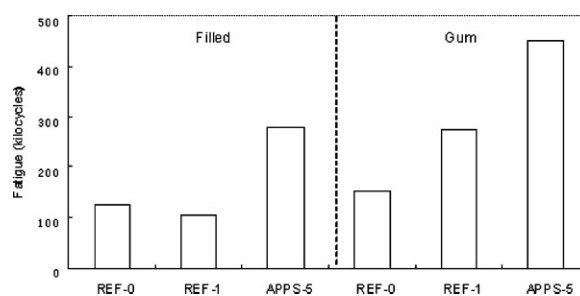


Modification of EPDM with Alkylphenol Polysulfide for Use in Tire Sidewalls, 1 – Mechanical Properties^a

Hongmei Zhang, Rabin N. Datta, Auke G. Talma, Jacques W. M. Noordermeer*

APPS has been used to modify EPDM in order to solve the cure incompatibility and heterogeneous filler distribution of NR/BR/EPDM blends for tire sidewall applications. The physical properties of the NR/BR/APPS-EPDM blends are compared with an NR/BR/EPDM blend and a conventional NR/BR tire sidewall. It is demonstrated that the application of APPS-EPDM leads to a significant improvement of the tensile properties, tear strength, and fatigue properties. The properties of the NR/BR/APPS-EPDM blends are equivalent or even superior to those of conventional NR/BR tire sidewall compounds. The dynamic viscoelastic properties of the NR/BR/APPS-EPDM blends are not quite comparable with the conventional NR/BR sidewall blend, but still greatly improved, compared to using virgin EPDM.



Introduction

Ethylene/propylene/diene rubber (EPDM) possesses excellent ozone, heat, and aging resistance due to its highly saturated chemical structure. It is well known that incorporation of saturated EPDM rubber into diene rubbers, such as natural rubber (NR) and butadiene rubber (BR), is a way to achieve non-staining ozone resistance for tire

sidewall applications instead of using conventional anti-ozonants, such as *N*-1,3-dimethylbutyl-*N'*-phenyl-*para*-phenylenediamine (6PPD), which have staining effects and leach out via migration.^[1] However, vulcanizates of the EPDM/diene rubber blends are generally poor in mechanical properties. The main problems associated with such elastomer blends are the difference in molar concentrations of carbon-carbon double bonds in each of the elastomers, resulting in differences in polarity, number of allylic sites for sulfur vulcanization, and reactivity of the cross-link sites.^[2] Curatives, which are commonly polar molecules, generally diffuse preferentially into the higher unsaturated elastomers, i.e. the diene phases, resulting in differences in concentration of reactants and hence uneven cross-link distribution.^[3,4] Carbon black also prefers to migrate into the higher unsaturated polymers causing a heterogeneous filler distribution in the blends.^[5,6] Several approaches have been proposed to overcome these problems and to improve the properties of EPDM/high-diene rubber blends.

H. Zhang, R. N. Datta, A. G. Talma, J. W. M. Noordermeer
Department of Elastomer Technology and Engineering, Faculty of Engineering Technology, University of Twente, PO Box 217, 7500AE Enschede, The Netherlands
Fax: +31 53 489 2151; E-mail: j.w.m.noordermeer@utwente.nl
H. Zhang, R. N. Datta, A. G. Talma, J. W. M. Noordermeer
Dutch Polymer Institute (DPI), PO Box 902, 5600 AX Eindhoven, The Netherlands

^a Part 2: DOI: 10.1002/mame.200900126

Generally, these attempts have sought to increase the cure rate of EPDM, either by using curatives that have an increased reactivity toward EPDM, or by means of modifying the EPDM to make it more reactive toward curing^[7–13] and more attractive to fillers.

Cook^[14] made a similar attempt by a different procedure called “reactive mixing.” In his work, three commercially available sulfur donors, bis(alkylphenol)disulfide (BAPD), dithiodicaproloactam (DTDC), and dithiodimorpholine (DTDM) were used to modify EPDM by mixing at elevated temperatures in an internal mixer as part of a normal masterbatch mixing cycle. The modification is believed to be similar in nature to what was described by Hopper,^[15] in which a certain functionality: alkylphenolmonosulfide, caprolactam, or morpholine coming from the sulfur donor was attached to the EPDM polymer molecules via a sulfur linkage. During vulcanization, all of these groups could act as leaving groups, to be substituted by mercaptobenzothiazol, which is known as a vulcanization intermediate. In this way a cross-link precursor site on the EPDM polymer chain was formed.

In the present work, alkylphenol polysulfide (APPS) has been selected as modification agent for EPDM. Alkylphenol sulfides were introduced in the 1940s as sulfur donors for synthetic elastomers. They are particularly recommended for butyl- and halobutyl rubber-based applications.^[16–19] There are several benefits by using alkylphenol sulfides as curing agents: they are nitrosamine-free, have no blooming problems, provide better heat resistance, improve dynamic fatigue properties, enhance adhesion, and may act as tackifier. Moreover, due to the phenol group in their structure, they are believed to have a good affinity with carbon black, which may improve the carbon black distribution after EPDM modification and consequently the mechanical properties.

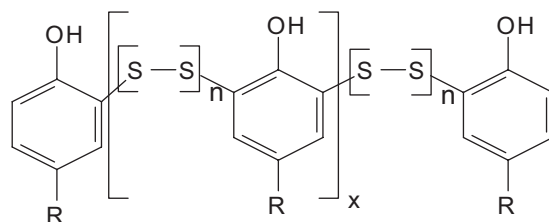
Experimental Part

Materials

Poly(*p*-*tert*-butylphenoldisulfide) (APPS) or Vultac TB7 (Arkema, France) was used as the modification agent. Its chemical structure is shown in Scheme 1.

The elastomers selected for the blends were NR (SIR20, Standard Indonesian Rubber), BR (Kosyn KBR01, Korea Kumho Petrochemical Co. Ltd), EPDM rubber containing 4.5 wt.-% ethylidene norbornene (ENB) as third monomer and 70 wt.-% of ethylene (Keltan 5508, DSM Elastomers B.V., The Netherlands).

The other compounding ingredients used were extra pure grade zinc oxide (Merck, Germany), finely divided sulfur (Merck, Germany), 95% pure stearic acid (Aldrich, Germany), poly(2,2,4-trimethyl-1,2-dihydroquinoline), or TMQ (Flexsys B.V., The Netherlands) and *N*-cyclohexyl-2-benzothiazolesulfenamide (CBS) or Santocure (Flexsys B.V., The Netherlands). High abrasion furnace (HAF) carbon black (HAF-N330, Cabot Corporation) and naphthenic



R = *t*-Butyl

■ Scheme 1. Chemical structure of APPS.

oil Sunthene 4240 (Sun Petroleum Products Co. Ltd) were used in the case of filled blends.

Grafting of APPS onto EPDM

Grafting of APPS onto EPDM was done in a Brabender PL2000 laboratory internal mixer with a chamber volume of 50 cm³, using a rotor speed of 80 rpm, a fill factor of 0.8, and an initial temperature of 165 °C. The amount of APPS varied from 2 to 10 wt.-%, relative to the EPDM. The EPDM was first masticated for 1 min, then APPS was added and the mixing was continued for another 10 min. The final compound temperature as recorded before dumping from the mixer was in the range of 183 ± 2 °C.

Preparation and Vulcanization of the Compounds

The overall formulations of the compounds are given in Table 1. The blend compounds were prepared in a Brabender Plasticorder 350 S mixer having a mixing chamber volume of 370 cm³. The mixer was operated at a rotor speed of 80 rpm, fill factor of 0.7, and an initial temperature of 50 °C. In case of gum blends, NR was first masticated for 2 min, then BR and EPDM or APPS-EPDM were added and mixed for another 1 min. ZnO, stearic acid, and TMQ were subsequently added and the mixing was continued for another 2 min. The final compound temperature before dumping from the mixer was in the range of 110–115 °C. CBS and sulfur were added to the compounds on a two-roll mill.

In the case of HAF-carbon black filled compounds, the same mixer settings were applied. NR was first masticated for 2 min, then BR and EPDM or APPS-EPDM were added and mixed for 1 min. Then, oil, half the amount of HAF-black, and all the other additives were added. After 1 min, the other half amount of HAF-black was added and the mixing was continued for two more minutes, till the torque value of the mixer became stable. CBS and sulfur were again added to the compounds on the two-roll mill.

The resulting compounds were tested for their cure characteristics using a RPA 2000 cure meter (Alpha Technologies) according to ISO 6502. The optimum cure time ($t_{c,90}$) of the fully compounded blends was determined as the time needed to reach 90% of the maximum torque difference in the RPA 2000 at 140 °C, 0.833 Hz, and 0.2° strain. The blends were then vulcanized into 2 mm thick sheets for this optimum cure time $t_{c,90}$ in a Wickert WLP1600 laboratory compression press at 140 °C and 100 bar.

Table 1. Formulation of NR/BR/EPDM or grafted-EPDM compounds.

Component	Ref-0	Ref-1	APPS grafted	APPS straight
	phr	phr	phr	phr
NR SIR 20	50	35	35	35
BR Kosyn KBR01	50	35	35	35
EPDM Keltan 5508	–	30	–	30
APPS-EPDM	–	–	30 + 0.3X ^{a)}	–
APPS	–	–	–	2.1
Zinc oxide	4	4	4	4
Stearic acid	2	2	2	2
TMQ	1	1	1	1
6PPD	2	–	–	–
CBS	1.98	1.98	1.98	1.98
Sulfur	2.5	2.5	2.5	2.5
CB HAF N330	50	50	50	50
Oil	10	10	10	10

^{a)}X = wt.-% APPS, used for modification of 100 wt.-% EPDM.

Tensile and Trouser Tear Tests

Type 2 dumb-bell test pieces were die-cut from the compression-molded sheets and tensile tests were carried out according to ISO 37, with a Zwick tensile tester Model Z 1.0/TH1S at a constant cross-head speed of 500 mm · min⁻¹.

Trouser test specimens of 100 × 7.5 mm² with a 40 mm-deep cut were die-cut and the test was performed according to ISO 34, Method A with the Zwick tensile tester at a constant cross-head speed of 100 mm · min⁻¹.

Flex Fatigue-to-Failure Tests

Fatigue-to-failure tests were carried out on a Monsanto fatigue-to-failure tester at constant strain energy. To determine the strain energy, a cured fatigue specimen was first conditioned by cycling it 30 times to 140% extension. Using ASTM procedure D-412, a stress/strain curve was then generated from which the force per unit area from 10% to 140% extension in 10% increments was determined. From these data, three extension ratios and corresponding strain energies were selected for each sample.

Dumb-bell test specimens were subjected to stress/strain cycles at the pre-selected extension ratios and the number of cycles required to cause failure, as indicated by complete rupture of the test specimen, was recorded. 12 test specimens of each sample were tested and the median value of the number of cycles required to cause failure was recorded. For each sample, three fatigue life values were measured for the three pre-determined extension ratios, respectively.

The fatigue life at a reference strain energy was then interpolated from the three respective fatigue lives per sample, using the equation^[20]

$$\ln(\text{Fatigue Life}) = A + B [\ln(\text{Strain Energy})] \quad (1)$$

where *A* and *B* are coefficients characteristic for the particular compounds. The reference strain energy was 1.2 MPa for gum blends and 1.8 MPa for the HAF-filled blends.

Frequency Sweep Measurements

Frequency sweep measurements of the vulcanized compounds were performed in the RPA 2000. The specimens were first vulcanized at *t*_{c,90} at 140 °C, followed by a cooling step to 60 °C. The frequency sweeps of vulcanized compounds were then done at 60 °C and 3.5% strain. The frequency varied from 0.01 to 30 Hz.

Results and Discussion

Grafting of EPDM with APPS in an Internal Mixer

Grafting of EPDM with different APPS-amounts was done in the smaller Brabender PL2000 internal mixer. Figure 1 shows the representative torque and temperature curves during mixing. After the addition of APPS, the torque decreases and then rises to its previous value. The softening temperature for APPS is about 106 °C. Therefore, when added to the hot compounds at 160 °C, the viscosity of the mixing compounds decreases due to the melting of APPS, and consequent plasticization of the mixture. Higher APPS amounts make the compounds take more time to return to their previous torques. With mixing going on, the

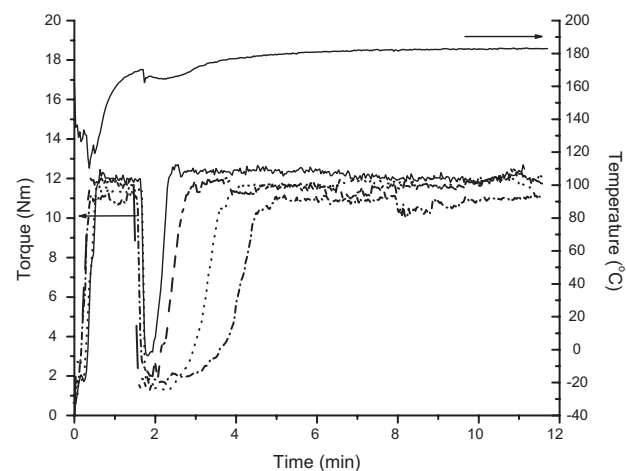


Figure 1. Torque and temperature curves during mixing of EPDM with different amounts of APPS: (—) 3 wt.-% APPS; (---) 5 wt.-% APPS; (···) 7 wt.-% APPS; (- · -) 10 wt.-% APPS.

temperature stays stable at about 183 °C and the torque values stay more or less at a constant value. The grafted rubber was then characterized by attenuated total reflection infrared (ATR-IR) spectroscopy to confirm that grafting has indeed occurred, which will be discussed in Part 2 of this series.

APPS-Modified EPDM in NR/BR/EPDM Blends

Curing Characteristics

Figure 2 shows the curing curves for HAF-filled NR/BR and NR/BR/EPDM (APPS-EPDM) blends after mixing according to the recipes in Table 1. A clear reversion can be observed for Ref-0, as opposed to the EPDM containing blends. The addition of unmodified EPDM to the NR/BR blend: Ref-1, increases both scorch and cure time. On the other hand, with APPS-EPDM, the scorch time decreases and becomes even shorter than that of the straight NR/BR blend: Ref-0. With respect to the Δ Torque values, which are the torque differences between the maximum torque and the minimum torque, as shown in Table 2: for APPS amounts higher than 5%, the blends with APPS-EPDM show higher Δ Torque values than the NR/BR and NR/BR/EPDM blends. The Δ Torque value further increases with higher APPS amounts. As APPS contains about 30 wt.-% sulfur, the consequence of the APPS-grafting is that more sulfur is introduced into the blends with APPS-EPDM, and therefore a higher state of cure is obtained.

For gum NR/BR and NR/BR/(APPS-EPDM) blends, similar results are found for their curing behaviors, as shown in Figure 3. However, the scorch time decreases more significantly with the addition of APPS-EPDM. The grafted

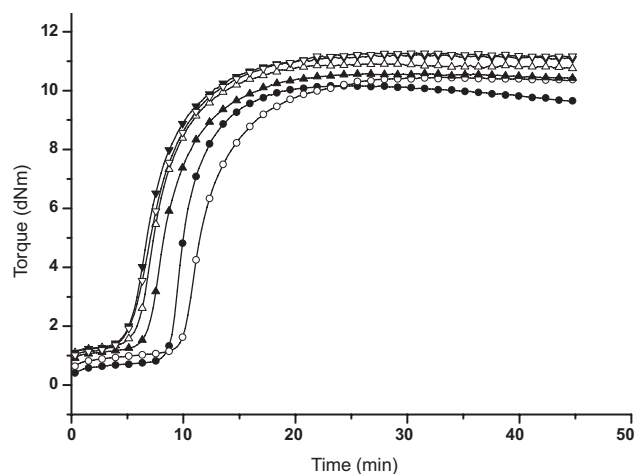


Figure 2. RPA curing curves for HAF-filled NR/BR and NR/BR/(APPS-EPDM) blends: (●): Ref-0; (○): Ref-1; (▲): APPS-3; (△): APPS-5; (▼): APPS-7; (▽): APPS-10.

Table 2. Δ Torque of NR/BR/EPDM(APPS-EPDM) compounds from curing curves.

Component	Δ Torque dN · m
Ref-0	9.75
Ref-1	9.79
APPS-3	9.77
APPS-5	9.83
APPS-7	10.10
APPS-10	10.21

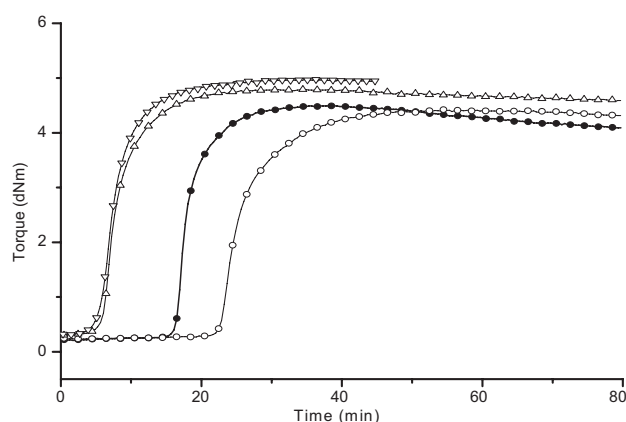


Figure 3. RPA curing curves for gum NR/BR and NR/BR/(APPS-EPDM) blends: (●): Ref-0; (○): Ref-1; (△): APPS-5; (▽): APPS-10.

APPS-group may react with CBS, accelerate the decomposition of CBS, and speed up the curing rate.

Tensile Properties

Figure 4 and 5 show the stress/strain curves for HAF-filled and gum blends, respectively. Both gum- and HAF-filled Ref-1 show much poorer tensile properties than the NR/BR blend, most probably due to some commonly existing problems in such kind of blends, as: viscosity mismatch, thermodynamic incompatibility, cure incompatibility, and inhomogeneous filler distribution, as will be further covered in the next part of this series. With APPS-EPDM, the tensile properties improve significantly compared to the blend with virgin EPDM and are comparable with the NR/BR blend. The characteristics data of the tensile properties are summarized in Figure 6–8.

Figure 6 shows the tensile moduli at 100 and 300% strain for both the HAF-filled and gum blends. For the filled blends, Ref-1 has a higher 100%-modulus but lower 300%-modulus compared to Ref-0. When APPS-EPDM is applied, the moduli increase continuously with higher APPS-amounts. For the

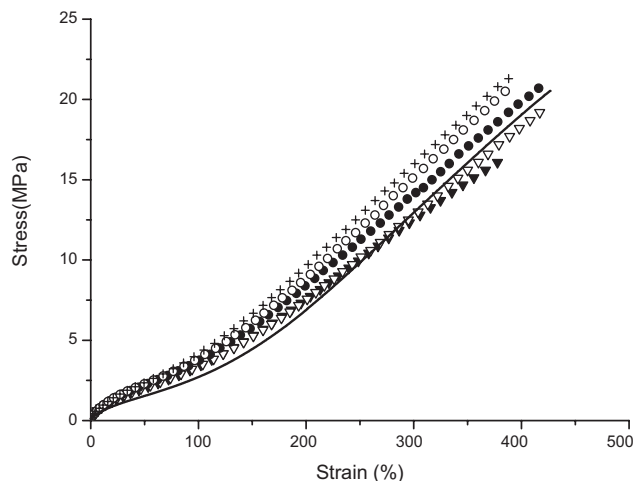


Figure 4. Tensile curves for HAF-filled NR/BR and NR/BR/(APPS)-EPDM blends: (—): Ref-0; (▼▼▼): Ref-1; (▽▽▽): APPS-3; (●●●): APPS-5; (○○○): APPS-7; (+ + +): APPS-10.

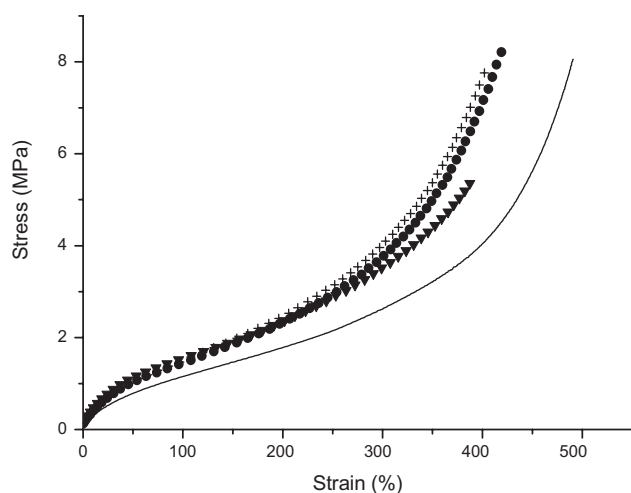


Figure 5. Tensile curves for gum NR/BR and NR/BR/(APPS)-EPDM blends: (—): Ref-0; (▼▼▼): Ref-1; (●●●): APPS-5; (+ + +): APPS-10.

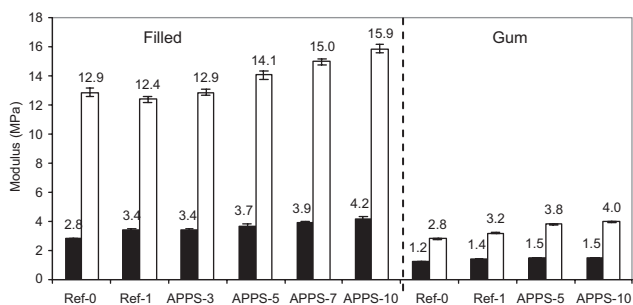


Figure 6. Modulus at 100 and 300% strain for NR/BR and NR/BR/(APPS)-EPDM blends: (■) at 100% strain; (□) at 300% strain.

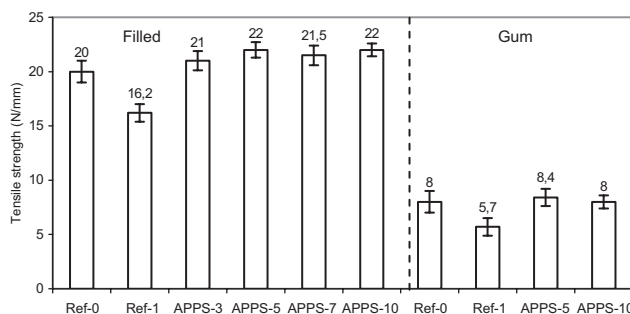


Figure 7. Tensile strength for NR/BR and NR/BR/(APPS)-EPDM blends.

case of the gum blends, all EPDM-containing blends exhibit higher moduli, at both 100 and 300% strain, than the gum NR/BR blend. After EPDM-grafting by APPS, the moduli increase as well. These results are consistent with the maximum torque values from the curing curves. As already discussed before, the extra sulfur content from the APPS and a higher resultant cross-link density may cause contribution to the higher modulus with APPS-EPDM.

The tensile strengths of the HAF-filled and gum blends are shown in Figure 7. Ref-1 has clearly lower tensile strength than Ref-0 in both the filled and gum cases. When APPS-EPDM is applied, a significant improvement is obtained, compared to the blend with virgin EPDM. The tensile strength with grafted EPDM is even higher than for the NR/BR blend for filled blends. However, between the different APPS-amounts grafted onto EPDM, there are no significant differences. 3 wt.-% APPS-EPDM already shows a large improvement. With APPS-amounts higher than 5 wt.-%, no further improvement of the tensile strength can be observed anymore. The significant improvement of the tensile strength may be attributed not only to a higher cross-linking density due to extra sulfur, but also to an improved solubility of curatives and better carbon black distribution in the EPDM phase after EPDM modification.

Figure 8 shows the elongation at break for the HAF-filled and gum blends. Both types of blends show a similar trend. From Ref-0 to Ref-1, a clear decrease can be seen like in the tensile strength. Compared to Ref-1, an improvement of the elongation at break can be observed again when 3 wt.-% APPS-EPDM is applied. With increasing APPS-amounts, the elongation at break subsequently decreases when the APPS-amount is higher than 5 wt.-%. It is clear that with higher APPS-amounts, modulus increases, while elongation at break decreases and the tensile strength remains more or less the same.

Comparison between EPDM-Pretreatment and Straight Mixing

From above results, it is clear that APPS-EPDM leads to significant improvements in the tensile properties, especially the tensile strength. However, it is not clear if

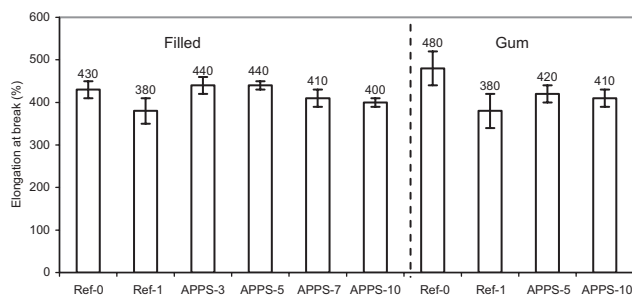


Figure 8. Elongation at break for NR/BR and NR/BR/(APPS)-EPDM blends.

those improvements are the results of the mere presence of APPS or of the grafting of APPS onto EPDM. Therefore, a comparison was made between EPDM-pretreatment and simple straight mixing, which means that the same amount of APPS was added directly to the blend compounds. Figure 9 shows the tensile curves and the characteristic data of the tensile properties of Ref-1 and the blends with and without EPDM-pretreatment.

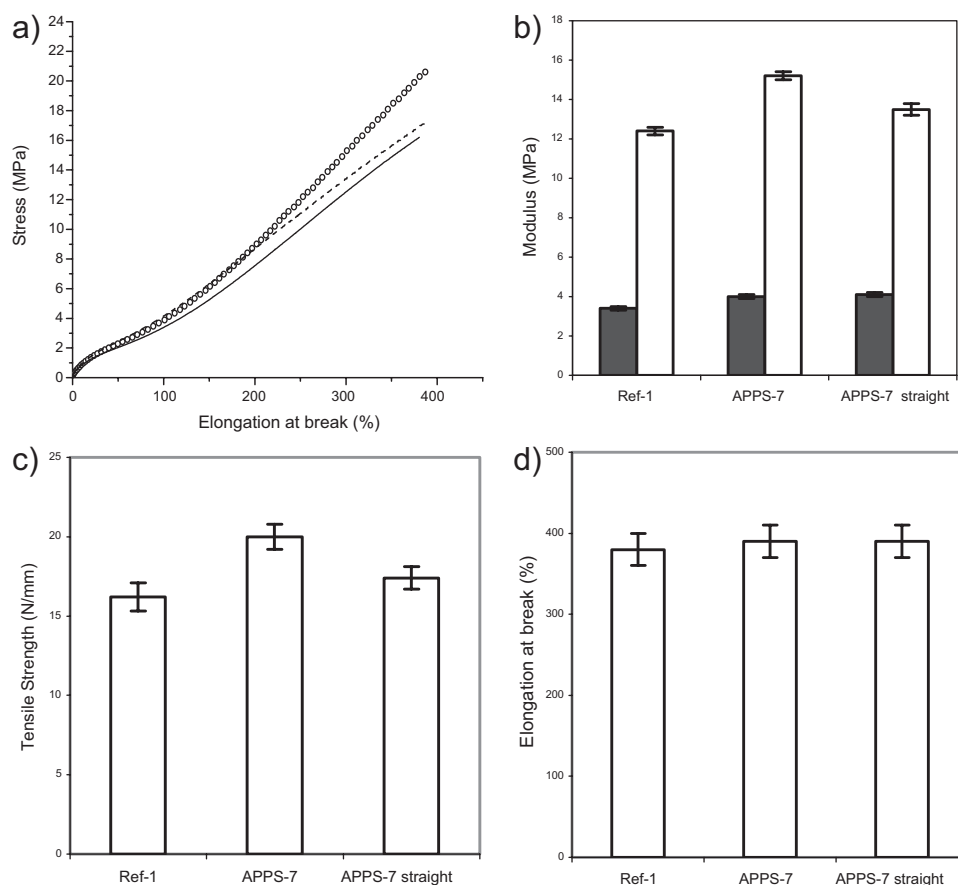


Figure 9. Comparison of tensile properties between Ref-1, APPS-7, and APPS-7-straight mixing: (a) tensile curves: (—): Ref-1; (○ ○ ○): APPS-7; (---): APPS-7-straight; (b) modulus: (■) at 100% strain; (□) at 300% strain; (c) Tensile strength; (d) Elongation at break.

Compared to the blend with APPS-EPDM, the blend by straight mixing shows lower tensile strength and similar elongation at break. It has a similar 100% modulus, while a lower 300% modulus than the blend with APPS-EPDM. Compared to Ref-1, the blend by straight mixing shows higher moduli but no significant improvement of the tensile strength and elongation at break.

It demonstrates that the EPDM-pretreatment step is necessary to obtain significant improvements of the tensile properties for NR/BR/EPDM blends. The straight addition of APPS only introduces extra sulfur into the compounds, which leads to some higher modulus values. This APPS tends to migrate to the NR and BR phases instead of to the EPDM. In that case, the presence of APPS does not overcome the cure incompatibility and will also not enhance the carbon black reinforcement of the EPDM phase to obtain a better overall filler distribution. Moreover, the extra sulfur in the NR/BR phase may result in overcure of this phase.

Tear Strength

The trouser tear strengths of the HAF-filled and gum blends are shown in Figure 10. A similar trend can be observed for

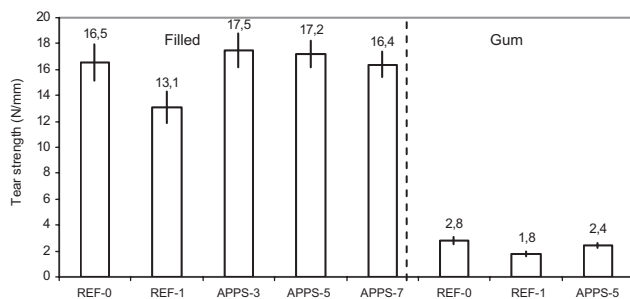


Figure 10. Trouser tear strength for NR/BR and NR/BR/(APPS-) EPDM blends.

the tear strength as for the tensile strength. The NR/BR blend exhibits a clearly higher tear strength than the blend with unmodified EPDM. When APPS-modified EPDM is applied, the tear strength increases significantly and is similar or even slightly higher than for Ref-0. The higher tear strength as well as the higher tensile strength of such NR/BR/EPDM blends suggests a better homogeneity of either cross-link distribution or carbon black distribution, or both. The better dispersion of the EPDM particles inside the NR/BR matrix may also impede the tear propagation and hence increase tearing energy and tear strength.

Fatigue-to-Failure

Fatigue-to-failure is defined as the tendency of a material to rupture by means of progressive cracks under stress/strain cycles. The modulus of a sample plays a very important role for the fatigue life, if based on the same extension. The reason is that, for the same extension ratio, more energy will be consumed during each cycle for higher modulus specimen and therefore, a shortened fatigue life will be obtained. Above results have shown that the NR/BR/APPS-EPDM blends have higher moduli as compared to Ref-0 and Ref-1. Therefore, in order to exclude the influence from the different modulus of the different samples, this test was carried out at the same strain energy by adjusting the fatigue extension ratio.

The fatigue lives at constant energy of the filled and gum blends are shown in Figure 11. For both the filled and gum cases, the use of APPS-EPDM leads to a large improvement in fatigue life, not only compared to Ref-1, but also in comparison with the NR/BR blends. Therefore, EPDM-modification by APPS does result in much better fatigue-to-failure properties for such a NR/BR/EPDM blend. The primary controlling parameters affecting the fatigue life are inhomogeneities or flaws present in each sample,^[21] caused by the blending, mixing, curing, and sample cutting steps. It is furthermore well known that APPS as sulfur donor can bring better dynamic fatigue properties to rubber compounds. In this study, after APPS was grafted onto EPDM, the longer fatigue life of the NR/BR/APPS-EPDM blend can also result from a better blend homogeneity

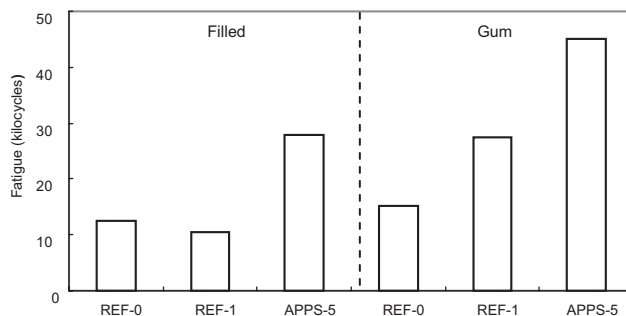


Figure 11. Fatigue-to-failure of the blends at constant strain energy: HAF-filled blends at 1.8 MPa; gum blends at 1.2 MPa.

because of improved co-cure, and the improvement of filler distribution among the various rubber phases in the blend.

In the EPDM-containing blends, the EPDM disperses as particles in NR/BR matrix. These particles may block crack propagation and thereby improve the fatigue life of the blends. However, in case of carbon black-filled blends, it is more complicated. The blends' homogeneity or carbon black distribution also has a strong influence on the fatigue life. The carbon black distribution in filled Ref-1, is very bad, which may be held responsible for its shorter fatigue life compared to filled Ref-0, in contrast to the gum case.

Dynamic Viscoelastic Properties

Rolling resistance is one of the major parameters of a tire accounting for energy consumption. The tire sidewall contributes approximately 10% of the total rolling resistance for both passenger car tires and truck tires.^[22] Because the dynamic viscoelastic properties are indicative for rolling resistance, they are essential parameters for tire sidewalls.

Elastomers are viscoelastic materials possessing both viscous and elastic behavior. Therefore, upon deformation, part of the energy is elastically stored, while the rest is dissipated through viscous behavior. The loss angle δ , the phase angle between stress and strain during oscillatory loading, and the tangent of the loss angle ($\tan \delta$) can be taken as a good parameter for the viscoelastic behavior of rubber:

$$\tan \delta = \frac{G''}{G'} \quad (2)$$

where G'' is the loss modulus and corresponds to the viscous behavior, and G' is the storage modulus, corresponding to the elastic behavior of the rubbers.

The results of frequency-sweep measurements performed at 60 °C and 3.5% strain on the vulcanized HAF-filled blends are shown in Figure 12. The storage moduli of all the blends increase with higher frequency. The increasing trend for all EPDM-containing blends is steeper

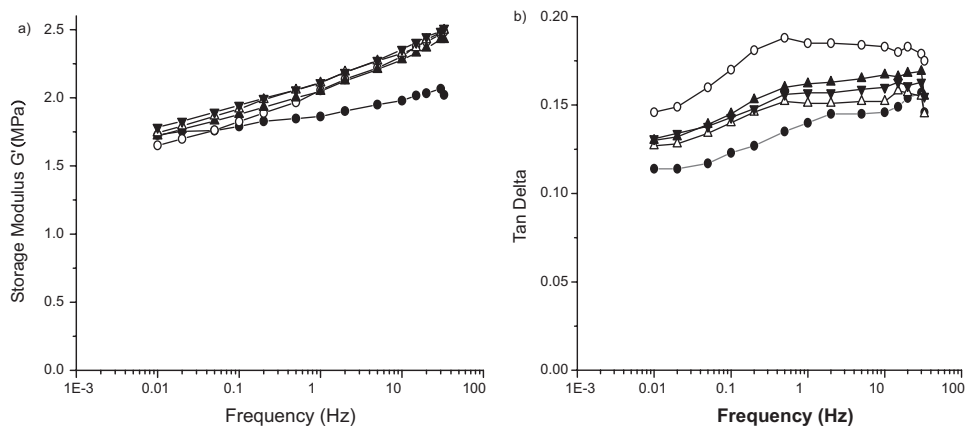


Figure 12. (a): Storage modulus; (b): $\tan \delta$ of vulcanized HAF-filled blends as function of frequency: (●): Ref-0; (○): Ref-1; (▲): APPS-3; (△): APPS-5; (▼): APPS-7.

than for the NR/BR blend. The difference of the storage moduli between the unmodified and grafted EPDMs is not very pronounced. The rolling resistance of tires is commonly related to the loss tangent of rubber compounds at the low frequency region within the rubbery state. $\tan \delta$ at 60 °C around 15 Hz is often taken as a good indicator for rolling resistance of a tire. A lower $\tan \delta$ corresponds to a lower rolling resistance.^[23,24] The $\tan \delta$ value of the NR/BR blend is much lower than the straight unmodified NR/BR/EPDM blend, which means that the addition of unmodified EPDM to the tire sidewall compound not only results in poor mechanical properties but also poor dynamic properties. After EPDM-grafting by APPS, the $\tan \delta$ value is still some higher than the NR/BR blend. However, compared to Ref-1, a significant improvement can again be found as a pronounced decrease of the $\tan \delta$ value, indicative for a lower rolling resistance. For different APPS-amounts, 5 wt.-% APPS-modified EPDM shows the lowest $\tan \delta$, but the difference is not very great.

Conclusion

The physical properties of the NR/BR/APPS-EPDM blends investigated are much better compared with compounds using virgin EPDM, and are equivalent or even superior to conventional NR/BR tire sidewall compounds. The tensile strength and tear strength of the NR/BR/APPS-EPDM blends and the reference NR/BR tire sidewall compounds, are more or less equivalent. The straight addition of APPS to the NR/BR/EPDM blend does not lead to significant improvements of the tensile properties. Therefore, pretreatment of EPDM with APPS is a necessary step. The NR/BR/APPS-EPDM blends show superior fatigue-to-failure properties to straight NR/BR/EPDM and the NR/BR tire sidewall compound. Dynamic viscoelastic properties are also improved

by using APPS-EPDM compared to virgin EPDM, although there is still some room for improvement, relative to the conventional NR/BR sidewall blend.

Acknowledgements: This study is part of the Research Program of the Dutch Polymer Institute (DPI), PO Box 902, 5600 AX Eindhoven, The Netherlands, under project no. 356.

Received: May 6, 2009; Revised: September 2, 2009; Published online: December 2, 2009; DOI: 10.1002/mame.200900125

Keywords: alkylphenol polysulfide; blends; modification; rubber; tire sidewall

- [1] W. H. Waddell, *Rubber Chem. Technol.* **1998**, *71*, 590.
- [2] A. V. Chapman, A. J. Tinker, *Kautsch. Gummi Kunstst.* **2003**, *56*, 533.
- [3] F. Ignatz-Hoover, B. H. To, R. N. Datta, A. J. de Hoog, N. M. Huntink, A. G. Talma, *Rubber Chem. Technol.* **2003**, *76*, 747.
- [4] F. X. Guillaumond, *Revue Generale des Caoutchoucs et Plastiques* **1974**, *51*, 853.
- [5] M. Klüppel, R. H. Schuster, J. Schaper, *Rubber Chem. Technol.* **1999**, *72*, 91.
- [6] P. M. van de Ven, J. W. M. Noordermeer, *Rubber World* **2000**, *222*, 55.
- [7] J. Zhao, G. Ghebremeskel, *Kautsch. Gummi Kunstst.* **2001**, *3*, 84.
- [8] M. E. Woods, J. A. Davidson, *Rubber Chem. Technol.* **1976**, *49*, 112.
- [9] A. Y. Coran, *Rubber Chem. Technol.* **1988**, *61*, 281.
- [10] M. G. Oliveira, B. G. Soares, *Macromol. Rapid Commun.* **1999**, *20*, 526.
- [11] K. C. Baranwal, P. N. Son, *Rubber Chem. Technol.* **1974**, *47*, 88.
- [12] R. T. Morrissey, *Meeting of the Rubber Division*, Am. Chem. Soc. Miami, Florida, April 1971.

- [13] K. Hashimoto, M. Miura, S. Takagi, H. Okamoto, *Int. Polym. Sci. Technol.* **1976**, *3*, T84.
- [14] S. Cook, in: *Blends of Natural Rubber*, Chapman & Hall, London 1998, p. 169.
- [15] R. J. Hopper, *Rubber Chem. Technol.* **1976**, *49*, 341.
- [16] R. L. Zapp, *Rubber Chem. Technol.* **1973**, *46*, 251.
- [17] M. B. Rodgers, S. C. Solis, N. Tambe, B. B. Sharma, *Rubber Chem. Technol.* **2008**, *81*, 600.
- [18] S. C. Solis, M. B. Rodgers, N. Tambe, B. B. Sharma, W. H. Waddell, *Meeting of the Rubber Division, Am. Chem. Soc.* San Antonio, Texas, October 2005.
- [19] D. D. Flowers, J. V. Fusco, D. S. Tracey, *Rubber World* **1994**, *209*, 32.
- [20] Monsanto technical service report no. 84-078, 1984.
- [21] D. G. Young, E. N. Kresge, A. J. Wallace, *Rubber Chem. Technol.* **1982**, *55*, 428.
- [22] L. Y. Chang, J. S. Schackleton, *Meeting of the Rubber Division of the American Chemical Society*, Chicago, October 1982.
- [23] K. H. Nordsiek, *Kautsch. Gummi Kunstst.* **1985**, *38*, 178.
- [24] M.-J. Wang, *Rubber Chem. Technol.* **1997**, *71*, 520.