expected.

As to the approach and rubber formulation components, agreement was made with the steering committee of the present project to try to avoid, as much as possible, disturbing factors which were thought not to be of importance for the friction and wear study. In particular this pertains to the choice of the type of elastomer, the fibres, use of silane coupling agents in combination with epoxy-amine pretreated fibres, sulphur vulcanization and omission of reinforcing and/or non-reinforcing fillers like carbon black or silica. The choice of silane coupling agents was made based on this literature survey as – possibly - the most promising candidate for epoxy-amine pretreated aramid fibre-elastomer interaction. A second reason was the extensive basis of know-how from the Elastomer Technology and Engineering Department wherein this research was to be carried out, in the silane-coupling technology between silica and rubber.

In this perspective, a holistic approach was chosen wherever possible as the basis for the research in this thesis. The focus of the project as a whole was on friction and wear properties, which are only preliminarily covered in this thesis. They will be the main subject of a second PhD project as a follow-up in the Department of Surface Technology and Tribology.

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3 Initial screening of control and noise factors in short-cut aramid fibre-reinforced elastomeric compounds with silane coupling agents

3.1 Abstract

This study concerns short-cut aramid fibre-reinforcement of styrene-butadiene rubber compounds with 4 types of silane coupling agents, with the objective of gaining greater insight into controllable factors and noise factors during processing. The major performance factors of interest are the mechanical properties. Two types of 3 mm cut aramid fibres are investigated: an untreated fibre and a fibre treated with an epoxy coating. The fibres are added at a concentration of 5 parts per hundred of rubber (phr). The coupling agents selected are: *Bis*-(triethoxysilylpropyl)-disulphide (TESPD), *S*-3-(triethoxysilylpropyl)-octanethioate (NXT), *Bis*-(triethoxysilylpropyl)-tetrasulphide (TESPT) and a mercapto silane (Si 363). They are compared on equimolar basis with regard to the amount of reactive ethoxy groups of TESP. The Mooney viscosity, vulcanization performance, tensile properties and hardness tests are used to assess the behaviour of the coupling agents in the rubber and to characterize the processability of the compounds. Apart from the unexpected results, that non-oriented fibres give higher Young's moduli than oriented fibres, the other results show that too many factors are influencing the properties of short-cut aramid reinforced elastomers, which makes it impossible to draw clear conclusions. Therefore, a more systematic investigation is needed, as will be set up in the following chapters with a Design of Experiments approach.

3.2 Introduction

Improving the abrasion resistance using short-cut aramid fibre reinforcement in rubber dates back to the 1970s.¹ At that time these fibres were first patented.² The term 'short fibre' refers to a length of a few mm, in comparison to 'fibres' which are continuous. In the meantime, it is generally accepted that the reinforcement by short fibres in a rubber matrix depends on the following interrelated factors: 1) fibre volume fraction, 2) fibre length and length distribution, 3) fibre orientation, 4) the properties of the components: rubber / type of fibre, and 5) the fibre-matrix interface strength.³ The subject of this chapter and of the whole thesis is to quantify the relative importance of these factors, with the emphasis on short-cut aramid fibres in a solution Styrene-Butadiene Rubber (S-SBR), without adding reinforcing or non-reinforcing fillers: a so-called gum-compound.

This work is based on the recent works of Shirazi⁴ and Hintze⁵. Both did extensive research on the important factors for short-cut fibre reinforcement in a highly carbon black filled compound, assuming the factors are not mutually affecting each other. This resulted in an ongoing discussion about the relative importance of other factors for the interpretation of the results. For example, as to factor 4: properties of the components: the reinforcing system that was used in the compound was two-fold: it contained a high amount of carbon black filler and a low amount of only 5 phr fibres. When the fibre-matrix interfacial strength is considered, it is necessary to vary a given factor to such an extent that a clear effect is observed. The standard deviation in the experimental data further needs to be as low as possible. When only small changes are observed, this leads to a 'significance' discussion. Small changes become more critical when systems without reinforcing fillers like carbon black or silica are concerned.

Therefore in most cases no detailed explanation is given of interrelated factors, and for the reinforcement no mechanism is presented,^{2,5-8} although interfacial strength between fibre and rubber seems to play a role.^{5,9} To further improve the quality of the fibre-reinforcement, it is essential to know the influencing factors and how to control them.

In this study a synthetic well-defined styrene-butadiene rubber (SBR) was chosen. To decrease the complexity of the system, oil and reinforcing filler were excluded. First, a 3 mm short-cut aramid without finish, virgin fibre (VF), was used of poly-p-phenylene-terephthalamide (PPTA). Aramid fibres are generally very inert and consequently difficult to adhere to. The interfacial strength of the surface of an aramid fibre with a rubber can further be influenced by two main elements: an adhesive coating and an agent which can interact with this coating, a coupling agent. To make sure that a proper interaction is established such a coating was selected, which has the ability to chemically react with a coupling agent. The aramid fibres selected were treated with an epoxy-amine coating^{10, 11} (EF), a reaction product of which a model system is shown in Figure 3.1. The figure shows that the epoxy groups have reacted away and OH groups are formed. Based on the work of De Lange et al.¹¹ increases in oxygen-atoms on the fibre surface from approx. 11% to approx. 22% were achieved with the epoxy-amine coating, based on XPS measurements. The fibre concentrations were used in quantities of 5 phr, carrying forward the work of Shirazi and Hintze.^{5, 6} To improve the fibre-matrix interfacial interaction a silane coupling agent was introduced. Silane coupling agents represent a class of materials used for a very broad range of purposes. A classification of the variety of these products can be found in the literature.¹² The chemical structure of the coupling agents determines the polymer-fibre interaction which in turn influences the mechanical properties. Four silanes were selected, representing different classes in their ability to react with the polymer and fibre. The coupling agents *Bis*-(triethoxysilylpropyl)-disulphide (TESPD, Figure 3.2a) and *Bis*-(triethoxysilylpropyl)-tetrasulphide (TESPT, Figure 3.2b) belong to the class of sulphur silanes. The coupling agents S-3-(triethoxysilylpropyl)-octanethioate (NXT, Figure 3.2c) and alkylpolyether-mercapto-silane (Si 363, Figure 3.2d) are both mercapto silanes, the first a blocked one, the last having a free mercapto group. All should be able to react with the OH groups resulting from the epoxy treatment on the fibre surface¹¹ and with the elastomer during the sulphur vulcanization. The coupling agents were added in low quantities: 1 phr based on TESP. NXT, TESPT and Si 363 were equimolar used based on the number of ethoxy groups per molecule. The amount of free sulphur in the system was also kept constant (Appendix I). The influences of the coupling agents on the fibre and rubber interactions and their effect on the processing characteristics of these compounds are presented, as well as their influence on the mechanical properties.

Figure 3.1 — Schematic representation of the reaction product observed in the epoxy-based finish model system.

The results are compared with those obtained for a compound containing no coupling agent and with and without fibre. The test results are used to characterize the controllable factors and noise factors within this system, the latter factors which cannot be independently set, but are the implicit results of the chosen controllable factor settings.

Figure 3.2 — Silane coupling agents a) TESPd, b) TESPT, c) NXT and d) Si 363.

3.3 Experimental

3.3.1 Materials and compound preparation

A solution-polymerized styrene-butadiene rubber (S-SBR, Buna VSL VP PBR 4045 HM, from Arlanxco, Leverkusen, Germany) was used in this study. It has a styrene content of 25%, 75% butadiene-content of which a vinyl content of 25%, and a Mooney viscosity ML(1+4) 100°C (*MV*) of 54 MU. The two types of poly-p-phenylene-terephthalamide (PPTA) fibres¹¹ investigated were provided by Teijin Aramid B.V., Arnhem, The Netherlands. Both types are 3 mm long. The characteristics, structures of the four types of coupling agents are given in Table 3.1 and depicted in Figure 3.2.

Table 3.1 — Characteristics of coupling agents used in this research.

Silane coupling agent	Chemical formula	Cas nr.	MW, g/mol	Density, g/cm ³
TESPD ^a	C ₁₈ H ₄₂ O ₆ S ₂ Si ₂	56706-10-6	475	1.03
NXT ^b	C ₁₇ H ₃₆ O ₄ SSi	220727-26-4	365	0.97
TESPT ^a	C ₁₈ H ₄₂ O ₆ S ₄ Si ₂	254-896-5	539	1.08
Si 363 ^a	C ₅₅ H ₁₁₄ O ₁₅ SSi	69011-36-5	1075	1.01

^aSi 75, Si 69, Si 363 Evonik Industries AG, Essen, Germany, ^bNXT*silane Momentive GE Silicones, Wilton, CT, USA

The compounds were prepared on the basis of the formulations given in Table 3.2a and b, based on a common silica-reinforced passenger car tyre tread.¹³ It was decided to omit the silica reinforcing filler to highlight the effect of the fibres in concert with the coupling agents. For the same reason the type of non-oil-extended S-SBR chosen for this study is different from the one containing extender oil used for passenger car tyre treads, because otherwise the compound viscosity would have been too low in the present study for proper mixing of the rubber with the ingredients. Finally, all compound formulations were based on 5 phr fibres, the same amount used in the works of Shirazi⁴ and Hintze⁵, so as to be comparable.

In the acronyms, the first letters represent the type of fibre used and the second part represents the type of coupling agent used. The levels of sulphur, zinc oxide and stearic acid, from Sigma Aldrich, St. Louis, United States, was kept constant throughout the study to

represent a commonly accepted optimum level.¹⁴ The vulcanization accelerators N-Cyclohexyl-2-Benzothiazole Sulphenamide (CBS) and DiPhenyl Guanidine (DPG) were from Flexsys, Brussels, Belgium.

Table 3.2a — Rubber compound formulations (phr).

Formulation	Ref.	VF	EF	TESPD	VF-TESPD	EF-TESPD
S-SBR	100	----->				
Fibre VF or EF	0	5	5	0	5	5
Coupling agent	0	0	0	1	1	1
Zinc oxide	2.5	----->				
Stearic acid	1.5	----->				
Sulphur	1.4	----->				
CBS	1.7	----->				
DPG	2	----->				

Table 3.2b — Rubber compound formulations (phr).

Formulation	NXT	VF-NXT	EF-NXT	EF-TESPT	EF-Si 363
S-SBR	100	----->			
Fibre VF or EF	0	5	5	5	5
Coupling agent	1.5	1.5	1.5	1.1	12.3
Zinc oxide	2.5	----->			
Stearic acid	1.5	----->			
Sulphur	1.4	----->			
CBS	1.7	----->			
DPG	2	----->			

The compounds were prepared in a 350 ml Brabender 350S tangential internal mixer using a four-stage mixing procedure. The four-stages mixing procedure is presented in Table 3.3. The internal mixer chamber volume was 390 cm³. In stage 1, the raw rubber was loaded into the mixer. After 1 minute the fibres and the coupling agents in 2 portions, after 2 minutes the zinc oxide and stearic acid were added. After 3 minutes the residue was swiped back in the hopper. After four minutes the compound was discharged.

The end temperature was closely monitored between 120 and 140°C to ensure a high level of coupling reaction between the silane and the fibre.¹⁵ A second stage remix was done on the mill, to disperse the fibres in 6 minutes time.¹⁶ To ensure equal distribution treatment the masterbatch was divided into 5 parts and treated separately, 6 minutes each, like shown in Figure 3.3. A nip width of 0.03 mm was used. After a maturation time of approximately 24 hours, the second stage masterbatch was returned to the mixing chamber of the internal mixer, stage 3, and mixed with the curatives up to a temperature of 100°C with 75 rpm rotor speed for 3 minutes. The fourth stage was used to orient the fibres on the mill and make a flat sheet with a nip width of approximately 50 µm, see Figure 3.4 left. A narrow nip width was the most efficient way to orient the fibres.¹⁷

Samples were vulcanized in a Wickert press WLP 1600 at 100 bar and 150°C to sheets of 110x110 mm with thicknesses of 2 mm for tensile tests, according to their *t*₉₀ optimum vulcanization time + 2 minutes, as determined with a Rubber Process Analyzer (RPA 2000) of Alpha Technologies, according to the procedure described in ISO 3417. To ensure that the flow pattern of the rubber in the mould does not interfere with the following test, lines were drawn in longitudinal direction with the mill direction, so that the flow pattern after the

vulcanization is visualized. Figure 3.4 right shows the flow pattern of the compound after vulcanization of a tensile test sheet. The areas of strong deviating flow pattern were avoided when test samples were cut.

Table 3.3 — Four stages mixing procedure.

1st stage: Brabender 350 S		
Rotor speed	110	rpm
Initial temperature setting	50	°C
Fill factor	70	%
Steps in mins:	0	Add polymer
	1	Add 2x50% fibre, Silane
	2	Zinc Oxide, Stearic Acid
	3	Sweep
	4	Dump @ ~ 120-140°C
2nd stage – remix: Two-roll mill, add to mill to further disperse fibres		
Friction ratio	1:1.3	
Nip width	~30	µm
Steps in mins:	6	min
3rd stage - curatives: Brabender 350 S		
Rotor speed	75	rpm
Initial temperature setting	50	°C
Fill factor	70	%
Steps in mins:	0	Add batch from stage 2
	1	Add curatives
	3	Dump @ ~ 80-100°C
4th stage: Two-roll mill, orient fibres on mill and make sheet		
Time	2	mins
Nip width:	~50	µm

Figure 3.3 — Milling stage 2.

3.3.2 Characterization methods

Mooney viscosity measurements were performed using a Mooney 2000VS from Alpha Technologies, using the large type rotor (L), at 100°C according to ISO 289. The hardness of the vulcanized compounds was measured using a Zwick 3150 Shore A Hardness Tester. Tensile strength measurements were performed in the tensile mode with an Instron tensile tester with a load cell of 1000 N, according to ISO 37 at a crosshead speed of 500 mm/min.

Figure 3.4 — Managing the flow pattern: a) before and b) after vulcanization in the mould.

3.4 Results

3.4.1 Compound Mooney viscosities

Tables 3.4a and b list the compound Mooney Viscosities (*MV*) at 100°C for all investigated green compounds.

Table 3.4a — Elastomer compound properties.

Properties	Ref.	VF	EF	TESPD	VF-TESPD	EF-TESPD
MV: ML(1+4) at 100°C, MU	34.3	34.7	35.3	44.3	48.5	45.2
St. dev., MU	0.6	0.2	0.4	0.1	0.7	0.6
Cure t_{s1} , min	2.19	1.38	1.37	1.95	1.38	1.68
data: St. dev., min	0.046	0.005	0.005	0.008	0.047	0.025
t_{90} , min	8.2	4.6	5.6	10.3	9.2	8.3
St. dev., min	0.1	0.3	0.4	0.2	2.3	0.3
M_i , dN·m	0.134	0.205	0.201	0.156	0.224	0.197
St. dev., dN·m	0.004	0.000	0.001	0.002	0.006	0.001
M_h-M_i , dN·m	2.60	3.06	3.04	2.36	3.04	2.95
St. dev., dN·m	0.02	0.03	0.03	0.03	0.11	0.01
$t_{90}-t_{s1}$, min	6.0	3.2	4.3	8.3	7.9	6.7
St. dev., min	0.02	0.08	0.13	0.03	2.1	0.12

Table 3.4b — Elastomer compound properties.

Properties	NXT	VF-NXT	EF-NXT	EF-TESPT	EF-Si 363
MV: ML(1+4) at 100°C, MU	38.5	36.5	37.2	45.8	74.9
St. dev., MU	0.8	0.4	0.1	0.1	0.8
Cure t_{s1} , min	2.46	2.12	2.05	2.04	2.21
data: St. dev., min	0.017	0.036	0.012	0.009	0.069
t_{90} , min	10.5	8.6	9.3	12.2	12.4
St. dev., min	0.1	0.3	0.4	0.3	0.2
M_i , dN·m	0.155	0.181	0.184	0.187	0.279
St. dev., dN·m	0.003	0.008	0.012	0.004	0.008
M_h-M_i , dN·m	2.44	2.62	2.91	3.10	2.66
St. dev., dN·m	0.01	0.02	0.02	0.02	0.02
$t_{90}-t_{s1}$, min	8.1	6.5	7.2	10.1	10.2
St. dev., min	0.01	0.11	0.20	0.07	0.04

The increase in Mooney torque can be considered to be caused by e.g. 1): the addition of fibres; 2): the fibre type; 3): coupling reaction of the silane with the epoxy-coated fibres (EF) or reaction with itself; or 4): because of a premature scorch reaction within the matrix. The *MV* of the compounds containing only coupling agent, or fibre and coupling agent, Table 3.4a, are all increased compared to the reference compound containing no fibres and no coupling agent. The samples containing VF and EF without coupling agent show no significant increase in *MV*, given the scatter in the data. The compounds containing coupling agent together with fibres show the largest increase in *MV*, compared to the compounds with fibres or coupling agent only. VF-TESPD shows a higher *MV* compared to EF-TESPD. The coupling agents increase the torque of the system, regardless of the fibre type, indicating an effect of coupling agent to cause (some) scorch. The effect of NXT is least pronounced compared to the other coupling agents. EF-NXT shows a higher *MV* than VF-NXT. The coupling reaction is an uncontrollable noise factor in this set of experiments and can either be positively or negatively influenced by the conditions during mixing.^{7, 18} Although the temperature after the 1st step was well within the reaction range, between 120°C and 140°C, the efficiency of the process is still unknown. The *MV* results of EF-TESPD and EF-TESPT are comparable, due to the similarity of the two molecules. This only applies if the dump temperature was below 140°C, otherwise there is a higher risk of pre-scorch for TESPT. NXT cannot lead to a scorch reaction at 140°C. The *MV* value of EF-Si 363 is almost double the value of EF-TESPT, so Si 363 is extremely scorch sensitive. It is likely that Si 363 interacts via alkylpoly(ether) groups with each other, causing the scorch.

3.4.2 Curing behaviour

The curing properties of the various compounds are presented in Table 3.4a and b and Figures 3.5-7. Figure 3.5 shows that the addition of 5 phr fibres influences the curing curve significantly. 5 phr fibres increase the torque value, as seen in the M_h-M_l , see Table 3.4a, compared to the reference compound. There is no difference observed between VF and EF. The addition of coupling agent only (with no fibre) decreases the M_h-M_l , as shown in Figure 3.6. For the compounds with coupling agents TESPD, NXT and fibre, see Table 3.4a and b, and Figure 3.7 and 3.8, the scorch times (t_{s1}) are increased slightly vs. VF and EF without coupling agent. Figure 3.7 shows that a large scatter in the curve of VF-TESPD occurs after 20 minutes and this explains the high standard deviation in Table 3.4a for M_h-M_l . It could be that the fibre-silane-elastomer bonds become unstable and start to degrade, so that the modulus starts to decrease, as also seen for EF-TESPD but then in a later stage. The values of the minimum rheometer torque M_l are qualitatively comparable with the Mooney viscosities. Figure 3.9 shows the curing curves of all the EF-fibres containing compounds with all the coupling agents tested. A clear overall shape difference is observed in the various curing curves from the start at t_{s1} till t_{90} . It makes it difficult to make a comparison between all the curves belonging to the various coupling agents and fibres. Coupling agent Si 363 shows a clear lower M_h-M_l and higher t_{s1} value, probably caused by some plasticizing effect due to the large amount added. TESPT shows a marching modulus which makes it difficult to determine the correct t_{90} of the EF-containing compound EF-TESPT. EF-TESPD is the most reactive of all the coupling agents, which is seen in the $t_{90}-t_{s1}$ results compared to for example EF-NXT. Large differences are seen in the optimum vulcanization time's t_{90} , clearly influenced by the coupling agents.

Figure 3.5 — Curing behaviour of compounds with 0 phr fibre vs. 5 phr fibre, no coupling agent.

Figure 3.6 — Curing behaviour of compounds with 0 phr coupling agent vs. 1 phr CA's, no fibre.

Figure 3.7 — Curing behaviour of compounds with TESPd with and without fibre.

Figure 3.8 — Curing behaviour of compounds with NXT with and without fibre.

Figure 3.9 — Curing behaviour of 4 compounds with phr EF with different CA's.

The testing times in the rheometer were kept the same for each compound, which precludes a realistic determination of the t_{90} properties.

3.4.3 Mechanical properties

Tables 3.5a and 3.5b list the tensile properties for all compounds, after being vulcanized till $t_{90} + 2$ min. These tables also give an indication of the scatter in the results for the compounds. Figure 3.10 presents the tensile stress-strain curves of the reference compound containing 0 phr fibre, and 5 phr fibres VF and EF. The median curve was chosen out of each data set and is shown in the graph. For the fibre-containing compounds with different fibre orientations the samples with the highest modulus value were chosen, based on Table 3.5a; these were the compounds with random orientation. Orientation differences are discussed later. To have a realistic presentation of the scatter in the data in Figure 3.10, the averages of the data points at 2, 5, 10 and 50% strain are given with their corresponding error bars. The YM of the fibre-containing compounds increases strongly, while the strain at break decreases, compared to the reference compound without fibres. It is highly surprising that the strength at break stays the same, irrespective of whether fibres are included in the compound or not. There is further no significant difference between the VF- and EF-fibres. The conclusion seems justified that only the YM , or moduli at small strain, can be taken as representative indicators for the reinforcing power of the different fibre-coupling agent combinations.

Table 3.5a — Rubber compound properties: X = random orientation, 0° = longitudinal direction, 90° = transverse direction.

	Ref.	VF			EF			TESPD	VF-TESPD			EF-TESPD		
		X	0°	90°	X	0°	90°		X	0°	90°	X	0°	90°
Strength at break, MPa	2.52	2.44	2.40	1.91	2.67	2.45	1.91	2.99	3.03	2.52	1.94	2.80	2.04	2.29
St. dev., MPa	0.35	0.30	0.05	0.12	0.33	0.15	0.12	0.34	0.32	0.18	0.06	0.20	0.09	0.20
Strain at break, %	495	173	263	322	206	249	322	476	204	235	306	244	214	293.3
St. dev., %	57	43	27	29	53	25	29	31	41	10	24	26	23	37
YM, MPa	0.59	3.10	1.36	1.11	2.56	1.38	1.11	0.71	2.55	1.49	1.20	1.97	1.30	1.29
St. dev. MPa	0.04	0.94	0.12	0.03	0.92	0.14	0.03	0.10	0.10	0.06	0.04	0.40	0.08	0.14
Hard., Shore A	43	62	53	53	58	51	49	43	58	53	51	58	51	51
St. dev., Shore A	0.3	0.5	1.1	1.2	0.4	0.7	0.9	1.1	0.7	1.1	0.4	1.0	1.0	0.2

Table 3.5b — Rubber compound properties.

	NXT	VF-NXT			EF-NXT			EF-TESPT			EF-Si 363		
		X	0°	90°	X	0°	90°	X	0°	90°	X	0°	90°
Strength at break, MPa	2.50	2.14	1.98	1.75	2.32	2.07	1.67	2.42	2.72	2.11	2.88	1.91	1.51
St. dev., MPa	0.77	0.10	0.08	0.05	0.09	0.05	0.08	0.33	0.06	0.09	0.37	0.11	0.09
Strain at break, %	508	292	352	316	203	359	252	193	313	277	257	357	278
St. dev., %	98	51	35	33	8	27	32	21	32	27	39	17	26
YM, MPa	0.62	1.59	0.97	1.15	2.36	0.95	1.27	1.99	1.01	1.22	1.7	0.74	0.86
St. dev. MPa	0.05	0.23	0.03	0.07	0.14	0.03	0.07	0.32	0.09	0.09	0.44	0.02	0.05
Hard., Shore A	42	52	49	47	58	51	50	58	51	49	45	40	39
St. dev., Shore A	0.4	0.2	0.7	1.2	0.7	0.7	1.7	1.7	0.8	1.0	1.5	0.6	0.5

Figure 3.10 — Tensile stress-strain curve of reference compound with 0 phr fibre, 5 phr VF and 5 phr EF.

The strength at break, or even more so the absence of a yield point in the tensile curves are of no value in this respect, at least so far for the low amount of only 5 phr fibres used in the non-filler-extended compound used in the present investigation.

Figure 3.11 shows the tensile test curves for the coupling agents TESPD- and NXT-containing compounds, compared to the reference. All the compounds are without fibres. All these compounds show no significant differences among one another, in the most relevant range of low strain. In Figure 3.12 the compounds VF-TESPD and EF-TESPD are compared with a compound without fibres and TESPD only. Figure 3.13 shows the same for VF-NXT,

EF-NXT vs. NXT. The differences between VF-TESPD and EF-TESPD in Figure 3.12 are not significant, within the error range. In Figure 3.13 EF-NXT stands out above VF-NXT, a significant effect outside the error range. The curves for VF and EF with TESP (Figure 3.12) reach a slightly higher strength at break than those with NXT: Figure 3.13. Figure 3.14 shows the tensile test results for all the coupling agents in combination with EF-fibres, all randomly oriented. No convincing difference is observed in relation to the coupling agent chosen, except for Si 363 which is lower than the other three. Figure 3.15 presents the tensile curves at different orientations for VF fibres. Surprisingly, random orientation shows the largest reinforcement in all the compounds, second is the longitudinal orientation direction. Figure 3.15 is representative for all the other compounds, see 3.5a and 3.5. Table 3.5 shows that the addition of coupling agent has the tendency to marginally decrease the hardness, for the VF containing compounds. However, the EF-TESPD and EF-NXT compounds show comparable hardness to VF and EF.

Figure 3.11 — Tensile stress-strain curve of the Reference compound, with and without TESP and NXT.

Figure 3.12 — Tensile stress-strain curve of compounds with TESP with and without VF and EF, all X oriented.

Figure 3.13 — Tensile stress-strain curve of compounds with NXT with and without VF and EF, all X oriented.

Figure 3.14 — Tensile stress-strain curves of all compounds with CA and with EF, all X oriented.

Figure 3.15 — Tensile stress-strain curve of VF-containing compounds with different orientation directions.

3.5 Discussion

The results of the experiments presented in this chapter are quite surprising. Although it is tempting to expect that aramid fibres in the classical sense are reinforcing fillers like carbon black or silica, this is fundamentally wrong. The specific surface area of the 12 μm diameter

aramid fibres, calculated with a density of 1.45^{19} g/cm^3 is ca. $0.2 \text{ m}^2/\text{g}$. This is to be compared with specific surface areas in the order of $100 \text{ m}^2/\text{g}$ for typical rubber reinforcing fillers like carbon blacks of the N300- to N100-series²⁰, or even more for reinforcing silica fillers: 3 orders of magnitude higher. Compared to those conventional reinforcing fillers, there is practically no surface offered by the aramid fibres to interact with the polymer matrix more than a nanometrically small layer around the fibres. From the classical perspective the fibres need to be classified as 'non-reinforcing', like mineral-based fillers with typical particle sizes in the μm -range.

The reinforcement effect coming from the flexible aramid fibres must rather be seen in the model-sense of reinforcement of concrete with steel: there is no adhesion necessary between the concrete and the steel, but the steel keeps the intrinsically brittle concrete together. The decision to leave classical reinforcing fillers out of the formulation has resulted in an intrinsically weak matrix material with e.g. a tensile strength of only 2.5 MPa, extremely low compared to more common practical formulations with reinforcing/active fillers. With the help of this model, the results in the present chapter can be understood.

Concerning the *MV*-results as shown in Tables 3.4a and b, it is very surprising that 5 phr VF- or EF-fibres without coupling agent and those with NXT coupling agent all have practically the same viscosity. In the perspective of the model-view presented above, the fibres may become elongated in the still unvulcanized compound, align themselves along the streamlines in the Mooney apparatus and, by lack of molecular interaction with the rubber matrix, contribute little or nothing to the viscosity anymore. The reason for the somewhat higher Mooney viscosity of the compounds with the sulphur-containing coupling agents TESP and TESPT can most probably be related to the tendency of these coupling agents to spend some elementary sulphur into the compound during the mixing stage and so create some premature scorch.²¹ The *MV* result for compound EF-Si 363 is somewhat difficult to judge because of the excessive amount of this coupling agent added, the strong scorch, probably caused by the possibility that this coupling agent reacts with itself rather than with the fibre and/or the polymer matrix.

The curing/vulcanization performance of the compounds shows no large differences, which seems to relate directly to a reinforcing effect of the fibres. Just the M_h - M_i , a modulus measurement after the vulcanization is complete, is slightly increased to values around 3.0 dN-m compared to $\sim 2.5 \text{ dN-m}$ for the compounds without fibres, with or without coupling agents present: a slight modulus enhancement can be seen as well as in the Young's modulus, as discussed later. The curing speed is reduced in the presence of coupling agents, but that is more an effect of the different shape of the rheometer curve at longer curing times, where the coupling agents tend to lead to some marching modulus compared to the compounds wherein no coupling agents are used, which reach a quick and stable M_h without marching modulus or reversion. For NXT this is a well-known side-effect, because of the retarded de-blocking reaction of the mercapto silane; for the other silane coupling agents this is not the case.

The most interesting results are the tensile results obtained after vulcanization. Compared to the reference compound without fibres, there is a strong increase in Young's modulus in all cases where fibres are included, some more, some less. The most striking result is that the compounds **without fibre orientation** give the highest Young's moduli compared to those tested along or perpendicular to the fibre direction after orientation! The tensile strength data for the non-oriented compounds and those measured along the fibre

direction (0°) are all more or less similar and differ only slightly from the tensile strength of the compound without fibres. The tensile strengths for the compounds measured in perpendicular direction to the orientation (90°) are all reduced relative to the reference. It indicates that along the fibre direction, the contribution of the fibres to the tensile strength is basically negligible or only very small and perpendicular to the orientation, the fibres only act as nuclei for failure. In the perspective of the concrete-reinforcement model presented above, the interaction/bonding of the fibres to the matrix does not reach further than a nanometric layer around the fibres and not into the bulk of the matrix. The higher tensile strength for the TESP- and TESPT-containing fibre-reinforced compounds measured perpendicular to the orientation does not necessarily mean that there is interaction/bonding, but may again be related to the tendency of these sulphur-containing coupling agents to interact more with the vulcanization system. Therefore, the rise of the moduli and strength occurs relative to the reference, see Table 3.4a and b, where the tensile strength and Young's modulus for compound TESP (without fibres) relative to the reference compound is increased, and not for the compound with coupling agent NXT.

The yield point or stress plateau at the first 50% elongation is commonly observed in the tensile stress-strain curves of compounds classically filled with carbon black or silica reinforced rubber and high amounts of fibres: see later in Chapter 11. A yield point is not seen in any of the compounds tested in the present case; basically the vulcanized rubber matrix is too weak to sustain sufficient stresses before it breaks or tears. This means that with the non-reinforced compound formulations as used in this chapter, a yield point or otherwise the tensile strength cannot be used as a discriminating factor to judge the effect of interaction/adhesion between the fibres and the rubber matrix.

The hardness results more or less confirm the overall results. Where hardness is a sort of easy modulus measurement, the data can be compared with the Young's modulus measurements (at infinitesimal deformation) or the M_n-M_l data at somewhat larger deformations. Hardness has additionally a complicating aspect: the results of hardness tests on these compounds with the relatively large fibres are influenced by whether the hardness needle points on top of a fibre or next to it. In the latter case, only the hardness of the matrix is sensed.

All this finally leaves only the Young's modulus, or similarly the modulus at very small strains – typically at 10 or 25% – as the only feasible criterion to judge eventual effects of interaction between the fibres and the rubber matrix. The most surprising thing in this study is that the highest Young's moduli are observed for the non-oriented compounds. However, if the range of the interaction between fibre and matrix does not extend any further than a few nanometres at most, the reinforcement due to the fibres needs to be seen again in the model-perspective of the concrete reinforcement: the steel is not simply embedded as straight bars, but in the form of woven nets: the non-oriented fibres are embedded in an intermingled “knitted” configuration, rather than nicely aligned with one next to the other. In order for the whole mass to fail either in tension or shear, the fibres need to be unravelled, or complete chunks of rubber plus fibres have to be broken out of the material as a whole; with or without interaction, which plays only a minor role. This causes the highest Young's modulus values for the non-oriented fibre compounds. Even though this may be a little disappointing from a mechanical performance point of view, it may be anticipated that this breaking-out of whole chunks will have a very positive effect on the friction and wear properties of these materials, as demonstrated in the next chapter with the first screening of these properties, which was

the main objective of this thesis. But in order to quantify the effect of interaction/adhesion between the aramid fibres and the rubber matrix, it has become clear that this effect is largely overruled by other factors. In particular:

- the amount of fibres,
- orientation of the fibres,
- the effect of orientation of the fibres, resp. the direction of measuring the tensile properties of oriented fibres,
- potential polymer breakdown during the orientation processing step, although not explicitly studied in this chapter,
- optimization of the amount(s) of coupling agent(s) added,
- optimization of the curing system,
- side-effects of the coupling agents, in particular their interaction with the curing agents and tendency to cause some premature scorch,
- contribution of reinforcing fillers, in the present case primarily silica, on the mechanical properties.

Therefore, another approach is needed to quantify all these in a more systematic manner, to see how all these various factors are related with one another. For that purpose, the Chapters 5, 6 and 7 will make use of tests which are set up on the basis of Design of Experiments, also including larger amounts of fibres than only the 5 phr employed in this chapter. This should allow quantifications of the various effects. Furthermore, this thesis will later cover experiments that are executed with classical, highly silica-reinforced compounds for which yield points are to be expected as an extra criterion besides the Young's modulus, because the vulcanized rubbers are then basically much stronger.

3.6 Conclusion

A basic SBR rubber compound was mixed with 5 phr of two types of aramid fibres: with and without epoxy treatment, and different types of coupling agents. The highest *YM* values are found for random orientation of the fibres and second best is the longitudinal orientation. Yield strengths were not obtained, because of the low overall mechanical strength of the compounds without reinforcing fillers. All tensile strengths at break were nearly the same. The higher the *YM*, the lower the strain at break. The differences between fibre-reinforced compounds and compounds without fibre are very dissimilar, in the processing and mechanical properties. Overall, no proper conclusions can be drawn based on the approach chosen in this chapter for the fibre-reinforced compounds. The approach chosen in this chapter does not lead to a real quantification of the effect of interaction/adhesion of fibre coatings and coupling agents, since it is overruled by other factors. Hence, a more systematic investigation is needed, as will be set up in the following chapters with Design of Experiments.

3.7 References

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4 Initial screening of randomly oriented short-cut aramid fibre-reinforced elastomeric compounds: friction and wear

4.1 Abstract

The major purpose of this chapter is an initial screening of the friction and wear behaviour of randomly oriented short-cut aramid fibre-reinforced styrene-butadiene rubber compounds. Two types of 3 mm aramid fibres are investigated: untreated fibres and fibres treated with an epoxy-amine coating. The fibres are added in concentrations of 3 and 5 parts per hundred of rubber (phr). The coupling agents employed are: *Bis*-(triethoxysilylpropyl)-disulphide (TESPD) and S-3-(triethoxysilylpropyl)-octanethioate (NXT), and compared on equimolar basis relative to the amount of reactive ethoxy groups within TESP. Laboratory scale Dynamic Mechanical Analyses (DMA) in the temperature (TDMA) and frequency sweep modes, and pin-on-disk friction tests were used to assess the behaviour of the coupling agents in the aramid-reinforced elastomer. The TDMA results show a slightly decreasing glass transition peak when short-cut fibres are added to the system. The addition of fibres increases the $\tan \delta$ value at 0°C and the moduli at 1 Hz, independent of the type of fibre or coupling agent, compared to the reference compound without fibres. Pin-on-disk friction tests are performed with a granite sphere under controlled environmental conditions. Fibre-reinforced compounds give much lower friction coefficients than those without fibres. The deformation component of the total friction coefficient has a dominant contribution over the adhesion component for the epoxy-coated fibres, quite opposite to the virgin fibres. The interaction between fibres and matrix achieved by adding coupling agents consequently lowers the total friction and the adhesion component in particular. The wear rate for the fibre-reinforced compounds is 25-30 times lower than for unreinforced, but there are no clear differences observed between the various fibre-containing compounds: VF vs. EF with coupling agents. Therefore, a more systematic investigation is needed to separate the interfacial interaction factor between the matrix and fibre from other influencing factors, which forms the basis of the following chapters.

4.2 Introduction

The largest benefits quoted of adding short-cut fibres to elastomers is an improvement in tear strength, reduced friction and wear.¹ The purpose of this chapter is a first attempt at quantifying these improvements based on the mechanical testing previously presented in Chapter 3.

Abrasion resistance is the ability of a material to resist mechanical action such as rubbing or scraping, which tends to progressively remove material from its surface. When an elastomeric material comes into contact with moving parts, a process of micro-tearing occurs. Gradually the elastomer is removed, finally ending the functional life of rubber products. Especially for tyre tread rubber, it is important to improve the abrasion resistance in order to increase the lifetime and to lead to a reduction in environmental pollution because of tyre debris.¹

Improving the abrasion resistance using short-cut aramid fibre reinforcement in rubber dates back to the 1970s.² At that time these fibres were first patented.³ The term 'short fibre' refers to a length of a few millimetres. In the meantime, it is generally accepted that the

reinforcement by short fibres in a rubber matrix depends on the following interrelated factors: 1) fibre volume fraction, 2) fibre length and length distribution, 3) fibre orientation, 4) the properties of the components: rubber/ type of fibre, and 5) the fibre-matrix interface strength.⁴ The aim of this chapter is to investigate how the preliminary results, obtained in Chapter 3 on the systems studied there, translate into friction and wear performance. The same basic formulations were used, comparing virgin fibres (VF) and epoxy-amine coated fibres (EF).⁵ The fibre concentrations were used in quantities of 0, 3 and 5 phr, carrying forward the work of Shirazi and Hintze.^{6, 7} To improve the fibre-matrix interfacial interaction, two silane coupling agents were used: TESP and NXT, as introduced in the previous chapter. The coupling agents were added in low quantities: 1 phr for TESP. The concentration of NXT was equimolar based on the number of ethoxy groups per molecule. The amount of sulphur in the system was kept the same. Refer to Appendix I to see how these values were calculated. The influences of the coupling agents on the fibre and rubber interactions and their effect on the friction characteristics of the compounds based thereon are presented, as well as their influence on the dynamic mechanical properties.

Classifying the friction between an elastomer and a rigid surface, two main contributors to the overall force F_{total} are commonly defined: a hysteretic/deformation component F_{def} and an adhesion/shear component F_{adh} , as shown in Figure 4.1 and Equation 4.1.

Figure 4.1 — Major components in elastomer friction.

$$F_{total} = F_{def} + F_{adh} \quad (4.1)$$

The first factor F_{def} is generated by the deformation of the 'softer' elastomer, caused by the ploughing of the harder asperities of the rigid contacting material.⁹ In the present study, it is assumed that the asperities only cause a small indentation, the ploughing is not permanent and the surface returns immediately to its original shape when the pressure is released. Because there is no energy loss, this factor can be neglected. The second factor F_{adh} is related to the attractive forces between the elastomer and a rigid surface¹⁰. If the attractive forces in the bulk material are stronger than the forces on the interface, the adhesion friction is determined by the shear strength of the elastomer, meaning that the surface will wear off. The friction force produced by adhesion, for dry contact, is therefore described by Bowden and Tabor⁹ with the following Equation 4.2.

$$F_{adh} = \tau A \quad (4.2)$$

Where τ is the frictional shear stress and A is the real contact area between the contacting surfaces. The adhesion strength can be decreased by reducing the surface interaction in the interface, by applying a very thin lubricant layer. Substitution of Equation 4.2 into Equation 4.1 results in Equation 4.3, where the overall friction F_{total} , depends on the tribological conditions, the shear stress and the area of contact.

$$F_{total} = F_{adh} = \tau A \quad (4.3)$$

Which contributor is the main factor to determine the overall friction force F_{total} , depends on the tribological conditions: the shear stress or the contribution from the real area of contact. The classical approximation of the force of friction, known as Coulomb friction¹⁰ (named after Charles-Augustin de Coulomb), is expressed as:

$$F_{total} = \mu F_n \quad (4.4)$$

Where μ is the friction coefficient and F_n the normal force to the contact surface.

Mokhtari et al.¹¹ showed the effect of different fibre orientations on the friction and wear properties of a highly silica filled short-cut fibre-reinforced compound. In this present study only randomly oriented fibre-reinforced compounds are used, because in Chapter 3 they show the highest reinforcement for the low amount of fibres used: 5 phr.

The present chapter focusses on the role of silane coupling agents with different fibre types (with and without epoxy-amine coating) on friction and wear in short-cut aramid fibre-reinforced elastomeric compounds. The results are compared with those obtained for a compound containing no coupling agent, with and without fibres. For the processing and mechanical properties of the compounds described in this chapter, reference is made to the previous chapter.

4.3 Experimental

4.3.1 Materials and compound preparation

A solution-polymerized styrene-butadiene rubber (S-SBR, Buna VSL VP PBR 4045 HM, from Arlanxeo, Leverkusen, Germany) was used in this study. It has a styrene content of 25%, 75% butadiene-content of which a vinyl content of 25%, and a Mooney viscosity ML(1+4) 100°C of 54 MU. The two types of poly-p-phenylene-terephthalamide (aramid) fibres investigated were provided by Teijin Aramid B.V., Arnhem, The Netherlands: fibres without finish (VF) and fibres coated with an epoxy-amine coating (EF).⁵ Both types are 3 mm long. For further information reference is made to Chapter 3.

The compounds were prepared on the basis of the formulations given in Table 4.1, i.e. the formulation used in Chapter 3, based on a common silica-reinforced passenger car tyre tread.¹² Silica reinforcing filler was omitted to highlight the effect of the fibres in concert with the coupling agents. For the same reason, the type of non-oil-extended S-SBR chosen for this study is different from the one containing extender oil used for passenger car tyre treads, because otherwise the compound viscosity would have been too low for proper mixing of the rubber with the ingredients.

Table 4.1a — Rubber compound formulations (phr).

Formulation	Ref.	5VF	3EF	5EF	0F-TESPD	5VF-TESPD	3EF-TESPD	5EF-TESPD
S-SBR	100	----->						
Fibre VF or EF	0	5	3	5	0	5	3	5
Coupling agent	0	0	0	0	1	1	1	1
Zinc oxide	2.5	----->						
Stearic acid	1.5	----->						
Sulphur	1.4	----->						
CBS	1.7	----->						
DPG	2	----->						

Table 4.1b — Rubber compound formulations (phr).

Formulation	0F-NXT	5VF-NXT	3EF-NXT	5EF-NXT
S-SBR	100	----->		
Fibre VF or EF	0	5	3	5
Coupling agent	1.5	1.5	1.5	1.5
Zinc oxide	2.5	----->		
Stearic acid	1.5	----->		
Sulphur	1.4	----->		
CBS	1.7	----->		
DPG	2	----->		

Finally, the compounds were based on 3 and 5 phr fibres, as employed in the works of Shirazi⁶ and Hintze⁷, so as to be comparable. In the acronyms, the first number represents the amount of fibres used, followed by the type of fibres: VF or EF, and the third part represents the type of coupling agent used. The levels of sulphur, zinc oxide and stearic acid, all from Sigma Aldrich, St. Louis, United States, were kept constant throughout the study to represent a commonly accepted optimum level.¹³ The other ingredients, the vulcanization accelerators CBS and DPG were from Flexsys, Brussels, Belgium.

The compounds were prepared using a four-stage mixing procedure. The four-stage mixing procedure was presented in Table 3.3 (Chapter 3) and described in the corresponding text. For the vulcanization, only a small amount of excess unvulcanized rubber was used to prevent a flow pattern in the boundaries of the friction sample mould. Figure 4.2 a) shows a schematic sketch of the test samples and b) a SEM picture of the top view of a real randomly oriented fibre-reinforced sample. Samples were vulcanized in a Wickert press WLP 1600 at 100 bar and 150°C to sheets of 110x110 mm with a thickness of 2 mm for DMA tests, and for the friction tests 60x60x10 mm sheets, according to their t_{90} optimum vulcanization time + 1 minute for 1 mm extra thickness, as determined with a Rubber Process Analyzer (RPA 2000) of Alpha Technologies, according to the procedure described in ISO 3417.

Randomly oriented

Sliding direction

a)

b)

Figure 4.2 — Sample for tribometer test: a rubber disk with randomly oriented fibres, a) schematic, b) SEM picture of top view.

4.3.2 Characterization methods

Dynamic mechanical analyses of the vulcanized compounds were performed in tension mode in a Metravib DMA2000 dynamic spectrometer, to determine the glass transition temperature of the samples. The samples were cut from the vulcanized sheets (150x150x2mm) of the rubber compounds. For storage E' and loss E'' moduli as functions of temperature, measurements were performed between -90°C and +80°C in steps of 2°C at a

dynamic strain of 0.1%, static strain of 0% and a frequency of 10 Hz. Frequency sweep measurements of the vulcanizates were performed at a constant dynamic strain of 0.1% from -25°C till 50°C, with the frequency ranging from 1 to 200 Hz. Frequency-temperature superposition of the results was done with horizontal shifting only, by using the WLF (Williams-Landel-Ferry) procedure and a reference temperature of 21°C.

The friction tests were executed as follows. A ball-on-rubber disk experiment was selected as schematically represented in Figure 4.3. The ball was a rough granite sphere, 30 mm in diameter and with a root mean square roughness of 2.1 μm .⁸ As the disk 60x60x10 cm rubber samples were used. The viscoelastic losses during shearing of the rubber samples with the rigid ball were used to determine the friction. The experiments were done at room temperature. The sliding velocity was 0.5 m/s, corresponding to the sliding velocity in the tyre/road contact at a driving speed of a car at approximately 80 km/h and a nominal contact pressure (P_m) of 0.2 MPa, corresponding to a common passenger car tyre pressure, between the rigid ball and the elastomers. The elementary Hertz theory can be used to obtain a first estimation of the nominal load F_n , see Equation 4.4. The Hertz Theory is explained in more detail in Appendix III of this thesis. The specific wear rate is calculated after the dry friction tests.

Figure 4.3 — Rough granite ball in contact with an elastomeric disk.

The ball-on-disk experiment results in a dry contact friction coefficient. To check if the assumption to neglect the deformation force was correct, an extra experiment was performed where the sample surfaces were wetted with a very thin layer of low-viscosity oil, Ordina 927, Shell Oil Cie. The friction coefficient μ_{wet} in wet contact can be calculated by decoupling of the hysteretic contribution to the total friction. Ordina 927 had a dynamic viscosity of 78 mPa·s at 20°C, to make sure that the lubricated tribo-system remains in the boundary lubrication regime. This is the level of lubrication where only the bearing load of the sample is transmitted by mechanical contact.

A Jeol NeoScope JCM-500 Benchtop Scanning Electron Microscope was used for the pictures included in this chapter.

4.4 Results

4.4.1 Dynamic properties

Tables 4.4a and 4.4b show for 5VF, 5EF, 5VF-TESPD, 5EF-TESPD, 5VF-NXT and 5EF-NXT no significant difference between each other in the $\tan \delta$ values at 0°C and the $\tan \delta$ at 60°C, but when they are compared with the compounds without fibres: Ref. 0F-TESPD and 0F-NXT, the whole group shows a large decrease in $\tan \delta$ values at 0°C and 60°C. The

differences between 5VF and 5EF without coupling agents, to see the factor effect of the fibre coating, are too small to be significant. 3EF-NXT values show no clear trend in comparison with 0F-NXT and 5EF-NXT. The tendency of a lower $\tan \delta$ peak position, as a measure for the glass transition temperature, is directly related to the amount of fibres and can be related to the increased stiffness due to the fibres. From these data it can be concluded that neither the coupling agent nor the type of fibre shows a clear effect among each other. It might be that effects aimed for, such as interfacial interaction between EF-fibres and rubber matrix by the coupling agent, are overshadowed by other factors, like the amount of coupling agent used, fibre dosage and fibre orientation, and suchlike.

Table 4.4a — Rubber compound properties: DMA indicators.

Properties	Ref.	5VF	5EF	0F-TESPD	5VF-TESPD	5EF-TESPD
DMA: $\tan \delta$ at 60°C, -	0.18	0.10	0.10	0.20	0.10	0.12
$\tan \delta$ at 0°C, -	0.22	0.17	0.16	0.22	0.17	0.18
$\tan \delta$ at peak, -	2.0	1.3	1.0	1.8	1.2	1.2
$\tan \delta$ at peak, °C	-25	-30	-29	-27	-29	-30
E' at 1 Hz, MPa	1.5	6.4	11	1.7	5.1	3.2
E'' at 1 Hz, MPa	0.1	0.62	1.3	0.2	0.54	0.43

Table 4.4b — Rubber compound properties: DMA indicators.

Properties	0F-NXT	5VF-NXT	3EF-NXT	5EF-NXT
DMA: $\tan \delta$ at 60°C, -	0.19	0.11	0.08	0.11
$\tan \delta$ at 0°C, -	0.21	0.17	0.22	0.17
$\tan \delta$ at peak, -	1.9	1.3	1.8	1.2
$\tan \delta$ at peak, °C	-26	-30	-27	-30
E' at 1 Hz, MPa	1.6	9.0	2.1	6.3
E'' at 1 Hz, MPa	0.2	1.1	0.55	0.77

The shifted master curves for the moduli of elasticity at 1 Hz are shown in Table 4.4a and b for the compounds with fibres for the reference temperature of 20°C. In all cases, the short-cut fibre-reinforced samples show higher storage moduli, compared to the compounds without fibres. When the 5EF and 5VF containing compounds without coupling agents are compared, the 5EF shows a large increase in values for the storage modulus as well as for the loss modulus. The opposite trend is found in the fibre coupling agent combinations; here 5VF-NXT and 5VF-TESPD are higher compared to the 5EF-NXT and 5EF-TESPD.

4.5 Friction tests

The measured steady-state coefficients of friction for the samples of Tables 4.1a and 4.1b under dry conditions are shown in Figure 4.4. The contributions from the hysteresis deformation component of friction are decoupled from the total friction and measured with the elastomer surface being wetted with a very thin layer of oil, Ondina 927. The measured hysteresis/deformation contribution to the total friction is shown in Figure 4.4 as the shaded area. The measured coefficients of friction differ drastically, but bear no relationship to the DMA-properties in the previous paragraph. The friction coefficients are approximately 3 times lower for the fibre-reinforced samples than for the reference compound without fibres. The adhesion part is dominant for the Reference and virgin fibre-containing compounds, with and without coupling agents. The contribution of the deformation component, the shaded area in

Figure 4.4, is dominant for the 5EF, 5EF-NXT and 5EF-TESPD samples. Figure 4.4 shows a clear influence of fibre vs. non-fibre-containing compounds, the coupling agent vs. non-coupling agent containing compounds, and VF vs. EF containing.

Figure 4.4 — Total measured friction coefficients under dry contact (grey) and with a very thin layer of oil (shaded).

Figure 4.5 shows the total friction force under dry contact for all samples, which were calculated with Equation 4.4. The figure shows the importance of the fibre addition in reducing the friction force, as highlighted by 3EF-NXT, which positions itself in between the Reference without fibres and all other sample with 5 phr fibres. The type of fibre, respectively coupling agent, shows no large effect considering the errors involved in the experiments.

Figure 4.5 — The total friction force on dry contact after the value is stabilized.

Long run-in times, the times needed to reach constant friction coefficients, for fibre-reinforced compounds are observed compared to the non-fibre-reinforced compounds, see Figure 4.6, where the Reference compound and 3EF-NXT are taken as examples.

Figure 4.6 — Friction coefficients and run-in distance after the measurement stabilizes.

4.5.1 Wear

The specific wear rate can be calculated with Equation 4.5¹⁴:

$$k = \frac{V}{F_n s} \quad (4.5)$$

where k is the specific wear rate (m^3/Nm), V is the wear volume (m^3), F_n is the force in (N) and s the sliding distance (m). The wear rates, calculated with Equation 4.5, of the compounds presented in Figures 4.4 and 4.5, are presented in Figure 4.7. The wear rate for the reinforced samples is 25-30 times lower than for the unreinforced Reference sample. This highlights the beneficial effect of the addition of short fibre-reinforced compounds in reducing the friction. There are only minor differences in the friction and wear rates of the fibre-reinforced samples with coupling agents compared to the samples without a coupling agent. Even the 3EF-NXT sample does not stand out against the other fibre-containing compounds.

Figure 4.7 — Degrees of wear.

The debris produced from the Reference compound is dust-like, while the fibre-containing compounds had the tendency for this debris to clog together. Differences in structure of worn debris are clearly visible, see Figure 4.8.

Figure 4.8 — SEM of wear debris of ball-on-disk experiments for: 1) Reference, 2) EF no coupling agent, 3) 3EF-TESPD and 4) 3EF-NXT.

4.6 Discussion

Concerning the DMA results in Table 4.4 and in view of the minor differences between the compounds with 5 phr VF and EF without coupling agent seen in Chapter 3, it is not surprising that they show practically the same indicators: $\tan \delta$ at 0 and 60°C. In the perspective of the model introduced in Chapter 3, the fibres are only embedded within the matrix and without interaction with the rubber matrix. The lower peak and peak temperature: T_g positions are directly related to modulus increases due to the fibres. The moduli at 1 Hz show a strong increase in all cases where fibres are included, compared to the Reference compound without fibres, and it is surprising that the compounds **without coupling agent** give the highest moduli compared to those tested with coupling agent. This is probably an effect of some plasticizer effect of the coupling agents used. The DMA is not sensitive enough to detect differences between the types of fibres or types of coupling agents in the quantities used.

The hysteresis component in the friction tests cannot be used as a discriminating factor to judge the effect of interaction/adhesion between the fibres and the rubber matrix. The deformation part remains the only feasible criterion to judge eventual effects of interaction between the fibres and the rubber matrix. It is a fact that the lowest friction coefficients are observed for the 5 phr epoxy-coated fibres with coupling agents NXT and TESP. In the perspective of the reinforcement model of concrete presented in Chapter 3: if the range of the interaction between fibres and matrix does not extend any further than a few nanometres at most, the fibres need to be unravelled, or complete chunks of rubber plus fibres have to be

broken out of the material as a whole, with or without fibre-elastomer interaction, which only plays a minor role. This causes the highest wear rate values for the Reference compound, without fibres. The lowest wear rates are found in the fibre-reinforced compounds, with little difference between the fibre types and coupling agents used. A purely mechanical effect: the rubber matrix is too weak to sustain sufficient stresses before it breaks or tears to really show effects of differences in interactions. Even though this may be a little disappointing from a chemical performance point of view, this breaking-out of whole chunks is what causes the positive effect on the friction and wear properties of these materials, which ultimately was the main objective of this whole project.

In order to quantify the effect of interaction/adhesion between the aramid fibres and the rubber matrix, it has become clear that this effect is insufficiently able to demonstrate itself, which needs to be included in further studies. In particular:

- the amount of fibres,
- orientation of the fibres, studied in the work of Mokhtari et al.¹¹
- the effect of orientation of the fibres, resp. the direction of measuring the tensile or DMA properties, to determine the E-moduli,
- optimization of the amount(s) of coupling agent(s) added,
- optimization of the curing system,
- side-effects of the coupling agents, in particular their interaction with the curing agents and tendency to cause some premature scorch (see Chapter 3),
- contribution of reinforcing fillers, in the present case left out, on the mechanical properties.

Clearly another, more systematic approach is needed to separate the effect of interfacial interactors of the aramid fibres with the rubber matrix in combination with a coupling agent in a more systematic manner, to see how each of all these various factors make their own contribution. For that purpose, the Chapters 5, 6 and 7 will make use of experiments, which are set up on the basis of Design of Experiments, and which also include larger amounts of fibres than only the 5 phr employed in this chapter, because this does allow for real quantifications of the various effects, still always with the non-classically non-reinforced compound. And later in this thesis, in Chapter 10, experiments will also be covered which are executed with higher coupling agent and fibre concentrations of reinforced compounds, for which higher moduli are to be expected as an extra criterion next to only the Young's modulus, because the vulcanized rubbers are then basically much stronger.

4.7 Conclusions

A basic SBR rubber compound was mixed with 3 and 5 phr of two types of aramid fibres: with and without epoxy coating, and different types of coupling agents: TESP and NXT. The addition of any type of fibre in the SBR compound improves the abrasion resistance significantly, compared to the Reference compound without fibres. The friction is dominated by the adhesion component for all compounds, except for the adhesion-activated EF containing compounds 5EF, 5EF-NXT and 5EF-TESP. For the epoxy-coated fibres containing compounds, the deformation contribution to the friction coefficient is dominant. The friction coefficient of the fibre-reinforced samples is approximately 3 times lower compared to non-fibre-reinforced compounds, but expressed in friction force approximately 20 times lower, with or without coupling agents. The wear rates for fibre-reinforced samples, with or without coupling agents, are **25-30 times lower** than for unreinforced samples, even in the absence

of a coupling agent. The friction forces and the wear rates show the same factor of improvement. Hardly any significant differences were observed between the coupling agents themselves. Debris produced from the Reference sample is dust-like, while for the other samples it has the tendency to clog together. Clear differences in the structure of worn debris are found in the SEM pictures.

The approach chosen in this chapter does not lead to a real quantification of the effect of interaction/adhesion of fibre coatings and coupling agents, since it is probably overruled by other factors. Hence, a more systematic investigation is needed to enlarge the effect of interfacial interaction, as will be set up in the following chapters.

4.8 References

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5 Understanding the relative importance of controllable factors on the processability and mechanical properties of short-cut aramid fibre-reinforced elastomers

5.1 Abstract

This study concerns short fibre reinforcement of synthetic elastomer compounds, to gain insight into the behaviour of short p-phenylene terephthalamide (aramid) fibres on the processability and mechanical properties. Short fibre reinforcement is complex, because it depends on many factors, which are also interrelated; fibre concentration, fibre orientation distribution, fibre length and distribution, fibre-matrix interfacial strength and properties of the matrix. This manuscript highlights the relationship between influencing factors in an S-SBR compound by Design of Experiments. Two 3 mm long aramid fibres were chosen: one epoxy-coated and one without. Two coupling agents were selected *Bis*-(triethoxysilylpropyl)-disulphide and S-(3-(triethoxysilyl)propyl)-octanethioate. The results clearly show that some factor effects are fully or partially overshadowed by other factors. In particular, fibre concentration and orientation are by far the most influential, grossly overshadowing for example the effect of fibre matrix interaction. The reactivity of the coupling agent is related to the interaction with adhesion active fibres, which in turn affects either the molecular integrity of the reinforced elastomer or enhances elastomer cross-linking. For each mechanical properties response an optimization prediction is calculated and confirmed with an experimental run, showing for example a 330% improvement of the Young's modulus.

5.2 Introduction

Research into the fundamentals of interfacial strength improvement of short aramid fibres in carbon black or silica-reinforced elastomer compounds turns out to be extremely complex.¹⁻⁵ Short fibre reinforcement depends mainly on: 1) fibre concentration; 2) fibre orientation distribution; 3) fibre length and distribution; 4) fibre-matrix interfacial strength and 5) properties of the matrix^{6, 7}; respectively on the interdependencies between all these factors. Typical elastomer formulations contain many ingredients such as reinforcing and non-reinforcing fillers and curatives, with the fibres coming in addition, which interact either chemically or physically with each other. Many analytical tests like Fourier Transform Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) are inconclusive in elucidating these interactions. Because of the need to investigate these interactions as well as the influence of processing, a systematic study was carried out making use of a very simple/basic elastomer formulation. In particular, various publications⁸⁻¹³ showed sometimes large and otherwise small improvements in mechanical properties when the interfacial strength was improved in short fibre-reinforced elastomer compounds. These were mainly derived from elementary tensile tests, where the effect of fibres was most conspicuous at low strains as an increase in tensile stress vs. non-fibre-containing.

As the basis for this study a formulation was chosen, derived from the silica-reinforced passenger car tyre tread technology with silane coupling agents¹⁴, normally employed to establish chemical coupling between silica and the elastomer. The formulation was stripped to its basics by taking out the butadiene rubber (BR) and the silica, or by adding just a minor

amount of silica and using the coupling agent as potential chemical binder between the fibres and the elastomer, a solution-polymerized SBR (S-SBR). Following this procedure, the separation of the impact of the single ingredients and process conditions should be possible. A Design of Experiments (DoE) approach was chosen, the Taguchi method¹⁵ for a robust design. In this approach a distinction is made, with a minimal amount of experiments, between controllable factors and noise factors. The controllable factors can be manipulated directly, for example the concentration of a specific ingredient, and correspond to the factors that are normally varied in a statistical experimental design. The noise factors, for example the temperature after mixing, result from the choice of the controllable factors and also have an effect on the responses, but cannot be individually influenced. Taguchi proposed that the controllable factors are varied together by means of an inner and outer array system, as shown in Figure 5.1. In this figure, VF and EF are virgin short-cut fibres and epoxy-coated fibres. Coupling agent stands for the absence (0) or use (1) of a coupling agent; fibre concentration for the use of 5 resp. 15 phr fibres. There are several ways to approach the analysis of the responses. A common way is to use a statistical analysis of variance and perform F-tests to see which factors are statistically significant.¹⁵ In this chapter a conceptual way of graphing the responses is employed, also proposed by Taguchi, which involves visualizing the effects and identifying the factors and their interactions, which appear to be significant.¹⁵⁻¹⁷

Figure 5.1 — Part of the experimental design with low and high levels, without central point.

The experimental data, 4 multiple data points per response per run, are analysed by a response graph, in which the averages per experimental run (see later, Table 5.2) and the noise average are included. It enables the detection of scatter in responses for a particular run. So, next to the average response, it is important to register the variation in a particular response and to determine the signal to noise ratio (S/N), as introduced by Taguchi.¹⁵ The S/N ratio is in its simplest form the ratio of the average to the standard deviation. The method used to compute the ratio depends on the situation, because the S/N ratio is directly related to the choice of the qualifier. The qualifier 'the higher the better'¹⁵, was chosen as an approach, because the main interest is in the mechanical properties of the vulcanizates; even though for certain other responses, e.g. Mooney viscosity or optimum cure time, the opposite is preferred. But the DoE allows only one qualifier throughout the whole set-up.

The control factors varied in this DoE are shown in Table 5.1. The fibre-reinforced elastomer compounds contain a variety of ingredients and involve various processing steps. Therefore, in this design a selection was made of 11 factors. These factors were identified in

a first assessment described in Chapter 3, showing which ones could have an influence on the short-fibre reinforcing behaviour.

Table 5.1 — Taguchi design: varied control factors.

Control factors:		Level 1	Level 2	
A	Fibre type:	Not coated	Coated	
B	Fibre conc.:	5 phr	15 phr	
C	Filler:	0	10 phr silica	
D	Coupling with TESPd:	0	1 phr	
E	Coupling with NXT:	0	1.5 phr*	
F	Orientation**:	0°	90°	to fibre orientation
G	Curatives conc.:	single	double	
H	Internal mixer mixing time:	4 mins	8 mins	at 110 rpm
I	Internal mixer T _{in} :	30°C	50°C	
J	Mill mixing time in stage 2:	6 mins	12 mins	
K	Curing time:	t _{90%} mins	t ₉₀ + 2 mins	at 160°C

*Corresponds to equal amounts of ethoxy function groups to TESPd.

**0° Longitudinal orientation and 90° transverse rel. to milling direction.

The involvement of 11 factors limits the use of a statistical approach in spreadsheet form. Therefore, the conceptual approach of graphing the responses was used instead. A standard experimental plan with L_{12} array of experiments was created, as shown in Table 5.2. In this table each row corresponds to one compound and processing combination. Two types of 3 mm long fibres were chosen, see Table 5.1, factor A. This means that the choice of a centre point is not possible in the DoE, only low (level 1) and high levels (level 2). The fibre types were level 1: not coated/virgin; and level 2: pretreated with an epoxy coating. This second type of fibre was selected because of its possible reactivity¹⁸ towards silane coupling agents.

Two commonly used coupling agents were selected for this study, see Figure 3.2: *Bis*-(triethoxysilylpropyl)-disulphide (TESPD) and *S*-(3-(triethoxysilyl)propyl)-octanethioate (NXT). These coupling agents were supposed to react with the epoxy groups coming from the fibre coating and with the elastomer. A proposed mechanism of the coating with, for example, the coupling agent TESPd is shown in Figure 5.2. The first step is the coupling reaction, where an ethoxy-silyl group of the coupling agent reacts with the coating at elevated temperature. The next step is the integration of sulphur into the sulphur chain of TESPd, breaking of the sulphur bridge and finally the coupling of the sulphur radical to the elastomer in allylic position.

The fibre concentration was varied between 5 and 15 parts per hundred elastomer (phr); the silica concentration from 0 to 10 phr. Silica is an inorganic filler with Si-OH groups on its surface that can form hydrogen bonds with each other and thus create filler-filler interactions to generate aggregates and agglomerates.¹⁹⁻²¹ Generally, silica-filled compounds are improved with the help of silane coupling agents, because this creates silica-elastomer chemical bonds and so decreases the silica-silica interaction.¹⁹ The silica was added to the compound to test whether it might create an additional network contribution of fibre-silane-silica-silane-fibre or fibre-silane-silica-silane-elastomer bonds. Small amounts of silica, like 10 phr, are also commonly used as adhesion promoters in elastomers in general.²² Silane coupling agent concentration is used between 0 and 1 phr for TESPd; for NXT 0 and 1.5 phr to keep the concentration of functional ethoxy groups the same (Si-isomolar). The coupling agent has the ability to react with the elastomer as well as with the pretreated fibre and/or the silica. The curing agent concentration was varied between the standard amount¹⁴ (level 1)

and a double amount (level 2). The mixing time in the internal mixer was varied between 4 and 8 minutes, and the initial temperature setting of the mixer between 30°C and 50°C. The milling time after the internal mixer was varied between 6 and 12 minutes, to ensure further fibre dispersion; the vulcanization time between t_{90} and $t_{90} + 2$ minutes.

Figure 5.2 — Proposed reaction mechanism of TESPd with epoxy-coated fibre and elastomer.

This study concerns the short fibre-reinforcement of synthetic elastomer compounds, with the objective to gain insight into the behaviour of short-cut aramid fibres on the processability and mechanical properties. With this approach the impact of variation in the chosen factors on the responses - processing performance and mechanical properties - was investigated and optimized.

Table 5.2 — Short fibre-reinforced compound Taguchi based experimental plan.

Run	Control factors (f)											Compound 1		Compound 2		M _k	S _k	(S/N) _k
k	A	B	C	D	E	F	G	H	I	J	K	a _{k,1}						
1	1	1	1	1	1	1	1	1	1	1	1	a _{1,1}	a _{1,2}	a _{1,3}	a _{1,4}	M ₁	s ₁	(S/N) ₁
2	1	1	1	1	1	2	2	2	2	2	2	a _{2,1}	a _{2,2}	a _{2,3}	a _{2,4}	M ₂	s ₂	(S/N) ₂
3	1	1	2	2	2	1	1	1	1	2	2	⋮	⋮	⋮	⋮	⋮	⋮	⋮
4	1	2	1	2	2	1	2	2	2	1	1	⋮	⋮	⋮	⋮	⋮	⋮	⋮
5	1	2	2	1	2	2	1	2	1	2	1	⋮	⋮	⋮	⋮	⋮	⋮	⋮
6	1	2	2	2	1	2	2	1	2	1	1	⋮	⋮	⋮	⋮	⋮	⋮	⋮
7	2	1	2	2	1	1	2	2	1	2	1	⋮	⋮	⋮	⋮	⋮	⋮	⋮
8	2	1	2	1	2	2	2	1	1	1	2	⋮	⋮	⋮	⋮	⋮	⋮	⋮
9	2	1	1	2	2	2	1	2	2	1	1	⋮	⋮	⋮	⋮	⋮	⋮	⋮
10	2	2	2	1	1	1	1	2	2	1	2	⋮	⋮	⋮	⋮	⋮	⋮	⋮
11	2	2	1	2	1	2	1	1	1	2	2	⋮	⋮	⋮	⋮	⋮	⋮	⋮
12	2	2	1	1	2	1	2	1	2	2	1	⋮	⋮	⋮	⋮	⋮	⋮	⋮
												∇	∇	∇	∇	∇	∇	∇
																M _{total}		

*The numbers 1 and 2 refer to level 1 and level 2.

5.3 Experimental

5.3.1 Materials and compounds preparation

The standard formulation used in this study is given in Table 5.3. The levels of elastomer, stearic acid and zinc oxide were not varied and represent a commonly accepted level for silica-reinforced passenger tyre tread compounds.²³

Table 5.3 — Standard elastomeric compound composition (phr).

Formulation*	(phr)
S-SBR	100
Coupling agent TESPD or NXT	1/1.5
Silica	0/10
Zinc oxide	2.5
Stearic acid	1.5
Short fibre VF or EF	5/15
Sulphur	1.4 or 2.8
CBS ^a	1.7 or 3.4
DPG ^b	2.0 or 4.0

*varied depending on experimental plan, see Table 5.1 and 5.2, ^aN-Cyclohexyl-2-benzothiazole sulphenamide, ^bDiphenyl Guanidine

Solution-polymerized styrene-butadiene elastomer (S-SBR) Buna VSL VP PBR 4045 HM from Arlanxco, Leverkusen, Germany was used. It has styrene content of 25w% and has 25w% butadiene content in the 1,2-vinyl configuration, and a Mooney viscosity ML(1+4) 100°C (MV) of 54. Zinc oxide and stearic acid were from Sigma Aldrich, St. Louis, United States. The other ingredients, which in the context of this DoE were varied, are: fibres, silica, coupling agents and curing system. Two types of p-phenylene terephthalamide fibres were provided by Teijin Aramid B.V., Arnhem, The Netherlands: virgin aramid fibre without (VF) finish and an epoxy-amine coated aramid fibre (EF).¹⁸

The characteristics and structures of the two types of coupling agents (CA) are given in Table 3.1 and depicted in Figure 3.2. The sulphur was obtained from Sigma Aldrich, St. Louis, United States. The vulcanization accelerators n-Cyclohexyl-2-Benzothiazole Sulphenamide (CBS) and Diphenyl Guanidine (DPG) were provided by Flexsys, Brussels, Belgium.

The compounds were prepared based on the general mixing procedure described in Table 5.4.

Table 5.4 — Five stages mixing procedure.

1 st masterbatch stage: Brabender 350 S		
Rotor speed	110 rpm	
Initial temperature setting*	30/50°C	
Fill factor	70%	
Steps in mins:	0	Add polymer
	1	Add 50% fibre and silane*
	1.5	Add 50% fibre and silane
	2	Silica*, zinc oxide, stearic acid
	3	Sweep
	4	Dump @ ~120-140 °C
2 nd masterbatch stage – remix: Two-roll mill		
Add to mill to further disperse fibres		
Friction ratio	1:1.3	
Nip width	~0.03 mm	
Steps in mins:	6 min or 12 min*	
3 rd masterbatch stage		
Rotor speed	130 rpm	
Initial temperature setting	50°C	
Fill factor	70%	
Steps in mins:	0	Add 2 nd masterbatch
	3	Dump @ ~120-140°C
4 th masterbatch stage: Brabender 350 S		
Rotor speed	75 rpm	
Initial temperature setting	50°C	
Fill factor	70%	
Steps in mins:	0	Add batch from stage 2
	1	Add curatives
	3	Dump @ ~ 100°C
5 th masterbatch stage: Two-roll mill		
Orient fibres on the mill and make sheet		
Time	~2 mins	
	~0.05 mm	

*varied depending on experimental plan, see Tables 5.1 and 5.2.

The asterisk shows which factors were varied based on the descriptions in Tables 5.1 and 5.2. A five stages mixing procedure was used. The compounds were first mixed in a Brabender 350S internal mixer: stage 1. The internal mixer chamber volume was 390 cm³ and a fill factor of 70% was used. A fixed rotor speed was employed. In stage 1, at 0 min the raw elastomer was loaded into the mixer. After 1 min 50% of the fibres, coupling agents, zinc oxide and stearic acid were added, closely followed by the addition of the other 50%. After 2 min the silica*(see table 5.4), zinc oxide and stearic acid were added. After 3 mins the residue was swept back into the hopper. After 4 or 8 mins the compound was discharged, depending on factor H, level 1 or 2. The dump temperature was closely monitored in order to later link this to the coupling reaction between the silane and the fibres²⁴, or some unwanted side-reactions of the coupling agent with the elastomer matrix, in particular scorch. A second masterbatch

stage was employed to further disperse and homogenize the fibres on a two-roll mill during 6 or 12 mins. The nip width of the mill was determined with a measuring gauge: $\sim 30\ \mu\text{m}$.

By such a thin elastomer sheet undispersed fibres could well be visually detected. After a storage time of approximately 24 hours, the second stage masterbatch was returned to the internal mixing chamber: stage 3, and the next day mixed with the curatives up to a temperature of maximum 100°C at 75 rpm in 3 mins stage 4. The fibres in the compound were oriented in stage 5, on the mill with a nip width of $\sim 50\ \mu\text{m}$.

With increasing mixing time the chance of fibre breakage increases. Hintze¹² demonstrated that this effect plays a small role for highly reinforced elastomer compounds. As the compounds employed in this study are all non-reinforced and of the same basic composition, it is assumed that this effect may be neglected or is at most of the same magnitude in all compounds. The obtained orientation of the fibres is shown in Figure 5.3, prepared with a Leica microscope DMRX. The fibres are oriented in longitudinal direction of the milling direction.

Figure 5.3 — Orientation of the fibres, visualized with a Leica microscope DMRX.

Samples were vulcanized in a Wickert press WLP 1600 at 100 bar and 160°C to sheets of $110\times 110\ \text{mm}$, with a thickness of 2 mm, according to their t_{90} or $t_{90} + 2$ mins optimum vulcanization times, as determined with a Rubber Process Analyzer (RPA 2000) of Alpha Technologies, according to the procedure described in ISO standard 3417.

5.3.2 Characterization methods

The Mooney viscosity $ML(1+4)_{100^\circ\text{C}}$ of the compounds was measured using an Alpha Technologies Mooney 2000VS according to ISO 289. The RPA 2000 was used at 160°C to determine the curing properties: cure rate ($t_{90}-t_{s1}$) and torque increment (M_h-M_i), during 1 h maximum, at a frequency of 0.833 Hz and 2.79% strain. Stress-strain tests of all the vulcanized compounds were performed on a 3343 series Tensile Tester from Instron, at crosshead speed of 500 mm/min, according to ISO 37, to determine the tensile strength at break, strain at break, Young's Modulus (YM) and Tangent Modulus (TM). The TM at 20% and 50% strain are included to emphasize the typical shape of the tensile strength vs. strain curve at low deformations below $\sim 50\%$ for short-cut fibre-reinforced elastomers, reflected in some sort of yield strength and flattening off of the curve afterwards. Figure 5.4 shows the difference between the moduli in more detail. In this study the tangent modulus at 50% strain (TM_{50}) is discussed in detail, to emphasize the measured tensile stress vs. non-fibre-reinforced compounds at low strain. The hardness of the vulcanized compounds was measured using a Zwick 3150 Shore A Hardness Tester according to ISO 7619.

Each formulation run was mixed and duplicated and each separate mix was tested twice. Such an approach in repeating tests is needed to determine the degree of the experimental

variation, designated as the replicate error.

Figure 5.4 — Tensile test properties; difference between secant modulus, tangent modulus and stress at predefined strain.

5.4 Results

5.4.1 Mooney viscosity

To demonstrate the benefit of the conceptual way of graphing the responses, it is necessary to focus on measurable responses. First, a start is made with the processing and curing responses and later the mechanical properties are evaluated, like tensile strength at break, strain at break, moduli and hardness. As an example, the Mooney viscosity (MV) values can be evaluated by looking at the raw data in a replicate plot, as shown in Figure 5.6a. In this plot the factually measured Mooney values: $a_{k,1}$, $a_{k,2}$, $a_{k,3}$ and $a_{k,4}$, are plotted versus the number of each experimental run k . Value $a_{k,2}$ is a duplicated measurement of $a_{k,1}$ of compound 1 and $a_{k,4}$ is a duplicated measurement of $a_{k,3}$ of compound 2, both compounds are produced with the same control factor settings as for run 1 shown in Table 5.2.

Figure 5.6a shows that the results per compound: $a_{k,1}$ and $a_{k,2}$, resp. $a_{k,3}$ and $a_{k,4}$ are very similar and that some more variation between the compounds occurs, as might have been expected. M_k is the average of all 4 measurements $a_{k,i}$ per experimental run, see Equation (5.1):

$$M_k = \frac{1}{4} \sum_{i=1}^4 a_{k,i} \quad (5.1)$$

Since the variation in each experimental run is smaller than the spread in the averages of all runs, it can be concluded that the replicate error within a run does not complicate the overall data analysis. From here on the average M_k of the experimental run k is used to present the results.

The standard deviation s_k of the 4 $a_{k,i}$ is calculated as shown in Equation 5.2:

$$s_k = \sqrt{\frac{1}{3} \sum_{i=1}^4 (a_{k,i} - M_k)^2} \quad (5.2)$$

In Figure 5.5a S/N represents the Signal to Noise ratio 'the larger, the better', as calculated with Equation 5.3:

$$(S/N)_k = {}^{10}\log\left(\frac{M_k}{S_k} - \frac{1}{4}\right) \quad (5.3)$$

The average responses M_f for Mooney viscosity level 1 resp. level 2 for each control factor f , are plotted in Figure 5.5b. To obtain an impression of the sensitivity of the mean response M_f towards the selected level 1 or 2, a difference coefficient is defined as follows:

$$\Delta M_f = M_{f, \text{level } 1} - M_{f, \text{level } 2} \quad (5.4)$$

where ΔM_f is the difference coefficient and $M_{f, \text{level } 1 \text{ or } 2}$ the average per control factor of level 1 or 2. To enlighten this calculation, see the following as an example:

$$\Delta M_A = \Delta M_{A, \text{level } 1} - \Delta M_{A, \text{level } 2} = (M_1 + M_2 + M_3 + M_4 + M_5 + M_6)/6 - (M_7 + M_8 + M_9 + M_{10} + M_{11} + M_{12})/6 \quad (5.5)$$

The difference in S/N-ratio $\Delta(S/N)$ between levels 1 and 2 for a given control factor f is shown in Figure 5.5c and is calculated with Equation 5.6:

$$\Delta(S/N)_f = (S/N)_{f, \text{level } 1} - (S/N)_{f, \text{level } 2} \quad (5.6)$$

For example:

$$\Delta(S/N)_A = \Delta(S/N)_{A, \text{level } 1} - \Delta(S/N)_{A, \text{level } 2} = ((S/N)_1 + (S/N)_2 + (S/N)_3 + (S/N)_4 + (S/N)_5 + (S/N)_6)/6 - ((S/N)_7 + (S/N)_8 + (S/N)_9 + (S/N)_{10} + (S/N)_{11} + (S/N)_{12})/6 \quad (5.7)$$

Figure 5.5d shows the difference coefficient and $(S/N)_k$ for Mooney viscosity, calculated with Equations 5.4 and 5.6. Positive values correspond to larger effects for level 1 (factors A and J) and negative values for level 2 (factors B, C, D, H and I).

Figure 5.5 — Mooney viscosity (MU): a) raw data replicate plot, b) mean per level per factor, c) mean S/N ratios per level per factor and d) difference coefficients per factor.

For example: factor B, fibre concentration, shows the largest effect to increase the Mooney viscosity when 15 phr fibre is added (level 2), vs. 5 phr (level 1). The $\Delta(S/N)$ ratio difference also points towards level 2, as having the largest effect and is additionally rather large compared with the other factors. This effect is commonly seen in the literature.²⁵ Factor J, milling time on the two-roll mill, shows a large effect towards 6 mins (level 1) vs. 12 mins (level 2).

This may be assigned to polymer breakdown during the mixing stage or a bad fibre dispersion.²⁶ The effect of factor C, a silica concentration of 10 phr (level 2) vs. 0 phr (level 1), increases the MV , but the $\Delta(S/N)$ favours level 1. For factor A, fibre type, virgin fibre (level 1) produces a higher MV than epoxy-coated (level 2). The addition of coupling agent TESP, factor D, has an increasing effect on the Mooney value: 1 phr (level 2) vs. 0 phr (level 1). This is an indication that the coupling agent TESP has reacted in some form or the other in the mixing stage.

5.4.2 Curing behaviour

The curing behaviour can be evaluated by looking at the data of $t_{90-t_{s1}}$ and M_h-M_l . The raw data of the $t_{90-t_{s1}}$ measurements are presented in Figure 5.6a. Figure 5.6a shows that the highest $t_{90-t_{s1}}$ are found in the experimental runs 5 and 9. Both compounds contain low dosage

curatives, factor G level 1 and double internal mixer mixing time level 2. Figure 5.6b shows the mean $t_{90}-t_{s1}$ calculated per level per factor. The largest difference between the levels can be seen, besides for E, G and H, in particular for the factors C, and D: silica concentration, coupling agent NXT concentration. The S/N ratios are given in Figure 5.6c. The highest S/N ratio differences are found for factors D and E, coupling agent additions, and factor J, milling time and factor C, silica addition. The difference coefficients are summed and shown in Figures 7d. The highest influence is caused by factor G (28%): curatives concentration. Factor C level 1, the formulation containing no silica, and G level 1, the formulation with the standard low curatives concentration, show their effects in the longest $t_{90}-t_{s1}$ value. The fibre concentration (factor B) has practically no influence on the $t_{90}-t_{s1}$ values. Both coupling agents, factors D and E, have a large, shortening effect (level 2) on the curing speed $t_{90}-t_{s1}$. Factor A, coated fibre has a slight prolonging effect on the $t_{90}-t_{s1}$ vs. virgin fibre. Factors H, mixing time of 8 min (level 2), and factor I, high mixer temperature setting of 50°C (level 2) also has a prolonging effect on the $t_{90}-t_{s1}$.

Figure 5.6 – $t_{90}-t_{s1}$ (mins): a) raw data replicate plot, b) mean per level per factor, c) mean S/N ratios per level per factor and d) difference coefficients per factor.

Figure 5.7a shows the raw data of the M_h-M_l measurements. This figure shows that the highest M_h-M_l values are found for experimental runs 4, 6 and 12. These compounds have in common (see Table 5.2) that they contain a high concentration of fibres (factor B) and a double amount of curatives (factor G). Figure 5.7b shows the mean M_h-M_l calculated per level per factor. The largest difference between the levels can be seen for factors B and G. The S/N ratios are given in Figure 5.7c. The highest S/N ratio differences are seen for the initial temperature of the internal mixer (factor 1). The differences between levels 1 and 2 (coefficients) are summarized in Figure 5.7d. The mixing time in the internal mixer, factor H, shows large preference towards level 2. Factor J, milling time, shows no preference towards a longer milling time, level 1. The addition of 10 phr silica shows only a minimal effect on the M_h-M_l . Both coupling agents, factors D and E, show a small effect on the M_h-M_l value: D, TESPd decreasing and E, NXT increasing.

Figure 5.7 — $M_{II}-M_I$ (dN·m): a) raw data replicate plot, b) mean per level per factor, c) S/N ratio per level per factor and d) difference coefficients per factor.

5.4.3 Mechanical properties

Figure 5.8a shows the replicate plot of the tensile strength at break results. The highest strength at break values are found for runs 4, 6 and 10, 11, 12. All these runs (see Table 5.2) correspond with a fibre concentration (factor B) of 15 phr of fibre vs. 5 phr of fibre. This effect is also observed in Figure 5.8b. The second largest difference between the levels is seen for factor G, curative concentration. Followed by factor F, fibre orientation. The S/N values in Figure 5.8c show the largest difference between factors B fibre concentration, factor C silica concentration, F orientation and factor H mixing time in the internal mixer. Figure 5.8d is constructed out of 5.8a-c and shows the different coefficients of the tensile strength at break. Factor D, use of TESPd coupling agent, increases the strength at break slightly and factor E, addition of NXT shows no significant effect. On the other hand, the factor effect A, epoxy-coated fibres seem to have a clear effect (10%) on the tensile strength at break.

Figure 5.9a shows the raw data for the tensile strain at break (%). The S/N ratio values are enlarged and shown in the right upper corner of Figure 5.9a. The S/N ratio values show a large deviation between the experimental runs. A low S/N ratio indicates a large variation in the raw data per run, which is clearly observed in Figure 5.10a for runs 1 and 4. All these compounds contain virgin fibre, factor A level 1 and a single curatives system, factor G level 1. The strongest effect (Figure 5.9b) on the tensile strain at break is for factors A, B, C, D, G and J. Factor A, virgin fibre type, level 1 shows an S/N ratio difference, shown in Figure 5.9c, in the opposite direction (level 2). For factor B, fibre concentration of 5 phr (level 1) and factor J, longer milling time, level 2, the $\Delta(S/N)$ points towards higher significance, less experimental scatter for the lower fibre concentration. For factor C, silica addition (level 2), factor D, addition of TESPd and factor G, single curatives concentration (level 1), the $\Delta(S/N)$ ratios point towards opposite directions (see Figure 5.9d) vs. their ΔM 's; the significance of the factor effects is equally good for both levels, as reflected in the small difference in $\Delta(S/N)$ ratios. Orientation of the fibres, factor F, tensile test in the longitudinal direction (level 1), shows no significant effect.

The Young's modulus (YM) is difficult to accurately measure in an elastomeric compound, because of difficulties with tensile tester zero-settings. However, when the results are averaged in the context of this DoE, they turn out to be reasonably good. The results for YM are shown in Figure 5.10a-d. The tangent modulus at 50% strain was not possible to

construct because the whole data set broke already before 50% strain. The effects at 20% strain are already relatively constant in relation to the *YM*, see Figure 5.11a-d, confirming the main effect of fibre loading at low strains. Figure 5.10d shows for factor B, fibre concentration, the largest effect to increase the *YM* when 15 phr fibre is added (level 2), vs. 5 phr (level 1). The $\Delta(S/N)$ ratio difference points towards level 2. Higher fibre dosage gives less scatter in the data. Factor H, internal mixer mixing time of 4 mins (level 1) produces a higher *YM* difference vs. 8 mins (level 2) and the $\Delta(S/N)$ ratio indicates a small spread in the data. For factor A, fibre type, epoxy-coated fibres (level 2) produce a higher *YM* than virgin fibres (level 1). The effect of C, no silica added (level 1) vs. 10 phr (level 2), increases the *YM*, and also the $\Delta(S/N)$ favours level 1. Adding coupling agent NXT factor E has a small increasing effect on the *YM* value: 1.5 phr (level 2) vs. 0 phr (level 1). Factor D TESPd shows no significant effect on the *YM*. This is an indication that coupling of the fibres and subsequent reaction with the elastomer have occurred, more pronounced for NXT than for TESPd. For factor G, vulcanization system, the double amount (level 2) produces a higher *YM* vs. single (level 1) as expected. The signal of factor I, initial temperature setting of the internal mixer, shows a preference for 50°C (level 2). Factor J, milling time on the two-roll mill, shows an effect towards 12 mins (level 2) vs. 6 min (level 1).

Figure 5.8 — Tensile strength at break (MPa): a) raw data replicate plot, b) mean per level per factor, c) S/N per level per factor and d) difference coefficients per factor.

Figure 5.9 — Tensile strain at break (%): a) raw data replicate plot, b) mean per level per factor, c) S/N per level per factor and d) difference coefficients per factor.

d)

Figure 5.10 — Young's modulus (MPa): a) raw data replicate plot, b) mean per level per factor, c) S/N per level per factor and d) difference coefficients per factor.

a)

b)

Figure 5.11 — Tangent modulus at 20% strain (MPa): a) raw data replicate plot, b) mean per level per factor, c) S/N ratio per level per factor and d) difference coefficients per factor.

Hardness data are presented in Figure 5.12a-d. Higher amounts of fibres and silica additions increase the hardness significantly, as expected. NXT decreases the hardness slightly. NXT can couple only to the fibre but cannot react with a second $\text{Si}(\text{OEt})_3$ -group towards another fibre. TESPd can do that. TESPd increases the hardness, just like the increase in Mooney viscosity. An increased curing time did not affect the hardness. This indicates that between t_{90} and $t_{90} + 2$ mins there is not much difference anymore in the degree of cure obtained.

a)

b)

c)

Figure 5.12 — Hardness (Shore A): a) raw data replicate plot, b) mean per level per factor, c) *S/N* ratio per level per factor and d) difference coefficients per factor.

5.5 Discussion

5.5.1 Understanding the relative importance of controllable factors on processability and mechanical properties

The Mooney viscosity (*MV*) results were calculated with the qualifier ‘the higher, the better’, although in general this is not always preferred in practice, because of possible processing problems. The *MV* difference coefficient indicates that primarily the fibre concentration (factor B, level 2) and short milling time (factor J, level 1) with a consequently lower polymer breakdown, together contribute for about 64% to an *MV* increase in the DoE. The other 36% are mainly influenced by the choice of coated vs. virgin fibres (factor A, 10%) in combination with the use of coupling agent (factors D, 10%) and silica (factor C, 11%). There is no plasticizing effect caused by the coupling agents. Or this could mean some premature scorch for TESP (factor D). NXT shows no premature scorch and only coupling occurred with the coating. TESP, having two Si(OEt)₃-groups, might create some silane bridges in addition, which NXT cannot do because of its single Si(OEt)₃-group. The *MV* data are not sensitive enough to separate/detect coupling from the scorch; the DoE is not able to resolve this question, which makes it a typical noise factor. The decrease in the *MV* (factor A, level 2), which occurs because of the coating, may be a result of the coating itself.²⁷

The use of fibre generally results in a higher vulcanization torque value $M_h - M_i$. The $M_h - M_i$ is most pronounced when no silica is added (factor C, level 1) and at low curatives concentration (factor G, level 1). Factors C, D, E and G contribute with ~70% to the $t_{90} - t_{s1}$ system. The combination of silica and coupling agents has an accelerating effect. On the other hand, the impact of the addition of the coupling agents is small for the difference coefficient of the torque $M_h - M_i$. Just like in Figure 5.5d for the *MV*, the coupling agent (level 2) effect is not prominently represented in the torque results. Factor B, fibre concentration and factor G, curative concentration, are contributing for ~64% to the $M_h - M_i$.

The effects of short fibres are most clearly seen in properties at low strains²⁸, like schematically shown in Figure 5.4. After the yield point, the interaction between fibres and elastomer becomes too weak and the curve follows the elastomer path. A yield point was not observed for all the compounds and thereby it couldn't be used as a response. The DoE shows that the overall strength at break is primarily improved: Figure 5.8d, while the strain at break decreases: Figure 5.8d for factor A, epoxy-coated fibre preferred: level 2; B, fibre

concentration level 2 and G, curatives concentration level 2. The addition of silica: factor C, level 2; coupling agents TESP level 2; factor J, long milling time, level 2, increases the strain at break. This combination points to a beneficial effect in the use of some silica and the coupling agent TESP, as might have been expected on the basis of the use of silica as a reinforcing filler together with coupling agents in modern passenger tyre technology¹⁴. The combination of coupling agent NXT with the epoxy-coated fibres shows a minor positive effect vs. no coupling agent for the tensile strength at break. However, the logical sequence is a reduction in tensile strain at break, where the virgin fibres, factor A, favour higher tensile strains. It can be taken as an indication of some better interaction, whether chemical or physical, between the epoxy-coated fibres and elastomer via the NXT coupling agent.

Comparing Figures 5.8d and 5.10d shows that for all factors the strength at break increases, also the Young's modulus rises, except for factors B, C, E and K. Factors B and E, addition of coupling agents, show a relatively low effect on the (S/N) ratios. Leaving the silica out (factor C, level 1), increases the *YM* but lowers the strength and strain at break. As it turns out, the addition of silica increases the strain at break substantially due to the discussed coupling reaction as proposed in the introduction. This is also confirmed by the difference coefficient in the *TM*₅₀ data, already representing higher strains: Figure 5.11d shows that factor C, 10 phr of silica, favours level 2 instead of level 1. All the other factors in Figure 5.11d contribute to an increase of the *TM*₅₀ in the other direction or in a much lower effect than for *YM*. This means that before 50% strain the main events happen in properties change. For example, the effect of TESP is not significant at *TM*₂₀ and for strain at break, and for the coupling agent NXT the opposite is visible (level 1). This is a clear indication of interaction. The addition of high amounts of fibre has a large effect on the moduli, but significantly decreases the strain at break as well. Overall, the effects of the coupling agents are weak compared to other factors, like fibre concentration, fibre orientation and silica usage.

The strength at break, strain at break and *YM* difference coefficients of factor J milling time, seem to be favoured by a longer duration: level 2. These better tensile properties are clearly related to a better dispersion of the fibres. This makes it unlikely at the same time that fibre breakage has a significant negative effect on the results. The low $\Delta(S/N)$ of factor H, mixing time, shows a large spread and minimizes the importance of this effect.

5.5.2 Optimal mechanical properties

A DoE has to be completed with a confirmation run. A grand total average over all experimental runs can be calculated with Equation 5.8:

$$M_{total} = \frac{1}{12} \sum_{k=1}^{12} M_k \quad (5.8)$$

A prediction of the possible improvement for a particular response can then be made with the following equation:

$$\varepsilon = M_{total} + \sum_{f=1}^{12} (M_{f, optimum \text{ level 1 or 2}} - M_{total}) \quad (5.9)$$

Where ε is the overall optimized response and $M_{k, \text{ level 1 or 2}}$ is the best level (highest average value) of the two *M*_{f, optimum levels 1 or 2}. In Table 5.4 these results are summarized. The table shows the optimal ε obtainable for each given response, by selecting the best level of each controllable factor. The optimization results show very large improvements in comparison with the average *M*_{total} values. To experimentally validate the calculated results,

an optimization run was performed for a maximum Young's modulus: the optimized tensile test curve, presented in Figure 5.13, is based on the highest mean effect results for YM. The M_{total} is used for comparison. An improvement is found of ~330% for the YM and ~320% for the TM_{20} . This proves that this DoE does indeed enable identifying the most important properties and finding the optimum compound, despite the sometimes large differences in $\Delta(S/N)$ ratios.

A limitation of the DoE used in this study is its sensitivity to the optimum coupling temperature. The dump temperature of the run differs between 120 and 140°C. A reaction temperature study needs to be done to get the optimum coupling temperature.

Table 5.5 — Optimal responses for given control factors.

Factors	MV	$t_{90}-t_{s1}$	M_h-M_l	Stress	Strain	YM*	TM_{20}	TM_{50}	Hard.
Fibre type:	1	2	2	2	1	2	2	n/a	2
Fibre conc.:	2	2	2	2	1	2	2		2
Filler:	2	1	1	2	2	1	1		2
CA TESP:	2	2	1	2	2	0	0		2
CA NXT:	0	2	2	1	0	2	2		1
Orientation**:	-	-	-	1	0	1	1		-
Curatives conc.:	0	1	2	2	1	2	2		2
Internal mixer mix. time:	2	2	1	1	2	1	1		1
Tin:	2	2	2	2	1	2	2		1
Mill mix. Time	1	0	2	0	2	2	2		0
Curing time:	-	-	-	2	1	1	1		1
M_{total}	41	4	6	5	206	9	1.5		96
ϵ	62	11	10	8	640	29	5.0		87
$(\epsilon 100)/M_{total}$ (%)	151	243	167	161	310	332	324		128

Figure 5.13 — Tensile curve optimized for YM sample vs. M_{total} values of some response factors.

5.6 Conclusions

This study concerns the understanding of the relative importance of controllable factors on the processability and mechanical properties, and the optimization of the performance of short fibre-reinforced elastomers with the help of a DoE approach. A Taguchi conceptual way

of graphing approach in DoE is a valuable tool to investigate the relative importance of controllable factors on the processability and mechanical properties of short-cut fibre-reinforced elastomers. Every factor is compared based on equal footing, which highlights the relative importance of each factor's response. The experimental objective was to determine the impact of both compounding ingredients and process parameters on the mechanical properties of the resulting vulcanizates.

The results clearly show that some factor effects are fully or partially overshadowed by other factors: fibre concentration and curatives concentration grossly overrule all other factors in their response to the Young's modulus. To increase the effect of the factors which are now overshadowed, the difference between levels 1 and 2 needs to be increased. For instance, to investigate the effect of silane coupling agents, factor E (NXT content) needs to be varied, while the other factors are kept constant. To obtain a large increase in mechanical properties, in particular at low strains, *YM*, the fibre concentration, rather than the curing time, needs to be increased by 2 minutes. For each mechanical property response an optimization prediction was calculated on the basis of the mean values of all the runs, varying between 126 and 300% improvement. A confirmation run confirmed this optimization for the *YM* and *TM₂₀*. The effect on the *YM* and *TM₂₀* can be increased with 330% and 320%, just by choosing the higher level value in the DoE factor setting. The eventual mechanical properties reached in the confirmation run are comparable to the predicted results, confirming the value of the DoE approach. This method is also suitable to visualize smaller effects, just by changing the lower level, as this will influence ϵ .

5.7 References

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6 Understanding the behaviour of the coupling agents TESPT and Si 363 in short-cut aramid fibre-reinforced elastomer

6.1 Abstract

The coupling agent mercaptopropyl-mono-ethoxypolyether-silane (Si 363) has been developed for the tyre industry, as a successor to coupling agent *Bis*-(triethoxysilylpropyl) tetrasulphide (TESPT). In this study the coupling agents TESPT and Si 363 are compared to each other in a standard SBR formulation, however, not in the presence of silica but for adhesion-active epoxy-coated short-cut aramid fibres.

Comparing TESPT with Si 363 with the help of a Design of Experiments approach gives a better understanding of the relevant factor effects, in order to judge and to quantify the relative importance of all varied factors on measured properties. Factors like fibre concentration, the vulcanization system concentration and the concentration of the coupling agents control the Young's modulus of the elastomer compounds most significantly. Optimization towards a higher Young's modulus of the elastomeric compounds can be obtained by adjustments in the factors leading to the optimum level.

6.2 Introduction

Poly- and disulphide silanes like *Bis*-(triethoxysilylpropyl)-tetrasulphide TESPT and *Bis*-(triethoxysilylpropyl) disulphide TESP are effective coupling agents in silica reinforced passenger tyre tread compounds.¹⁻³ The rubber world is interested in the alternative coupling agent mercaptopropyl-mono-ethoxypolyether-silane (Si 363), because besides the fact that it can improve the rolling resistance of silica tyres by 10%, it also provides a solution for the ecological need to decrease the ethanol emission by 80% vs. TESPT during mixing.⁴

The molecular structure of Si 363 is shown in Figure 6.1; Si 363 contains one ethoxy group, two polymeric, amphiphilic substituents and a free mercapto-group.

Figure 6.1 — Molecular structure of a) Si 363⁴; b) TESPT and c) Si 263.

The reaction mechanism of the coupling agent with silica proceeds via the ethoxy- and/or polyether- substituents on the silicon atom. They are cleaved during the mixing process and the silanes bond covalently to the reactive silanol-groups on the silica-surface. The long polymeric chains in Si 363 are polar, which ensures a high affinity with a polar surface like

silica, which guarantees a fast absorption and reaction on the reactive surface. Klockmann et al.⁴ claimed that this reaction compensates for the steric hindrance given by the bulkiness of the polymeric chains, e.g. it acts as a shield covering the silica surface, which improves the hydrophobation. This shielding/hydrophobation effect is shown in Figure 6.2.

Figure 6.2 — Si 363 connected to a reactive silica surface.⁴

Besides the hydrophobation of the reactive silica surface, the long chains generate a certain steric hindrance for the mercapto-group; its reaction with accelerators and sulphur is slowed down. Consequently, a higher scorch safety together with reinforcement is claimed by Klockmann et al.⁴. The mercapto-group is responsible for an efficient coupling of this silane to the elastomeric chains, because it has a yield of almost 100% due to a changed coupling mechanism, whereas a silane like TESPT only reaches approximately 50%.^{5, 6}

In the present study the coupling agent Si 363 is compared with the coupling agent TESPT, not in reaction with silica, but with adhesion-activated aramid (poly-p-phenylene-terephthalamide) fibres instead. A synthetic styrene-butadiene rubber (SBR) was chosen, based on a 'green tyre' tread formulation for passenger cars. First, 3 mm short-cut aramid fibres without finish were used: virgin fibres (VF). Aramid fibres are generally very inert and consequently difficult to adhere to. The interfacial strength of the surface of an aramid fibre with a rubber can further be influenced by two main elements: an adhesive coating and an agent which can interact with this coating, a coupling agent. To make sure that a proper interaction could be established such a coating was selected that has the ability to chemically react with a silane coupling agent. These aramid fibres were treated with an epoxy coating (EF) onto the finish. During the coating reaction epoxy groups reacted away and OH-groups were formed.⁷ Based on the work of De Lange et al.⁸ increases of oxygen-atoms on the fibre surface from ~11% (theoretical percentage of aramid) to ~22% were achieved with epoxy-amine coating, based on XPS measurements. To improve the fibre-matrix interfacial interaction TESPT and Si 363 were introduced. Both silanes differ in molecular weights: 539 vs. 968 g/mol, and coupling efficiency due to the number of ethoxy groups. Because polyether-alcohol can be released as well, the dosage applied was based on ethoxy-isomolar amounts. The silane coupling agent concentration is therefore varied between 0 and 12.3 phr for Si 363 and 0 and 1.1 phr for TESPT. Both coupling agents are also compared on equal footing with the sulphur concentration.

Figure 6.3 proposes a mechanism for the TESPT coupling agent reaction with the adhesion activated fibres during mixing. Under vulcanization conditions a chemical link

between the silane and rubber is created, see Figure 6.4. The combined fibre-silane-elastomer couplings lead to an improved reinforcement of such compounds.⁹⁻¹¹

For the activation of the fibre-elastomer coupling, curatives such as elemental sulphur and accelerators play an important role in the silane elastomer reaction.¹² In the presence of elementary sulphur, the poly-sulphide of the silane is activated due to the insertion of elemental sulphur, like also shown in Figure 6.4. According to Debnath et al.¹³ the TESPT coupling agent can also reversely act as a sulphur donor. So, the elementary sulphur in the vulcanization package, together with the sulphur taken up and released from the coupling agent, 'plays an intricate dance' in both the polymer cross-linking and polymer-fibre coupling.

Figure 6.3 — Proposed reaction mechanism TESPT a) primary reaction and b) secondary reaction.

Figure 6.4 — Silane-elastomer coupling in the presence of accelerator, * the adhesion active fibre.

To confirm this reaction mechanism an extra test is done with (mercaptopropyl)-triethoxysilane Si 263, see Figure 6.1c. This silane coupling agent contains a very reactive thiol-group, which readily reacts with the polymer, but may also react with the fibre coating. By comparing the results with a bifunctional mercapto silane like Si 363, which can only react at one side with the fibre and at the other side with the elastomer, some indication of the reaction mechanism might be obtained.

In this study the coupling agent Si 363 is compared with coupling agents TESPT and Si 263. The relative importance of controllable factors on the processability and mechanical properties is investigated in detail. The formulation is subsequently optimized based on these

relevant factors. The surface activity of the aramid fibre is further enhanced with the extra addition of a blocked isocyanate to the system.

6.3 Experimental

6.3.1 Design of Experiments, materials and compounds preparation

A Design of Experiments (DoE) approach was chosen, the Taguchi method for a robust design as described in the work of Vleugels et al.¹⁴ and in detail in Chapter 5 of this thesis. The control factors varied in this DoE are shown in Table 6.1. The factors D and E in the present study are the coupling agents: factor D, TESPT and factor E, Si 363. The experimental plan is presented in Table 6.2.

Table 6.1 — Taguchi design: varied control factors.

Factor <i>f</i>		Level 1	Level 2	
A	Fibre type:	Not coated	Coated	
B	Fibre conc.:	5 phr	15 phr	
C	Filler:	0	10 phr silica	
D	Coupling with TESPT:	0	1.1 phr	
E	Coupling with Si 363:	0	12 phr*	
F	Orientation**:	0°	90°	Fibre direction
G	Curatives conc.:	single	double	
H	Internal mixer mixing time:	4 mins	8 mins	at 110 rpm
I	Internal mixer T_{in} :	30°C	50°C	
J	Mill mixing time in stage 2:	6 mins	12 mins	
K	Curing time:	t_{90} mins	$t_{90} + 2$ mins	at 160°C

Corresponds to equal amounts of ethoxy functional groups of TESPD. ** 0° longitudinal orientation and 90° transverse rel. to milling direction

The fibre-reinforced elastomer compounds contain a variety of ingredients and involve various processing steps. A standard experimental plan with L_{12} array of experiments was created, as shown in Table 5.2. In this table each row corresponds to one compound and processing combination.

The standard rubber compound composition used in this study is shown in Table 6.2. The quantities are in parts per hundred rubber (phr). The ingredients are the same as given in the previous chapters. The system is further tested with a (mercaptopropyl) tri-ethoxysilane: Si 263 from Evonik Industries, Germany.

Table 6.2 — Standard rubber compound composition (phr).

Formulation*	(phr)
S-SBR	100
Coupling agent TESPT or Si 363	1.1/12.3
Silica	0/10
Zinc oxide	2.5
Stearic acid	1.5
Short fibre	5/15
	VF/EF
Sulphur	1.4 or 2.8
CBS	1.7 or 3.4
DPG	2.0 or 4.0

*vary depending on experimental plan: see Tables 5.2 and 6.1.

The compounds were prepared based on the general mixing procedure described in detail in Table 5.4. The optimized mixing sequences, results from Table 6.1, are further tested with a (mercaptopropyl) tri-ethoxysilane (Si 263) from Evonik Industries, Germany. The pertinent mixing sequences are shown at the end of this chapter in Table 6.4.

6.3.2 Characterization methods

The characterization methods for Mooney viscosity, RPA, Hardness, tensile test and calculations necessary for the conceptual graphing of the results of the DoE are described in detail in Chapter 5.

6.4 Results

6.4.1 Mooney viscosity

The raw data of the Mooney viscosity (*MV*) measurement results are presented in Figure 6.5a. It shows that the highest Mooney viscosity is found for experimental runs 5 and 10. Both compounds contain a high amount of fibres of 15 phr, level 2; 10 phr silica, level 2; and no coupling agent TESPT nor Si 363; all indicators for a higher *MV*. Figure 6.5b shows the mean Mooney value calculated per level per factor. This figure enlarges the effect of each factor and by visual observation the largest difference between the levels can be seen for factors B and C. The signal to noise ratios are given in Figure 6.5c. The other factor differences can be better pictured in a separate graph, as shown in Figure 6.5d. Positive values correspond to larger effects for level 1 (factors A, D, G and J) and negative values for level 2 (factors B, C, E, H and I). For example: factor B, fibre concentration, shows the largest effect (~30%) to increase the *MV* when 15 phr fibre is added (level 2), vs. 5 phr (level 1). The effect of C, a silica concentration of 10 phr (level 2) vs. 0 phr (level 1), increases the *MV* (~20%). The largest spread per experimental run is found for runs 5, 6 and 10, see Figure 6.5a, resulting in a low signal to noise ratio (*S/N*). The $\Delta(S/N)$ ratio difference of factor B, in Figure 6.5d, fibre concentration, points towards level 2, but the $\Delta(S/N)$ for both levels 1 and 2 differ practically nothing compared with the other factors. The $\Delta(S/N)$ effect of C, silica concentration, favours level 1.

Figure 6.5 — Mooney viscosity (MU): a) raw data replicate plot, b) mean per level per factor, c) S/N per level per factor and d) difference coefficients per factor.

Adding coupling agent TESPT, factor D in Figure 6.5d, has a decreasing effect on the Mooney value: 1.1 phr (level 2) vs. 0 phr (level 1). This is an indication that the coupling agent acts somewhat as a plasticizer and as a hydrophobation agent. On the one hand, coupling agent Si 363, factor E, increases the MV , level 2. Both have a small S/N ratio which makes these results qualitatively less significant. On the other hand, for the factors G, H, I and J the effects seem to be more significant. Factor G, curatives concentration, low (level 1) produces a higher

MV vs. high (level 2). Factor H, internal mixer mixing time of 8 mins (level 2) produces a higher *MV* difference vs. 4 mins (level 1). This indicates that a better dispersion is obtained at longer mixing times, but the $\Delta S/N$ ratio is rather low, so this effect is of little significance. Factor I, initial temperature of the internal mixer, shows a preference for 50°C (level 2). Factor J, milling time on the two-roll mill, shows a small effect towards 6 mins (level 1) vs. 12 min (level 2). Increasing the milling time can contribute to polymer breakdown during the mixing process.¹⁵ For factor A, virgin fibre (level 1) produces a higher *MV* than epoxy-coated fibres (level 2). This indicates that the coating on the fibres has a small effect on the *MV* values, which effect is emphasized because of the $\Delta(S/N)$ ratio points in the same direction as the preferred level.

6.4.2 Curing behaviour

The curing behaviour $t_{90}-t_{s1}$ can best be evaluated by means of the plots in Figures 6.6a-d. Figure 6.6a shows clear differences in low and high curing speed, e.g. runs 3, 4, 5 and 9. The only factor they have in common, see Tables 6.1 and 5.2, are factor E, coupling agent Si 363 of 12.3 phr, level 2. This effect is also seen in Figure 6.6b, for factor E. Other factors which show a large difference between level 1 and level 2 are factors D, addition of coupling agent TESPT and factor G curative concentration decrease. So these factors have a high increasing effect on the curing speed $t_{90}-t_{s1}$. Figure 6.6c shows the *S/N* ratio results. The largest effects are seen for factor E, the addition of no coupling agent Si 363, level 1, factor H internal mixer mixing time of 4 min, level 1 and factor J longer milling time, level 2. Figure 6.6d summarizes the differences between level 2 and level 1 of ΔM and $\Delta(S/N)$ ratio values. The fibre type (factor A) and milling time (factor J) have practically no influence on the $t_{90}-t_{s1}$ value. Factor C level 1, the formulation containing no silica shows a small effect in the $t_{90}-t_{s1}$ value. Factor B, low fibre concentration, produces a small positive effect on the $t_{90}-t_{s1}$ vs. higher loadings.

a)

Figure 6.6 — $t_{90}-t_{s1}$ (mins): a) raw data replicate plot, b) mean per level per factor, c) S/N per level per factor and d) difference coefficients per factor.

Figure 6.7a shows the raw data of the M_h-M_l values. The lowest values of the torques differences values, cross-link density are for runs 1, 2, 3 and 9. The only factor they have in common, see Tables 6.1 and 5.2, is factor B, low fibre concentration. This effect is also seen in Figure 6.7b, for factor B. Another factor which shows a large difference between level 1 and level 2 is factor G, curatives concentration. So for these factors, level 1 low curatives concentration has a strong decreasing effect on the torque difference value. Figure 6.7c

shows the S/N ratio results: factor B shows a strong effect in the level 1 direction. Figure 6.7d summarizes the results of Figure 6.7b and 8c. Factor G shows a $\Delta(S/N)$ ratio difference in the same direction as the factor effect: level 2 factor D, addition of TESPT, level 2, increases the M_h-M_l (12%), while factor E, the addition of 0 phr Si 363, level 1, shows a small increasing effect on the M_h-M_l value. The M_h-M_l difference effects of factor H is rather large compared to the other factors and the effect of factor I, internal mixer initial temperature, is lower. The fibre concentration, factor B, has, as expected, a large influence on the M_h-M_l .

a)

b)

c)

Figure 6.7 — M_h-M_l (dN·m): a) raw data replicate plot, b) mean per level per factor, c) S/N ratio per level per factor and d) difference coefficients per factor.

6.4.3 Mechanical properties

Figure 6.8a shows for runs 6, 7 and 11 the highest tensile strength values. The only factors which these runs have in common are the addition of TESPT, D level 2, and no Si 363 coupling agent, level 1. This observation is the same in Figure 6.8b. The largest differences are found for factors B, C, D and E. The mean S/N ratio values per level are shown in Figure 6.8c. The largest differences are found for factor E and H. The difference coefficients of the tensile strength at break are shown in Figure 6.8d. Positive values correspond to a larger effect on tensile strength at break for level 1 (factors E, F, H, I and K) and negative values for level 2 (factors A, B, C, D, G and J). For example: leaving out the coupling agent, factor E Si 363, has a significant (23%) positive effect on the tensile strength at break: 0 phr (level 1) vs. 12 phr (level 2); so coupling agent Si 363 decreases the tensile strength; on the other hand, coupling agent TESPT increases the strength at break. The effect of C, a silica concentration of 10 phr (level 2) vs. 0 phr (level 1), increases the tensile strength at break (16%), and the $\Delta(S/N)$ favours level 2.

Figure 6.8 — Tensile strength at break (MPa): a) raw data replicate plot, b) mean per level per factor, c) S/N per level per factor and d) difference coefficients per factor.

Factor B, fibre concentration, shows an effect (15%) to increase the tensile strength at break when 15 phr fibre is added (level 2), vs. 5 phr (level 1). An increase in tensile strength when more fibre is added is commonly seen in the literature.¹⁶ The $\Delta(S/N)$ ratio difference points towards level 1. Factor J, milling time on the two-roll mill, shows a decreasing effect on the tensile strength for 12 mins (level 2) vs. 6 min (level 1). Increased milling leads to a better dispersion of the fibres.

Figure 6.9a presents the raw data for the elongation at break; y-axis is added in the figure to enlarge the S/N data. The S/N ratio has a certain distribution, which is practically not visible in the original graph. The lowest strain at break values are found for runs 4, 6, 11 and 12. The only factor these 4 runs have in common is a high fibre loading, factor B, level 2 and a low S/N ratio, compared to the other runs, Figure 6.9b confirms that the factor B (fibre loading at 15 phr) has the highest influence, together with factor C, silica concentration and factor G, curatives concentration. Figure 6.9c shows the $\Delta(S/N)$ ratio for level 1 and 2 for the strain at break vs. the control factors. Figure 6.9d shows the M_i difference coefficient results of the strain at break on the right y-axis and the S/N difference ratios are shown in the right y-axis. The results show that factor B, fibre concentration, factor C, silica concentration, factor E coupling agent Si 363 concentration and factor G, curatives concentration, show the largest effects on the strain at break. The difference coefficients for the S/N ratios for C, D, E, F, G, I, J and K are very low. This indicates the large spread of the raw data, making them of little significance.

Figure 6.9 — Tensile strain at break (%): a) raw data replicate plot, b) mean per level per factor, c) S/N per level per factor and d) difference coefficients per factor.

Figure 6.10a shows the raw data replicate plot of Young's modulus (YM). The figure shows the highest YM values for run 6 and run 11. Both runs have the following factors in common: B, high fibre concentration level 2, factor D coupling agent TESPT level 2, factor E no coupling agent Si 363 level 1, factor F orientation level 2 and factor H internal mixer mixing time of 4 min level 1. Figure 6.10b shows the highest difference between levels 1 and 2 for the same factors: B, D, E, F and H. Figure 6.10c shows the S/N ratio of the corresponding factors for YM for level 1 and 2. A clearly improved S/N ratio pointing in the same direction as observed for the preferred level is found for factor A, fibre type level 2, factor D addition of coupling agent TESPT and factor I low internal mixer temperature level. Figure 6.10d shows the difference coefficients for the Young's modulus. Factor E, coupling agent Si 363 concentration, shows the largest effect (24%) to increase the YM for no coupling agent Si 363 added (level 1) vs. 12.2 phr (level 2). On the other hand, the $\Delta(S/N)$ ratio difference shows a large preference towards level 2. The addition of coupling agent TESPT has a strong increasing effect on the YM value: factor D 1.1 phr (level 2) vs. 0 phr (level 1). Factor B, fibre concentration, increases the YM when 15 phr fibre is added (level 2), vs. 5 phr (level 1). The $\Delta(S/N)$ ratio difference points towards level 1, there is less scatter in the data. Factor H, internal mixer mixing time, of 4 mins (level 1) produces a higher YM difference vs. 8 mins (level 2), but the $\Delta(S/N)$ points towards level 2 ratio, indicating a larger spread in the data.

Hardness raw data results are shown in Figure 6.11a. The lowest hardness values are

measured for run 3 and run 8. Both contain factor B low fibre concentration level 1, factor C silica concentration level 2, factor E Si 363 concentration level 2, factor H internal mixer mixing time level 1 and factor K higher curing time, level 2. Figure 6.11b shows the mean values and Figure 6.11c the *S/N* ratios between level 1 and 2. The difference coefficients are presented in Figure 6.11d. More fibres (21%) and more silica (9%) increase the hardness, as expected. The addition of coupling agent Si 363 decreases the hardness. TESPT increases the hardness with 14%. The increased curing time, factor K, affected the hardness with 12%. This indicates an unexpected phenomena where a longer curing time is not related to an increase in hardness. This means that the degree of cure obtained is caused by interaction with another (noise) factor(s). Figure 6.11a shows that the highest Shore A values are found for the compounds with a 15 phr fibre content and are oriented in longitudinal direction of the mill.

Figure 6.10 — Young's modulus (MPa): a) raw data replicate plot, b) mean per level per factor, c) S/N ratio per level per factor and d) difference coefficients per factor.

Figure 6.11 — Hardness (Shore A): a) raw data replicate plot, b) mean per level per factor, c) S/N ratio per level per factor and d) difference coefficients per factor.

6.5 Discussion

As already mentioned, Si 363 is a compound with a significantly higher molecular weight and only one ethoxy-functionality compared to the other silane TESPT. For this reason a higher amount of silane had to be applied: a factor of approx. 10. The coupling efficiency of Si 363 was not further investigated or improved, because the present Design of Experiments points towards an optimized formulation without the addition of Si 363. Tables 6.3a and b give

an overview for each measured property, which factor sequence gives the highest values.

Table 6.3a — Optimal responses for given control factors part a.

Factors	MV	$t_{90}-t_{s1}$	M_h-M_l	Stress	Strain	YM*
A Fibre type:	1	1	2	2	1	2
B Fibre conc.:	2	1	2	2	1	2
C Filler:	2	1	2	2	2	1
D CA TESPT:	1	2	2	2	2	2
E CA Si 363:	2	2	1	1	2	1
F Orientation:	n/a	n/a	n/a	-	2	2
G Curatives conc.:	1	1	2	2	1	2
H Int. mixer mix. time:	2	2	1	1	2	1
I Int. mixer Tin:	2	2	1	1	2	1
J Mill mix. time	1	1	1	2	2	2
K Curing time:	n/a	n/a	n/a	1	1	1
M_{total}	65	6	5	3	240	3
ε	137	18	9	9	450	7
$(\varepsilon \cdot 100)/M_{total} (\%)$	211	300	180	300	188	233

1: preference for level 1, 2: preference for level 2, - : preferences are equally divided, n/a: not applicable, *sequence used for optimization tests.

Table 6.3b — Optimal responses for given control factors part b.

Factors	Moduli at predefined strain (%):					Stresses at predefined strain (%):					
	2	5	10	20	50	2	5	10	20	50	Hard.
A	2	2	2	2	2	2	2	-	2	2	2
B	2	2	2	2	2	2	2	2	2	2	2
C	-	-	-	-	1	-	-	-	-	-	1
D	2	2	2	2	2	2	2	2	2	2	2
E	1	1	1	1	1	1	1	1	1	1	1
F	2	2	2	2	2	2	2	2	2	2	n/a
G	2	2	2	2	2	2	2	2	2	2	2
H	1	1	1	1	1	1	1	1	1	1	2
I	1	1	1	1	1	1	1	1	1	1	1
J	2	2	2	2	2	2	2	2	2	2	2
K	1	1	1	1	1	1	1	½	1	1	1
M_{total}	3	3	3	3	2	0.04	0.14	0.3	0.5	1	60
ε	8	8	7	7	5	0.09	0.30	0.7	1.4	3	83
$(\varepsilon \cdot 100)/M_{total} (\%)$	267	267	233	260	230	225	214	233	280	300	138

Practically all properties give best results for factor E, level 1: no coupling agent Si 363 added. The focus of this study was to increase the moduli. So the YM factor sequence is most representative for all the factor effects, as shown in Table 6.3a in the column indicated with an asterisk*. With the help of Equation 5.9, Chapter 5, a theoretical optimization percentage can be calculated. Where ε is the overall optimized response and is the best level (highest average value) of the two M_r levels 1 or 2 of each factor. In general, optimizations can be reached between 200-300% of the various properties under consideration, with omission of Si 363 but with TESPT included in the formulation.

Tables 6.3a and b show that only the tensile strain at break is improved by the addition of Si 363. More optimization tests are needed, such as done by Klockmann et al.⁴ In their

article the concentration of Si 363 was lowered, and in a highly silica-filled system an optimum level was found between 8-10 phr. The ratio coupling agent silica used in the present study was very different. 10 phr silica was not chosen as a reinforcement factor but rather as an activator for adhesion/interaction between fibre and rubber. Notably, the addition of a 10 phr silica seems to have an interrelated factor effect in combination with the coupling agents Si 363 and TESPT. This means that, because factors C and E are interrelated, the effect on one of these two, in this case the silica, is diminished by the other. Figure 6.7d shows a similar effect for the M_h - M_l data, with the same diminishing effect.

In the study by Klockmann et al.⁴, the silica concentration of 80 phr is well above the percolation threshold. Therefore, the assumption that this high amount of Si 363 also works for the present formulation well below the percolation threshold turned out to be incorrect. Si 363 has the tendency to delay the curing speed to the same extent as needs to be corrected by double curatives addition, Factor G. Klockmann et al.⁴ claim that this is related to the accelerator system. In general, silica-filled rubber compounds require a high amount of DPG as a secondary vulcanization accelerator and additional hydrophobation agent. DPG is often added in the 2nd stage of a 3rd stage mixing process, so that it can be absorbed on the silica surface. This will prevent the absorption of the more active CBS. It seems that for Si 363 containing compounds the addition of DPG should be avoided, because of the large decrease in scorch safety.¹⁷ Different cross-linking reactions occur with the mercapto silane: more CBS in the system slows down the starting reaction, DPG speeds it up.

In the DoE design the option of doubled curatives concentration was included. This could explain the large influence of curatives amount, in Figures 6.6d and 6.7d, factor G. Less DPG in the rubber compound leads to longer curing times because of reduced vulcanization speed.

The DoE is completed with a confirmation run. The optimized results ϵ are depicted in Table 6.3 (a and b) and Figure 6.12.

Figure 6.12 — Tensile test curve for optimized sample vs. M_{total} values of response factors YM and M.

Based on the results of the mechanical properties TESPT showed the highest positive effect on the system and was then further analysed in the following. Figure 6.12 depicts the expected optimized data ϵ in a tensile test curve for YM and tensile stresses at predefined strains 2, 5, 10, 20 and 50% strain (M). As reference the M_{total} data before optimization are used. The

choice for *YM* could be equal to the stresses for predefined strains 2% till 50%, because the optimal factor choice was the same for all, see Table 6.3b. The experimental run follows the prediction very well. A clear reinforcement is presented, and reproducibility is well within an acceptable range. This system can still further be optimized by altering certain factors.

Figure 6.13 shows the confirmation run again of the optimized formulation for *YM*. In this experiment a double amount of the vulcanization system was used, see Table 6.1, factor G. Figure 10d shows that factor G is only pointing a little towards level 2. This means that there is only a slight effect of the curatives level seen. To test this, an extra confirmation experiment (line B) was performed, with the addition of the single amount of curatives: factor G level 1 instead of level 2, and all the other factors the same. The reinforcement is lowered as is represented by line B, in Figure 6.13. Indeed, the *YM* is slightly reduced, but not by a factor of 2, as would have been expected.

Figure 6.13 — Tensile test curve for optimized sample vs. confirmation run.

The addition of 10 phr silica in combination with the low amount of curing system, line C, increased the modulus and the strain at break again, overcompensating the loss from A to B due to the single curing package. Table 6.4 summarizes the changes.

Table 6.4 — Optimal levels settings.

Factors	Optimized samples			
	A	B	C	D
A Fibre type	2	2	2	2
B Fibre conc.	2	2	2	2
C Filler conc.	1	1	2	1
D CA TESPT	2	2	2	1
E CA Si 363	1	1	1	Si 263
F Orientation	2	2	2	2
G Curative conc.	2	1	1	2
H Time internal mixer	1	1	1	1
I Temp. internal mixer	1	1	1	1
J Time on mill	2	2	2	2
K Time vulcanization	2	2	2	2

The use of two different types of aramid fibres (non-coated and epoxy-coated) to reveal whether the fibre type had a significant effect on enhancing interaction/bonding between short aramid fibres and the rubber: factor A, gave relatively small effects compared to the other factor effects. To understand in which way the coupling agents are reacting with the epoxy coating, the coupling agent TESPT was replaced by Si 263: 3-(triethoxysilyl)-propane-thiol, see Figure 6.1c and Table 6.4, optimized sample D. This experiment was based on the preliminary concept that the epoxy coating on the EF-fibres still contained epoxy groups. In such case, the thiol-group of the Si 263 would have reacted with the epoxy group. However, as shown in Figure 6.13, line D, the result is negative. Afterwards it became clear that these epoxy groups do not exist anymore and have been replaced by OH-hydroxyl groups.^{7, 8} A thiol-group cannot react with hydroxyl-groups and the results of line D do in fact confirm this.

6.6 Conclusions

Compared to the Design of Experiments in the previous chapter, the change here is the replacement of the coupling agents by TESPT and Si 363. The results clearly show that some factor effects are fully or partially overshadowed by other factors: fibre concentration and curatives concentration grossly overrule all other factors in their effect on the Young's modulus, the latter being most representative for the mechanical properties. Interaction between fibres and elastomer again plays only a secondary role, whereby the epoxy-amine coated fibres in combination with coupling agent TESPT gave overall the best results.

To increase the effect of the factors which are now overshadowed, the difference between levels 1 and 2 needs to be increased. To obtain a large increase in mechanical properties, in particular at low strains, Young's modulus, the fibre concentration needs to be increased rather than the curatives level or curing time. For each mechanical property response an optimization prediction was calculated on the basis of the mean values of all runs, varying between 180 and 300% improvement. A confirmation run confirmed this optimization for the Young's modulus. The eventual mechanical properties reached in the confirmation run are comparable to the predicted results ϵ , confirming the value of the DoE approach. This method is also suitable to visualize smaller effects, just by focusing on one factor at a time and changing the levels, to see how this will influence ϵ .

High fibre concentration along with TESPT as a coupling agent have a significant effect on enhancing modulus properties of the elastomeric compound employed. Yet, the best level combination which was obtained from the DoE optimization could be further improved to obtain an even higher Young's modulus by adding a little silica, even though the DoE had not signalled this.

Si 363 at a loading of 12 phr was not effective as a coupling agent in this study. Instead of working as a coupling agent, this silane acts as a plasticizer resulting in easy fibre dispersion and soft elastomer vulcanizates, compared to SBR compounds containing coupling agent TESPT. DPG used in this study seems to be a critical factor and could be further investigated.

6.7 References

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7 Understanding the importance of di- and poly-sulphide silane on the processability and mechanical properties of short-cut aramid fibre-reinforced elastomeric compounds

7.1 Abstract

Although the coupling agents *Bis*-(triethoxysilylpropyl)-tetrasulphide TESPT and *Bis*-(triethoxysilylpropyl)-disulphide TESPd are chemically very similar, their behaviour is rather different. The main focus of this chapter is the comparison between the coupling agents TESPT and TESPd in a short-cut aramid fibre-reinforced elastomer. Both coupling agents compete between the elastomer-fibre interaction and the matrix cross-linking for the added free sulphur during vulcanization. Therefore a conceptual Design of Experiments is performed, with variation in the amount of sulphur-functional silane: TESPT and TESPd.

It is observed that an increase in the amount of silane leads to an increase in reinforcement, resulting in a higher Young's modulus and a strongly reduced strain at break; more so for TESPd than for TESPT. During mixing in the presence of TESPT a little sulphur is released resulting in premature scorch, causing a slightly reduced matrix cross-link density later after vulcanization. Due to the simultaneity of both cross-linking reactions, this noise factor in the sense of the Design of Experiments cannot be mapped independently. In order to achieve an optimum reinforcement, the ratio of silane to sulphur needs to be adjusted. Coupling agent TESPd showed the best overall results in mechanical properties: the Young's modulus reached an optimization of more than 300%.

7.2 Introduction

The use of bifunctional silanes like *Bis*-(triethoxysilylpropyl)-tetrasulphide TESPT and *Bis*-(triethoxysilylpropyl)-disulphide TESPd in a sulphur-cured, short aramid fibre-reinforced rubber compound is new. During mixing the silane reacts just like with silica, with an adhesion activated fibre¹ which leads to hydrophobation of the fibre surface. The hydrophobation reduces the tendency to generate fibre-fibre bundles; in other words, it improves the fibre dispersion. Furthermore, it makes the polar fibre more compatible with the non-polar elastomer, which leads to lower compound viscosities.^{2, 3} Under vulcanization conditions a chemical link between the silane and rubber is created. This fibre-silane-elastomer coupling leads to an improved reinforcement of such compounds^{4, 5}. The proposed reaction of adhesion activated fibre with e.g. TESPT is shown in Figure 6.3.⁶ For the activation of the fibre-rubber coupling, curatives such as elemental sulphur and accelerators play an important role in the silane elastomer reaction.⁷ Silane-elastomer coupling takes place during the vulcanization process. In the presence of elementary sulphur, the poly-sulphide of the silane is activated due to the insertion of elemental sulphur into the poly-sulphide of the silane, as shown in Figure 6.4. According to Debnath et al.⁸ the TESPT coupling agent can also reversely act as a sulphur donor. So, the elementary sulphur in the vulcanization package, together with the sulphur taken up and released from the coupling agent, 'plays an intricate dance' in both the polymer cross-linking and polymer-fibre coupling like with silica.⁶

Consequently, the amount of silane and the amount of added sulphur both influence the vulcanizate properties strongly, as both the fibre-silane-elastomer and the elastomer-

elastomer matrix-cross-linking are responsible for reinforcement. In this chapter the changes of the vulcanizate properties in a short fibre-reinforced SBR compound by variation of the amount of silane and the amount of sulphur are described in more detail, using the same conceptual Design of Experiments as in the previous Chapters 5 and 6. The experimental design is basically the same as described in Chapter 5, Introduction. Also, in the present study A-K factors are selected, see Table 7.1, including material and processability aspects to assess the behaviour of short-cut fibre-reinforced elastomers. The experiments in Chapter 5 and 6 for short fibre-reinforced elastomers showed that several relevant factors are interrelated, but for the sake of consistency this was left unchanged in this chapter.

7.3 Experimental

7.3.1 Materials and compound preparation

The coupling agents TESPT and TESPД are produced by and obtained from Evonik Industries, Germany, under the trade names Si 69 and Si 266. Silane coupling agent's concentrations are used between 0 and 1 phr for TESPД and 0 and 1.1 for TESPT. Both coupling agents are compared on equal footing with respect to sulphur concentration and molecular weight. The other rubber ingredients and respective suppliers are described in Chapter 5. The rubber compound formulation is shown in parts per hundred rubber (phr) in Table 7.1.

Table 7.1 — Standard rubber compound composition.

Formulation*	phr
S-SBR	100
Coupling agent TESPT or TESPД	1.1/1
Silica	0/10
Zinc oxide	2.5
Stearic acid	1.5
Short fibre	5/15
	VF/EF
Sulphur	1.4 or 2.8 (TESPT 1.3 or 2.7)
CBS	1.7 or 3.4
DPG	2.0 or 4.0

*varied depending on experimental plan see Table 5.2, Chapter 5.

Table 7.2 presents the varied control factors in this study. Factor D will represent the data for 0 and 1.1 phr TESPT coupling agents, and factor E for 0 and 1 phr coupling agent TESPД. The other factors are kept the same as Table 5.1, Chapter 5. The design sequence is shown in Table 5.2, Chapter 5.

7.3.2 Characterization methods

The characterization methods used and the calculations necessary for the conceptual graphing of the results of the DoE are described in detail in Chapter 5.

Table 7.2 — Taguchi design: varied control factors

Factor <i>f</i>		Level 1	Level 2	Notes and remarks
A	Fibre type:	Not coated	Coated	
B	Fibre concentration:	5 phr	15 phr	
C	Filler:	0	10 phr silica	
D	Coupling with TESPT:	0	1.1 phr*	
E	Coupling with TESP:	0	1 phr	
F	Orientation**:	0°	90°	Fibre direction
G	Curatives concentration:	Single	Double	
H	Internal mixer mixing time:	4 mins	8 mins	at 110 rpm
I	Internal mixer T_{in} :	30°C	50°C	
J	Mill mixing time in stage 2:	6 mins	12 mins	
K	Curing time:	t_{90} mins	$t_{90} + 2$ mins	at 160°C

*The sulphur concentration is kept the same corresponding to TESP, ** 0° longitudinal orientation and 90° transverse rel. to milling direction

7.4 Results

7.4.1 Mooney viscosity

The data of the Mooney viscosity (*MV*) results are shown in Figure 7.1a. This figure shows that the highest Mooney viscosity values are found for experimental runs 4, 6 and 10. With the help of Table 5.2, Chapter 5, the runs can be compared. The factor effects that the runs 4, 6 and 10 have in common are factors B, fibre concentration and J, milling time level 1. The effect of factors B and J can be seen as a first indication of the relative importance of the milling behaviour. The mean value for each level, level 1 or 2, based on the conceptual approach can be calculated with Equation 4, Chapter 5, and is presented in Figure 7.1b. Factors which show the largest mean difference between level 1 and level 2 are more significant than the factors with small differences. Figure 7.1b confirms a large difference between the two levels for factors B and J. Other factors with large differences between the two levels are: factor D, the addition of coupling agent TESPT, and factor I, temperature setting of the internal mixer 50 vs. 30°C. Figure 7.1c shows the mean *S/N* ratio difference per level per factor as calculated with Equation 5, Chapter 5. For factor J the *S/N* ratio is higher for level 2; indicating better reproducibility of the respective experiments. For factors B and D the *S/N* ratio is almost equal for both levels, which is good for either of the two levels as long as their mean factor effects are large, which they are. The data from Figures 7.1b and 1c are summarized in Figure 7.1d, the ΔM_i mean difference coefficient and $(S/N)_i$ plot per factor. Positive values correspond to larger effects for level 1 (factors J) and negative values for level 2 (factors A, B, C, D, E, H and I). The largest factor effect comes from factor B, fibre concentration (31%). Factor B, 15 phr fibre (level 2), vs. 5 phr (level 1), increases the *MV* significantly. The $\Delta(S/N)$ ratio difference also points towards level 2, the high filler loading. Factor J, milling time on the two-roll mill, shows a large effect (24%) for 6 mins (level 1) vs. 12 mins (level 2). This effect can be assigned to more polymer breakdown during longer milling.⁹ The $\Delta(S/N)$ ratio difference shows a preference for level 2. The addition of coupling agent TESPT, factor D, has a significant increasing effect on the Mooney value: 1 phr (level 2) vs. 0 phr (level 1). The $\Delta(S/N)$ ratio difference also points towards level 2 and is additionally rather large compared with the other factors. This can be an indication that silanization of the fibres has occurred, or it can be the result of some premature scorch of the compound by free-active sulphur released by the coupling agent TESPT. The addition of coupling agent TESP, factor E level 2, shows the same effect, but less pronounced, because it does not release free

sulphur to cause premature scorch. The signal of factor I, initial temperature of the internal mixer, shows a preference for 50°C (level 2), and shows a significant effect on the $\Delta(S/N)$ ratio difference towards the same level 2. For factor A (3%), fibre type, the epoxy-coated fibre (level 2) produces a higher MV than the virgin fibre (level 1). This proves that the coating on the fibre has a small increasing effect on the MV, although this effect is not very convincing, because of the positive $\Delta(S/N)$ ratio pointing towards the other level 1 direction, which means that the observed effect is not very clear or accurate. Factor H, internal mixer mixing time of 8 mins (level 2) produces a higher MV vs. 4 mins (level 1), and shows a significant effect on the $\Delta(S/N)$ ratio difference, just like for factor I. This indicates that a better dispersion may have been reached at longer mixing times. The effect of C, silica concentration of 10 phr (level 2) vs. 0 phr (level 1), increases the MV slightly (3%), the $\Delta(S/N)$ favours level 2. Factor G, single vulcanization system (level 1), produces a slightly higher MV vs. the double (level 2), probably because the still unreacted curatives have a slight plasticizing effect. The plot contains also irrelevant factor effects: e.g. F, orientation, cannot be of influence on the MV and K, additional curing time of 2 mins, is also irrelevant at this instance because the compound is still unvulcanized.

Figure 7.1 — Mooney viscosity (MU): a) raw data replicate plot, b) mean per level per factor, c) S/N ratio per level per factor and d) ΔM and $\Delta(S/N)$ per factor.

7.4.2 Curing behaviour

The curing behaviour $t_{90}-t_{s1}$ and M_h-M_l can best be evaluated by means of the plots in Figures 7.2a-d and 7.3a-d. Figure 7.2a shows short curing speeds for runs 3 and 9. Both runs have a low fibre concentration (factor B) in common, both contain coupling agents TESPT and TESPd (factors D and E) and a low curatives concentration (factor G), resp., an initial internal mixer temperature of 30°C (factor I). The mean $t_{90}-t_{s1}$ values per level are shown in Figure 7.2b. The figure shows large level differences between factors D, E, G and J. The difference coefficients plot in Figure 7.2d shows, as expected, that the highest relevant influence is caused by factor G: curatives concentration (28%) level 1. Higher curatives concentration increases the amount of cross-links, in particular the torque and decreases the curing time: the system becomes more reactive. The increasing torque is confirmed in Figure 7.3d M_h-M_l difference coefficients, see factor G (36% towards level 2). Both coupling agents, factors D (13%) and E (23%), have a large negative (level 2), so shortening effect on the curing speed $t_{90}-t_{s1}$ and a small effect on the M_h-M_l value: factor D, TESPT (4%) level 2 and for factor E, addition of 0 phr TESPd (11%) level 1.

Figure 7.2 — $t_{90}-t_{51}$ (mins): a) raw data replicate plot of, b) mean per level per factor, c) mean S/N ratios per level per factor and d) difference coefficients per factor.

Figure 7.3 — $M_h - M_l$ (dN·m): a) raw data replicate plot, b) mean per level per factor, c) S/N ratios per level per factor and d) difference coefficients per factor.

Factor I, internal mixer temperature, shows that 50°C (level 2) vs. 30°C (level 1) doesn't influence the $t_{90-t_{s1}}$ values and only slightly the $M_h - M_l$ values. Factor H, internal mixer mixing time of 8 mins (level 2), shows an effect on the $t_{90-t_{s1}}$. On the other hand, the $M_h - M_l$ difference effect of factor H is rather large compared to the other factors. Factor A, epoxy-coated fibre vs. virgin fibre shows a small effect on the difference coefficient $t_{90-t_{s1}}$ and a slight effect on the $M_h - M_l$. The fibre concentration has practically little influence on the $t_{90-t_{s1}}$ value, and as expected a large influence on the $M_h - M_l$. Factor C level 2, the formulation containing 10 phr silica, shows a very small effect on the $t_{90-t_{s1}}$ while $M_h - M_l$ a higher curing torque value presents and indicates that the silica is somewhat activating the systems.

7.4.3 Mechanical properties

Figure 7.4a presents the raw data of the tensile stress at break and an extra ordinate axis added in the figure to enlarge the S/N data. Figure 7.4a shows for run 12 the highest and for runs 1, 2 and 9 the lowest tensile strength values. The factors which these lower tensile strength at break runs have in common are: low concentration of fibre, factor B level 1 and no addition of silica, factor C level 1. This is also observed in Figure 7.4b. The largest differences between levels 1 and 2 are found for factors A, B, C, E, F and G. Less pronounced differences can be found for factors D, H, I, J and K. Figure 7.4d shows the difference coefficients of the tensile strength at break for each factor. The factors A, B, C, D, E, G, I and J show large

effects corresponding to level 2, and values corresponding to level 1 are obtained for factor F, orientation, factor H internal mixer mixing time and K, curing time. Factor B, fibre concentration, shows an effect (21%) to increase the tensile strength at break when 15 phr fibre is added (level 2), vs. 5 phr (level 1). Factor G, double curatives concentration level 2 leads to a higher strength at break (13%). Factor J, milling time on the two-roll mill, shows an increasing effect for 12 mins (level 2) vs. 6 mins (level 1) (17%). An increased milling time leads to a better dispersion of the fibres. Factor A, fibre type, shows an increasing effect (13%) for EF level 2 vs. VF level 1, with a significant S/N ratio. Factor K, curing time of t_{90} (level 1) instead of $t_{90} + 2$ mins (level 2), shows a small effect towards a higher strength at break. A clear difference is observed between the behaviour of the two coupling agent factors D and E. The coupling agent TESP_D (factor E) increases the strength at break, while coupling TESPT weakens the compound. The effect of C, a silica concentration of 10 phr (level 2) vs. 0 phr (level 1), increases the tensile strength at break (9%) and the $\Delta(S/N)$ is significantly pointing towards the same direction: level 2.

c)

d)

Figure 7.4 — Tensile strength at break (MPa): a) raw data replicate plot, b) mean per level per factor, c) S/N ratios per level per factor and d) difference coefficients per factor.

Figure 7.5a presents the raw data of strain at break and an extra axis on the right is added in the figure to enlarge the S/N data. The S/N ratio has a distribution, which is not properly visible in the original graph. The highest strain at break values are found for runs 3 and 5, both with a large scatter, a low S/N ratio. The factors which these two runs have in common are factor A, virgin fibre level 1, factor C, addition of silica level 2, factor E level 2 addition of coupling agent TESP, factor G, low curatives concentration level 1, factor H level 2, longer internal mixer mixing time and factor J, longer mill mixing time, level 2. Figure 7.5b confirms that factor B has the highest influence, together with factor C, silica concentration, factor A, virgin fibre and factor G, curatives concentration. Figure 7.5c shows the S/N ratios of levels 1 and 2 for the strain at break. Figure 7.5d shows the difference coefficient results for the strain at break. The results show that factor A, fibre type (13%), factor B (14%), fibre concentration, factor C, silica concentration (18%), factor E coupling agent TESP (14%) concentration and factor G, curatives concentration, show the second largest effect on the strain at break. Orientation, factor F, in the longitudinal direction (level 2), seems to have only a small effect. The difference in S/N ratios for C, F, and G are very low. This indicates a large spread in all these raw data.

a)

b)

c)

Figure 7.5 — Strain at break: a) raw data replicate plot, b) mean per level per factor, c) S/N ratios per level per factor and d) difference coefficients per factor.

Figure 7.6a shows the raw data replicate plot of Young's modulus (YM). The figure shows by far the highest YM values for runs 10, 11 and 12. All runs have the following factors in common: factor A, epoxy-coated fibres level 2 and factor B, high fibre concentration level 2. Figure 7.6b shows the highest difference between levels 1 and 2, for the same factors as mentioned before; A, B, C, G, H and J. Figure 7.6c shows S/N ratios for YM for levels 1 and 2. A high S/N ratio in the same level direction is found for factors A, B, C, E, F, H, I, J and K. Figure 7.6d shows the difference coefficients for the Young's modulus. Factor D, use of coupling agent TESPT, shows the largest effect (5%) to higher YM when no CA is added (level 1) vs. 1 phr (level 2). On the other hand, the $\Delta(S/N)$ ratio difference shows a large tendency to a higher value for level 2, which makes this result questionable. The addition of coupling agent TESP factor E has a strong increasing effect on the YM value: 1 phr (level 2) vs. 0 phr (level 1). Factor B, fibre concentration, increases the YM when 15 phr fibre is added (level 2), vs. 5 phr (level 1). The $\Delta(S/N)$ ratio difference points towards level 2. Factor H, internal mixer mixing time of 4 mins (level 1), produces a higher YM difference vs. 8 mins (level 2), but the $\Delta(S/N)$ pointing towards level 2 indicates a large spread in the data for level 1.

Figure 7.6 — Young's modulus: a) raw data replicate plot, b) mean per level per factor, c) S/N ratios per level per factor and d) ΔM and $\Delta(S/N)$ per factor.

Table 7.3 gives an overview of the optimal response of all properties measured. If there is an increasing preference towards level 1, the symbol 1 is used, and 2 for level 2; if there is no preference, so 0%, the symbol – is used. The M_{total} , Equation 5.8 Chapter 5, represents the mean value of all the experimental runs and ε the predicted value calculated based on Equation 5.9, Chapter 5. It can be concluded that the factor effects improving the mechanical properties are almost always deteriorating the processability factor effects. The YM sequence,

see the bold section Table 7.3, is used for the experimental confirmation runs, as is presented in Figure 7.7. The curves can be compared with the reference data in Table 7.3. To compare the optimization results between the two coupling agents, also TESPT is added to Figure 7.7.

Table 7.3 — Optimal responses for given control factors.

Factors	MV	$t_{90-t_{s1}}$	M_h-M_l	Strength at break	Strain at break	YM	TM ₂₀	TM ₅₀	M ₂	M ₅	M ₁₀	M ₂₀	M ₅₀
A	1	1	2	2	1	2	2	2	2	2	2	2	2
B	2	2	2	2	1	2	2	2	2	2	2	2	2
C	2	2	2	2	2	1	1	1	1	1	1	1	1
D	2	2	2	2	2	1	1	2	1	1	1	1	1
E	2	2	1	2	2	2	2	2	2	2	2	2	2
F	-	-	-	1	2	1	1	1	1	1	1	1	1
G	0	1	2	2	1	2	2	2	2	2	2	2	2
H	2	2	1	1	2	1	1	1	1	1	1	1	1
I	2	0	2	2	1	2	2	2	2	2	2	2	2
J	1	2	1	2	2	2	2	1	2	2	2	2	2
K	-	-	-	1	1	1	1	2	1	1	1	1	1
M_{total}	47	6	5	5	230	5	5	4	0.08	0.3	0.5	1.0	2.3
ϵ	75	13	9	10	650	20	17	7	0.21	0.8	1.7	3.5	7
ϵ (%)	160	220	170	210	280	380	350	180	280	310	320	340	300

Figure 7.7 — Tensile curve for optimized sample vs. M_{total} values of response factors M_{10} , M_{50} and strength at break.

7.5 Discussion

During the vulcanization with sulphur and accelerators the elastomer is cross-linked by sulphur bridges, resulting in a network structure, strongly depending on the ratio between sulphur and accelerators: see the results for factor G, concentration of curatives in Figures 7.2d $t_{90-t_{s1}}$ and 7.3d M_h-M_l data. Both show that the curative concentration is the largest relevant factor compared to the others; for Figure 7.2d, 28% and for Figure 7.3d, 36%. With the addition of silica (10 phr) and TESPT also some silica-silane-elastomer bonds are formed. Both cross-linking reactions, the matrix-cross-linking and silane elastomer coupling, take place at the same time during vulcanization. In Figure 7.3d, for the M_h-M_l difference coefficients, the additions of silica and TESPT increase the torque values. TESPd, factor E, has practically no effect on the M_h-M_l . TESPT releases some of its sulphur, supposed to join

the elemental sulphur added in the curing package, to add to the degree of cross-linking. However, in comparison with TESP_D there is still some difference to be seen. Taking this into account, it is reasonable to assume that pre-scorch by TESP_T occurred in this system and not so much for TESP_D. This also explains the higher *MV* increase of TESP_T (22%) vs. lower for TESP_D (5%) in Figure 7.3d. This sensitivity towards mixing temperature could also be confirmed by the relatively high factor *H* in Figure 7.3d, low initial mixing temperature (level 1) of the first mixing stage. It all indicates that free sulphur released from TESP_T during mixing is a disturbing 'noise factor' in the sense of the Design of Experiments approach.

For the TESP_T-containing compounds the amount of sulphur in the curing packages was reduced (Table 7.2) corresponding to the higher sulphur content of TESP_T vs. TESP_D. A result could be for TESP_T that the amount of sulphur built into the silane-fibre bonds and matrix cross-links is reduced. Due to the fact that the silanes might incorporate sulphur for the activation, the following coupling reactions, the matrix and silica-rubber couplings, compete for the added silane in the compound. Once the free sulphur is consumed for both cross-linking reactions, no further bonds are created. Therefore, it is logical that an increase in the amount of sulphur leads to higher coupling efficiencies, as well as an increased cross-link density of the matrix, which results in much higher moduli and reduced elongation at break. This behaviour is clearly observed in the mechanical properties for TESP_D. TESP_D improves the tensile strength at break, strain at break and the *YM* much more compared to TESP_T. The work of Hasse et al.⁶ made clear that the highest couplings efficiency with silica is found for TESP_T rather than for TESP_D. From this contradiction it can be concluded that, because of the premature scorch, the coupling efficiency of the TESP_T is most likely reduced. The coupling agent efficiency must therefore be optimized by adjusting the temperature profile during mixing.

The effects in the mechanical properties, such as strength at break and *YM*, are largely improved when epoxy-coated fibres are added over virgin fibres. The combined effect of epoxy-coated fibres and coupling agents are interrelated factors, which cannot be confirmed by the set-up of the present Design of Experiments: the two factors are treated as independent of each other. This will be covered explicitly in the next chapter.

Table 7.3 shows the M_{total} , (average of all the experimental runs) and the calculated optimization possibilities. The experimental confirmation run for coupling agent TESP_D is presented in Figure 7.7. An improvement of more than 300% in *YM* can be reached using the combination of optimized factors. The experimental confirmation run is a good fit compared with the predicted performance. The same run was repeated using the coupling TESP_T, see Figure 7.7. This experiment confirmed the trend from the experimental design and showed a clearly lower reinforcement in tensile strength at break and *YM* for TESP_T. The strain at break was slightly increased for TESP_T. The results from previous Chapters 5 and 6 for coupling agents NXT, TESP_D, and TESP_T are largely in agreement with the results for TESP_D and TESP_T in the present chapter, except for Si 363 which showed a very different behaviour.

7.6 Conclusions

Comparing the two coupling agents TESP_D and TESP_T in the present chapter, the main difference between the two is that TESP_T contains approximately two times more sulphur than TESP_D. As is known from the silica reinforcement technology, TESP_T gives indications of releasing active elementary sulphur into the fibre-reinforced compound during the mixing stage, resulting in premature scorch. It seems to do this more so than TESP_D. Evidence for

that is the higher Mooney viscosity of the compound with TESPT and the higher Young's modulus, tensile strength and elongation at break for TESP vs. TESPT. Also, the slower cure properties $t_{90-t_{51}}$ for TESPT point to that. Consequently, the silane-fibre coupling and the matrix cross-linking reaction are then no longer efficient for TESPT. The higher Mooney viscosity of the TESPT-containing compounds may explain their higher M_h-M_l , even though the amount of cross-linking (in an absolute sense) might be somewhat lower. This makes TESP the more favourable choice of the two, because the controllability is better.

For each of the mechanical property responses, an optimization prediction could be calculated on the basis of the mean values of all the runs, varying between 150% and 400%, just by choosing the higher level values in the design factor settings. The eventual mechanical properties reached in the confirmation runs are comparable to the predicted results, confirming the value of the DoE approach.

7.7 References

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8 Influence of increasing coupling agent concentration in short-cut aramid fibre-reinforced elastomeric compounds

8.1 Abstract

This chapter concerns the influence of an increasing concentration of silane S-3-(triethoxysilylpropyl)-octanethioate (NXT) coupling agent in short-cut aramid fibre-reinforced styrene-butadiene elastomeric compounds. Based on the results of the previous chapters, the objective is to check whether the concentration of the optimal coupling agent NXT - used at a constant dosage of 1.5 phr in the previous chapters - needs further optimization for optimal performance. The major performance factors studied are the mechanical properties, in particular: moduli at low strains and hysteretic behaviour. Three types of 3 mm short-cut aramid fibres are tested: untreated fibres, untreated fibres but with oily finish and fibres treated with an epoxy coating. The fibres are added at a concentration of 15 parts per hundred rubber (phr) and the coupling agent NXT is added in quantities between 0 and 7.5 phr. Tensile tests are used to assess the interaction of the fibres with the rubber matrix, with emphasis on low strain properties. The results show that the treated fibre-filled compounds oriented in the milling direction give a significant increase in tensile moduli and hysteresis. A clear optimum is observed in tensile moduli at 6 phr of coupling agent NXT. The results show that all moduli at low strain and the tensile curve itself need to be considered to determine the relevance of the different factors involved in fibres-silane elastomer interaction. An extra check for the ability of the EF and NXT to react in a simplified curing test confirms the reactivity of this system vs. the other two fibre systems.

8.2 Introduction

An ideal rubber is defined as one that stores all energy during deformation, followed by return of the energy upon release of the deforming force and coming back to its un-deformed shape.¹ When short stiff fibres are embedded in a rubber and aligned in the longitudinal direction and are 'ideally' bound to the elastomer matrix, no stresses are transmitted over the blunt face of the fibres, only via axial stresses along the fibres. Near the fibre end region, the axial stress is small, less than or equal to the matrix stress.² Unfortunately, in reality short fibres cannot be perfectly aligned and bound to rubber; the critical stresses of the bonds are easily reached and will lead to catastrophic failure. To prevent this from happening necessary measures need to be taken based on a proper understanding of the underlying phenomena, depending on many factors.^{3, 4} Among these factors are the type of elastomer, the type and level of ingredients incorporated in the elastomer, processing conditions (orientation of the fibres, homogeneity of the mix), and the degree to which the polymer molecules in an elastomer are cross-linked. Long polymer chains require only two cross-links along their length to form a network structure. These factors play an important role in many rubber products that are designed for a range of applications. In short-cut fibre-reinforced elastomeric compounds, improvements can be expected if the fibres can be covalently coupled within the rubber-network.⁵⁻⁸ This requires that other factors involved in short-fibre reinforcement of elastomers, like fibre concentration and fibre orientation, are under control. In Chapters 5-7 it was concluded that the differences between various fibre types, as may be reflected in

different fibre-rubber interactions, are best visible in the Young's modulus. Nevertheless, more methods are needed to demonstrate clearer differences between the different types of fibres. Tests which reflect changes in the conformation of the molecules in the rubber compound and permit subsequent deformations to occur more readily are, for example, tensile tests and dynamic experiments.

The above discussion deals primarily with chemical issues involved in rubber compounds. Different chemical factors are involved with various types of rubber, but also with the myriad vulcanization systems that are used to cross-link the rubber molecules. The type of cross-links and eventual coupling via a coupling agent substantially affects many other important engineering properties like fatigue resistance, compression set, and resistance to degradation by heat.⁹ In the present chapter the curatives system is kept the same, to avoid confounding herewith.

A factor causing a communication gap between rubber technologists and mechanical engineers is that hardly any compound information is included in mechanical engineering education. Mechanical engineers are generally more familiar with high modulus materials such as concrete and steel, which function at very small strains in service. Young's modulus and bulk modulus successfully predict the behaviour of the latter materials. Rubber engineers are antipodal, they focus on 'low' moduli and large strains. It is of great importance to improve the engineer's understanding of rubber behaviour. Rubber technologists typically use the term 'percent modulus', when referring to stress-strain properties. For example, the stress required to elongate a tensile specimen by 300% is designated as the 300% modulus M_{300} . This term often confuses mechanical engineers because the 300% modulus is not a modulus. Rather, it is a stress at 300% strain, as shown in Figure 5.4. The slope of the dashed line drawn tangent to the stress-strain curve is the tangent modulus at 300% strain. Figure 5.4 shows a schematic graph of a highly filler-reinforced rubber compound. In the present study no reinforcing filler is added, which results in much lower elongations at strain than 300%. Even more so when short fibres are added: 50-200%, depending on the fibre concentration and orientation. This means that in the present study the emphasis lies on the moduli at low strain. This is quite unusual for rubber engineers.¹⁰

In this chapter the changes in the vulcanized properties in a short-cut aramid fibre-reinforced SBR rubber compound are studied in detail by variation of the concentration of silane coupling agent S-3-(triethoxysilylpropyl)-octanethioate NXT, using the optimized formulation derived from previous Chapter 5. Three types are used of 3 mm long poly-p-phenylene-terephthalamide (aramid fibre)¹¹ fibres: untreated fibres (VF), untreated fibres with an oily finish (SF) and fibres treated with an epoxy-amine coating (EF). The latter has the ability to react with the coupling agent. The optimized formulation as derived from Chapter 5 gives the highest Young's modulus, and is used as the basis to study the influence of the fibre types and NXT silane coupling agent concentration 0-7.5 phr. The latter was limited to low values in the previous chapters, because the Taguchi design of experiments approach limited the amount to only two levels: 0 and 1.5 phr NXT. It could not be checked if this amount of 1.5 phr was the optimum level. In the present chapter much higher concentrations of NXT are employed. Processability aspects are also taken into account. Extra experiments are invoked like: hysteresis tests and comparing the reactivity of the different fibres with the rubber, with and without coupling agent and without a vulcanization system added, in an RPA experiment. These experiments make it possible to investigate the mutual interactions between the fibre types and the rubber matrix with the coupling agent concentration as variable.

8.3 Experimental

8.3.1 Materials and compound preparation

In the present study the compound with the largest Young's modulus from Chapters 5, 6 and 7 was selected: the one with NXT coupling agent. The formulations are shown in Tables 8.1 and 8.2. All materials were kept the same. Solution-polymerized styrene-butadiene rubber (S-SBR, Buna VSL VP PBR 4045 HM, from Arlanxeo, Leverkusen, Germany) and three types of poly p-phenylene terephthalamide (Aramid) fibres provided by Teijin Aramid B.V., Arnhem, the Netherlands, were used: untreated fibres (VF), untreated fibres but with oily finish (SF) and fibres treated with an epoxy coating (EF). All types were 3 mm long. The coupling agent used was NXT, provided by Momentive, Wilton, CT, United States. The acronyms in Tables 8.1 and 8.2 refer to the following: the numbers represent the concentrations of coupling agent, the letters the type of coupling agent and type of fibre used. The levels of sulphur, zinc oxide and stearic acid, from Sigma Aldrich, St. Louis, United States, were kept constant throughout the study to represent the optimum level as determined in Chapter 5 based on the design of experiments. The other ingredients, n-Cyclohexyl-2-Benzothiazole Sulphenamide CBS and Diphenyl guanidine DPG, were from Flexsys, Brussels, Belgium. In the formulations in Table 8.2 the fibres are left out to see the effect of the coupling agent alone, and as a reference for the formulations with fibres.

Table 8.1 — Rubber compound compositions (phr) with fibres and varying NXT-amount.

Formulation (VF, SF or EF)	0 NXT-VF	1.5 NXT-VF	3 NXT-VF	4.5 NXT-VF	6 NXT-VF	7.5 NXT-VF
S-SBR	100	----->				
Fibre (VF, SF or EF)	15	----->				
Coupling agent NXT	0	1.5	3	4.5	6	7.5
Zinc oxide	2.5	----->				
Stearic acid	1.5	----->				
Sulphur	2.8	----->				
CBS	3.4	----->				
DPG	4	----->				

Table 8.2 — Rubber compound compositions (phr), without fibres and varying NXT-amounts.

Formulation	Reference	1.5 NXT	3 NXT	4.5 NXT	6 NXT	7.5 NXT
S-SBR	100	----->				
Fibre	0	----->				
Coupling agent NXT	0	1.5	3	4.5	6	7.5
Zinc oxide	2.5	----->				
Stearic acid	1.5	----->				
Sulphur	2.8	----->				
CBS	3.4	----->				
DPG	4	----->				

Compounds were prepared according to the same procedure as described in Chapter 5, materials and compound preparation. Samples were vulcanized in a Wickert press WLP 1600

at 100 bar and 150°C to sheets 110x110 mm with a thickness of 2 mm for tensile tests, according to their t_{90} optimum vulcanization times, as determined with a Rubber Process Analyzer (RPA 2000) of Alpha Technologies, according to the procedure described in ISO 3417. To ensure the flow pattern of the rubbers will not interfere with following tests, line marks were drawn, in longitudinal orientation along the mill direction, so that the flow pattern in the vulcanization mould could be visualized. Figure 3.5, Chapter 3, shows clearly that the outer layers of the sheets should be avoided when the dumb-bell samples were cut.

8.3.2 Characterization methods

Tensile strength at break measurements were performed in tensile mode in an Instron tensile tester with a load cell of 1000 N, according to ISO 37 at a crosshead speed of 500 mm/min. Hysteresis tests were performed as a sort of ‘Mullins’ test by extending the tensile bars to consecutively 5, 10 and 20% strain in three cycles each, at a crosshead speed of 500 mm/min, and by letting the samples recover in between. The average permanent deformations of the three cycle’s pre-deformation were recorded.

Extra experiments were invoked to compare the reactivity of the different fibres with the rubber, with and without coupling agent and without a vulcanization system added, in an RPA experiment at 120°C and 140°C at a strain of 2.78% and 0.8 Hz for 60 minutes. These experiments made use of formulations 0 NXT-VF and 1.5 NXT-VF in Table 8.1, and the corresponding formulations with EF, with the omission of all vulcanization ingredients.

8.4 Results

8.4.1 Processability

Table 8.3a presents the end temperatures of each mixing stage and Mooney viscosities (*MV*) of the various finished compounds.

Table 8.3a — Compound properties: end temperatures of mixing stages and *MV*.

Samples	T ₁	T ₂	T ₃	MV	St. dev
	(°C)			(MU)	
0 NXT-VF	129	129	92	39.6	0.5
1.5 NXT-VF	129	124	93	34.8	0.1
3 NXT-VF	118	134	95	33.1	0.1
4.5 NXT-VF	121	131	94	32.2	0.1
6 NXT-VF	118	126	93	31.3	0.2
7.5 NXT-VF	117	127	98	30.6	0.1
0 NXT-SF	130	129	95	34.6	0.1
1.5 NXT-SF	128	132	94	34.2	0.2
3 NXT-SF	121	132	95	32.6	0.0
4.5 NXT-SF	120	132	94	31.7	0.3
6 NXT-SF	130	126	95	30.3	0.8
7.5 NXT-SF	119	136	96	29.3	0.5
0 NXT-EF	123	131	94	33.8	1.0
1.5 NXT-EF	122	134	95	34.5	0.5
3 NXT-EF	120	134	93	34.1	0.2
4.5 NXT-EF	120	132	97	32.4	0.1
6 NXT-EF	122	128	96	31.8	0.6
7.5 NXT-EF	117	129	98	31.4	0.5

In the table the standard deviation values are included, to provide an indication of the scatter within the measurements. Silanization occurs between 120°C and 140°C. Table 8.3a shows that the end temperatures, measured with the temperate probe inside the mixing chamber, of mixing stages 1 (T_1) and 2 (T_2) are within this reactivity range. The temperature in the rubber compound itself is slightly higher but was not further measured in this study. No clear effect is seen in the end temperature T_3 with an increasing amount of coupling agent. A clear decreasing mixing temperature trend in mixing stage 1 is observed for increasing coupling agent concentration: for stages 2 and 3 this effect is gone. Table 8.3a and Figure 8.1 shows the MV results in graphical form. Increasing concentration of coupling agent decreases the MVs . For SF and EF there is no difference observed between 0 and 1.5 phr. The EF with 3, 4.5, 6 and 7.5 phr NXT shows higher values compared to SF and VF. This is a possible indication that the epoxy coating is most reactive.

Figure 8.1 — MV results vs. increasing coupling agent concentration and fibre type.

8.4.2 Curing behaviour

Tables 8.3b and c present the rheometer data of the various finished compounds. The M_i values decrease with increasing coupling agent concentration: Figure 8.2. In elastomer compounding the M_i bears a relationship to the Mooney viscosity, because both values are measurements of torque in the unvulcanized state. Figures 8.1 and 8.2 show that the same trend is observed for M_i as well as for MV . $M_h - M_i$ is related to the cross-link density; it seems to be constant for VF and SF at 0, 1.5, 3 and 4.5 phr coupling agent: Figure 8.3, but the torque decreases significantly for 6 and 7.5 0 phr NXT. For EF the same trend is observed, except that the decrease in torque starts at 6 phr NXT instead of 4.5 phr. Above this loading the coupling agent softens the system and starts to act as a plasticizer.

The t_{s1} values slightly increase with increasing coupling agent concentration, see Table 8.3. The $t_{90} - t_{s1}$ values are presented in Figure 8.4. The $t_{90} - t_{s1}$ values decrease with increasing coupling agent concentration, more so for VF than for SF and EF containing compounds. The vulcanization time was kept the same though for all the compounds, because the t_{90} values show only minor differences.

Table 8.3b — Compound properties: RPA rheometer data at 150°C data in mins.

Samples	t_{90}	St. dev	t_{s1}	St. dev	$t_{90}-t_{s1}$	St. dev
	(mins)					
0 NXT-VF	12.1	0.0	1.6	0.1	10.5	0.07
1.5 NXT-VF	12.4	0.1	1.8	0.0	10.6	0.02
3 NXT-VF	12.1	0.1	1.7	0.0	10.4	0.02
4.5 NXT-VF	11.6	0.1	1.8	0.0	9.8	0.01
6 NXT-VF	11.1	0.0	1.8	0.0	9.3	0.02
7.5 NXT-VF	10.7	0.3	2.0	0.0	8.7	0.05
0 NXT-SF	12.7	1.1	1.7	0.0	11.0	0.09
1.5 NXT-SF	12.3	0.5	1.7	0.0	10.6	0.06
3 NXT-SF	11.9	0.2	1.7	0.0	10.2	0.03
4.5 NXT-SF	12.4	0.1	2.0	0.1	10.4	0.07
6 NXT-SF	12.7	0.2	2.1	0.1	10.7	0.05
7.5 NXT-SF	12.3	0.6	2.2	0.0	10.1	0.06
0 NXT-EF	12.8	0.7	1.9	0.1	11.0	0.11
1.5 NXT-EF	11.8	0.5	1.7	0.0	10.1	0.05
3 NXT-EF	12.6	0.6	1.8	0.0	10.9	0.06
4.5 NXT-EF	12.1	0.3	1.8	0.0	10.3	0.03
6 NXT-EF	12.0	0.2	1.9	0.0	10.1	0.02
7.5 NXT-EF	12.6	0.5	2.7	0.1	10.0	0.07

Table 8.3c — Compound properties: RPA rheometer data at 150°C in dN·m.

Samples	M_l	St. dev	M_h-M_l	St. dev
	(dN·m)			
0 NXT-VF	0.39	0.00	6.81	0.01
1.5 NXT-VF	0.35	0.01	6.78	0.05
3 NXT-VF	0.34	0.01	7.17	0.03
4.5 NXT-VF	0.33	0.01	6.62	0.06
6 NXT-VF	0.27	0.01	5.76	0.11
7.5 NXT-VF	0.25	0.01	4.85	0.10
0 NXT-SF	0.38	0.00	7.18	0.01
1.5 NXT-SF	0.38	0.01	7.25	0.05
3 NXT-SF	0.36	0.03	7.04	0.13
4.5 NXT-SF	0.32	0.06	7.49	0.19
6 NXT-SF	0.27	0.02	6.38	0.08
7.5 NXT-SF	0.26	0.06	5.31	0.26
0 NXT-EF	0.36	0.03	7.42	0.11
1.5 NXT-EF	0.39	0.01	7.51	0.04
3 NXT-EF	0.38	0.01	7.17	0.04
4.5 NXT-EF	0.37	0.03	7.38	0.10
6 NXT-EF	0.31	0.03	7.24	0.17
7.5 NXT-EF	0.29	0.03	5.48	0.20

8.4.3 Mechanical properties

Table 8.4 lists the tensile properties for the various finished compounds after optimum vulcanization: tensile strength at break, strain at break and *YM*. This table is useful to obtain an indication of the scatter within the compounds. All fibre-containing compounds are measured in the longitudinal direction of milling. In this chapter only the longitudinal results are presented, the next chapter will focus more specifically on orientation effects.

Figure 8.2 — M_l results vs. increasing coupling agent concentration and fibre type.

Figure 8.3 — $M_h - M_l$ results vs. increasing coupling agent concentration and fibre type.

Figure 8.4 — $t_{90} - t_{51}$ results vs. increasing coupling agent concentration and fibre type.

The tensile strength at break values stay constant for all the fibre types, except for the EF samples which show a decrease in strength at break at 7.5 phr. The EF-fibres combined with coupling agent have a significantly higher strength at break compared to the SF- and VF-containing samples.

The strain at break values show a similar behaviour for each fibre type, when the coupling agent concentration is increased: a decrease and subsequent increase. All the tensile curves show no yield point.

The Young's modulus is derived in the tensile tester software from the slope drawn from 0 N to 5 N for the tensile test curve. In that range between 0 and 5 N, the highest value is presented as the *YM*. The *YM* values, see Table 8.4 and Figure 8.5 for VF and SF, show an increase till 4.5 phr NXT and a decrease in value for 6 and 7.5 phr NXT. There is no difference between the VF- and SF-containing compounds. For EF the *YM* increases till 6 phr and decreases also at 7.5 phr NXT. This *YM* is therefore the most favourable property to compare the three fibre types with each other. EF shows generally a +50% increase in *YM*-value vs. the VF and SF samples. This demonstrates that the coupling agent NXT has an interactive effect with the type of fibre, in particular EF.

Table 8.4 — Compound mechanical properties (phr).

Samples	Strength at break (MPa)	St. dev	Strain at break (%)	St. dev	YM (MPa)	St. dev
0 NXT-VF	5.2	0.5	100.0	2.3	6.8	0.5
1.5 NXT-VF	4.6	0.2	96.9	4.8	8.3	0.2
3 NXT-VF	5.0	0.1	67.7	8.0	8.9	1.2
4.5 NXT-VF	5.8	0.2	58.8	4.2	9.1	0.8
6 NXT-VF	5.6	0.3	84.2	5.7	9.5	0.4
7.5 NXT-VF	5.2	0.2	125.3	7.0	5.3	0.3
0 NXT-SF	5.2	0.7	82.3	11.5	7.8	0.3
1.5 NXT-SF	5.2	0.3	92.0	1.2	7.4	0.8
3 NXT-SF	5.9	0.4	66.3	6.3	9.6	0.6
4.5 NXT-SF	4.9	1.6	48.8	13.0	10.7	2.6
6 NXT-SF	5.8	0.2	110.5	13.7	6.7	0.8
7.5 NXT-SF	5.0	0.3	118.3	8.7	5.1	0.4
0 NXT-EF	6.9	0.6	81.3	4.8	11.0	2.1
1.5 NXT-EF	6.5	0.4	73.6	6.9	10.7	0.7
3 NXT-EF	7.4	0.5	61.7	6.4	14.6	1.7
4.5 NXT-EF	6.9	0.6	52.1	7.4	17.8	1.3
6 NXT-EF	8.1	0.3	56.8	3.5	20.3	2.0
7.5 NXT-EF	5.8	0.5	90.2	6.2	8.2	0.7

The differences are most conspicuous at high NXT-amounts, higher than the 1.5 phr used in the DoE study in Chapter 5. It may be taken as clear evidence for the reactivity of NXT towards the EF for enhanced fibre-elastomer interaction.

Table 8.5 shows the results of the tangent moduli. For 2, 5, 10 and 20% strain the same trend is observed as for the *YM*. The higher the strain, the smaller the differences between the samples with varied NXT-loadings, due to the shape of the tensile curves. The *YM* is the most pronounced compared to the tangent responses. At 50% strain the tensile curves are coming close to their yield points, although they are never reached. EF-containing compounds

show again significantly larger tangent moduli than SF- and VF-containing compounds, except for 7.5 phr NXT wherefore the elongation at break increases again.

Figure 8.5 — Tensile test result of YM (MPa).

Table 8.5 — Compound tangent moduli at 2, 5, 10, 20 and % strain (MPa).

Samples	TM ₂	St. dev	TM ₅	St. dev	TM ₁₀	St. dev	TM ₂₀	St. dev	TM ₅₀	St. dev
0 NXT-VF	6.0	0.7	7.0	0.3	6.7	0.6	6.7	0.5	5.0	3.8
1.5 NXT-VF	8.0	0.7	8.5	0.2	8.6	0.6	7.7	0.2	5.2	0.6
3 NXT-VF	7.9	0.6	8.4	0.9	8.4	1.3	8.6	1.3	6.8	0.3
4.5 NXT-VF	9.5	0.4	10.3	0.3	10.6	0.7	11.8	0.6	7.9	1.1
6 NXT-VF	7.9	0.2	8.3	0.3	8.6	0.3	9.5	0.4	7.8	0.7
7.5 NXT-VF	4.1	0.1	4.3	0.2	3.7	0.4	3.8	0.2	4.8	1.9
0 NXT-SF	6.8	0.4	7.4	0.6	7.2	0.8	7.2	0.9	7.2	2.6
1.5 NXT-SF	6.0	0.3	6.6	0.3	6.1	0.6	6.4	0.5	7.2	1.0
3 NXT-SF	7.7	0.3	8.1	0.4	7.9	0.4	8.7	0.5	8.6	0.6
4.5 NXT-SF	9.2	1.5	9.4	1.9	10.2	2.3	10.8	2.8	5.9	1.2
6 NXT-SF	4.9	0.5	5.2	0.4	4.8	0.6	5.0	0.7	6.6	0.9
7.5 NXT-SF	4.0	0.4	4.5	0.3	4.0	0.3	4.0	0.3	4.9	0.4
0 NXT-EF	7.9	0.6	7.5	0.5	7.8	0.6	8.9	1.0	10.1	2.0
1.5 NXT-EF	8.4	0.9	9.4	1.2	9.4	1.2	10.2	1.2	9.4	0.2
3 NXT-EF	10.3	1.5	11.4	1.5	12.3	2.0	14.1	2.3	11.0	1.2
4.5 NXT-EF	13.7	1.4	15.7	1.5	16.9	1.6	17.6	1.2	2.9	5.5
6 NXT-EF	15.6	1.3	17.4	0.9	20.1	1.9	20.5	2.1	8.3	6.9
7.5 NXT-EF	5.4	0.3	5.9	0.3	5.3	0.6	5.9	0.5	8.0	0.7

Table 8.6 shows the results of the stresses at predefined strains: 2, 5, 10, 20 and 50%. These results may be a bit more accurate than the Tangent Moduli, although the results are overall comparable. At 50% strain the stress values are less sensitive towards scatter than in the tangent modulus data. EF-containing compounds have again significantly higher values than SF- and VF-containing compounds, except for 7.5 phr NXT.

Table 8.6 — Compound stresses at predefined strains of 2, 5, 10, 20 and 50% (MPa).

Samples	M ₂	St. dev	M ₅	St. dev	M ₁₀	St. dev	M ₂₀	St. dev	M ₅₀	St. dev
0 NXT-VF	0.077	0.010	0.28	0.02	0.6	0.0	1.3	0.1	3.1	0.2
1.5 NXT-VF	0.093	0.005	0.35	0.02	0.8	0.1	1.6	0.1	3.5	0.2
3 NXT-VF	0.100	0.008	0.36	0.04	0.8	0.1	1.6	0.2	4.1	0.5
4.5 NXT-VF	0.113	0.003	0.43	0.01	0.9	0.0	2.1	0.1	5.4	0.2
6 NXT-VF	0.100	0.002	0.35	0.01	0.8	0.0	1.7	0.1	4.4	0.9
7.5 NXT-VF	0.062	0.002	0.20	0.01	0.4	0.0	0.8	0.0	2.0	0.1
0 NXT-SF	0.086	0.002	0.31	0.02	0.6	0.1	1.4	0.1	3.5	0.2
1.5 NXT-SF	0.081	0.003	0.29	0.04	0.6	0.1	1.2	0.3	3.4	0.3
3 NXT-SF	0.099	0.004	0.35	0.02	0.7	0.1	1.6	0.2	4.3	0.2
4.5 NXT-SF	0.111	0.016	0.40	0.07	0.9	0.2	1.9	0.4	5.0	1.3
6 NXT-SF	0.067	0.004	0.23	0.02	0.5	0.1	1.0	0.1	2.7	0.4
7.5 NXT-SF	0.060	0.003	0.20	0.01	0.4	0.0	0.8	0.2	2.1	0.2
0 NXT-EF	0.100	0.006	0.340	0.07	0.7	0.0	1.6	0.2	4.3	0.4
1.5 NXT-EF	0.100	0.010	0.390	0.04	0.9	0.1	1.8	0.2	4.9	0.4
3 NXT-EF	0.123	0.016	0.463	0.06	1.0	0.1	2.4	0.1	6.5	0.8
4.5 NXT-EF	0.150	0.015	0.600	0.04	1.4	0.1	3.2	0.2	7.1	0.3
6 NXT-EF	0.179	0.014	0.69	0.06	1.6	0.1	3.7	0.3	7.9	0.4
7.5 NXT-EF	0.076	0.004	0.26	0.01	0.5	0.0	1.1	0.1	3.3	0.2

Figure 8.6 presents the tensile stress-strain curves for 1.5 NXT-SF, 1.5 NXT-EF and 1.5 NXT. 1.5 NXT-VF is not added because it is very similar to 1.5 NXT-SF. Figure 8.6 nicely shows the reinforcing effect of the fibres vs. the compound without fibres, all with 1.5 phr NXT. Because the fibres are all oriented in longitudinal direction, the difference between the interaction mechanisms for EF and SF is very eye-catching in the much higher curves for the EF than for the SF. In comparison with the compound without fibres the stress at a preset strain of e.g. 50% (M_{50}) is increased for SF with 1000% and for EF with ~1300%. Figure 8.7 presents the tensile stress-strain curves for 6 NXT-SF, 6 NXT-EF and 6 NXT. Again, compared to the compounds without fibres SF reinforces the system with ~850% and EF with ~2500%.

Figure 8.6 — Tensile stress-strain curve of 1.5 NXT-EF, 1.5 NXT-SF and 1.5 NXT at predefined strains of 2, 5, 10, 20 and 50%.

Figure 8.7 — Tensile stress-strain curve of 6 NXT-EF, 6 NXT-SF and 6 NXT at predefined strains of 2, 5, 10, 20 and 50%.

Tables 8.7, 8.8 and 8.9 show the tensile test results for the compounds without fibres. These data are added as a reference. The tensile strength at break values stay constant for the compounds with silane NXT concentration from 0 to 6 phr. The tensile strength at break drops significantly at 7.5 phr NXT. The elongation at break is independent of the concentration of NXT. The Young's modulus decreases slightly with increasing coupling agent concentration. The tangent moduli at 2% strain show negative values. This is an artefact of the tensile test, caused by irreproducibility during clamping of the test samples. The tangent moduli (TM) and stresses at predefined strain (M) (see Figure 5.4) at 5-50% show a comparable picture for different NXT loadings. The large differences seen in the performance of the EF vs. SF in combination with NXT are not caused by NXT alone, and indeed point at much stronger fibre-matrix interaction for EF than for SF and VF.

Table 8.7 — Compound mechanical properties without fibres

Samples	Strength		Strain		YM (MPa)	St. dev
	at break (MPa)	St. dev	at break (%)	St. dev		
0 NXT	1.9	0.2	413	32	0.71	0.03
1.5 NXT	1.9	0.1	460	18	0.66	0.01
3 NXT	1.8	0.1	485	28	0.66	0.01
4.5 NXT	1.9	0.1	460	33	0.64	0.02
6 NXT	1.9	0.2	417	31	0.61	0.01
7.5 NXT	1.5	0.1	464	28	0.65	0.02

Table 8.8 — Compound Tangent Moduli at 2, 5, 10, 20 and 50% strain (MPa), without fibres.

Samples	TM ₂	St. dev	TM ₅	St. dev	TM ₁₀	St. dev	TM ₂₀	St. dev	TM ₅₀	St. dev
0 NXT	-0.19	0.09	1.14	0.07	0.97	0.13	0.78	0.14	0.56	0.07
1.5 NXT	-0.08	0.07	1.02	0.07	0.76	0.06	0.64	0.08	0.56	0.12
3 NXT	-0.09	0.25	0.83	0.10	0.72	0.05	0.63	0.08	0.58	0.19
4.5 NXT	-0.18	0.22	0.79	0.10	0.83	0.12	0.7	0.11	0.50	0.17
6 NXT	-0.25	0.02	0.83	0.22	0.87	0.06	0.73	0.07	0.42	0.09
7.5 NXT	-0.13	0.15	0.79	0.09	0.80	0.10	0.61	0.15	0.46	0.04

Table 8.9 — Compound stresses at predefined strains: 2, 5, 10, 20 and 50% (MPa), without fibres.

Samples	M ₂	St. dev	M ₅	St. dev	M ₁₀	St. dev	M ₂₀	St. dev	M ₅₀	St. dev
0 NXT	0.017	0.0002	0.041	0.0010	0.088	0.002	0.17	0.003	0.36	0.005
1.5 NXT	0.016	0.0003	0.039	0.0015	0.084	0.008	0.16	0.004	0.34	0.007
3 NXT	0.015	0.0011	0.039	0.0008	0.083	0.001	0.16	0.001	0.34	0.001
4.5 NXT	0.018	0.0006	0.039	0.0003	0.082	0.001	0.16	0.001	0.33	0.002
6 NXT	0.015	0.0004	0.036	0.0010	0.079	0.002	0.15	0.003	0.32	0.008
7.5 NXT	0.015	0.0004	0.037	0.0006	0.078	0.001	0.15	0.002	0.32	0.002

8.4.4 Hysteresis properties

Table 8.10 shows the hysteresis results of the SF and EF compounds with 6 NXT and 0 NXT, and one without fibres but with 6 NXT. The interaction effect of EF-fibres with the rubber via the coupling agent is increased with 50% at 5% strain and with 80% at 10% strain vs. SF, as seen in the tensile stresses, see Figure 8.8 for examples. Surprisingly, the effect of 6 NXT vs. 0 NXT only starts to show at 10% strain and not yet at 5%.

Table 8.10 — Compound mechanical properties: hysteresis (MPa).

Samples:		6 NXT-SF	6 NXT-EF	6 NXT	0 NXT-SF	0 NXT-EF
5% strain	Tensile stress (MPa)	1.9	2.8	0.2	2.0	2.7
	St. dev. (MPa)	0.1	0.2	0.0	0.4	0.5
	Perm. Def. (%)	0.7	0.8	0.2	1.8	0.6
	St. dev (%)	0.1	0.1	0.0	0.1	0.0
10% strain	Tensile stress (MPa)	4.0	7.3	0.4	2.4	2.7
	St. dev. (MPa)	0.5	0.7	0.0	0.1	0.9
	Perm. Def. (%)	1.6	1.8	0.4	2.4	1.0
	St. dev (MPa)	0.2	0.2	0.0	0.1	0.1
20% strain	Tensile stress (MPa)	-	-	0.8	-	-
	St. dev. (MPa)	-	-	0.2	-	-
	Perm. Def. (%)	-	-	0.8	-	-
	St. dev (MPa)	-	-	0.1	-	-

Figure 8.8 shows that both compounds show the highest modulus during the first cycle, with each subsequent strain cycle showing progressively reduced stress at a given strain (stress softening). The stronger the coupling, the lower the hysteresis expected in terms of permanent deformation. The average permanent deformations of the 3 cycles each, as given in Table 8.10 for 5 and 10% strain are just slightly worse for EF compared to SF, but it has to be realized that EF was subjected to about double the stresses compared to SF. This may be taken as an extra proof of the stronger interaction of the EF with the rubber, in combination with the NXT, compared to SF. The hysteresis tests at 20% strain were in most cases not successful, because in this test set-up most samples failed before.

8.4.5 Fibre-matrix interaction without vulcanization

Extra experiments were executed to compare the reactivity of the different fibres with the rubber, with and without coupling agent and without a vulcanization system added. The experiments were done in an RPA experiment at 120 and 140°C at a strain of 2.78% and 0.8 Hz for 60 minutes. The formulation 0 NXT-VF in Table 8.1 was used, and the corresponding formulation with EF, with the omission of all vulcanization ingredients.

Figure 8.8 — Tensile hysteresis curve of 6 NXT-EF and 6 NXT-SF.

Figure 8.9 shows the RPA results. The figure shows that there is no significant difference between EF and VF. The steep incline at the beginning of the curve is caused by inertia of the machine. It clearly demonstrates that in the absence of a coupling agent there is no difference between EF- and VF-fibres in their interaction with the rubber, if any.

Figure 8.9 — RPA curve of 0 NXT-SF and 0 NXT-EF at 120°C.

Figure 8.10 presents the RPA data for 1.5 NXT-VF and 1.5NXT-EF, again without curatives. The EF now shows a significantly higher torque compared to VF. This phenomenon is again a clear indication of interaction between the EF and rubber matrix via the NXT. The test was repeated at 140°C and for 3 phr NXT, and showed the same difference.

8.5 Discussion

Coupling agent NXT is a bifunctional molecule, wherefore under elevated temperatures the ethoxy groups may react with the epoxy coating on the fibres, and later the mercapto group with the rubber matrix during vulcanization. Because the virgin fibres contain no reactive groups, any reaction which could happen must have another reason. One possibility is silane-silane coupling by oligomerization of the NXT: see Figure 8.11 for an example of dimerization. Hereafter, the sulphur atoms in the NXT-oligomer are still available for reaction with the rubber matrix towards cross-linking.

Figure 8.10 — RPA curve of 1.5 NXT-SF and 1.5 NXT-EF at 120°C.

Figure 8.11 — Dimerization of NXT.

The ‘strongest’ cross-linking reaction possible with the rubber matrix would be the elastomer-silane-silane-elastomer link. So, the higher the coupling agent concentration, the higher the chance that more elastomer-silane-silane-elastomer cross-links are formed.¹² However, for NXT to react with an elastomer, first the octanoic shielding groups need to be released, which only happens in the presence of a curatives system. Any reaction seen in NXT with fibres in the absence of a curatives system must therefore be due to chemical interaction with the fibre; in particular the EF: Figures 8.10 vs. 8.9. Comparing both figures it may be commented that the torque levels are lower in the NXT-containing compounds vs. those without. This is obviously due to the plasticizing effect of the low molecular weight coupling agent.

This so-called plasticizing effect is also visible in the Mooney viscosity results and in curing data: it lowers the *MV* and *M_i* values for all fibre-containing compounds, irrespective of the type of fibre. This effect is also seen in the mechanical properties: tensile strength at break and moduli at low strain. The SF-containing compounds are comparable to the VF-containing compounds, which means that the oily finish on the fibre is not interfering with the reaction mechanism(s), as discussed in the first paragraph. A minor difference between SF and VF is seen in the *MV* for 0 NXT-SF: 35 MU, and 0 NXT-VF: 40 MU, which must be related to some plasticizing effect of the oily finish.

After vulcanization the EF- and NXT-containing compounds show a clear reinforcement in all moduli compared to the SF and VF compounds. It must be concluded that reaction of the NXT with the epoxy coating and the rubber matrix is the cause of the moduli increase and the hysteresis effects, as seen in Table 8.10. In contrast with the mechanical interlocking effect discussed in Chapter 3, where no significant difference was found for the various fibres, in the present chapter the EF in the presence of sufficient NXT coupling agent stands out: 4 or 6 phr. This demonstrates that mechanical interlocking is not the main factor involved.

In the present chapter the RPA seems to be a valuable tool to prove the reactivity of the

EF vs. SF in formulations as shown in Tables 8.1 and 8.2, additional to the model compounds used by De Lange et al.¹¹ in their study to prove that the epoxy-amine coating contains reactive OH groups and derives reactivity therefrom.

The mechanical results show that the Young's modulus presents the largest differences between the samples, and is therefore preferred as parameter to signal fibre-rubber interaction. However, it is unfortunately very sensitive to clamping problems in the tensile test, like schematically shown in Figure 8.12. Somehow, if fibre is present, the clamps sometimes cannot properly grab the tensile bars. The tensile samples tend to slip a little in the clamps.

This could give a wrong interpretation of the results if the stress at such a point is needed for the automatic (machine software) calculation of the moduli at that strain. In order to correct for that artefact the moduli were calculated by hand instead of by the computer software of the tensile tester. Consequently, it is important to look at all moduli and not only at the Young's modulus to obtain a proper understanding of the phenomena. Determining the difference between YM and TM_2 is a good first indicator of an unsmooth curve due to inhomogeneous tearing or clamping problems.

Figure 8.12 — Artefacts in the tensile test curve.

Unfortunately the strains at break, obtained with the model formulations without fillers and used in this study, are too low to reach typical yield points. For that, the tear strengths need to be increased. This requires the application of common reinforcing fillers like carbon black or silica. In the previous works of Shirazi⁶ and Hintze⁸ carbon black-reinforced compounds were used, where such yield points were obtained. In the case of the use of silica-reinforced rubber compounds, the reaction mechanism between the EF-fibres and the coupling agent becomes more complicated, because there will be a competition in the system between the fibres and the silica. This will be studied in more detail in Chapter 11.

8.6 Conclusions

Coupling agent NXT reinforces the EF-fibre-containing elastomeric compounds, because it can form silane bridges with the matrix. This coupling causes fixation of the EF-fibres in the elastomer matrix, which greatly improves the mechanical properties compared to VF- and SF-fibres. Coupling agent NXT with SF-fibres also reinforces somewhat, but far less because it cannot form fibre-matrix bridges, but adds to the cross-linking due to oligomerization. The mechanical properties show no significant differences between the VF- and SF-containing compounds. This means that the oily finish on the SF-fibre is not interfering with any of the mechanisms above, except that it seems to improve the processability as shown in lower

Mooney viscosity results. Even without a coupling agent, 15 phr epoxy-amine coated fibres do give some reinforcement relative to standard fibres.

The combination of EF-fibres with 4-6 phr NXT clearly performs best in terms of mechanical properties: moduli at low strain. 7.5 phr NXT is too much, as it starts to act as a plasticizer. There is a large gain in properties achieved vs. 1.5 phr NXT, as employed in Chapters 3 and 5. After all, this 4-6 phr NXT is surprisingly comparable to what is more or less common in silica reinforcement of elastomers: see Chapter 11. This secondary study to optimize the amount of NXT vs. the 1.5 phr used earlier is an important added value for the whole study presented in this thesis.

8.7 References

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9 A multidimensional investigation into orientation in a short-cut aramid fibre-reinforced elastomeric compound using X-ray diffraction and computed tomography

9.1 Abstract

This study concerns a characterization of the mesoscopic orientation of short-cut aramid fibre-reinforced elastomeric compounds, with the objective of understanding the hierarchical structure and inhomogeneity in the compounds using X-ray diffraction and computed tomography.

The X-Ray Diffraction (XRD) data show that the rubber and the fibre signals are situated in the same diffraction angle range, where the latter becomes visible when the fibre concentration is sufficiently high. It is important that diffraction signals from other compounding ingredients are relatively low in intensity compared to the signals from rubber and fibres. Volume-surface reconstruction of the composite material and subsequent analyses reveal that the aramid fibres look like they are macroscopically arranged in bundles in the Y-X plane of the sample, where the fibre bundles are oriented in the Y-direction. The aligned fibre bundles have a mean thickness of 65 μm because of the lower resolution limit of the technique, so that individual fibres are not visible. However, even with this limitation it is, after all, a good quantification method of fibre orientation at much lower costs and scanning times, which would have been needed to see the individual fibres.

DiPhenyl Guanidine (DPG), as a secondary accelerator, shows a large orientation preference in bloom, towards the direction of the fibres. The explanation is that an excess amount of DPG forms crystals on the surface of the compound, which oriented themselves just like the fibres.

9.2 Introduction

In the introductory Chapter 2 of this thesis it has been emphasized that a holistic approach was necessary to fully comprehend the performance of short fibres-reinforced composites. The various factors involved were specified in that chapter. One of the major factors involved was the degree of short fibre orientation. In the previous chapters, it became very clear that fibre orientation indeed plays a major role in the mechanical performance of such fibre-reinforced composites. Because there is no easy method to quantify the degree of orientation, the approach was taken of an orientation step after mixing the fibres into the rubber compounds and this was carried through in the Design of Experiments in Chapters 5, 6 and 7, as oriented versus non-oriented, and tensile measurements parallel and perpendicular to the mill orientation direction. Unfortunately, detailed quantification of the orientation and the spread therein was not possible in this way. To build on the preliminary work on this subject of Hintze¹, as briefly covered in Chapter 2, the company PANalytical B.V. in Almelo, the Netherlands, was approached, to jointly further develop the X-Ray technology towards a more easily accessible technique.²⁻⁵

Much effort has been invested in the analysis of the structure of aramid fibres.⁶⁻¹⁵ Aramid is a highly crystalline polymer, with a typical pseudo-orthorhombic crystal structure. Inter-molecular hydrogen bonding between the C=O and the N-H groups of the amide units leads

to the formation of hydrogen bonded sheets: aramid fibres exhibit structural hierarchy at the smallest length scale. At larger scales short fibre-reinforced matrices exhibit also structural hierarchy, by placing the fibres in different orientation directions in a matrix the modulus can be increased or decreased.^{8, 9}

In an elastomeric compound multiple structures are present, which are generally regarded as amorphous and crystalline phases. These entities have a complex organization. A rubber compound including short-cut aramid fibres is a composite of very many ingredients, of which the diffraction signals may overlap. In order to investigate where the diffraction peaks of the separate ingredients are located, an X-Ray Diffraction (XRD) study was first carried out on the single components. Once the relevant ingredients have been identified with XRD, and it has been safeguarded that they do not mutually influence each other, they can be used to build a 3D spatial Computed Tomography distribution, primarily via differences in density or crystallinity. This is then done with X-ray absorption in transmission.

A model that describes the semi-crystalline compound in terms of two phases has been found to be adequate for many practical purposes.¹⁶ The fraction of the material that is crystalline is an important parameter in the two-phase model. Crystallinity can be determined with a wide-angle XRD scan by comparing the areas under the crystalline peaks to the total scattered intensity, such as shown in Figure 9.1.¹⁶

Figure 9.1 — A four-cycle diffractometer. The settings of the orientations of the components are controlled by computer; each reflection is monitored in turn, and its intensity recorded.¹⁶

The accuracy or the precision of these measurements can be improved by drawing a proper baseline, using an appropriate amorphous template, and by carefully selecting the crystalline peaks.^{14, 15} The disorder in the crystalline domains can be evaluated by measuring the radial widths $\Delta(2\theta)$ of the reflections at a scattering angle 2θ by using the Deybe-Scherrer technique. They used monochromatic radiation (X-ray beam with fixed wavelength λ) and the sample was a powder. The reflections can then be monitored electronically when the detector is rotated around the sample in a plane containing the incident beam, as shown in Figure 9.1. The diffraction technique used in the present study is generally employed to identify a sample of a solid substance by comparison of the position of the diffraction lines and their intensities with the diffraction pattern stored in a large databank. Diffraction is also used to determine phase diagrams, for different solid phases, and to determine the relative amounts of each phase present in a mixture. XRD measurements in this study are performed in reflection mode with line focus, while computed tomography measurements are performed as absorption in transmission with point focus.

The diffraction technique is used for the initial determination of the interspace distance d and symmetries of unit cells. The equation developed by Bragg made it possible to calculate the angle ϑ the crystal must make to the incoming beam of X-rays for interference to occur. For example, consider the reflection of two parallel rays of the same wavelength by two adjacent planes of a lattice, as shown in Figure 9.2.¹⁷ Figure 9.2 shows that one ray strikes point D on the upper plane, but the other ray must travel an additional distance AB before striking the plane immediately below. Similarly, the reflected rays will differ in path length by a distance BC. The net path length difference of the two rays is then:

$$AB + BC = 2d \sin \theta = n\lambda \quad (9.1)$$

Figure 9.2 — XRD-principle obeying Bragg's law.¹⁷

Where d is the interspace distance, and ϑ is the angle of incident radiation. For many incident radiation angles the path length difference is not an integer number of wavelengths, and the waves interfere largely to extinguish each other. However, when the path length difference is an integer number of wavelengths ($AB + BC = n\lambda$), the reflected waves are in phase and interfere, as is shown in Equation 9.1, where λ is the constant wavelength of the X-ray (for the copper target used in the present study 1.54 Å) and n a positive integer indicating the order of the reflection.

In order now to measure the spatial distribution of the various phases in the short-cut aramid fibre-reinforced compounds: crystalline vs. amorphous, or high vs. low density, X-ray absorption in transmission can be employed. In practice, directly a 3-dimensional image can be calculated with CT. A slice image is composed of voxels (volume elements), by stacking all of its voxels, a complete volumetric representation of an object is obtained. The grey levels in a CT voxel image correspond to X-ray attenuation, which reflects the proportion of X-rays scattered or absorbed as they pass through each voxel. X-ray attenuation is primarily a function of X-ray energy and the density and composition of the material being imaged.

Recently, Sieker and Brunke¹⁸ showed that CT systems are frequently more often used through the complete process of development up to the final non-destructive quality check of elastomeric products. Their experimental results illustrate a relation between the material composition, the density and the porosity. However, the precision of the set-up requires high resolution and accuracy of the measurements to see the distribution of the different ingredients. Robin and Alshuth¹⁹ showed that 3D high resolution CT in highly filled elastomers is a successful method to determine the microstructure of the composites and distribution of the fillers. The resolution reached in the latter article was limited to approx. 50 µm, a priori too low to detect individual aramid fibres with a typical diameter of 12 µm. In 2014 Hintze¹ showed with steps of 1.5 µm that it was possible to detect a single aramid fibre and its orientation,

resp. the dispersion of zinc oxide. However, no quantification method was provided for the orientation of multiple fibres. The study was not continued due to high costs and the long scanning times required.

From the above it is clear that studies on structure-property relations of short aramid fibre-reinforced elastomers are still limited and resolution of the CT is of great importance to detect small changes. To detect only fibre-matrix phase separation a lower resolution can be used. In the present study the synthetic well-defined styrene-butadiene rubber (SBR) of the previous chapters was chosen, together with 5, 15 resp. 30 phr with 3 mm short-cut aramid fibre without finish: virgin fibre (VF) and with epoxy-amine coating.²⁰ The coupling agent used was S-3-(triethoxysilylpropyl)-octanethioate NXT in quantities of 6 phr.

In view of the above, this present study is composed of two main parts. First the XRD-responses of the different compound ingredients, including the fibres, are all individually registered in reflection, in order to separately identify these, resp. their mutual interactions, in the final compound containing all constituents. Once the signals for the aramid fibres are sufficiently clearly identified vis-à-vis the other ingredients, rotational CT in transmission is performed in order to construct a morphological 3D model of their orientation distribution. The effect of coupling agent, fibre type and blooming is also included. The properties and structures are carefully measured and all relative structure parameters are investigated.

9.3 Experimental

9.3.1 Materials and compound preparation

In this study the compound with the highest Young's modulus was selected from Chapter 8. The formulations are shown in Table 9.1a and b. A solution-polymerized styrene-butadiene rubber S-SBR, Buna VSL VP PBR 4045 HM, from Arlanxeo, Leverkusen, Germany, was used. Two types of poly(p-phenylene terephthalamide) aramid fibres were provided by Teijin Aramid B.V., in Arnhem, the Netherlands: an untreated fibre (VF) and a fibre treated with an epoxy coating (EF), both types are 3 mm long.²⁰ The coupling agent (CA) used was NXT silane from Momentive GE Silicones, Wilton, CT, USA as shown in Figure 3.2. The levels of sulphur, zinc oxide and stearic acid, from Sigma Aldrich, St. Louis, USA, were kept constant throughout the study to represent a commonly accepted optimum level²¹ determined in Chapter 5 based on Design of Experiments.²² The other ingredients are n-Cyclohexyl-2-Benzothiazole Sulphenamide CBS and DiPhenyl Guanidine DPG from Flexsys, Brussels, Belgium. Compounds were prepared according to the same procedure as described in Chapter 8, materials and compound preparation.

Table 9.1a — Unvulcanized rubber compound compositions (phr).

Formulations	Ref.	1	2	3	4	5	6	7	8
S-SBR	100	----->							
Fibre VF	5	5	15	5	5	5	5	5	5
EF		-	-	-	-	-	-	-	-
CA: NXT	6	-	-	-	-	-	-	-	-
Zinc oxide	2.5	-	-	2.5	2.5	2.5	2.5	2.5	2.5
Stearic acid	1	-	-	-	1	1	1	1	1
Sulphur	1.4	-	-	-	-	1.4	-	1.4	1.4
CBS	1.7	-	-	-	-	-	-	1.7	1.7
DPG	2	-	-	-	-	-	2	2	2

Table 9.1b — Vulcanized and aged rubber compound compositions (phr).

Formulations	9	10	11	12	13	14	15	16	17
S-SBR	→								
Fibre VF	15	-	-	15	30	15	-	15	-
EF	-	-	-	-	-	-	15	-	15
CA: NXT	-	-	-	-	-	-	-	6	6
Zinc oxide	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Stearic acid	1	1	1	1	1	1	1	1	1
Sulphur	2.8	2.8	1.4	1.4	1.4	2.8	2.8	2.8	2.8
CBS	3.4	3.4	1.7	1.7	1.7	3.4	3.4	3.4	3.4
DPG	4	4	2	2	2	4	4	4	4
	vulcanized						Aged/blooming		

Table 5.4, Chapter 5 describes which mixing stages were used. Samples were vulcanized in a Wickert press WLP 1600 at 100 bar and 150°C to sheets 110x110 mm with a thickness of 2 mm according to their t_{90} optimum vulcanization times in minutes, as determined with a Rubber Process Analyzer (RPA 2000) from Alpha Technologies, according to the procedure described in ISO 3417. To ensure the flow pattern of the rubber will not interfere with following tests, stripes were drawn longitudinally with the mill direction so that the flow pattern after vulcanization could be visualized.

9.3.2 X-Ray measurements

The XRD and computed tomography measurements were performed at PANalytical B.V. in Almelo, the Netherlands. The sample compositions and microstructure properties of the short fibre-reinforced elastomeric compounds were evaluated by means of wide-angle XRD at a broad angular range with an Empyrean diffractometer using monochromatic Cu K α radiation (wavelength 1.542 Å) at a 2 θ scan rate of 2° min⁻¹ with an acceleration voltage and beam current of 45 kV and 40 mA. The experimental conditions are shown in Table 9.2. These experiments were done on the pure materials and stepwise build-up of the compound.

The specifications of the CT X-ray technique on a vulcanized sample are shown in Table 9.3. These tests were performed on a dumb-bell test piece of the tensile test. The tomography calculations were performed with the Data Collector 5.1a-3 and 5.3 (instrument control), the High Score Plus 3.0e (MAC calculations) and Volume Graphics Studio MAX 2.2.6. The latter contains the modules for: Wall Thickness analysis, Porosity/Inclusion analysis, Coordinate measurement, Cone beam CT reconstruction and analysis and finally fibre orientation analysis.

9.4 Results

9.4.1 XRD studies

Before investigating the rubber compounds with XRD, first the individual ingredients are discussed. S-SBR is a random copolymer of butadiene and styrene, produced by anionic living polymerization, e.g. with a butyl-lithium catalyst. The SBR in the present study consists of 25% styrene, 75%butadiene of which 25% in the vinyl configuration.

Table 9.2 — X-ray specifications XRD analysis.

Instrument type	Empyrean
X-ray tube	Empyrean Cu-LFF
Focus type	Line
Power	40 mA, 45 kV
Diffraction radius	240 mm
Goniometer	Theta / Theta
Measurement mode	Reflection
Incident Beam Optics	
PreFIX	Fixed Divergence Slit
Filter	Ni 0.02 mm
Divergence	1/2°
Soller Slit	0.02 rad
Mask	10 mm
Anti-scatter slit	1°
Sample Stage	
Reflection-Transmission Spinner	
Spinning	1s/revolution
Diffracted Beam Optics	
PreFIX	X'Celerator with Fixed Anti-scatter Slit
Anti-scatter slit	5.0 mm
Soller Slit	0.04 rad
Detector	X'Celerator
PHD Settings	35 to 80% (6.20 to 12.88 keV)

Table 9.3 — X-ray specifications Powder CT

Instrument type	Empyrean
X-ray tube	Empyrean Cu-LFF
Focus type	Point
Power	20 mA, 10 kV
Diffraction radius	240 mm
Goniometer	Theta / Theta
Measurement mode	Transmission
Incident Beam Optics:	
PreFIX: CT Collimator Block	
Divergence	7 mm
Mask	7 mm
Filter	Nickel
Sample Stage: CT rotational stage	
Diffracted Beam Optics	
Detector	PIXcel-3D 2x2
Distance source-detector	480 mm
Distance source-sample	452 mm

Figure 9.3 shows the XRD pattern for SBR. The SBR is amorphous and gives only broad peaks, indicating a randomly ordered SBR, with two peaks with average domain d -spacings of 4.5 and 2.2 Å (calculated with Equation 9.1), where the high intensity peak is corresponding to the butadiene and the low intensity peak to the styrene.

Figure 9.3 — XRD data SBR.

Figure 9.4 shows the XRD curve for short-cut VF aramid fibres. The very broad peak indicates that the crystallite sizes are small.²³ Miller indices which are shown like Equation 9.2, in the graph, and estimated d-spacings from left to right are, for the strongest reflections visible: (110) 4.3 Å, (200) 3.9 Å, (211) 3.1 Å and (310) 2.3 Å.

$$\begin{array}{c} h \\ k \text{ or } (hkl) \\ l \end{array} \quad (9.2)$$

The peaks are unique and specific to aramid fibres, the layers of hydrogen bonded chains which lie in the (200) planes.²⁴

Figure 9.4 — XRD data short-cut VF aramid fibre.

The different bond lengths and bond angles can contribute to the following: 1) restricted elongation of the molecular chain, 2) strong intermolecular interaction expected from the good packing of the benzene ring, and 3) strong inter-chain forces via hydrogen bonding contribute to a high crystallite modulus.²³⁻²⁵ It is known from the literature that aramid fibres are characterized by a layer structure and differ in stacking sequence. Comparing Figures 9.3 and 9.4 shows that the main peaks of SBR and VF aramid fibres overlap around 2θ of 20° , which makes it difficult to distinguish the two.

Figure 9.5 shows the influence of an increasing concentration of VF aramid fibres in SBR: 0, 5, 15 phr, (samples 1, 2 and SBR).

Figure 9.5 — XRD data SBR with an increasing VF amamid fibre content.

A higher concentration of aramid fibres increases the peak intensity into two distinct peaks between the (110) and (200) reflections. The smaller reflections observed in Figure 9.5 are again overlapped by the broad SBR peak. However, if fibres are added in sufficient amounts, they can still be sufficiently identified as their characteristic peaks above the broad SBR peak.

Figure 9.6 shows the XRD pattern of another component in the compound: ZnO. ZnO is crystalline, with hexagonal plates with preferred orientation (001) and is mainly located in the higher 2θ range, meaning a small spatial distance of the molecules.^{26, 27}

Stearic acid, as shown in Figure 9.7, is crystalline, with a crystal structure which is monoclinic.²⁸ The first two reflections were not measured due to the measurement set-up. The largest reflections are found: for (300) at 2° and (311) 22° .

The XRD data of compound ingredient DPG (diphenyl guanidine) are shown in Figure 9.8. DPG is also crystalline; only the strongest reflections are indexed.²⁹

Figure 9.6 — XRD data of ZnO.

Figure 9.7 — XRD data of stearic acid.

Figure 9.8 — XRD data of DPG.

Sulphur is shown in Figure 9.9 and has an orthorhombic unit cell.^{30, 31} The figure shows that the crystal structure is rather complex due to the high number of peaks.

Figure 9.9 — XRD data of sulphur.

CBS (n-cyclohexyl-2-benzothiazole sulphenamide) is also a relatively complex structure, as shown in Figure 9.10, due to the large amount of low intensity peaks. Unfortunately, no information about the unit cell or miller indices could be found because CBS is not included in the database in use for interpretation of X-ray data of various substances.

Figure 9.10 — XRD data of CBS.

Figure 9.11 now shows the results for the reconstruction or build-up of a 5 phr VF fibre-reinforced unvulcanized compound: see Table 9.1 for samples pure SBR, 1, 3-7. The main peaks in the curves are reflections from the fibres and ZnO and overlap the other components in the unvulcanized samples.

Figure 9.11 — XRD build-up of short-cut fibre-reinforced compound, unvulcanized.

Figure 9.12 shows the influence of curatives in the un- and vulcanized states: Compound 7. No new peaks are formed because of vulcanization. A higher curatives concentration did not influence the XRD data either.

Figure 9.12 — Effect of vulcanization, VF-containing compounds.

Figure 9.13 shows the effect of blooming, which showed on vulcanized samples after storage of ± 6 months. A large peak is observed around $2\theta 10^\circ$ and a very small at 14° , both corresponding to DPG: (101) and (012) planes. The pink line, representing fresh compound, shows no explicit DPG, while the older samples showing blooming exhibit clear DPG peaks caused by DPG-crystals formed on the rubber surface. This is a migration effect caused by limited solubility of DPG in the rubber compound.

Figure 9.14 shows the effect of a silane coupling agent and fibres containing compound compared to a compound without coupling agent: formulations 14 and 16. There are additional peaks seen at 9° and 26° , which represent the NXT.

Figure 9.15 shows the influence of the epoxy-coated (EF) fibres versus virgin fibres (VF); the additional peaks are marked in the figure. The compounds according to formulations 14 and 15 in Figure 9.15 contain no coupling agent. Figure 9.16 shows the results of the influence of the EF-fibre versus VF-fibre, including a coupling agent NXT: formulations 16 and 17; an additional small peak occurs in the 25° range.

Figure 9.13 — Effect of blooming in a VF-containing compound.

Figure 9.14 — Effect of coupling agent.

Figure 9.15 — Effect of EF-fibres versus VF-fibres, without coupling agents.

Figure 9.16 — Effect of EF-fibres versus VF-fibres, with coupling agent.

Figure 9.17 shows the influence of orientation: formulation 16. The figure shows that the intensity of the peaks differs depending on the meso-orientation of the fibres, particularly the DPG-peak at 9°. This is an indication that the distribution of DPG bears some relation to the meso-orientation of the fibres.

Figure 9.17 — Effect of orientation.

9.4.2 Tomography

With the characteristic reflections of the various components identified, the individual entities in the composite spectra of the fibre-reinforced rubbers can now be recognized: the main ones from the SBR and the fibres. As these two components have different densities, SBR $\sim 0.9 \text{ g/cm}^3$ and aramid $\sim 1.44 \text{ g/cm}^3$, they will cause different absorptions in a CT transmission measurement that can be linked to the previous reflection data. The colour schemes used to represent the CT volume reconstruction and section views are depicted in Figure 9.18. A typical example of the amount of transmission, left over from absorption, is given in Figure 9.18, running from low to high density of the substrate. Somewhat arbitrarily, the transmission versus density graph is divided into four regions, making sure that the fibres and rubber are represented in different regions, respectively colours. From left to right: black, for the background or empty holes; cyan, surface; yellow, for rubber and red for the fibres.

Low density ←

→ High density

Figure 9.18 — Grey values and colour scheme used for volume reconstruction and section views.

For the volume reconstruction different views are chosen depending on the X-, Y- or Z-axis, as defined in Figure 9.19 (left). An example of a test piece tensile bar is shown on the right in Figure 9.19. The fibres are preferentially oriented in the y-direction in the tensile bar in this case (perpendicular to the length of the bar).

Figure 9.19 — Coordinate axis with reference to the test piece chosen for fibre orientation.

Figure 9.20 shows the X-Y cross section, looking in the Z-direction, where the fibre lengths are oriented in the Y-direction. Figure 9.21 shows an X-Z cross section, looking in the Y-direction: no preferred orientation is observed because it shows the blunt fibre ends. The figures also reveal voids and undispersed fibre bundles: resp. the black and fully red areas.

Figure 9.20 — Cross section through X-Y plane at 2 random cuts.

Figure 9.21 — Cross section through X-Z plane at 2 random cuts.

Figure 9.22 now shows a histogram of the orientation distribution in the X-Y plane, where 0° corresponds with the X-direction and 90° with the Y-direction. Figure 9.23 shows the distribution in the X-Z plane, where 90° corresponds again with the orientation in the Y-direction, and 0° and 180° with looking at the blunt fibre ends. The colours have no specific meaning; they are related to the projected angle in the equipment.

Figure 9.22 — Cross section through X-Y plane.

Figure 9.23 — Cross section through X-Z plane.

9.5 Discussion

In the fibre-reinforced elastomeric compounds multiple structures are present. They contain an amorphous SBR phase and highly crystalline phases like aramid fibre, ZnO, SA, sulphur, CBS and DPG, as was shown in the XRD data results. The entities of CBS and sulphur seem to have a more complex behaviour, especially because of the multiple peaks. However, the content of these additives is low enough not to disturb the SBR and aramid fibre signals.

The XRD data show that a clear distinction can be made between the elastomer and the aramid fibre phase. The higher the fibre concentration, the higher the intensity of the characteristic (110) and (200) reflections of the (VF) aramid fibres. On the other hand, both aramid peaks are overlapping with the SBR in the 20° range. The computed tomography (CT), which created a 3-D representation of the sample, did not make use of crystal structure differences, but distinguished only on density: SBR and aramid fibres 0.9 versus 1.4 g/cm^3 .

The CT experiments show two clear distinct phases, despite the low resolution, as was shown in Figures 9.20 and 9.21. The densities of the other compounding ingredients are

overlapping and consequently it is not possible to determine the distribution of these materials amongst themselves and quantify them, such as is done for the fibre-containing phase. In other words, the other ingredients must be considered to be part of the matrix due to the fact that they only exist in small quantities. Although no separate peaks are visible, by adjusting the section views a distribution of the fibres and rubber can be observed, independent of the sections and cuts. With these orientation differences it is possible to calculate the orientation distributions as shown in Figures 9.22 and 9.23 in the form of histograms. As the lower resolution of the present technique is limited to 65 μm , only fibre bundles of these dimensions are visible. The diameter of a single fibre is around 12 μm . This means that the resolution is a limiting factor. However, even with this limitation it is, after all, a good quantification method. Such a quantification can easily be made by taking either the peak height or peak half width from the histograms in Figures 9.22 and 9.23.

Although the CT was not able to detect dimensions smaller than 60 μm , the existence of the extra peaks are observed of which the interpretation is not clear. The XRD-data did in addition show orientation of crystalline ingredients, most conspicuously in the DPG (101) reflections. The use of DPG, as an indicator for orientation, seems to be a surprising aspect of this study. DPG, as shown in Figure 9.24, belongs to the group of guanidines and is used in the rubber industry to boost the vulcanization speed by activation of the primary accelerator CBS. The use of secondary accelerators increases the speed of the vulcanization substantially, but at the expense of scorch safety.³² The dosage of the secondary accelerator is generally between 10-30 % of the primary accelerator.

Figure 9.24 — DPG.

The DPG was primarily found in crystalline form after the aging, as blooming on the surface, around 10° in Figure 9.13. With some preliminary experiments on the bloom, zooming in to specific peaks of DPG, there is information to be gained on the orientation of its crystals. As DPG crystallizes in monoclinic needles³³, these needles tend to orient themselves as bloom on the surface. This is worth exploring further.

The experiments have shown that it is possible to obtain a quantitative measure for orientation, for the system under study. A minor disadvantage is that a resolution of 12 μm could not be reached. Hintze¹ showed in his work that CT can be done using a resolution of about 1.5 μm , but only at high costs and long scanning times 24h. For that reason the latter could not be further pursued. The method presented in this study is an enormous step forward in costs and scanning time 1h.

9.6 Conclusions

A short-cut aramid fibre-reinforced elastomeric compound was investigated using X-ray diffraction and computed tomography. Volume-surface reconstruction of the composite material and subsequent analyses with VGStudioMax reveal the following properties of the sample: the aramid fibres are arranged in the YZ plane of the sample with fibre direction running along the Y-direction. The fibres demonstrate themselves in bundles of 65 μm , due to

the limited resolution. However, in spite of this, the overall orientation is very well visible. Sometimes large inclusions of undispersed aramid material are visible, indicating inhomogeneities in the samples. The technique as developed offers potential to be used as a relatively quick method to quantify the aramid fibre orientation and distribution in SBR rubber.

The XRD data show that DPG is the main component of bloom and oriented on the sample surface along the direction of the fibres. This shows that the technique offers possibilities for much more information about the distribution of other rubber compounding ingredients. This needs further exploration.

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10 The tribological behaviour of short-cut aramid fibre-reinforced elastomers: the effect of coupling agents as interaction promoters

10.1 Abstract

The advantage of fibre-reinforced elastomers to withstand large deformations plays a significant role in their friction behaviour. The existence of an adhesion-active coating on aramid fibres for a silane coupling agent to act as an intermediate between the fibres and the elastomer matrix, resp. the importance thereof on the friction performance of elastomers has not been investigated before. The role of the coupling agent in the fibre-elastomer matrix interaction and how it influences the specific macroscopic wear of the corresponding rubber samples is studied in this chapter. The wear is compared for two types of fibres: one with and one without an adhesion-active coating, measured in two different directions: transverse and longitudinally aligned along the sliding direction. A styrene-butadiene elastomer is used as the rubber base. Pin-on-disk friction tests are performed under controlled operational conditions. The total friction coefficient is approximately 15% lower for samples reinforced with adhesive active epoxy-coated fibres in combination with a coupling agent, compared to fibres without coating. Samples with transversely oriented fibres give higher friction than for longitudinal orientation. The hysteretic contribution to the overall friction plays only a minor role, while the adhesion contribution is dominant in the present tribo-system. Further investigation of the contact area shows that it is largely influenced by the material properties. The specific wear rate of the rubber samples with epoxy-coated fibres is lower than for the non-reactive fibre-containing samples. The specific wear rate of rubber samples with transversely oriented fibres is much higher than for longitudinally oriented fibres. SEM pictures show the higher interaction effect with the elastomer for epoxy-coated fibres vs. non-reactive in the presence of the silane coupling agent.

10.2 Introduction

In Chapter 4 preliminary friction and wear tests were executed on vulcanized short-cut aramid fibre-reinforced SBR samples without reinforcing fillers like silica or carbon black. 5 phr fibres: epoxy-amine treated coated aramid fibres (EF) were positioned against virgin fibres (VF) with and without the addition of 1 phr coupling agents NXT or TESP. The approach chosen in that chapter did not lead to a real quantification of the effect of interaction/adhesion of fibre coatings and coupling agents, to create interaction between the fibres and the rubber matrix. This is probably because the effects were overruled by other factors, not included in the testing, requiring a holistic approach as employed in the previous Chapters 5 till 8. In particular, it has become clear that larger amounts of fibres and coupling agents are required to see significant differences in mechanical properties. Therefore the tribology experiments are revisited in the present chapter, with 15 phr fibres and 6 phr coupling agent NXT and orientation effects of the fibres. Reference is made to Chapter 4 for terminology and theory of friction and wear. In the present study the contact area between orthotropic viscoelastic compounds and the rigid sphere under sliding are studied in more detail and the following coordinates system is used as shown in Figure 10.1.¹

Figure 10.1 — Schematic of the coordinates system used in the present study.

Because the fibres are differently oriented along the x- and y-axes, the corresponding moduli differ, and the resulting elliptical contact area must, in general, be characterized by the following equations:

$$a_x(t) = \left(\frac{3RF_n}{4} \right)^{\frac{1}{3}} [I_1 \bar{\phi}(t)]^{\frac{1}{3}} \quad (10.1)$$

$$a_y(t) = \left(\frac{3RF_n}{4} \right)^{\frac{1}{3}} \left(\frac{I_2^{\frac{1}{2}}}{I_1^{\frac{1}{6}}} \right) [\bar{\phi}(t)]^{\frac{1}{3}} \quad (10.2)$$

Where a_x and a_y are the principal axes of the ellipse in x and y direction, respectively.¹ R is the radius of the sphere. F_n is the normal force employed, and $\bar{\phi}(t)$ is the creep compliance function as a function of time t , normalized with respect to the fully relaxed compliance.² In the fully elastic case the normalized creep compliance function $\bar{\phi}(t) = 1$. I_1 and I_2 are the numerical solutions of two contour integrals, which depend on nine material properties of the orthotropic material ($E_x, E_y, E_z, G_{xy}, G_{xz}, G_{yz}, \nu_{xy}, \nu_{xz}, \nu_{yz}$), where the E 's are the elastic moduli in the principal directions, G are the shear moduli, and ν the Poisson's ratios in the principal directions. The stiffness matrix $[S]^3$ of an orthotropic material is shown in Equation 10.3:

$$[S_{orthotropic}] = \begin{bmatrix} \frac{1}{E_x} & \frac{-\nu_{xy}}{E_x} & \frac{-\nu_{xz}}{E_x} & 0 & 0 & 0 \\ \frac{-\nu_{yx}}{E_y} & \frac{1}{E_y} & \frac{-\nu_{yz}}{E_y} & 0 & 0 & 0 \\ \frac{-\nu_{zx}}{E_z} & \frac{-\nu_{zy}}{E_z} & \frac{1}{E_z} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{G_{yz}} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{G_{zx}} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{G_{xy}} \end{bmatrix} \quad (10.3)$$

where E are the elasticity moduli of the compound and can be determined by tensile tests and G the shear moduli can be calculated using Equation 10.4, assuming the compound is a quasi-incompressible material, with Poisson's ratio ~ 0.5 , common for elastomers.

$$G = \frac{E}{2(1 + \nu)} \quad (10.4)$$

A choice was made in the present study to orient the friction test sample fibres longitudinally and transversely. This means for the longitudinally oriented fibre-containing

compounds that the elasticity moduli E_y and E_z are the same and E_x is different. The elasticity moduli E_y and E_z can be determined from tensile tests at 2% strain measured with short fibre-reinforced compounds transversely oriented to the mill direction, and E_x can be measured longitudinally oriented to the mill direction. The model is described in detail by Rodriguez Pareja et al.¹ and Swanson⁴. The principle axes of the contact can be calculated with equations 10.1 and 10.2, and the area of the corresponding ellipse with:

$$A = \pi a_x a_y \quad (10.5)$$

This equation is valid because the roughness of both materials is assumed to be perfectly smooth. The elliptical contact area together with the total friction performance is used to gain insight into the abrasion/wear resistance of the fibre-elastomer system.

The fibre concentrations were used in quantities of 15 phr, carrying forward the work of Chapter 8. To improve the fibre-matrix interfacial interaction 6 phr NXT coupling agent was used, see molecular structure in Chapter 3. The mechanical properties in Chapter 8 indicated that the modulus of the fibre-reinforced elastomer is also largely dependent on the orientation of the fibres, as is shown by the tensile test results in Chapter 8 and in the paper by Vleugels et al.⁵, and is therefore included in the present chapter.

The present study focusses on the role of fibre-matrix interaction and fibre orientation on friction and wear of short-cut aramid fibre-reinforced elastomeric compounds. The results are compared with those obtained for a compound containing non-reactive, non-interacting fibres.

10.3 Experimental

10.3.1 Materials and compounds preparation

The rubber formulations employed in this study are based on a solution-polymerized styrene-butadiene rubber type (S-SBR, Buna VSL VP PBR 4045 from Arlanxeo, Leverkusen, Germany), with a styrene content of 25w%, 75w% butadiene-content of which a vinyl content of 25%, and a Mooney viscosity ML(1+4)@100°C of 54 MU. The two types of poly-p-phenylene-terephthalamide (aramid) fibres investigated were provided by Teijin Aramid B.V., Arnhem, The Netherlands: fibres with standard finish (SF) and fibres coated with an epoxy-amine coating (EF). The present investigations were executed with SF, contrary to virgin fibres employed in Chapter 4. The differences seen in the previous chapters were minor and the SF-fibres represent the more commonly available types versus the virgin fibres. The fibres were cut to 3 mm length from continuous filaments, and have a diameter of 10-12 µm. 3-octanoylthio-1-propyltriethoxysilane (NXT) from Momentive, New York, United States, was used as a coupling agent to provide interaction between the elastomer matrix and the EF-fibres. An overview of the formulations of the elastomeric compounds is given in Table 10.1, with the amounts of ingredients expressed in parts per hundred rubber (phr).

The compounds were prepared in multiple mixing stages. The first one in a 390 mL Brabender 350S internal mixer with tangential rotors, mixer temperature setting 50°C, 110 rpm rotor speed. The fibres, NXT, zinc oxide and stearic acid were added to the prior loaded elastomer after 1 to 2.5 minutes. At 3 minutes any residue in the hopper or on the plunger was swept back into the mixing chamber. The mixes were discharged from the mixer after 4 minutes. In the second stage the fibres were further dispersed on a Polymix 80T mill for 6 minutes at 50°C, at 1.13 friction ratio rotor speeds. For the third stage the masterbatches of the second stage were returned to the Brabender mixer to ensure coupling between the EF-fibres and NXT between 120°C and 140°C, for 3 minutes at a mixer temperature setting of 50°C and 130 rpm rotor speed.

Table 10.1 — Formulations.

Compound description	1 phr	2 phr	3 phr	4 phr
S-SBR	100	100	100	100
NXT	6	6	6	6
ZnO	2.5	2.5	2.5	2.5
Stearic acid	1.5	1.5	1.5	1.5
Sulphur	2.8	2.8	2.8	2.8
CBS ^a	3.4	3.4	3.4	3.4
DPG ^b	4	4	4	4
Aramid fibres	15 EF	15 EF	15 SF	15 SF
Orientation (ball-on-disk test samples)	transverse	longitudinal	transverse	longitudinal

^aN-Cyclohexyl-2-Benzothiazole Sulphenamide, ^bDiPhenyl Guanidine

After cooling at room temperature the third stage masterbatches were returned for a stage 4 to the mixing chamber again, to mix the curatives at a temperature of 100°C at 75 rpm for 3 minutes. The end temperatures of the various mixing stages correspond with their equivalents in Chapter 8. After cooling, the batches were milled into flat sheets with nip width setting of the mill of approximately 30 µm, to ensure orientation where necessary, and subsequently stacked to fill the tensile and friction test sample moulds.⁶ Only a small amount of excess of rubber was used to prevent a flow pattern in the edges of the moulds. Figure 10.2 shows a schematic sketch of the friction test samples of the fibre-reinforced samples for two different orientations. Transverse means that the fibres were aligned in perpendicular direction to the sliding direction: see Figure 10.2a, while longitudinal means that fibres were aligned in longitudinal direction along the sliding direction: see Figure 10.2b. Therefore, it means that the vulcanizates have different elastic moduli depending on the direction in which the fibres are oriented. In this study, transverse orientation means they are assumed to be equal in the x and z direction, in longitudinal orientation but different in the z direction ($E_x = E_y \neq E_z$).

Figure 10.2 — Samples for tribometer tests; rubber disks with a) transversely and b) longitudinally oriented fibres.

The samples were vulcanized in a Wickert press WLP 1600 at 100 bar and 150°C to sheets of 110x110 mm with a thickness of 2 mm for tensile tests, while for the friction tests disks with a thickness of 5 mm were prepared, according to their t_{90} optimum vulcanization time minutes, as determined with a Rubber Process Analyzer (RPA 2000) from Alpha Technologies, according to the procedure described in ISO 3417.

10.3.2 Characterization methods and friction tests

Stress-strain measurements of the vulcanized compounds were performed on a 3343 series Tensile Tester from Instron, to determine the tensile strength at break, strain at break and

Young's modulus, according to ISO 37 Type 2 dumb-bell size see Figure 10.3. A crosshead speed of 500 mm/min. was employed. Creep properties of the compounds were determined using a Dynamic Mechanical Analyser Metravib Viscoanalyser DMA 150 in shear mode at constant stress, at ambient temperature.

Figure 10.3 — Tensile test samples with different orientations.

The friction tests were executed with a ball-on-disk experiment, as schematically represented in Chapter 4, Figure 4.3. The ball was made out of granite, with a surface roughness of a root mean square $0.97\ \mu\text{m}$ determined with a confocal microscope, 35 mm in diameter, the rubber disk samples were 5 mm thick with a diameter of 34 mm. The viscoelastic losses during shearing of the rubber samples with the rigid ball were used to determine the friction. The experiments were done at room temperature. The sliding velocity was 0.2 m/s, corresponding to the sliding velocity in the tyre/road contact at a driving speed of a car of 80 km/h, and a nominal contact pressure (P_m) of 0.2 MPa, corresponding to the tyre pressure. The Equations 1, 2 and 5 can be used to specify the nominal load. The specific wear rate is calculated after the dry-friction tests.⁵

A Jeol JCM-6400 Scanning Electron Microscope (SEM) was used to make pictures and a Keyence Confocal Microscope VK 9700 was used to measure the average asperities of the granite ball.

10.4 Results

10.4.1 Mechanical results

The mechanical stress-strain curves determined with help of the tensile test are presented in Figure 10.4 and Table 10.2, which quantify the following properties: tensile strength at break, strain at break, Young's modulus (YM) and elasticity moduli (E) at 2% strain. The compounds containing EF-coated fibres show the highest strength at break and YM values, dependent on the fibre orientations. There is a significant difference between SF-containing compounds compared to the EF-containing compounds, where the longitudinal orientations show better mechanical properties compared to the transversely oriented fibre-containing compounds. However, the higher strength at break for the longitudinally oriented fibre-containing compounds are accompanied by a significantly lower strain at break.

Figure 10.4 — Tensile stress-strain diagram of two types of fibres and fibre orientations, see Figure 10.3.

Table 10.2 — Compound mechanical properties (phr).

Samples	Strength		Strain		YM		E	
	at break MPa	St. dev. MPa	at break %	St. dev. %	MPa	St. dev. MPa	at 2% strain MPa	St. dev. MPa
*EF 0°	8.1	0.3	57	4	20.3	2.0	15.6	1.3
EF 90°	3.9	0.9	151	18	4.5	0.3	2.7	0.2
*SF 0°	5.8	0.2	111	13.7	6.7	0.8	4.9	0.5
SF 90°	3.8	0.1	184	17	3.1	0.2	2.2	0.2

*results from Chapter 8

Figure 10.5 shows the creep of the fibre-reinforced compounds, transversely oriented on the mill. The EF compound shows less creep compared to the SF compound. The creep results can be fitted using a series of discrete exponential terms given by Equation 10.6.⁷

$$\phi(t) = \phi_r - \sum_{i=1}^3 \phi_i e^{-\left(\frac{t}{\lambda_i}\right)} \quad (10.6)$$

The equation indicates the initial creep due to instantaneous elastic deformation where t represents time and λ_i three retardation times used for fitting purposes. As can be seen in Figure 10.5, the creep behaviour of the compounds is very well described by Equation 10.6. The parameter values of the fit equation can be found in Table 10.3 for all compounds.

10.4.2 Contact area

The contact area can be calculated using Equations 10.1, 10.2 and 10.5. The Elasticity Modulus at 2% strain of the compounds can be found in Table 10.2. The creep properties of the compounds can be obtained by putting the parameter values of Table 10.3 into Equation 10.6. The shear moduli of the compounds are calculated using Equation 10.4, assuming the compound is a quasi-incompressible material (Poisson's ratio $\nu \sim 0.5$), common for elastomers. The elliptical contact areas are calculated and plotted over time in Figure 10.6. It shows that the contact areas increase with time; after 5 to 6 seconds the contact areas become constant. The contact area of the transversely oriented compound is the same as the longitudinally oriented compound, as simply the x - and y -axes are interchanged. The contact areas of the EF compounds are smaller than for the SF compounds.

Figure 10.5 — Creep versus time diagram.

Table 10.3 — Compound mechanical properties (phr).

	SF transversely*	EF transversely
ϕ_r , Pa ⁻¹	1.09×10^{-6}	1.02×10^{-6}
ϕ_1 , Pa ⁻¹	4.31×10^{-9}	1.40×10^{-8}
ϕ_2 , Pa ⁻¹	1.13×10^{-8}	1.56×10^{-8}
ϕ_3 , Pa ⁻¹	8.23×10^{-8}	1.09×10^{-7}
λ_1 , s	0.302	0.009
λ_2 , s	0.808	1.097
λ_3 , s	1.687	1.903

*oriented to the mill direction

Figure 10.6 — Contact area versus time diagram.

10.4.3 Friction tests

To check whether the assumption that was made in the introduction was correct - to neglect the deformation contribution to the friction force - an extra experiment was performed where the sample surfaces were wetted with a very thin layer of low-viscosity oil, Ordina 927, Shell. The friction coefficient μ_{wet} in wet contact can be calculated by decoupling of the

hysteretic contribution from the total friction, which was done in Chapter 4 as well.

The experiments performed under dry contact give the total friction, see Equation 4.3, Chapter 4. A typical measured signal is shown in Figure 10.7. The coefficient of friction takes some time to equilibrate and is taken as the mean value when the signal is stabilized.

Figure 10.7 — The coefficient of friction as a function of sliding distance.

The friction force at steady state for all compounds can be seen in Figure 10.8, all calculated with Equation 4.4 from Chapter 4. It shows that the friction force for the transversely oriented fibres containing compounds is nearly the same as for the longitudinally oriented ones. The friction force of the EF compounds is significantly lower than for the SF compounds. The adhesion contribution, measured as the decrease in friction force with the thin oil layer, is dominant in all cases. Therefore it was correct to neglect the deformation friction for the calculation of the contact area, with Equations 10.1, 10.2 and 10.5, as was done for the circular contact area in Chapter 4 before. The results of friction force are caused by the different contact areas, lower for EF than for SF, and for transversely oriented fibres lower than for longitudinally oriented.

Figure 10.8 — The F_{total} under dry contact: grey, and F_{def} with a thin layer of oil: shaded.

10.4.4 Specific Wear rates

The specific wear rate can be calculated with Equation 4.5, Chapter 4. The specific wear rate of each compound can be seen in Figure 10.9. There is quite some scatter in the results, but the error bars of the SF vs. EF samples do not overlap. The average specific wear rates

of the epoxy-coated fibre compounds are lower than for the standard finished compounds for both orientations, longitudinal and transverse. In both cases the longitudinally oriented samples show some more wear than the transversely oriented. The combination of adhesion-reactive coating and coupling agent NXT has a clear positive effect on the wear behaviour of the compound.

Figure 10.9 — Specific wear rate vs. type of fibres and orientation.

10.4.5 Microscopic pictures

Figure 10.10 shows the wear tracks of the samples for the transversely oriented and longitudinally oriented samples after the friction experiments for the EF-fibres containing compounds. The corresponding compounds for SF fibres look similar. The figure shows a clear visual difference between transversely and longitudinally oriented fibres. Figure 10.11 shows a magnification of the wear tracks after the experiment for the transversely and longitudinally oriented EF-fibre-containing compounds measured with SEM. The transversely oriented fibre-containing compound shows that the orientation of the fibres is perpendicular to the sliding direction, where the fibres are partly detached from the matrix, and so will orient in the direction of the sliding. The longitudinally oriented samples show that the fibres remain aligned in the sliding direction.

Figure 10.12 shows a magnification of the wear tracks after the experiments for the longitudinally oriented compounds, SF- vs. EF-fibres. The SF-containing compound, Figure 10.12a, shows rectangular signs of fibre pull-out. Figure 10.12b shows no signs of fibre pull-out, which is an indication of stronger fibre-rubber matrix interaction compared to the SF-fibres. To further stress the increased interaction caused by the coated EF-fibres in combination with the NXT coupling agent, pictures were also taken from the debris generated in the wear tests: see Figure 10.13. The differences in structure of the worn debris are minimal, as visible in Figure 10.13, with a slight indication of more coherence for the EF-containing samples.

10.5 Discussion

The results in this chapter are quite intriguing. In the previous tribology Chapter 4 it was already observed that the reinforcement effect coming from the flexible aramid fibres in low amounts of 5 phr was mainly coming from the addition of the fibres themselves: there was no adhesion necessary between the aramid fibres and the rubber matrix, but the randomly oriented aramid fibres kept the intrinsically weak rubber together.

Figure 10.10 — Confocal microscope pictures of test sample wear tracks: a) transversely and b) longitudinally oriented EF-fibres.

Figure 10.11 — SEM pictures of wear tracks: a) transversely and b) longitudinally oriented EF-fibres.

Figure 10.12 — SEM pictures of longitudinally oriented compounds: a) SF- and b) EF-fibres.

Figure 10.13 — SEM pictures of wear debris of a) SF- and b) EF-fibres.

The surface offered by the EF aramid fibres interacts with the polymer matrix via the coupling agent, in a nanometrically thin layer around the fibres. The strength of the otherwise not reinforced rubber with reinforcing fillers was too low to properly transmit the load among neighbouring fibres without itself being fractured.⁸ This was clearly seen in the mechanical properties of Chapter 3. On the other hand, in Chapter 8 samples with higher fibres and coupling agent amounts were used based on the outcome of the Design of Experiments in the previous chapters. The interaction of the aramid fibres was increased in such a way that clear differences in the mechanical properties were observed. On these understandings, the question addressed in the present chapter was whether these differences could be seen in the friction and wear performance.

The friction test results are largely dependent on the stiffness of the material as it translates into the contact area between the rubber samples and the granite ball. The stiffness is a critical factor in the determination of the E-moduli. Mokhtari et al.⁹ determine the E-moduli with the help of DMA tests at 1 Hz, while Rodriguez Pareja et al.¹ used the tensile E-moduli at 2% strain. The reason was that the differences between EF and SF fibres were better visible in tensile testing than in DMA testing. Another argument was that DMA testing practically always measures at very small strains corresponding to Young's moduli, which are not really relevant to actual rubber applications. Therefore in this chapter tensile moduli at 2% strain were taken, different from Chapter 4. Because with this approach the moduli differences were larger than previously seen with the DMA measurements, it was not possible to perform experiments with the Reference compound without fibres such as in Chapter 4. The determination of the real contact area will depend thereon. It is the writer's opinion that this is worth a more in-depth investigation.

The ball-on-disk experiments are designed in such a way that a circular movement is applied. The orientation of the fibres in the x, y and z directions is not perfect, either by the distribution seen in Chapter 9 or by experimental problems to create properly oriented samples which are disturbed by e.g. the vulcanization process.

The total friction force results, Figure 10.8, can be used as a discriminating factor for interfacial interaction, because a significant difference is observed between the epoxy-coated fibres with coupling agent compared to the standard finish fibre values, to the benefit of epoxy-coated fibres with coupling agent. The deformation F_{def} component is less appropriate as a criterion because the significance is not good enough. The differences in orientation of the fibres, whether longitudinal or transverse, have a surprisingly small effect on the friction force. The transversely oriented fibres even show a lower friction force compared to longitudinally oriented ones, as was not expected.

Surprisingly, the specific wear rates in Figure 10.9 for the transversely oriented fibres were lower than for the longitudinally oriented fibres, although the significance is poor. However, the trend corresponds with the ranking of the total friction forces in Figure 10.8. The root cause of all this is the smaller contact area for EF-fibres with coupling agent at the same contact pressure, which, in turn, results in lower friction forces and as a result of that, a lower specific wear rate.

The increase in fibre amount and coupling agent, and monitoring the fibre orientation, has led to a more important role of the fibre–elastomer interfacial interaction in comparison with Chapter 4. This answers the main question of the entire project. It is the writer's opinion that, in order to further substantiate the effect of interaction/adhesion between aramid fibres and the rubber matrix, it is necessary to use rubber compounds which include reinforcing fillers

like silica or carbon black, because only in the latter case is the load carrying role of the rubber matrix between adjacent fibres guaranteed: see Chapter 12 later on.

10.6 Conclusion

An optimized SBR elastomeric compound was mixed with 15 phr of two types of 3 mm short-cut aramid fibres: with and without epoxy-amine coating, and coupling agent NXT. The addition of an adhesion active coating on the aramid fibres in combination with NXT improves the matrix interaction, resulting in a significantly reduced friction force, irrespective of whether the fibres were oriented longitudinally or transversely in the sliding direction. The friction is mainly dependent on the adhesion contribution of the granite ball to the rubber and not so much on the deformation part, for both types of fibres. The total friction coefficient is approximately 15% lower for samples reinforced with adhesive active epoxy-coated fibres (EF) in combination with a coupling agent, compared to fibres without coating (SF). Samples with transversely oriented fibres give lower friction than for longitudinal orientation. These results are mainly influenced by the contact area, lower for the EF-containing compounds compared to the SF-containing compounds, because of their higher moduli.

The specific wear rate of the rubber samples with epoxy-coated fibres is lower than for the non-reactive fibre-containing samples. The specific wear rate of rubber samples with transversely oriented fibres is lower than for longitudinally oriented fibres.

SEM pictures show the higher interaction effect with the elastomer for epoxy-coated fibres vs. non-reactive in the presence of the silane coupling agent. The approach chosen gives a good lead to further research on the effect of interaction/adhesion of fibre coatings with coupling agents and the rubber matrix.

10.7 Reference

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11 The influence of silane coupling agents on the performance of a silica-reinforced SBR/BR tyre tread compound, additionally strengthened with short-cut aramid fibres

11.1 Abstract

This study concerns short aramid fibre reinforcement of a highly silica-reinforced SBR/BR elastomeric compound. In the present study, a highly silica-loaded elastomer formulation is employed to investigate how the results from previous chapters, without reinforcing fillers, compare with a more realistic practical tyre tread compound. Two types of 3 mm short-cut aramid fibres are investigated: an untreated fibre and a fibre treated with an epoxy-amine coating. The fibres are added in amounts of 0, 5, 10, 15, 20, 30 and 40 parts per hundred rubber (phr). The coupling agent selected is *Bis*-(triethoxysilylpropyl)-tetrasulphane (TESPT) and added in amounts of 0, 2, 4 and 6 phr. To further investigate the role of the coupling agent, also a silica pre-modified with TESPT is used, and additional tests are performed with coupling agents *Bis*-(triethoxysilylpropyl)-disulphane (TESPD) and S-3-(triethoxysilylpropyl)-octanethioate (NXT). Material properties are determined on a laboratory scale by measuring the Mooney viscosity, rubber curing and tensile properties, hardness and dynamic mechanical performance. The results show that the reinforcement caused by the short aramid fibres in the elastomeric matrix depends on four main factors: 1) fibre volume fraction, 2) fibre orientation, 3) the properties of the components (elastomers / type of fibre) and 4) fibre-matrix interfacial strength (type and amount of coupling agent). The properties of highly silica-reinforced elastomeric compounds in combination with short-cut aramid fibres differ enormously in comparison with those for non-silica reinforced compounds. The strength at break and strain at break are greatly increased. Above 5 phr fibres a yield point in the tensile curves appears, which is a new indicator of fibre reinforcement. Enhanced epoxy-coated fibres show an increase in Young's modulus and a shift of the yield point towards higher stresses compared to virgin fibres. As tensile strength and elongation at break decrease with increasing Young's modulus and yield point, these two tensile characteristics don't lend themselves to quantify fibre reinforcement any further. Longitudinal orientation of the fibres increases their effect on the tensile strength, yield point and Young's modulus, compared to transverse and random orientations. The $\tan \delta$ values in the 60°C temperature range as indicative for Rolling Resistance of tyre treads based on compounds made thereof, are not affected by VF-concentrations in the presence of 7 phr TESPT, while the Skid Resistance, as indicated by the $\tan \delta$ in the 0°C region, is lower compared to the reference compound without any fibres, which needs to be valued negatively.

11.2 Introduction

Elastomers are used for many applications because of their high elasticity.¹ However, almost no elastomer can be used in its original form because of its low strength.² The strength can be improved by vulcanization^{3, 4} and by the inclusion of particulate fillers⁵ and/or fibres.⁶⁻¹⁰ The largest market for elastomers is the tyre industry.¹¹ In this field, a lot of research is performed on materials to improve the driving characteristics and the durability of elastomeric

tyre treads^{12, 13}, like adding strength at low strains by the use of short fibres.⁵ Despite the fact that short-cut fibres, ranging in lengths of a few millimetres, can significantly increase the modulus at low strains, a large shortcoming is the interfacial bonding of the fibres with the elastomer matrix, which is typically not seen for short fibre-reinforced thermosets.¹⁴ A reinforcement method that has not been examined in detail before is the implementation of short-cut fibres and silica in combination with a silane coupling agent.

The work in the present chapter is based on the recent works of Shirazi and Hintze^{6, 15}. Both did extensive research into the important factors for short-cut fibre reinforcement in a highly carbon black filled compound, assuming that the factors are not mutually affecting each other, not even by processing. This resulted in an ongoing discussion about the relative importance of other factors for the interpretation of the results. No mechanism could be presented which equivocally explains (small) interfacial strength differences of the fibre with the matrix.^{5, 16-18} According to other authors the interfacial strength between fibre and rubber seems to play a large role though.^{5, 10} To further improve the quality of short fibre-reinforced compounds, it is essential to know the mutually influencing factors and how to control them.

In the study described in this chapter a well-defined combination of styrene-butadiene rubber (SBR) with polybutadiene (BR) was chosen, based on a 'green tyre' tread formulation for a passenger car tyre.¹⁹ First, 3 mm short-cut aramid fibres without finish: virgin fibres (VF) were used of poly-p-phenylene-terephthalamide (aramid fibres). Aramid fibres are generally very inert and consequently difficult to adhere to, so no interaction between the VF and rubber is assumed. The interfacial strength of the surface of aramid fibres with a rubber can be enhanced, as demonstrated in previous chapters of this thesis, by two main elements: an adhesive coating and an agent which can interact with this coating, a coupling agent. To make sure that proper interaction is established, a type of coating was selected which has the ability to chemically react with a silane coupling agent. So, secondly, aramid fibres were selected treated with an epoxy-amine coating²⁰ (EF), for which a reaction product of a model system is shown in Figure 3.1. The figure shows that the epoxy has reacted away and OH groups have appeared. Based on the work of De Lange et al.²¹ increases of oxygen-atoms on the fibre surface from 11% to approx. 22% were achieved with epoxy-amine coating fibre surface, based on XPS measurements.²⁰

The fibre and coupling agent concentrations are varied in the present study, carrying forward the work of Shirazi and Hintze.^{6, 15} To improve the fibre-matrix interfacial interaction a silane coupling agent was introduced. Silane coupling agents represent a class of materials used for a very broad range of purposes. A classification of the variety of these products can be found in the literature^{22, 23}. The silane coupling agents in the present study serve a dual purpose: apart from fibre-rubber matrix interaction, they are also a prerequisite for the coupling of silica with the rubber^{23, 24}. The chemical structure of the coupling agent determines the polymer-fibre interaction which, in turn, influences the mechanical properties. The coupling agent *Bis*-(triethoxysilylpropyl)-tetrasulphane (TESPT, Figure 3.2) belongs to the class of sulphur silanes and should be able to react with the OH groups on the EF resulting from the epoxy treatment of the fibre surface²¹, the silica and with the elastomer during the sulphur vulcanization.

The coupling agents were added in different quantities. The amount of free sulphur in the system was kept constant. Multiple reactions will take place, the three main ones are shown in Figures 6.3 and 6.4: TESPT coupling with fibre and/or silica and reacting with the elastomer: vulcanization. During mixing the silane reacts with silica and with the adhesion activated fibre,

which leads to hydrophobation of the silica and fibre surface: Figure 6.3.²⁵ The hydrophobation reduces the tendency to generate large silica agglomerates and fibre-fibre bundles; in other words, it improves the dispersion. Furthermore, it makes the polar silica and fibre more compatible with the nonpolar elastomer, which leads to lower compound viscosities.^{26, 27} Under vulcanization conditions a chemical link (Figure 6.4) between the silane and rubber is created. This fibre-silane-elastomer coupling leads to an improved reinforcement of such compounds.^{23, 24, 28, 29} For the activation of the fibre-elastomer coupling, curatives such as elemental sulphur and accelerators play an important role in the silane-elastomer reaction.³⁰ In the presence of elementary sulphur, the poly-sulphide of the silane is activated due to the insertion of elemental sulphur into the poly-sulphide of the silane, as shown in Figure 6.4. According to Debnath et al.³¹ the TESPT coupling agent can also reversely act as a sulphur donor. So, the elementary sulphur in the vulcanization package, together with the sulphur taken up and released from the coupling agent plays an intricate dance in both polymer cross-linking and polymer-fibre coupling, resp. with silica.

The coupling agents *Bis*-(triethoxysilylpropyl)-disulphane (TESPD) and *Bis*-(triethoxysilylpropyl)-tetrasulphane (TESPT), both belong to the class of sulphur silanes. The coupling agent S-3-(triethoxysilylpropyl)-octanethioate (NXT) and is a blocked mercapto-silane. All should be able to react with the OH groups resulting from the epoxy treatment of the fibre surface^{20, 21} and with the elastomer during the sulphur vulcanization. The coupling agents were added in low quantities: 6 phr based on TESPT. NXT and TESPd were added in equimolar quantities based on the number of ethoxy groups per molecule. Consequently, the amount of silane and the amount of added sulphur both influence the vulcanizates properties strongly, as both the fibre-silane-elastomer and the elastomer-elastomer matrix-cross-linking are responsible for reinforcement.

In the foregoing set-up of experiments the silane coupling agents have to fulfil a dual purpose: to chemically couple the silica to the elastomers and to establish interaction between the fibres and the silica-reinforced compound. This adds an extra level of complexity. In an attempt to decouple these two purposes, an extra series of experiments are executed with silica pretreated with TESPT coupling agent: Coupsil 8113, consisting of Silica Ultrasil VN3 pretreated with 13 phf (parts per hundred filler) of TESPT. Assuming that most of the reactive sites on the silica have been captured, the role of the silane in the compound reduces to interaction promoter with the fibres. For proper comparison with this Coupsil system, the unmodified silica used for this study was also chosen as Ultrasil VN3, even though this silica does not represent the so-called easy-dispersion silicas commonly employed for low Rolling Resistance tyres.

The influences of the fibre and coupling agent's concentration on the fibre and elastomer interactions and their effect on the processing characteristics of these compounds are presented, as well as their influences on the mechanical properties. In the present study a complete 'green tyre' passenger car tyre tread formulation is employed, including silica as reinforcing filler. M. Shirazi, in his PhD thesis, made the observation that the addition of 5 phr RFL-coated aramid fibres in a carbon black-reinforced NR-formulation reduced the $\tan \delta$ at 60°C, as indicative for reduced Rolling Resistance of tyre treads made thereof.⁶ Therefore it is of interest to see whether, in the present formulation based on silica-reinforced SBR/BR, the same trend is observed. At the end of this chapter, dynamic mechanical experiments will be presented to verify this.

11.3 Experimental

11.3.1 Materials and compound preparation

The formulations, see Tables 11.1a-b, were based on a common^{23, 32} ‘green tyre’ passenger car tyre tread.¹⁹ A 70/30 blend of 37.5 wt% oil-extended solution styrene-butadiene rubber (SBR), Buna VSL 5025-2 HM (Arlanxo, Leverkusen, Germany) and KBR 01 (Kumho, Seoul, S-Korea) high-cis-polybutadiene was used. The two types of poly-p-phenylene-terephthalamide (aramid) fibres^{21, 25} investigated were provided by Teijin Aramid B.V., in Arnhem, the Netherlands. Both types are 3 mm long. Ultrasil VN3 silica granulates, Coupsil 8113 pretreated silica and coupling agent *bis*-(triethoxysilylpropyl) tetrasulphide (TESPT, Si 69) were obtained from Evonik Industries AG, Essen, Germany. The other two silane coupling agents used were: Bis-(triethoxysilylpropyl)-disulphane (TESPD, Si 75) from Evonik Industries AG, Essen, Germany and S-3-(triethoxysilylpropyl)-octanethioate (NXT) from NXT*silane Momentive GE Silicones, Wilton, CT, United States. The levels of sulphur, zinc oxide and stearic acid, from Sigma Aldrich, St. Louis, United States, were kept constant throughout the study to represent a commonly accepted optimum level.³³ The stabilizers 6PPD, TMQ, and vulcanization accelerators N-Cyclohexyl-2-Benzothiazole Sulphenamide (CBS) and DiPhenyl Guanidine (DPG) were from Flexsys, Brussels, Belgium.

For this research various highly silica-reinforced mixtures were prepared: one without fibres (0 parts per hundred rubber, phr), others with virgin fibres (VF) in different concentrations (5, 10, 15, 20, 30 and 40 phr VF) and compared with coated EF-fibres (5, 10 and 20 phr EF), see Table 11.1a. In the acronyms used in this table, the first numbers represent the amounts of fibre used (phr) and the second part represents the type of fibre used.

The influence of coupling agent TESPT was further investigated with the addition of pretreated silica Coupsil 8113 with TESPT, see Table 11.1b. The acronyms used in this table present first the amounts of fibre (phr), secondly the type of fibre, followed by the coupling agent dosage and type. When there is no fibre and/or coupling agent used, the abbreviations 0F and 0CA are used. The concentration of TESPT was varied from 0 to 6 phr for EF and VF; TESP and NXT were added at 6 and 9 phr respectively, representing equimolar quantities based on the number of ethoxy groups per molecule vs. TESPT. The sulphur amounts were also adjusted to equimolar quantities relative to the TESPT-containing compounds in order to – at best – avoid effects related to differences in degree of vulcanization between the different compounds.

The compounds were prepared in a 390 ml Brabender 350S tangential internal mixer using a six-stage mixing procedure. The six-stages mixing procedure is presented in Table 11.2. A fill factor of 0.7 was employed. A Schwabenthan 150 ml mill, with a friction ratio of 1:13, was used. After stage 5, 50% of the masterbatch was oriented in stage 6, while the other 50% was directly used for vulcanization. The six stages were used to orient the fibres on the mill and make a sheet with a narrow nip width of approximately 50 µm. A narrow nip width was the most efficient way to orient the fibres.³⁴

A Rubber Process Analyzer RPA 2000 from Alpha Technologies was used to determine the optimal vulcanization time at 160°C, according to the procedure described in ISO 3417. Samples were vulcanized in a Wickert press WLP 1600 at 100 bar and 160°C to sheets of 110x110 mm with a thickness of 2 mm for tensile and DMA tests, according to their t_{90} optimum vulcanization time + 2 minutes, as determined with the RPA 2000. To ensure that the flow pattern of the rubber in the mould does not interfere with the following tensile tests, lines were

drawn in longitudinal direction with the mill direction, so that the flow pattern after the vulcanization was visible.

Table 11.1a — Rubber compound formulations (phr).

Ingredients	Reference	5VF	10VF	15VF	20VF	30VF	40VF	5EF	10EF	20EF
SBR	97.3	----->								
BR	30.0	----->								
Silica VN3	80.0	80	80	80	80	80	80	80	80	80
Zinc oxide	2.5	----->								
Stearic acid	1.5	----->								
TDAE	6.7	----->								
Aramid	0	5	10	15	20	30	40	5	10	20
Type:		VF	VF	VF	VF	VF	VF	EF	EF	EF
TESPT	7.0	7	7	7	7	7	7	7	7	7
6PPD	2.0	----->								
TMQ	2.0	----->								
Sulphur	1.4	----->								
CBS	1.7	----->								
DPG	2.0	----->								

Table 11.1b — Rubber compound formulations (phr) containing pretreated silica.

Ingredients	0F-0CA	10VF-0CA	10VF-2TESPT	10VF-4TESPT	10VF-6TESPT	10VF-6TESPD	10VF-9NXT	10EF-0CA	10EF-2TESPT	10EF-4TESPT	10EF-6TESPT	10EF-6TESPD	10EF-9CANXT
SBR	97.3	----->											
BR	30.0	----->											
Silica	80.0	80	80	80	80	80	80	80	80	80	80	80	80
Coupsil													
Zinc oxide	2.5	----->											
Stearic acid	1.5	----->											
TDAE	6.7	----->											
Aramid	0.0	10	10	10	10	20	20	10	10	10	10	10	10
Type:		VF	VF	VF	VF	VF	VF	EF	EF	EF	EF	EF	EF
TESPT	0	0	2	4	6	0	0	0	2	4	6	0	0
TESPD	-	-	-	-	-	6	-	-	-	-	-	6	-
NXT	-	-	-	-	-	-	9	-	-	-	-	-	9
6PPD	2.0	----->											
TMQ	2.0	----->											
Sulphur	1.4	1.4	1.2	1.0	0.8	1.4	1.4	1.4	1.2	1.0	0.8	1.4	1.4
CBS	1.7	----->											
DPG	2.0	----->											

A few adjustments were made to the standard mixing procedure for the compound with 40 phr fibres. The mixture was mixed at 90 rpm in stage 1 and at 110 rpm in stage 3, because of the high torque caused by the high largeness of fibres. Furthermore, stages 2 and 3 were switched for this mixture because of difficult processability. A third adjustment was that, at stage 3 of mixing, the process was stopped at 155°C to prevent early vulcanization, i.e. premature scorch.

11.3.2 Characterization methods

Mooney viscosity measurements were performed using a Mooney 2000VS from Alpha Technologies, using the large rotor (L), at 100°C according to ISO 289. The hardness of the vulcanized compounds was measured using a Zwick 3150 Shore A Hardness Tester. Tensile measurements were performed in the tensile mode with an Instron tensile tester with a load cell of 1000 N, according to ISO 37 at a crosshead speed of 500 mm/min.

Dynamic mechanical analyses were done using a Metravib DMA200. For storage E' and loss E'' moduli as functions of temperature, measurements were performed in the tension mode between -80 and +80°C in steps of 2°C per minute at a dynamic strain of 0.1%, static strain of 0 % and a frequency of 10 Hz. Frequency sweep measurements of the vulcanizates were performed in tension mode at a constant dynamic strain of 0.1 % from -25 till 50°C, with the frequency sweep ranging from 1 to 200 Hz. From the results a Williams-Landel-Ferry (or WLF) temperature-frequency shift was applied with the help of the Metravib software. Room temperature was chosen as the reference temperature.

Table 11.2 — Compound preparation procedure.

Stage 1: Mixing			Internal mixer
Rotor speed: 110 rpm	Initial temp.: 50°C	Fill factor: 0.7	
Steps in mins:			
0	Add SBR + BR		
1	Add fibres + silane,		
2	Add ½ silica, ZnO, SA+ TESPT		
2.30	Add ½ silica, TMQ + 6PPD		
3	Sweep		
4	Take out		
Stage 2: Milling (fibre dispersion)		Mill	
Configuration: 1:1.13	Nip width: 1 mm	Duration: 6 minutes	
Stage 3: Silanization		Internal mixer	
Rotor speed: 130 rpm	Initial temp.: 50°C	Fill factor: 0.7	
Steps in mins:			
0 min	Masterbatch		
3 min	Take out ~155°C		
24 hours maturation time			
Stage 4: Curatives		Internal mixer	
Rotor speed: 75 rpm	Initial temp.: 50°C	Fill factor: 0.7	
Steps in mins:			
0	Masterbatch		
1	Add sulphur, CBS + DPG		
2	Sweep		
3	Take out		
Stage 5: Milling		Mill	
Configuration: 1:1.13	Nip width: 1 mm	Duration: 5 times guided through the mill	
Stage 6: Milling (orientation, optional)		Mill	
Configuration: 1:1.13	Nip width: 1 mm	Duration: 1 time guided through the mill	

11.4 Results

11.4.1 Compound Mooney viscosities

Tables 11.3a-c list the compound Mooney viscosities (MV) at 100°C for all investigated compounds. The MV of the compounds containing fibres and coupling agent are all increased

compared to the reference compounds containing no fibres, except for the 5VF- and 5EF-containing compounds. It was not possible to measure the sample with a VF-fibre concentration of 40 phr due to slippage. The *MV* results of 5, 10 and 20 phr fibres EF versus VF are more or less comparable.

Table 11.3a — Elastomer compound properties.

Properties	Ref.	5VF	10VF	15VF	20VF	30VF	40VF	5EF	10EF	20EF
Stage 1, °C	147	153	142	152	152	154	138	140	154	163
Stage 3, °C	132	130	135	137	149	155	154	132	135	149
Stage 4, °C	88	94	102	108	107	116	121	98	95	115
ML(1+4) at 100°C	40	36	53	57	62	86	n.m.	35	52	64
t_{s1} , min	4.6	3.6	2.6	2.1	1.6	1.5	1.9	3.5	2.6	1.5
t_{90} , min	13	13	12	13	12	12	13	13	12	12
M_i , dN·m	1.6	1.5	1.4	1.4	1.4	1.7	3.2	1.4	1.5	1.6
M_h-M_i , dN·m	7	8	10	11	11	13	16	8	11	10
$t_{90}-t_{s1}$, min	8	10	10	11	11	11	11	10	10	11

n.m. = not measurable because of rotor slip

The reaction of the coupling agent with the fibres is an uncontrollable factor in these experiments, see Table 11.3b, and can either be positively or negatively influenced by the conditions during mixing.^{35, 36} Although the temperature after the 1st step was well within the supposed reaction range, between 120 and 140°C, the efficiency of the process is still unknown. The somewhat higher *MV* for the EF-containing compounds vs. those with VF might be taken as an indication that the coupling agents improve the hydrophobation/compatibilization of the fibres with the elastomer. The *MV* of 10EF-6TESPT shows a higher torque compared to its equivalents with the coupling agents NXT and TESP, which could be a sign of premature scorch for TESPT, see Table 11.3c.

Table 11.3b — Elastomer compound properties with pretreated silica.

Properties	0F-0CA	10VF-0CA	10VF-2TESPT	10VF-4TESPT	10VF-6TESPT	10EF-0CA	10EF-2TESPT	10EF-4TESPT	10EF-6TESPT
Stage 1, °C	140	145	139	137	135	142	141	140	136
Stage 3, °C	140	135	138	136	126	133	136	133	127
Stage 4, °C	87	108	104	102	97	98	101	104	97
ML(1+4) at 100°C	56	72	95	101	103	68	100	106	114
t_{s1} , min	0.4	0.7	0.6	0.5	0.4	0.7	0.5	0.5	0.4
t_{90} , min	7	11	12	13	17	10	11	14	19
M_i , dN·m	0.8	0.9	1.0	1.1	1.3	1.0	1.1	1.1	1.3
M_h-M_i , dN·m	9	11	12	13	15	10	13	14	15
$t_{90}-t_{s1}$, min	7	10	11	12	16	9	10	13	17

Table 11.3c — Elastomer compound properties with pretreated silica.

Properties	10VF-6TESPD	10VF-9NXT	10EF-6TESPD	10EF-9NXT
Stage 1, °C	122	119	124	119
Stage 3, °C	131	118	132	127
Stage 4, °C	102	97	100	98
ML(1+4) at 100°C	95	98	106	100
t_{s1} , min	0.5	0.8	0.5	0.9
t_{90} , min	11	11	11	16
M_i , dN·m	1.1	1.0	1.1	1.0
M_h-M_i , dN·m	12	12	15	13
$t_{90}-t_{s1}$, min	11	10	11	15

11.4.2 Curing behaviour

The curing properties of the various compounds are presented in Tables 11.3a-c, and Figure 11.1. Figure 11.1 shows that the addition of fibres influences the curing curves significantly. Fibres increase the torque values, as seen in the M_h-M_i see Table 11.3a, compared to the reference compound. For the compounds with 5, 10 and 20 VF vs. EF and 7 phr TESPT, the M_h-M_i as well as the scorch times (t_{s1}) are comparable. This means that the epoxy coating is not acting as a plasticizer in this system, as sometimes stated. The M_h-M_i values in Table 11.3b for EF-containing compounds with variable amounts of diverse coupling agents, increase only marginally vs. the VF-containing compounds with the same amounts of fibres. The values of the minimum rheometer torque M_i are qualitatively comparable with the Mooney viscosities. A clear overall shape difference is observed in the various curing curves from start at t_{s1} till t_{90} . This makes it difficult to make a comparison between all the curves belonging to the 0, 2, 4 phr coupling agent concentrations and fibres. Compound 10EF-6TESPT shows a clearly higher M_h-M_i , probably caused by some scorch due to the large amount of TESPT added. In Table 11.3a and, see Figure 11.1, the t_{90} values are practically the same. However, large differences are seen in the t_{90} values for the compounds in Tables 11.3b and c, clearly influenced by the coupling agents and fibre concentrations.

Figure 11.1 — Curing behaviour of compounds (Table 11.1a) with increasing fibre concentrations VF 0-40 phr and 7 phr TESPT.

11.4.3 Mechanical properties

Tables 11.4a and b list the tensile properties for all compounds with silica VN3, after being vulcanized till $t_{90} + 2$ min. The vulcanizates were tested in three fibre directions:

randomly (X), longitudinally (0°) and transversely oriented (90°). Figure 11.2 presents the tensile stress-strain curves of the reference compound containing no fibres versus increasing VF-fibre concentrations, all measured in longitudinal direction with the mill. In this graph the best average curve was chosen out of each data set, and this procedure was also followed in the other stress-strain figures. The properties at low strain are improved with increasing fibre concentration, while the strain at break decreases. The curves show that above 10 phr fibre content a yield point becomes visible, which is increasing with higher fibre concentrations. The stress at break is clearly a bad indicator to quantify effects. At 40 phr fibre loading the rubber compound becomes too weak to withstand forces and breaks directly after the yield point. The strain at break decreases a lot with increasing fibre dosage.

Figure 11.2 — Tensile stress-strain curves of reference compound with increasing VF-fibre concentrations and 7 phr TESPT: Table 11.1, all in longitudinal direction of the mill.

Figure 11.3 presents the tensile curves for 20VF and 7 phr of TESPT-containing compounds, Table 11.1a, at different fibre orientations: random, longitudinal and transverse. Longitudinal orientation shows the largest reinforcement in the low strain range, second best is the random orientation direction of the fibres and lowest the transverse direction.

Figure 11.3 — Tensile stress-strain curve of different fibre orientations for 20 phr VF and 7 phr TESPT: Table 11.1a.

Table 11.4a — Rubber vulcanizates properties: Reference, 5VF, 10VF, 15VF and 20VF.

	Reference			5VF			10VF			15VF			20VF		
	X	0°	90°	X	0°	90°	X	0°	90°	X	0°	90°	X	0°	90°
Strength at break, MPa	19.7	19.9	18.60	19.6	19.9	19.7	18.2	19.6	16.8	15.7	16.9	13.4	11.4	13.0	10.3
St. dev., MPa	0.8	0.8	0.7	0.3	0.2	0.5	0.3	0.4	0.5	0.3	0.5	0.6	0.6	0.5	0.2
Strain at break, %	1483	1506	1568	921	930	920	700	703	695	599	575.7	642	663	401	785
St. dev., %	56	71	37	3	13	26	10	21	69	12	23	58	42	19	42
YM, MPa	1.8	1.8	1.7	2.2	2.4	2.3	9.1	14.4	3.5	9.6	26.8	5.0	30.6	50.3	36.1
St. dev. MPa	0.03	0.03	0.05	0.0	0.2	0.0	0.4	2.9	0.4	1.5	3.0	0.5	3.3	2.7	1.6
Stress at yield point, MPa	-	-	-	-	-	-	-	-	-	-	-	-	5.9	9.6	-
St. dev. MPa	-	-	-	-	-	-	-	-	-	-	-	-	0.2	0.1	-
Strain at yield point, %	-	-	-	-	-	-	-	-	-	-	-	-	73	44	-
St. dev., %	-	-	-	-	-	-	-	-	-	-	-	-	20	3	-
TM at 25% strain, MPa	1.4	1.3	1.3	4.4	4.2	3.5	5.1	11.2	3.8	8.0	13.7	4.6	7.8	13.3	34.3
St. dev., MPa	0.1	0.1	0.1	0.4	0.2	0.2	0.5	1.3	0.4	0.6	1.2	0.4	0.9	1.0	0.6
TM at 50% strain, MPa	0.8	0.8	0.8	2.3	3.2	2.4	4.8	3.3	3.3	5.1	1.8	3.4	0.2	-0.8	2.0
St. dev., MPa	0.1	0.1	0.1	0.1	0.2	0.2	0.4	0.5	0.4	0.5	0.4	0.5	0.6	0.4	0.3
Stress at 25% strain, MPa	0.61	0.64	0.59	1.5	1.37	1.26	1.6	3.5	1.4	2.6	5.4	1.7	5.3	8.2	2.5
St. dev., MPa	0.01	0.02	0.02	1.1	0.03	0.05	0.1	0.5	0.1	0.3	0.5	0.1	0.4	0.4	0.3
Stress at 50% strain, MPa	0.86	0.89	0.83	2.3	2.3	2.0	2.8	5.2	2.3	4.1	6.9	2.7	5.8	9.5	1.7
St. dev., MPa	0.02	0.03	0.02	0.1	0.1	0.1	0.2	0.5	0.2	0.3	0.6	0.2	0.2	0.1	0.2
Hardness, Shore A	61.1	60.0	61.0	72.2	74.3	71.2	78	81.0	77	85	86	84	87.0	82.1	85.3
St. dev. Shore A	0.2	1.5	1.5	0.2	0.1	0.2	0.1	0.3	0.2	0.3	0.1	0.3	0.5	1.4	0.5

Table 11.4b — Rubber vulcanizates properties: 30VF, 40VF, 5EF, 10 EF and 20EF.

	30VF			40VF			5EF			10EF			20EF		
	X	0°	90°	X	0°	90°	0°	0°	0°	X	0°	90°	X	0°	90°
Strength at break, MPa	9.3	11.1	8.9	7.0	9.3	6.6	18.7	17.4	11.7	11.7	13.1	11.0			
St. dev., MPa	0.6	0.7	0.4	0.4	0.4	0.2	0.8	0.23	0.3	0.3	0.6				
Strain at break, %	520	513	688	380	46	497	801	602	565	348	775				
St. dev., %	65	47	48	66	13	20	32	21	20	51	60				
YM, MPa	31.4	66.3	6.9	38.4	96.0	8.8	7.9	30.5	23.1	81.6	8.0				
St. dev. MPa	3.7	6.8	1.0	2.8	7.3	0.3	1.7	1.7	1.8	7.0	2.0				
Stress at yield point, MPa	6.6	10.2	-	6.9	12.8	-	-	-	-	13.0	-				
St dev. MPa	0.3	0.1	-	0.4	0.7	-	-	-	-	0.4	-				
Strain at yield point, %	65	28	-	54	22	-	-	-	-	29	-				
St. dev., %	15	1	-	12	1	-	-	-	-	2	-				
TM at 25% strain, MPa	9.0	5.2	4.6	9.8	14.5	3.9	7.1	7.3	7.9	2.1	5.5				
St. dev., MPa	1.5	2.0	0.4	0.9	3.8	0.2	0.2	0.7	0.7	3.5	0.8				
TM at 50% strain, MPa	0.7	-3.0	2.6	-0.3	-	2.6	3.7	0.5	1.6	-2.2	2.5				
St. dev., MPa	0.6	0.4	0.1	1.1	-	0.2	1.3	0.35	0.5	2.3	0.2				
Stress at 25% strain, MPa	5.2	10.1	1.8	6.0	11.8	1.8	2.2	5.5	4.3	13.0	2.1				
St. dev., MPa	0.6	0.2	0.1	0.5	0.8	0.1	0.5	0.1	0.2	0.5	0.3				
Stress at 50% strain, , MPa	6.0	8.8	2.7	6.6	-	2.6	3.6	6.5	5.2	11.7	3.0				
St. dev., MPa	0.6	0.3	0.2	0.4	-	0.1	0.3	0.1	0.2	0.1	0.4				
Hardness, Shore A	87.1	89.2	77.1	92	87	90	73.2	83.1	86	77	78				
St. dev. Shore A	2.3	1.1	0.5	0.9	0.7	1.2	1.3	1.0	0.7	2.4	1.3				

Figure 11.4 shows the tensile stress curves for 5, 10 and 20 VF- and EF-containing compounds all with 7 phr TESPT. The higher the fibre concentrations, the larger the differences in behaviour between VF and EF. At 10 and 20 phr fibre loadings the EF clearly

reinforces more than VF.

Table 11.4c shows the tensile test data for the Coupsil pretreated silica-containing compounds. All these fibre-containing compounds show the best properties for the EF in the low strain region, compared to the compound without fibres and coupling agent: 0F-0CA. Higher coupling agent concentrations of TESPT increase the difference between VF and EF.

Table 11.4c — Rubber vulcanizates properties, measured in 0° with the mill.

	0F-0CA	10VF-0CA	10VF-2TESPT	10VF-4TESPT	10VF-6TESPT	10VF-6TESPD	10VF-9NXT	10EF-0CA	10EF-2TESPT	10EF-4TESPT	10EF-6TESPT	10EF-6TESPD	10EF-9NXT
Strength at break, MPa	21.7	17.3	18.0	18.6	18.8	14.4	14.9	16.7	18.2	18.3	18.2	15.6	15.3
St. dev., MPa	1.2	1.8	1.3	0.5	0.3	1.7	0.7	0.3	0.3	0.6	0.4	0.5	0.4
Strain at break, %	1330	862	849	706	782	468	555	874	744	910	660	519	535
St. dev., %	47	97	68	29	61	55	35	56	28	38	19	15.7	15
YM, MPa	2.3	6.2	6.6	8.1	4.5	44.1	27.9	7.9	6.8	9.4	9.5	37.8	35.4
St. dev. MPa	0.1	0.5	1.3	0.7	0.4	4.4	3.5	1.0	1.2	1.3	1.1	7.6	4.3
Stress at yield point, MPa	-	-	-	-	-	7.3	6.9	5.5	5.5	5.6	6.7	7.7	8.0
St dev. MPa	-	-	-	-	-	0.1	0.2	0.1	0.1	0.0	0.1	0.13	0.1
Strain at yield point, %	-	-	-	-	-	32	44	97	81	77	82	36	39
St. dev., %	-	-	-	-	-	1	3	6.5	7	10	9	4	3
TM at 25% strain, MPa	1.3	6.0	6.1	8.3	4.0	4.0	11.9	7.4	6.6	9.1	7.9	12.8	12.0
St. dev., MPa	0.3	0.7	1.0	1.0	0.4	1.3	0.9	1.9	1.8	1.8	0.5	0.8	2.6
TM at 50% strain, MPa	1.0	6.7	7.2	7.3	4.5	-1.5	-0.87	7.6	8.3	7.8	9.9	-2.2	-3.4
St. dev., MPa	0.2	0.3	0.6	0.5	0.7	0.7	0.52	0.6	0.3	0.4	0.3	0.8	0.2
Stress at 25% strain, MPa	0.73	1.6	1.7	2.2	1.7	7.0	5.6	1.8	1.8	2.2	2.3	6.9	6.8
St. dev., MPa	0.03	0.2	0.2	0.2	0.1	0.14	0.2	0.2	0.3	0.3	0.1	0.5	0.3
Stress at 50% strain, MPa	1.0	3.3	3.4	4.3	2.7	7.0	6.8	7.6	3.7	4.5	4.6	7.3	7.7
St. dev., MPa	0.03	0.2	0.5	0.3	0.2	0.1	0.2	0.6	0.7	0.6	0.2	0.2	0.1
Hardness, Shore A	65.2	75.2	77.6	78.3	76.2	85	82	74.6	74.3	74.7	77.8	82.5	81.3
St. dev. Shore A	0.7	0.6	0.7	1.1	1.2	0.5	0.8	0.7	1.8	0.7	1.0	0.8	0.6

Figure 11.5 shows the tensile test results for three different coupling agents in combination with EF-fibre, all longitudinally oriented. The enlarged figure at low strain shows that the 6TESPT-containing compounds both for EF and even more so for VF give very low stresses compared to the 6TESPD- and 9NXT-containing compounds. This could be the result of an oversaturation from the TESPT already contained in the Coupsil silica and the amount added in the formulation. This also explains why the YM values for these two compounds in Table 11.4c are so low compared to the others.

Tables 11.4a and b show that the addition of fibre increases the hardness, for the VF- and EF-containing compounds. The EF-containing compounds show comparable hardnesses with VF. Table 11.4c shows that the hardness increases marginally which increases coupling agent concentration for VF as well as for EF. The coupling agents TESPD- and NXT-containing compounds show a clearly higher hardness compared to their TESPT-containing equivalents.

Figure 11.4 — Tensile stress-strain curves of epoxy coated fibres versus VF for 5, 10 and 20 phr fibre with 7 phr TESPT: Table 11.1a, all measured in longitudinal direction with the mill.

11.4.4 Dynamic mechanical analysis

Dynamic Mechanical Analysis (DMA) temperature sweep data are presented in Table 11.5. $\tan \delta$ at 0°C and at 60°C respectively, are commonly taken as indicators of wet skid resistance and rolling resistance for tyre treads made out of pertinent compounds. As this chapter is based on a ‘green tyre’ passenger car tyre tread formulation, it is worthwhile to have a look at these properties.

The $\tan \delta$ at 0°C decreases with increasing VF-fibre concentration for the compounds of Table 11.1a, prepared with regular silica and 7 phr TESPT coupling agent. However, the use of 20 phr EF-fibres restores the $\tan \delta$ at 0°C back to the value for the Reference compound without fibres added, while the $\tan \delta$ at 60°C stays constant, as shown in Figure 11.6. The $\tan \delta$ peak maximum decreases in height and slightly shifts to lower temperature for the VF-containing compounds. Again, for the 20 phr EF-containing compounds the peak height decreases only slightly relative to the Reference compound without fibres.

Figure 11.5 — Tensile tests in longitudinal direction for three different coupling agents and two types of fibre: Table 11.1b.

Table 11.5 — DMA, temperature and frequency sweep.

		Temperature sweep				Frequency sweep	
Sample		Tan delta		at Maximum		Storage moduli	
		0°C	60°C	Tan δ	Temp. (°C)	1 Hz (MPa)	10 ⁶ Hz (MPa)
Table 11.1a	Reference	0.18	0.11	0.50	-40.2	16	50
	20VF	0.14	0.11	0.28	-41.5	119	200
	30VF	0.12	0.11	0.24	-41.7	204	372
	40VF	0.11	0.10	0.22	-44.4	285	565
	20EF	0.18	0.11	0.39	-40.6	44	113
Table 11.1b	10EF-0CA	0.22	0.11	0.45	-28.8	36	88
	10EF-2TESPT	0.17	0.10	0.48	-38.1	31	82
	10EF-4TESPT	0.18	0.10	0.49	-38.3	29	77
	10EF-6TESPT	0.16	0.10	0.44	-38.7	38	87
	10VF-4TESPT	0.16	0.09	0.48	-40.8	31	83

Figure 11.7 shows an increasing storage modulus E' versus temperature for increasing VF-fibre concentration. From the perspective of tyre performance these results show that the use of 20 phr EF-fibres with 7 phr TESPT provides close to Reference values indicative for Skid Resistance as well as Rolling Resistance, contrary with VF-fibres, wherefore the Skid Resistance would deteriorate.

Figure 11.8 shows the $\tan \delta$ curves against temperature for the compounds with Coupsil pretreated silica and increasing coupling agent concentration: Table 11.1b. The addition of extra coupling agent lowers the temperature of the $\tan \delta$ peak by 10°C and increases its value slightly for 2 and 4 phr TESPT, but decreases it for 6 phr TESPT. Apparently the shift of the $\tan \delta$ peak to lower temperature already occurs at low coupling agent concentration.

Figure 11.9 shows the storage moduli values for the EF-containing compounds prepared with pretreated silica. To highlight the influence of the EF- versus the VF-fibres in this system, 10EF-4TESPT versus 10VF-4TESPT are plotted in Figure 11.10. For the 10 phr EF-fibre-containing compounds the temperature of the $\tan \delta$ peak is slightly increased by approx. 5°C, while the peak height is not significantly changed.

Figure 11.6 — $\tan \delta$ versus T for increasing VF-fibre concentrations, with 7 phr TESPT.

Figure 11.7 — E' versus T for increasing VF-fibre concentrations, with 7 phr TESPT.

Figure 11.8 — $\tan \delta$ versus T for increasing EF-fibre, TESPT concentrations and pretreated silica.

Figure 11.9 — Storage modulus E' versus temperature for increasing EF-fibre and TESPT concentrations and pretreated silica.

Table 11.5 shows the results of the frequency sweep data for 1 and 10^6 Hz, the first measured and the second calculated by horizontal time-temperature shifting of the data obtained at different temperatures with 20°C as a reference. The results show that the storage moduli at 1 and 10^6 Hz are strongly increased with an increasing VF-fibre concentration, but

not for 20 phr EF-fibre. The samples with the Coupsil pretreated silica show a slightly decreasing trend of the storage modulus with increasing coupling agent concentration, except for 6 phr TESPT.

11.5 Discussion

The observations on the Mooney viscosities and curing data are of limited value in the present context, because it is obvious that the MV and cure torque M_h-M_l will rise with increasing fibre concentration. A difference between the EF- vs. VF-fibres is practically not seen in the MV , because the interaction effects aimed for in the present context are not developed yet in the uncured state. The slight increase in M_h-M_l with increasing coupling agent concentration might well have to do with its participation in the vulcanization process.

The most interesting results are the tensile results obtained after vulcanization. The most striking result is the occurrence of yield point at the first 50% elongation, above 10 phr of fibre employed. Basically, the vulcanized matrix is strong enough to sustain sufficient stress to reach the yield point before it breaks or tears, even after the addition of 40 phr fibre, which is extremely large. This means that the yield point can now be used as a discriminating factor to judge the effect of interaction/adhesion between the fibres and the elastomer matrix. The results obtained for these silica-reinforced compounds in comparison with those for the non-silica-reinforced compounds in the previous chapters are enormous. The Young's modulus effects are much more pronounced. The vulcanized compounds show yield points and higher strengths at break thanks to the elongations at break which are increased by many factors. Consequently, the differences between the EF-fibre/coupling agent combinations and VF-fibre /coupling agent combinations are much more pronounced: see Figure 11.4. Also, the effects of orientation of the fibres are more clearly visible: Figure 11.3.

Figure 11.10 — Storage modulus E' versus temperature for increasing EF- vs. VF-fibre concentrations.

The observations on the tensile strengths at break deserve some extra discussion. The tensile strength data decrease with increasing VF-fibre concentration: Table 11.4a, opposite to the development in the yield points, respectively, the higher the Young's modulus the lower the tensile strength: Figure 11.2. The tensile strengths measured in the longitudinal direction along the fibres are always highest, followed by random orientation and transverse orientation. In fact, the same ordering as seen in the Young's modulus data, except much less pronounced. Looking at the results for the Coupsil pretreated silica with varied amounts of

TESPT coupling agent, Table 11.4c, there is little or any effect seen. The tensile strength is therefore not a good indicator for reinforcement compared to the Young's modulus or the yield points at low strain, nor is the elongation at break.

Of the various coupling agents investigated: TESPT, TESPd and NXT, the TESPT is, after all, not the most robust. In combination with the Coupsil pretreated silica, TESPd and NXT perform much better, leading to very high Young's moduli in comparison with TESPT. The reason for that remains a bit unclear. It might be the result of oversaturation from TESPT, where the Coupsil pretreated silica already contained a large amount of TESPT to start with. For the normal silica VN3 this is not clear, because similar experiments were not performed. All these experiments were executed at the very beginning of the overall project, but not further pursued, because they were outside the agreed scope of the project.

The reinforcing power of the fibres, EF as well as VF, becomes clear only in loadings of more than 5 phr, see Table 11.4a. At 5 phr, formulation 5VF, the Young's moduli for random, transverse and longitudinal orientation are still practically equal. At 10 phr, 10VF, the longitudinal Young's modulus stands out significantly against the random orientation, as second best, and against the transverse orientation as being the worst. Actually, in all cases the random orientation positions itself in between longitudinal and transverse orientation for all fibre dosages. This favourably compares with the observation in Chapter 3, where for 5 phr randomly oriented VF- and EF-fibres, but without silica employed, the Young's modulus was the highest compared to longitudinal and transverse orientation. In Chapter 8, where the amount of fibres was increased to 15 phr, still in the absence of silica reinforcement, the longitudinal orientation also showed the highest Young's modulus.

In Chapter 8 the optimum coupling agent concentration turned out to be 6 phr, above which the Young's modulus tended to decrease again. In the present study the coupling agent amount was only varied for TESPT in combination with the Coupsil pretreated silica: Table 11.1b. In spite of the large difference of the formulations in this table compared with those employed in Chapter 8, the same effect can be observed in the present case, in the sense that the Young's modulus for the VF-fibres tends to decrease at higher TESPT-loading than 4 phr. For EF-fibres this does not happen (yet) while the Young's modulus stays at a high level even for 6 phr TESPT added. This was also seen in essence in Chapter 8 for the non-silica reinforced formulations. Again, the EF-fibres stand out compared to the VF-fibres for the system with pretreated silica.

The dynamic mechanical experiments of the formulations in Table 11.1a are quite different compared to those for Table 11.1b, where the latter do not show much difference amongst themselves. For the regular VN3 silica with a constant amount of 7 phr TESPT, the $\tan \delta$ results at 0°C decrease with increasing amounts of VF-fibres, while the $\tan \delta$ results at 60°C remain unchanged. This would indicate a negative influence of the VF-fibres on the skid resistance of tyres made therefrom. The EF-fibres show much less of this negative effect, Table V, as their $\tan \delta$ at 0°C remains more or less on the level of the Reference compound without any fibres added. The EF-fibres also stand out in the sense that the storage moduli for 20EF remain low in contrast with the VF-fibres, be it a little higher than the Reference compound with fibres. For the second series of experiments with the Coupsil pretreated silica there is not much to be seen, except that the storage modulus remains low and that the $\tan \delta$ at 0°C also decreases somewhat. Overall, these results are still rather difficult to fully understand; much more research would have been required to fully elucidate the effects seen. But that was again outside the scope of the project.

Coming back to the analogy raised in Chapter 3 of reinforced concrete, in the present case this analogy can be further expanded on, in this case to silica reinforcement. The fibres are the analogues of the steel reinforcement, the silica the stones, and the elastomer the cement. All three cooperate towards creating the strength of the concrete. The silica reinforcement creates a so-called co-continuous filler network with the vulcanized elastomer, which gives strength throughout the matrix of the composite. The aramid fibres can now adhere/interact with this much stronger matrix along larger distances than they could do where no reinforcing filler is present, like in the previous chapters, where the coupling agents would at best adhere a thin layer of rubber around the fibres, but without strong interaction on a longer distance. This could also be a subject for future research.

11.6 Conclusions

In the current chapter a complete ‘green tyre’ passenger car tyre tread formulation was employed, including 80 phr silica as reinforcing filler. The influences of the fibre concentrations and coupling agent concentrations on the fibre and elastomer interactions and their effect on the processing characteristics of these compounds were presented, as well as how they influence the mechanical properties. There are enormous differences in mechanical properties between highly silica-reinforced elastomeric compounds in combination with short-cut aramid fibres, in comparison with those for non-silica reinforced compounds. Much higher strengths at elongations are obtained in comparison with non-silica reinforced compounds. The coupling agent TESPT can now form strong silane bridges with the silica as well as with the fibres and the elastomer matrix. A three-phase co-continuous network is created. This coupling creates a greatly improved fixation of the fibres in the elastomer matrix, in particular for the EF-fibres compared to the VF-fibre-containing compounds. Coupling agent TESPT with VF-fibres also reinforces the system, but to a lesser extent, because it cannot form fibre-matrix bridges. In the highly silica-filled system the Young’s modulus effects are much more pronounced than in the absence of silica. The vulcanized compounds show yield points above 5 phr fibres added, the higher the more fibres added and more for EF- compared to VF-fibres. The tensile strengths and elongations at break respond in an opposite manner towards the modulus and yield point changes, and are therefore not appropriate to quantify fibre reinforcement effects. The better performance of EF-fibre / coupling agent combinations is much more pronounced than for VF-fibre / coupling agents. Also, the effects of orientation of the fibres is more clearly visible.

Of the various coupling agents investigated: TESPT, TESP and NXT, the TESPT is after all not the most robust. In combination with Coupsil 8113 pretreated silica TESP and NXT perform much better in comparison with TESPT, leading to very high Young’s moduli.

Shirazi made the observation in his PhD thesis, that the addition of 5 phr RFL-coated aramid fibres in a carbon black-reinforced NR-formulation reduced the $\tan \delta$ at 60°C, as indicative for reduced Rolling Resistance of tyre treads made thereof. In the present formulation based on silica-reinforced SBR/BR this effect is much smaller. The $\tan \delta$ values in the 60°C temperature range are not affected by the VF-concentrations in the presence of 7 phr TESPT, while the Skid Resistance, as indicated by the $\tan \delta$ in the 0°C region is lower compared to the reference compound, which needs to be valued negatively. 20 phr EF-fibre-containing compounds are similar to the reference compound without any fibres, which is an indication that the fibre-elastomer-silica interaction/coupling for this type of fibre improves the dynamic properties. Adsorption of the coupling agents on the fibre surface improves the

immobilized polymer chains covering the surface of the fibres, to form an interphase between the elastomer matrix and the fibre, indicating better interfacial interaction.

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12 Proof of silane epoxy-amine coated fibre interaction on a larger scale internal mixer

12.1 Abstract

This study concerns the qualitative proof of principle in a 1.6 L mixer of the silanization reaction of epoxy-amine coated fibres embedded in a styrene-butadiene rubber compound with coupling agent S-3-(triethoxysilylpropyl)-octanethioate (NXT). Two types of 3 mm cut short-cut aramid fibres are tested: untreated fibres with an oily finish and fibres treated with an epoxy-amine coating. The fibres are added at a concentration of 15 parts per hundred of rubber (phr) and the coupling agent is added in a quantity of 6 phr. Fibres are tested in random, longitudinal and transverse orientation with the mill direction. Tensile tests are executed and used to assess the interaction between the fibres and the elastomer, with the emphasis on low strain properties.

The results show a positive silanization reaction of epoxy-amine coated aramid fibres in combination with NXT coupling agent. The highest Young's modulus was found for 15 phr epoxy-amine aramid fibre in combination with 6 phr NXT. Even without coupling agent 15 phr epoxy-amine coated fibres do give some reinforcement relative to standard fibres. In most cases the longitudinally oriented fibres show the largest reinforcement and transversely oriented fibres show the worst reinforcement. Random orientations give results surprisingly close to the longitudinal orientation for standard finish, epoxy-amine coated fibres and standard finish fibres with 6 phr NXT coupling agent. On the other hand, for the combination with the adhesion active epoxy-amine coating together with NXT coupling agent, the Young's modulus in longitudinal direction is significantly higher, as seen before in Chapter 8. The latter is the clearest sign of the positive effect of fibre-elastomer interaction by means of the coupling agent.

12.2 Introduction

The replacement of standard finish short-cut aramid fibres by adhesion active epoxy-amine coated fibres¹ in combination with NXT coupling agent compounds resulted in improved mechanical properties and abrasion resistance, see Chapters 8 and 10.²⁻⁵ However, these short-cut fibres were very difficult to mix properly. For that reason a series of experiments were set up in a larger 1.6 L internal mixer at Teijin Aramid B.V. in Arnhem, the Netherlands, as compared to the 350 cm³ internal mixer used throughout the studies in the previous chapters. Suitable mixing conditions were established for short-cut fibre-reinforced compounds for the 350 cm³ laboratory mixer. An important factor for proper silanization of the epoxy-amine coated fibres in combination with NXT coupling agent was the temperature trajectory during the mixing cycle, whereby the aim was to achieve end temperatures of 120-140°C. The larger the internal mixer, the more difficult it is to reach such high temperatures.⁸⁻¹⁰ By maintaining the conditions for the scale-up of different sized internal mixers, such as: same shear-stress, power input and same temperature profile during the mixing cycle, van Buskirk et al.¹¹ showed that closely matching the temperature profiles during the mixing cycle and mixer volume loading gave a successful scale-up for a given elastomeric compound. However, it is in practice difficult to match the temperature profile in a large mixer to that of a laboratory mixer because of the difference in heat transfer due to the changed surface/volume ratio with the size of the mixer.¹²

In the current study a few tests are performed on a 1.6 L internal mixer. The emphasis is on adjusting the mixing temperature of the internal mixer in order to enhance the efficiency of the reaction between the silane-based coupling agent and the short-cut aramid fibres. Two types of 3 mm cut short-cut aramid fibres are tested in the same SBR-rubber compound formulation as used in this thesis: untreated fibres with an oily finish (SF) and fibres treated with an epoxy-amine coating (EF).

In addition to the 1.6 L compared to the 350 cm³ internal mixer, the vulcanization and tensile properties are also measured in a somewhat different way at Teijin Aramid B.V., compared to the experiments in the previous chapters in this thesis. Because of the many different ways of executing the experiments, a direct one-to-one comparison with results from 350 cm³ internal mixer data is not appropriate. The purpose of this exercise is a qualitative proof of principle of the benefits of using epoxy-amine coated fibres in combination with NXT coupling agent on the mechanical properties.

12.3 Experimental

12.3.1 Materials and compound preparations

In this study the formulation with the largest Young's modulus difference was selected from Chapter 8. The variations on this formulation as tested are shown in Table 12.1.

Table 12.1 — Rubber compound compositions (phr)

	Reference	6 NXT-SF	6 NXT-EF	6-NXT-EF duplo	SF	EF
Formulation	1	3	4			
S-SBR	100	----->				
Fibres (SF or EF)	0	15SF	15EF	15EF	15SF	15EF
Coupling agent	0	6	6	6	0	0
Zinc oxide	2.5	----->				
Stearic acid	1.5	----->				
Sulphur	2.8	----->				
CBS	3.4	----->				
DPG	4	----->				

The experiments were executed in the Teijin Aramid B.V. laboratories based on the procedure described in Table 12.2.

A 1.6 L Banbury internal mixer was used with a fill factor of 70%. The mixing procedure was designed to mimic the procedure developed in Chapter 8 to reach the same end temperatures. The torque versus time, respectively the temperature-traces during the mixing cycle were recorded automatically, but the end temperatures were measured manually with a thermocouple, because the real temperature is commonly 10 to 20 degrees higher than recorded by the temperature sensor in the mixer.

Because the larger internal mixer also requires a larger two-roll mill for the subsequent mixing stages, the mill nip width could not be set narrower than 0.5 mm. Therefore, a separate series of extra tests were included to determine the effect of a smaller mill nip width of 0.3 mm with the same small mill as used in the previous chapters at the University of Twente. By including this step the dispersion could be better monitored. The curatives were added on the larger two-roll mill with a nip width of 1 mm after the large mixer, see Figure 12.1a.

A calender was used to orient the fibres instead of the two-roll mill in the previous chapters, respectively to make sheets which fitted directly in the mould, see Figure 12.1b.

Sample sheets 210x210 mm were vulcanized in a Fontijne Press Labpro 600, at 100 bar and 150°C to sheets. All sheets were moulded with a thickness of 2 mm for tensile tests, according to their t_{90} optimum vulcanization times, as determined with the locally owned Rubber Process Analyzers (RPA 2000) of Alpha Technologies, according to the procedure described in ISO 3417, with a strain of 2.8% and 0.8 Hz.

Table 12.2 — 5 stage mixing procedure for the large mixer.

Stage 1		
Rotor speed	50 rpm	
Initial temp.	50°C	
Steps	Time (s)	Add
	0	Elastomer
	60	33% of fibres+silane
	75	33% of fibres+silane
	90	33% of fibres+silane, ZnO, stearic acid
	105	Sweep
		Increase temperature to 115°C and leave for two minutes, adjust rotor speed to lower values necessary, dump
Stage 2		
Disperse fibres on a Troester two-roll mill		
Nip width	0.5 mm	
Stage 3		
Rotor speed	50-70 rpm	
Initial temp.	50°C	
Steps	Time (min)	Add
	0	Total compound
		Increase temperature to 115°C and leave for two minutes, adjust rotor speed to lower values necessary, dump
Stage 4		
Remix on 2-roll mill: 1 at Teijin Aramid, 2 at the University of Twente.		
Stage 5		
3-Calender	2 mm	nip width
Guthrie –Pullen		
LTD

a)

b)

Figure 12.1 — a) Mill and b) tensile sheet preparation.

12.3.2 Characterization methods

Mooney viscosity measurements were performed using a Mooney 2000VS from Alpha Technologies, using the large rotor (L), at 100°C according to ISO 289. Tensile test measurements were performed with an Instron 5800 R tensile tester and Instron BZ1.0 with Blue Hill software, with a load cell of 1000N, with type II dumb-bells, with an initial length of 50 mm, according to ISO 37 at a crosshead speed of 500 mm/min.

12.4 Results

12.4.1 Mixing performance

Figure 12.2 shows a typical example of a torque versus time and temperature profile for the compounds. The end temperatures of the mixing cycles, stage 1 and 3, as measured manually with a thermocouple are of particular importance and given in Table 12.3.

Figure 12.2 — Torques and temperatures versus time.

12.4.2 Mooney viscosity and vulcanization

Table 12.3 shows the *MV* of the compounds after stage 5, with 0.5 mill nip width. The second *MV* row shows the values after the 0.3 mm mill nip width. It shows that the *MV* decreases slightly by using a smaller nip width, by some polymer breakdown. The coupling agent has a plasticizing effect on the *MV*, as seen by comparing the data for the formulations without coupling agents SF and EF with those with coupling agent included: 6 NXT-SF, 6 NXT-EF and 6 NXT-EF duplo. The *MV* value for SF at 0.3 mm nip width is abnormally low, the reason is not clear. There is no clear effect seen yet of the fibre type.

Table 12.3 — Processability properties and vulcanization performance.

	6 NXT-SF	6 NXT-EF	6 NXT-EF duplo	SF	EF
Temp. stage 1, °C	135	140	138	137	137
Temp. stage 3, °C	138	135	139	134	133
MV 0.5 nip width, MU	34	35	36	41	41
MV 0.3 nip width, MU	31	33	34	33	38
t_{s2} , min	2.41	2.79	2.74	2.22	2.06
t_{90} , min	13.1	14.4	14.4	8.7	7.5
M_l , dN·m	0.28	0.32	0.34	0.34	0.36
M_h , dN·m	5.77	6.50	6.36	6.45	7.00
M_h-M_l , dN·m	5.49	6.19	6.03	6.12	6.64

Table 12.3 also shows the vulcanization properties and Figure 12.3 shows the full curing curves. The curves for compounds SF and EF without coupling agent show the highest torque, corresponding with the differences seen in the viscosity. Comparing the compounds with coupling agent, 6 NXT-EF gives a higher torque than 6 NXT-SF. This is the same trend as seen before in Chapter 8.

Figure 12.3 — Curing curves of compounds made in large mixer at 0.8 Hz.

12.4.3 Mechanical properties

Tables 12.4a-d list the tensile properties for the various finished compounds, after optimum vulcanization: tensile strength at break, strain at break and Young's modulus (0.25-0.5%) YM. All fibre-containing compounds are measured longitudinally (II), perpendicularly (=) and randomly (X) oriented towards the mill direction.

Table 12.4a — Mechanical properties averages, 0.5 mm mill nip width.

Samples:	6 NXT-SF			6 NXT-EF			6 NXT-EF duplo		
	II	=	X	II	=	X	II	=	X
Strength at break, MPa	2.2	1.5	2.4	3.1	1.8	2.6	2.8	1.9	2.1
St. dev., MPa	0.2	0.1	0.2	0.2	0.1	0.2	0.2	0.1	0.4
Strain at break, %	36	87	37	25	79	37	26	57	41
St. dev., %	3	4	9	3	12	3	4	6	10
Young's Modulus, MPa	10.3	4.3	10.3	19.0	5.6	11.1	17.9	4.1	10.8
St. dev., MPa	0.9	1.1	1.5	0.8	1.6	1.6	2.3	1.9	0.9

Table 12.4b — Mechanical properties, 0.5 mm mill nip width.

Samples:	SF			EF		
	II	=	X	II	=	X
Strength at break, MPa	2.5	2.1	3.1	2.5	2.3	3.1
St. dev., MPa	0.1	0.2	0.1	0.3	0.1	0.4
Strain at break, %	44	85	30	27	60	30
St. dev., %	6	15	4	6	15	3
Young's Modulus, MPa	7.0	4.0	12.4	11.3	5.2	12.3
St. dev., MPa	1.5	0.6	3	1.8	1.37	0.3

Table 12.4c — Mechanical properties, 0.3 mm mill nip width.

Samples:	6 NXT-SF			6 NXT- EF			6 NXT-EF duplo		
	II	=	X	II	=	X	II	=	X
Strength at break, MPa	2.6	1.7	2.3	2.9	1.9	2.4	3.2	1.9	2.4
St. dev., MPa	0.2	0.2	0.3	0.1	0.1	0.2	0.3	0.1	0.0
Strain at break, %	47	56	35	34	95	45	29	80	36
St. dev., %	9	9	13	3	11	9	4	5	3
Young's Modulus, MPa	11.2	4.8	10.5	15.5	3.3	11.5	15.7	3.3	10.5
St. dev., MPa	1.2	0.8	1.8	1.1	0.3	0.6	1.0	0.5	1.5

Table 12.4d — Mechanical properties, 0.3 mm mill nip width.

Samples:	SF			EF		
	II	=	X	II	=	X
Strength at break, MPa	3.1	2.2	2.9	3.0	2.2	2.8
St. dev., MPa	0.1	0.2	0.3	0.1	0.1	0.1
Strain at break, %	34	98	33	31	77	33
St. dev., %	6	16	6	3	11	7
Young's Modulus, MPa	8.9	3.5	12.3	11.5	4.0	11.8
St. dev., MPa	1.2	1.0	1.9	1.5	0.5	1.5

Figure 12.5 shows the tensile test curves of 6 NXT-EF, 6 NXT-SF, EF and SF, all measured in longitudinal direction of fibre orientation. The Young's moduli obtained for 0.5 mm mill nip width are higher than those for a 0.3 mm nip width. This is another indication that somewhat less polymer breakdown has occurred, as already seen in the *MV*. In the majority of cases, the longitudinally oriented fibres show the largest reinforcement and transversely oriented fibres give the worst properties. Random orientations give results surprisingly close to the longitudinal orientation for SF, EF and 6 NXT SF. On the other hand, for the combination 6 NXT-EF with the adhesion active epoxy-amine coating together with NXT coupling agent, the YM in longitudinal direction is significantly higher, as seen before in Chapter 8. Figure 12.6 highlights the orientation effects of 6 NXT-EF in more detail.

Figure 12.5 — Tensile stress-strain curves of 6 NXT-EF versus 6-NXT longitudinal prepared in the large mixer and with a mill nip width of 0.5 mm.

Figure 12.6 — Tensile stress-strain curves of 6 NXT-EF for different orientations.

12.5 Discussion

The results are considered as a check to characterize the influence of mixer size on the silanization effect of the epoxy-amine coating on aramid fibres in combination with NXT coupling agent. The reaction time-temperature window for the silanization was not the same as for the 350 cm³ mixer employed throughout this thesis and needed special attention.

The results are comparable with the observations in Chapter 8, where epoxy-amine coated fibres in combination with NXT coupling agent stood out against the others. In so far as it stands, this proves there is a reaction between coupling agent and epoxy-amine coating, and it seems to have a beneficial effect on the Young's modulus.

Actually, it turns out that the epoxy-amine coating by itself already gives a certain reinforcing effect, even without the coupling agent. The coupling agent does increase the effect, however. This corresponds, indeed, with the observation in Figure 8.6, in Chapter 8, where the epoxy-amine coated fibres without coupling agent already gave some increase in Young's modulus. Apparently, this only shows for 15 phr fibres, as used in Chapter 8 and in the present chapter, but not for 5 phr fibres in Chapter 3. It is difficult to imagine what the cause of this phenomenon is. A possible explanation could be that the epoxy-amine coated fibres are less prone to fibre breakage during mixing. Another explanation could be that the hydroxyl groups on the epoxy-amine coating interact in some way or the other with the vulcanization, in the sense that they contribute to the cross-link density of the rubber. To elucidate these phenomena, an in-depth chemical sulphur study would have been required. This was not embarked on further owing to a lack of remaining time.

12.6 Conclusions

The qualitative proof of principle of the silanization reaction of epoxy-amine coated aramid fibres in combination with NXT coupling agent has been positively confirmed in a larger mixer. The highest Young's modulus was found for 15 phr epoxy-amine aramid fibre in combination with 6 phr NXT.

Even without a coupling agent, 15 phr epoxy-amine coated fibres do give some reinforcement relative to standard fibres. In most cases the longitudinally oriented fibres show the largest reinforcement and the transversely oriented fibres show the worst reinforcement. Random orientations give results which are surprisingly close to the longitudinal orientation for SF, EF and 6 NXT SF. On the other hand, for the combination 6 NXT-EF with the adhesion

active epoxy-amine coating together with NXT coupling agent, the Young's modulus in longitudinal direction is significantly higher, as previously seen in Chapter 8. The latter is the clearest sign of the positive effect of fibre-elastomer interaction by means of the coupling agent.

12.7 References

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Appendix I Calculation of phr, w%, v% and molecular equivalents

The fibre fraction of the compounds in parts per hundred parts of rubber can be obtained by dividing the fibre mass m_{fibre} by the mass of the rubber m_{rubber} used in the compounds:

$$phr = \frac{m_{fibre}}{m_{rubber}} \cdot 100 \quad (A1.1)$$

The fibre w% in the compounds is given by the fraction of fibre mass divided by the total mass of the compound m_{total} .

$$w\% = \frac{m_{fibre}}{m_{total}} \cdot 100 \quad (A1.2)$$

The fibre v% in the compounds can be calculated according to:

$$v\% = \frac{V_{fibre}}{V_{total}} \cdot 100 \quad (A1.3)$$

Based on the relation that the volume V of a piece of material is dependent on its mass and density:

$$V = \frac{m}{\rho} \quad (A1.4)$$

The two equations can be combined to obtain the fibre v%:

$$v\% = \frac{m_{fibre} / \rho_{fibre}}{m_{total} / \rho_{total}} \cdot 100 \quad (A1.5)$$

The molecular equivalents of the coupling agents with respect to their number of ethoxy groups per molecule can be calculated based on molecular weight (MW g/mole) of the coupling agents divided by the molecular weight of the reference coupling agent, and multiplication by the amount of ethoxy groups of the reference coupling agent divided by the number of ethoxy groups of the coupling agent under consideration.

$$\frac{MW_{CA}}{MW_{CAreference}} \cdot \frac{ethoxy - groups_{CAreference}}{ethoxy - groups_{CA}} = Equivalent\ CA \quad (A1.6)$$

The equivalent CA can be replaced with CA concentration in phr in the formulation.

When extra sulphur is added to the system (due to coupling agent like TESPT) to take part in the cross-linking reaction, the sulphur needs to be compensated:

$$\frac{Equivalent\ CA}{MW_{CA}} * sulphur\ CA * MW_{Sulfur} = equivalent\ sulphur \quad (A1.7)$$

The equivalent sulphur can be subtracted from the sulphur concentration in phr in the formulation.

Appendix II Hertz equation

The maximum contact pressure P_{max} can be equally compared in N/mm², by adjusting the normal load F_n . The relationship between the maximum contact pressure P_{max} and the mean contact pressure P_m is given by $P_{max} = 3P_m/2$. The elementary Hertz theory can be used to get a first estimate of the nominal load F_n . In this formula the ball is not in motion. This means that there is a nominal circular contact of the ball with the disk, and the equation of Johnsonⁱ can be used to calculate the radius of the circular contact area, see Equation All.1:

$$r = \left(\frac{3F_n R'}{4E'} \right)^{1/3} \quad (\text{All.1})$$

where E' is the effective modulus of elasticity defined by:

$$\frac{1}{E'} = \left(\frac{1 - \nu_1^2}{E_1} \right) + \left(\frac{1 - \nu_2^2}{E_2} \right) \quad (\text{All.2})$$

where E_1 and ν_1 are the elastic modulus and Poisson's ratio of the granite ball (70 GPa and 0.3), E_2 and ν_2 correspond to the elastomer with fibres distributed therein, as was shown in Figure 4.3, Chapter 4, which can be determined with the tensile test. And R' is the effective radius related to the radii of the ball, as is shown in Equation All.3.

$$\frac{1}{R'} = \frac{1}{R_1} + \frac{1}{R_2} \quad (\text{All.3})$$

where R_1 is the radius of the ball and R_2 the radius of the elastomer. Because the elastomeric disk does not have a curvature, this radius can be assumed to be infinite and therefore can be neglected.

The Hertz theory is presented in Equation All.4a.

$$P_{max} = \frac{3}{2} P_m = \frac{3}{2} \frac{F_n}{\pi \cdot r^2} = \left(\frac{6 \cdot F_n \cdot E'^2}{\pi^3 \cdot R^2} \right)^{1/3} \quad (\text{All.4a})$$

Hence F_n can be calculated by substitution Equation All.1, All.2 and All.3 into All.4a and rewrite it into All.4b.

$$F_n = (\pi P_{max})^3 \frac{9}{64} \left(\frac{d}{E'} \right)^2 \quad (\text{All.4b})$$

Where d is the diameter of the sphere/ball. The normal load F_n can be used to make a first estimate of the contact area A , see Equation 4.3, Chapter 4.

ⁱK. L. Johnson, *Contact Mechanics*, Cambridge University Press, 92-93 (1985).

List of publications

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- N. Vleugels and W.K. Dierkes, A. Blume, and J.W.M. Noordermeer, *Understanding the behavior of the coupling agents TESPT and Si 363 in short-cut aramid fiber reinforced elastomers*, Kautschuk Gummi und Kunststoffe, manuscript in preparation.
- N. Vleugels and W.K. Dierkes, A. Blume, and J.W.M. Noordermeer, *Understanding main governing factors for mechanical properties of short aramid-fibres reinforced elastomers*, Kautschuk Gummi und Kunststoffe, manuscript in preparation.

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- M. Mokhtari, and D.J. Schipper and N. Vleugels and J.W.M. Noordermeer *Transversely isotropic viscoelastic materials: Contact mechanics and friction*, Tribology international, 97, 116-123 (2016).
- N. Vleugels and W.K. Dierkes, A. Blume, and J.W.M. Noordermeer, *Understanding main governing factors for mechanical properties of short aramid-fibres reinforced elastomers*, International Rubber Conference IRC2016, Kitakyushu, Japan, 24-28 October 2016, Kitakyushu, Japan, 94-98 (2016).
- N. Vleugels and W.K. Dierkes, A. Blume, and J.W.M. Noordermeer, *Main Governing Factors Influencing Mechanical Properties of Short-cut Aramid-fibres reinforced Elastomers*, Fall 190th Technical Meeting of American Chemical Society Rubber Division, 10-13 October 2016, Pittsburgh, Pennsylvania, USA, 1-39 (2016).
- N. Vleugels, W. Pille-Wolf, W.K. Dierkes and J.W.M. Noordermeer *Influence of oligomeric resins on traction and rolling resistance of silica tire treads*, Rubber, Fibres, Plastics International, **11**(1) 20-26 (2016).
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- M. Mokhtari, and D.J. Schipper and N. Vleugels and J.W.M. Noordermeer, *Existence of a Tribo-Modified Surface Layer on SBR Elastomers: Balance between Formation and Wear of the Modified Layer*, Tribology letters, **58**(22), 1-13 (2015).
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