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Influence of oligomeric resins on traction and rolling resistance of silica tire treads

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ABSTRACT

This study concerns the silica-reinforcement of synthetic rubber compounds for passenger tire treads with the objective to gain insight into the beneficial effects of oligomeric resins, derived from natural and synthetic monomers, on the major tire performance factors: Rolling Resistance and (Wet) Skid Resistance. This manuscript highlights the relationship between the performances of various oligomeric resins in different concentrations: 2, 4 and 6 phr, on the dynamic mechanical behavior of the silica reinforced passenger car tire tread compounds. Three types of resins were tested: a polyterpene, a terpene-phenolic and a pure vinyl-aromatic hydrocarbon resin. Dynamic Mechanical Analysis (DMA) was used, in addition to Mooney viscosity, cure meter, tensile and hardness tests to assess the behavior of these resins in the rubber and to characterize the processibility of the compounds. The DMA shows that the resins and rubber compounds are compatible at the resin quantities used. The tan δ loss angle versus temperature was used as an indication for wet skid and rolling resistance. The shift to a higher temperature in the tan δ peak belonging to the glass transition (Tg) of the rubber phase, due to the contribution of the higher T_g of the resins, is the reason for improved wet skid performance. A maximum improvement of ca. 35 % in the wet skid region (0 - 30 °C) is found. The improved tan δ at 60 °C, indicative for rolling resistance, accounts for reduced interaction between filler-particles. This is also confirmed by a decrease in Payne effect. A maximum improvement of ca. 15 % is found in the rolling resistance temperature range, dependent on the particular choice of the resin.

INTRODUCTION

The ever increasing demands on tire performance accounts for a continuous effort to raise the overall level of the so-called "Magic Triangle of Tire Technology": the balance between Rolling Resistance (RR), Traction or Wet Skid Resistance (WSR) and Wear or Abrasion Resistance. This is partly, but not only, triggered by governmental influences like the recent tire labeling regulation issued by the European Union,[1] or similar regulations in the USA, Japan and elsewhere. These requirements on RR and WSR are often conflicting, as improvement in one characteristic usually causes a decrease in the other. A compromise between these characteristics is therefore always aimed for. It has recently been demonstrated that oligomeric resins have a beneficial influence on this balance, particularly on the WSR with no or even a small positive influence on the RR of passenger tires, based on synthetic rubbers with silica reinforcement.[2,3,4,5]

Oligomeric resins represent a class of materials used for a very broad range of purposes. For a classification of the variety of these products the reader is referred to the overview given by Kim *et al.*[6]. They can be obtained from different sources: extracted from trees or purposely produced from hydrocarbon monomers. These resins are commonly divided into the main four groups: the naturally derived rosin acids and terpenes, and the synthetic C_5- and C_9-based hydrocarbons; various after-treatments are also applied.

It has become common practice to use laboratory scale dynamic mechanical testing to predict or simulate real tire performance. In particular, the dependence of the loss factor (tan δ), the ratio loss (G'') and the storage modulus (G'), as a function of temperature at a low frequency of typically 10 Hz can be used for such purpose.[7,8] As an indication of traction or WSR, the level of the loss factor tan δ around 0 °C till approximately +30 °C is commonly employed. The range between +40 °C and approximately +70 °C and frequency of 10 Hz represents the operating conditions of a tire and under these conditions the loss factor can be used as an indication for the degree of RR.

The objective of the present study was to elucidate the mechanistic role of such oligomeric resins on the WSR and RR of silica-reinforced passenger tire treads based on synthetic rubbers, which were already optimized for RR. Three oligomeric resins were selected, representing the classes of natural resins: poly-terpene resin (resin A) and a phenolic modified terpene resin (resin B); respectively a pure vinyl-aromatic hydrocarbon resin (resin C). The oligomeric resins were used as admixtures in low quantities: 2, 4 and 6 phr, in substitution of the corresponding amounts of extender oil in silica-reinforced tread compounds with a SBR/BR rubber blend. The influences of the oligomeric resins on the filler-filler and rubber-filler interactions and their effect on the processing characteristics of these compounds were investigated, as well as their influence on the dynamic and mechanical properties of their vulcanizates. These results are compared with those obtained for a compound containing no resin.

EXPERIMENTAL

MATERIALS AND COMPOUND PREPARATION

A blend of a 37.5 wt% oil-extended solution-polymerized styrene-butadiene rubber (S-SBR, Buna VSL 5025-2 HM from Lanxess, Leverkusen, Germany) and high-cis-polybutadiene (BR, KUMHO KBR, Seoul, S-Korea) with a rubber ratio of 70/30 was used in this study. The three types of oligomeric resins investigated were provided by Arizona Chemical B.V., Almere, the Netherlands. All types are from the Sylvatraxx^{TM} product line: the naturally derived oligomeric poly-terpene resin (resin A); the phenolic modified oligomeric terpene (resin B); the pure vinyl-aromatic hydrocarbon resin (resin C). The characteristic properties of the resins are given in Table I. Compounds were prepared based on basis of the formulations given in Table II, based on a common “Green Tire”, silica-reinforced passenger car tire tread.[9] In the acronyms employed the first letter represents the type of oligomeric resin, A, B and C, and the number represents the concentration in phr (parts per hundered rubber) of oligomeric resins used. Highly dispersible silica 1165MP from Rhodia Silices (Lyon, France) was used as reinforcing filler. The

amount of coupling agent bis(tri-ethoxy-silyl propyl)tetrasulfide (TESPT) was held constant throughout the study to represent the commonly accepted optimum amount.[10] The other ingredients and their suppliers are listed in Table II.

Compounds were prepared in a 350 mL Brabender 350S internal mixer using a three stage mixing procedure. The three stages mixing procedure is presented in Table III. The internal mixer chamber volume was 390 cm^3. The oligomeric resins to be added were physically mixed with the extender oil, ½ silane, TMQ and 6PPD in step 3 of the first mixing stage prior to adding them together to the mixer. After cooling down, the first stage master batch was returned to the mixing chamber for a second stage. This was done to ensure a high level of coupling reaction between the silane and the silica.[11] After a maturation time of approximately 24 hours, the second stage master batch was returned to the mixing chamber and mixed with the curatives till a temperature of 100 ^oC at 75 rpm during 3 minutes.

Samples were vulcanized in a Wickert press WLP 1600 at 100 bar and 160 ºC to sheets with a thickness of 1.5 and 2 mm, according to their t_{90} + 2 minutes optimum vulcanization time, as determined in a Rubber Process Analyzer RPA 2000 of Alpha Technologies, according to the procedure as described in ISO 3417.

CHARACTERIZATIONS

Mooney viscosity measurements were performed with an Alpha Technologies Mooney 2000VS, using the large type rotor (L), at 100 ^oC, according ISO 289. Dynamic mechanical analyses of the vulcanized compounds were done in shear and tension mode in a Metravib DMA2000 dynamic spectrometer. The samples were cut from the vulcanized sheets (150x150x2mm and 160x160x1.5mm) of the rubber compounds. For storage and loss moduli as function of temperature, measurements were performed between -80 ºC and +80 ºC in steps of five degrees at a dynamic strain of 0.1%, static strain of 1% and a frequency of 10 Hz. The glass transition temperatures were obtained from temperature sweep measurements in tension mode at a frequency of 10 Hz and dynamic strain of 0.1%. Strain sweep measurements of the vulcanizates

were performed at constant frequency of 10 Hz at 90 ºC, with strain amplitudes ranging from 0.1 to 100%. Hardness of the vulcanized compounds was measured with a Zwick 3150 Shore A Hardness Tester. Tensile and tear strength measurements were performed in tensile mode in a Zwick/Roell Z1.0 tensile tester, according to the ISO 37 at a crosshead speed of 500 mm/min.

RESULTS

MIXING, VULCANIZATION AND MECHANICAL PROPERTIES

The mixing behavior of the compounds containing the various resins is significantly changed relative to the non-resin containing Reference compound, particularly during the later steps in Stage 1 mixing. Figure 1 shows typical mixer torque versus time fingerprints for the three compounds containing 4 phr of the various oligomeric resins, in comparison to the non-resin containing Reference. In step 3 after loading of all the silica, silane and the oil as well as resins, and more so even in step 4 of the 1st mixing stage the torque levels progressively deviate for resins C and B resulting in higher, resp. resin A in lower torque levels relative to the Reference compound. When the concentration of oligomeric resins was changed, similar behavior was observed. This difference in mixer torque could be a consequence of the partial replacement of the low viscosity extender oil by the higher viscosity oligomeric resins; however, the effects are opposite of what might have been expected on basis of the natural viscosities of the respective resins (Table I), with Resin A having by far the highest and Resin C a very low viscosity. Table II lists the Mooney viscosities for the various finished compounds; these confirm the earlier observations: Resin A tends to decrease the Mooney viscosity at least for 2 and 4 phr loading; Resins B and C show a mutually comparable progressive increase in Mooney viscosity with increasing loading in comparison with the Reference compound. It is clear that the viscosity of the resins themselves cannot account for this effect.

It is well known for the present silica technology that an *in-situ* reaction of the coupling agent with the silica surface needs to take place during mixing, in order to hydrophobize the polar

nature of the silica particles and to provide a reactive surface which later-on during vulcanization can chemically couple the rubber polymers to the silica. The efficiency of this silanization is a crucial factor in this technology and can positively or negatively be influenced by the conditions during mixing.[7,12] The Mooney increase can be taken as a first indication that the addition of the resins enhances the hydrophobation/compatibilization achieved by the coupling agent TESPT somewhat. The more common way to judge this is by the so-called Payne effect discussed later.

The curing properties of the various compounds, as presented in Table II, are slightly influenced by the oligomeric resin addition. For Resins B and C, the scorch times tend to decrease slightly. The values of the minimum rheometer torque M_L are mutually the same and show no significant difference, corresponding with the small differences in Mooney viscosity. The differences seen in the optimum vulcanization time t_{90} and the maximum rheometer torque M_H are not significant in view of the experimental error, besides the fact that some compounds showed marching modulus, which precludes a realistic determination of these properties: in particular compounds B-2 and C-6. Overall it seems justified to state that the vulcanization properties of the compounds are only marginally influenced by the oligomeric resin additions.

The mechanical properties after optimum vulcanization are also presented in Table II. Oligomeric resin addition has the tendency to marginally increase the hardness, which could indicate enhancement of the degree of crosslinking. However, this could also be the consequence of the replacement of some of the plasticizing oil softener by the less softening resins. The M_{300} values within the Resin groups A and B show a decreasing trend; Resin C shows no trend. Given the somewhat large scatter in the data, also relative to the Reference this may not be very relevant. The tensile strength though increases significantly with oligomeric resin content. Resins B and C give a high reinforcing contribution to the tensile strength, already at 2 phr additions, without further increase at higher resin loadings. Similarly the elongations at break are increased already at 2 phr loading, but do not further increase at higher loadings. Resin A, on the other hand, shows a steady increase in tensile strength and - after an initial decrease - in the elongation at break, even

up to 6 phr addition. This might indicate a limit in the solubility of the resins in the compound, where Resins B and C apparently reach their limit in solubility at around 2 – 4 phr, while Resin A dissolves homogenously till 6 phr in this type of compound.

DYNAMIC PROPERTIES

The common way to judge the efficiency of the silanization/hydrophobation of the silica is by the so-called Payne effect, the difference in Storage (or Loss) Modulus at low and high strain, caused by breakdown of the filler-filler interactions at large strain.[13,14] Payne effect measurements of the storage modulus as executed on the optimally vulcanized compounds are presented in Figure 2. The lower the difference between low and high strain modulus, the better the silanization. It signifies a reduced interaction between the filler aggregates themselves: less filler-filler networking; more interaction/bonding between the fillers and the rubbers and possibly – but not necessarily - a better filler dispersion. All resins clearly show a positive effect on the silanization efficiency relative to the Reference, confirming the earlier observation in the Mooney results. Resins B and C are even better than Resin A. And as to the effect of concentration, all three resins seem to reach saturation at around 4 – 5 phr. Similar results were obtained with the loss modulus versus strain. As reduced filler-filler interaction and increased filler-polymer interaction is the essence of less hysteresis and consequently lower RR of tire treads, these reduced Payne effects anticipate improvements in RR.[15]

In order to judge the influence of these resins on RR in detail, the results of tan δ against temperature are presented in Figure 3 for the RR temperature-range of 30 – 80 ^{o}C. With the exception of sample C-6, which shows erratic behavior, and apart from the scatter in the curves resulting from the rounding off of the tan δ values to 2 decimals, all compounds containing Resins B and C clearly show a reduction in tan δ relative to the Reference, particularly at 60 ^{o}C. It predicts a 15% reduction in RR for tire treads made from these compounds. The effects for Resin A are less pronounced.

Figure 4 shows the tan δ data in the temperature range representative for WSR: 0 – 30 ^{o}C. Here a clear positive effect of higher tan δ values indicates a higher and thus improved WSR of tire treads made from these compounds. The largest relative improvements found for tan δ are around 35% for sample B-4 and Resin C at 2 phr. All curves converge at 30 ^{o}C to correspond with cross-over at around 40 ^{o}C, as seen in Figure 3. A closer look at the tan δ data at sub-zero temperatures, -25 – 0 ^{o}C, also sometimes referred to as relevant for Ice Grip properties of tire treads, is presented in Figure 5. It shows the increases in tan δ to be the result of a combined effect of a slight shift in the glass transition temperature (T_g) of the compounds to higher temperature as well as an increase in the peak heights themselves. The effects are again most prominent for Resins B and C relative to Resin A.

Table IV summarizes the dynamic data in terms of better or worse relative to the Reference, with the understanding that with respect to WSR an increase is preferred, and for RR a decrease. The overall best performing compounds are marked in bold, indicating again the preference for the Resins B and C over Resin A. In view of saturation or limited solubility effects, quantities of ± 4 phr of all types of resins seem sufficient to achieve more or less optimal results.

DISCUSSION

The results as presented clearly indicate the great potential value of oligomeric resins as admixtures to silica-reinforced tire tread compounds, to impart at the same time improvements in WSR and RR, without negative effects on other properties. A slight increase in hardness was noticed upon addition of the resins, which in commercial tire production could give reason to compound composition adjustments. But in the context of the present study this was not considered appropriate as it might have obscured the effects seen and made the interpretation difficult.

Overall Resin C and Resin B gave the best performance, better than Resin A. This obviously has something to do with the mutual compatibility of the resins with the polymers.–

From a phenomenological perspective comes the chemical nature of the resins of the vinyl-aromatic base of Resin C or the phenolic modification of Resin B at least closer in structure to the styrene-butadiene than the polyterpene structure of Resin A. This might explain the better compatibility.

The root cause of the phenomena seen is the influence of the respective resins on the glass transition performance of the compounds: a small shift in T_g to a higher temperature and an increase in the tan δ peak. One possible explanation for this T_g-shift is related to the earlier raised question about the solubility/compatibility of the three resins with the basic compound.[11] It is illustrative to use the approach of Fox to calculate the resulting Tg of two mutually soluble components with different individual T_g's. The well-known Fox equation is given as:

$$\frac{1}{T_{g,mix}} = \frac{w_A}{T_{g,A}} + \frac{w_B}{T_{g,B}} \qquad \text{Eq. (1)}$$

In Eq. 1. are w_i and $T_{g,i}$ the weight fraction and the T_g of component i. In case the components are mutually not compatible/soluble, the T_g's do not merge and keep their individual values and two T_g-peaks remain visible in the tan δ versus. temperature diagram, at least when the quantities of both components are both sufficiently high. This is not the case in the present study, but at least there is a tendency to increase seen in the T_g's of the compounds as given in Table II, which therefore can be taken as a sign of good/sufficient solubility at the low amounts as added. It indicates that the resin containing compounds are homogeneous and compatible.[16] The T_g-shifts obtained for Resin A are clearly the largest, and for Resin C the smallest, corresponding very well with the T_g's of the pristine resins, as presented in Table I.

Another explanation, also covering the increase in the peak height of tan δ as well as the lower tan δ at the RR-range at higher temperature, is related to the enhancement of the silanization of the silica by the oligomeric resins, as referred to before. The degree of silanization by the coupling agent TESPT and later by the chemical bonding of rubber molecules to the surface leads to the creation of a significant amount of immobilized rubber molecules, or at least heavily restricted in their segmental motions; sometimes also called a "glassy layer". This plays a

particularly important role for silica reinforcement, as this chemical bonding is a prerequisite for silica to work as reinforcing filler, in contrast with the more traditional carbon black, where this bonding is mainly physical of nature and therefore less strong. The silica fillers – if present in large enough quantity, like they are in the present compounds - therefore act in a way like multifunctional chemical crosslinkers, next to the crosslinks created by the sulfur vulcanization. As it is well known that crosslinking of polymers tends to raise the T_g by a few degrees, the multifunctional crosslinking effect of the rubber immobilized on the silica surface also results in a T_g-shift or broadening of the T_g-peak to higher temperature: therefore also the designation "glassy layer".

Apparently, the presence of the oligomeric resins enhances this immobilization of rubber molecules on the silica filler. This raises the hydrodynamic volume of the filler particles, which then can account for the viscosity increases as observed[17]. However, it also improves the silica dispersion and thereby releases more of the rubber molecules occluded in the void spaces of the silica aggregates. The Payne effect data support this phenomenon in the sense, that the mutual interactions between the filler aggregates are reduced. This raises the effective volume fraction of rubber in the compounds, which enhances the rubber elastic performance of the compounds versus the "dead, non-elastic" contribution of the filler, as is reflected in the lower tan δ in the RR-range, but also in the increased tan δ – peak at the glass transition. This challenging interpretation concurs with similar observations and analyses by others, e.g. as a result of functionalization of the polymers[18,19], or by variation of the type and chemical structure of the coupling agent used instead of TESPT.[20] It would require more fundamental in-depth studies, however, to confirm this further in detail.

CONCLUSIONS

Addition of low amounts of low molecular weight, oligomeric resins of natural and/or synthetic origin, bears the potential to enhance the (wet) skid resistance and at the same time

reduce the rolling resistance of silica-reinforced passenger tire treads based on synthetic rubbers. In the specific polymer matrix used for this investigation, the vinyl-aromatic based hydrocarbon resin and the phenolic-modified terpene resin perform better than the poly-terpene resin. The overall performance of the resins depends on the particular rubber formulation and the selection of rubbers which explains the necessity of a large variety of oligomeric resins derived from various monomers. The addition of 2 to 6 phr resin to the compounds to replace the same amounts of extender oil, has little influence on vulcanization behavior, hardly raises the hardness, but has a strong positive influence on tensile strength and elongation at break. The Payne-effect improvements resulting from the addition of the oligomeric resins indicate a reduced filler-filler interaction of the silica filler and tighter silica-rubber interaction, as obtained by enhancement of the silanization by the coupling agent TESPT. It results in a stronger immobilized rubber shell around the silica particles and more rubber released from occlusion in the void spaces of the silica aggregates. It improves the "elastic" performance of the compounds: reduced hysteresis, and consequently gives indication for lower RR of tire treads made thereof, versus increases in the tan δ temperature and peak-height in the glass-transition region, indicative for higher (wet) skid resistance of tire treads.

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Table I: Characteristics of Resins used in this research

Resin code	Main designation	Main components	M_n [g/mol]	PDI* [-]	T_g [^oC]	Softening point [^oC]	Density [kg/m^3]	Viscosity** [mPa·s]	Hydroxyl value [mg KOH/g]
A	Polyterpene (100% cyclo-aliphatic)	Terpene	630	1.6	72	120-126	1.05	10,000	-
B	Terpene phenolic	Terpene + Phenol	563	1.3	60	112-118	1.01	3,400	50
C	Aromatic hydrocarbon	Styrene + α-Methyl Styrene	723	1.6	43	80-90	1.064	650	-

* Polydispersity index: M_w/M_n

** at 150 ^oC

Table II: Rubber compound compositions (phr) and properties

Ingredient	Supplier	Compound sample code									
		Reference	A-2	A-4	A-6	B-2	B-4	B-6	C-2	C-4	C-6
S-SBR	Buna VSL 5025-2 HM Lanxess, Leverkusen, Germany	96.3	96.3	96.3	96.3	96.3	96.3	96.3	96.3	96.3	96.3
BR	Kumho KBR Seoul, S-Korea	30	30	30	30	30	30	30	30	30	30
Silica (1165MP)	Rhodia Silices, Lyon, France	80	80	80	80	80	80	80	80	80	80
TESPT[a]	Evonik GmbH, Essen, Germany	7	7	7	7	7	7	7	7	7	7
TDAE[b]	Hansen & Rosenthal, Hamburg, Germany	**6.7**	**4.7**	**2.7**	**0.7**	**4.7**	**2.7**	**0.7**	**4.7**	**2.7**	**0.7**
Zinc oxide	Sigma Aldrich, St. Louis, United states	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Stearic acid	Sigma Aldrich, St. Louis, United states	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
6PPD[c]	Flexsys Brussels, Belgium	2	2	2	2	2	2	2	2	2	2
TMQ[d]	Flexsys Brussels, Belgium	2	2	2	2	2	2	2	2	2	2
Resin	Arizona Chemical BV, Almere, the Netherlands	**0**	**2**	**4**	**6**	**2**	**4**	**6**	**2**	**4**	**6**
Sulfur	Sigma Aldrich, St. Louis, United state	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
TBBS[e]	Flexsys, Brussels, Belgium	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7
DPG[f]	Flexsys Brussels, Belgium	2	2	2	2	2	2	2	2	2	2
Properties											
Mooney viscosities:	[ML(1+4) at 100 ^{o}C]	70	69	70	72	72	76	77	72	74	75
Cure meter data:	Ts1 [min]	2.7	2.8	2.8	2.3	2.2	2.2	2.4	2.2	2.3	2.1
	t_{90} [min]	12.0	12.6	11.8	12.6	14.9	12.5	12.5	12.9	12.2	14.1
	M_L [dNm]	0.7	0.7	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
	M_H [dNm]	8.3	8.6	8.0	8.5	9.1	8.0	9.0	9.0	9.0	9.0
Mechanical properties:											
	Tensile Strength [MPa]	17.1	17.6	17.8	20.1	20.6	20.3	20.1	20.7	20.4	20.8
	Elongation at break, [%]	387	349	367	435	428	444	468	465	422	434
	M100 [MPa]	2.1	2.6	2.2	2.2	2.2	2.2	2.0	1.9	2.5	2.3
	M300 [MPa]	12.2	14.4	13.6	12.3	12.6	12.1	10.8	11.1	13.9	12.8
Hardness	[Shore A]	61	61	61	62	60	61	62	60	61	62
Glass transition temperature		-19	-19	-19	-18	-20	-19	-18	-19	-18	-17

[a] Coupling agent bis(triethoxysilylpropyl) tetrasulfide

[b] Treated distillate aromatic extract oil, Enerthene 1849 F

[c] Antiozonant N-phenyl-N'-1,3-dimethylbutyl-p-phenylenediamine

[d] Antioxidant 2,2,4- trimethyl-l,2-di-hydroquinoline

[e] Accelerator N-tert-butylbenzothiazole-2-sulphenamide

[f] Accelerator diphenyl guanidine

Table III: Three stage mixing procedure

1st master batch stage	
Rotor speed:	110 RPM
Initial temp. setting:	65 °C
Fill factor:	0.7
Actions	
(Min. sec.)	
0.0	Add polymers
1.0	Add ½ silica, ½ silane, ZnO + Stearic acid
2.0	Add ½ silica, ½ silane, Oil, TMQ, 6PPD and Resin
3.0	Sweep
4.0	Dump @ ~ 155 °C

2th master batch stage – remix	
Rotor speed:	130 RPM
Initial temp. setting:	50 °C
Fill factor:	0.7
Actions	
(Min. sec.)	
0.0	Load stage 1 batch
3.0	Dump @ ~ 155 °C

3th master batch stage	
Rotor speed:	75 RPM
Initial temp. setting:	50 °C
Fill factor:	0.7
Actions	
(Min. sec.)	
0.0	Add batch from Stage 2. Add curatives
3.0	Dump @ ~ 100 °C

Table IV: Summary of WSR and RR results

	Resin dosage (phr)	DMA		
		Ice grip (-25–0 °C)	Wet skid resistance (0-30 °C)	Rolling resistance (30-80 °C)
Reference	0			
Resin A	2	+	+	±
	4	++	+	++
	6	+	++	±
Resin B	2	+	+	++
	4	++	++	+
	6	+	++	+
Resin C	2	+	++	++
	4	++	++	++
	6	+	+	

(++): Best; (+): Improved; (±): Neutral; (-): Worse.

CAPTIONS TO THE FIGURES

Figure 1: Fingerprint of 1st Stage masterbatch mixing of the reference and 4 phr resin-containing compounds.

Figure 2: Payne effect (storage modules versus strain) of reference compound and resin containing compounds.

Figure 3: Tan δ against temperature in the RR range of 30 – 80 °C for all compounds.

Figure 4: Tan δ against temperature in the WSR range for all compounds.

Figure 5: Tan δ of resin group A, B and C (10 Hz and 0.1% dynamic strain) in the ice grip temp. range.

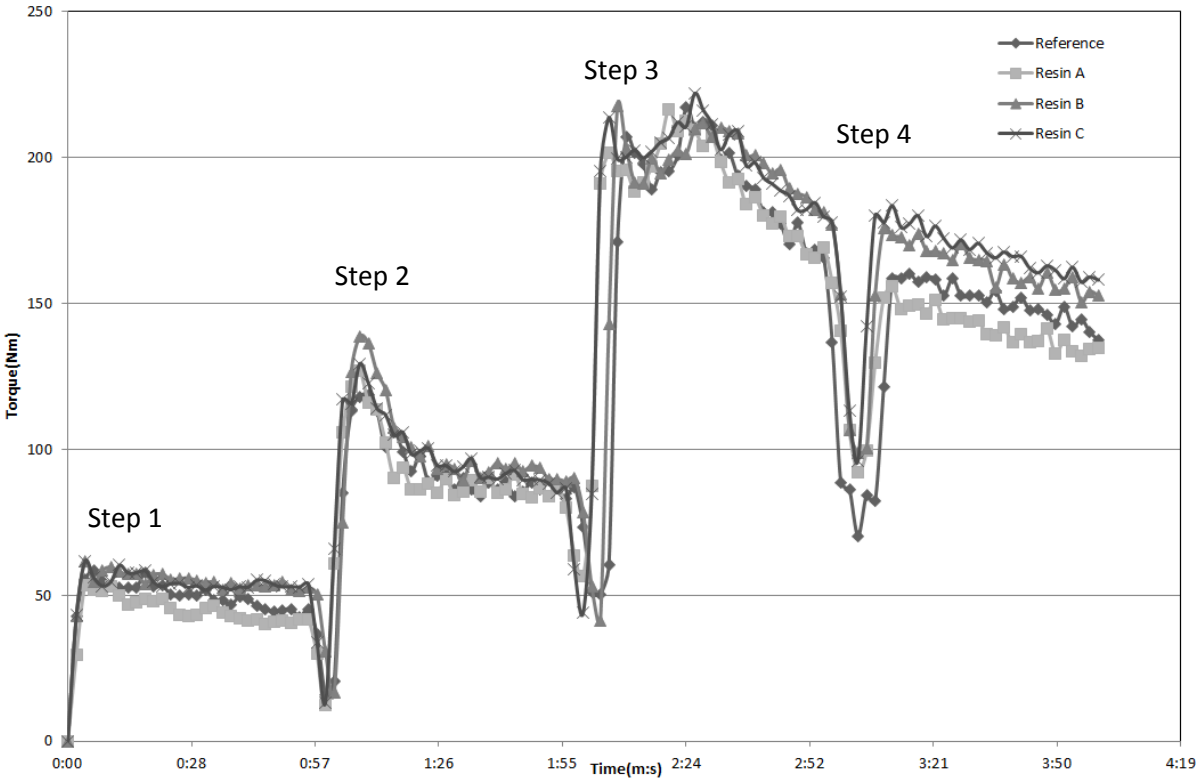
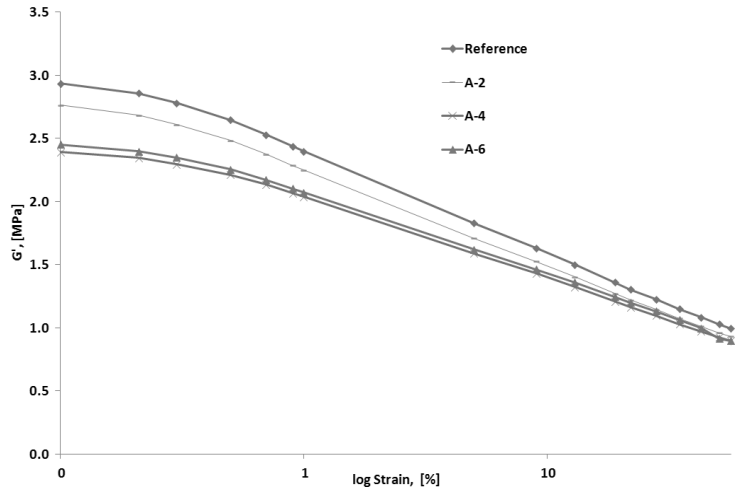


Figure 1: Fingerprint of 1st Stage masterbatch mixing of the reference and 4 phr resin-containing compounds.



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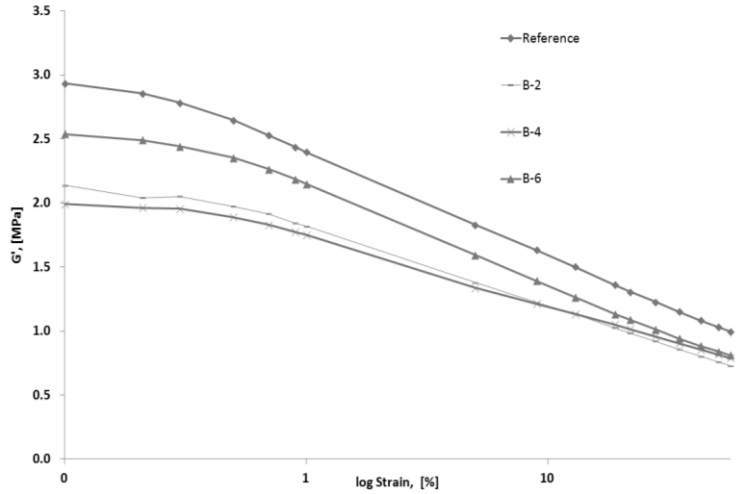

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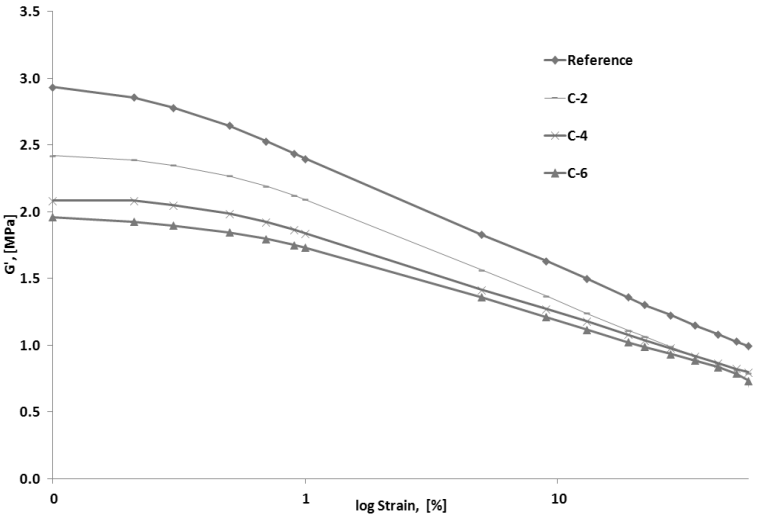
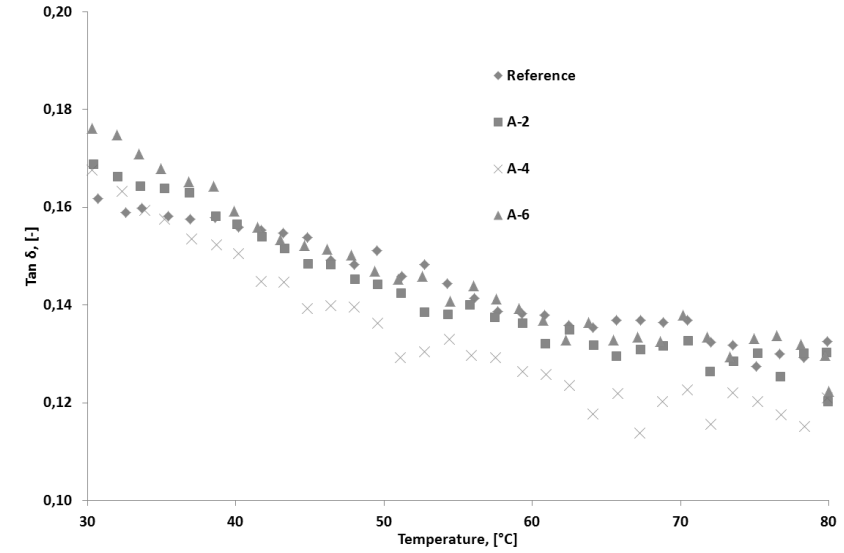


III

Figure 2: Payne effect (storage modules versus strain) of reference compound and resin containing compounds



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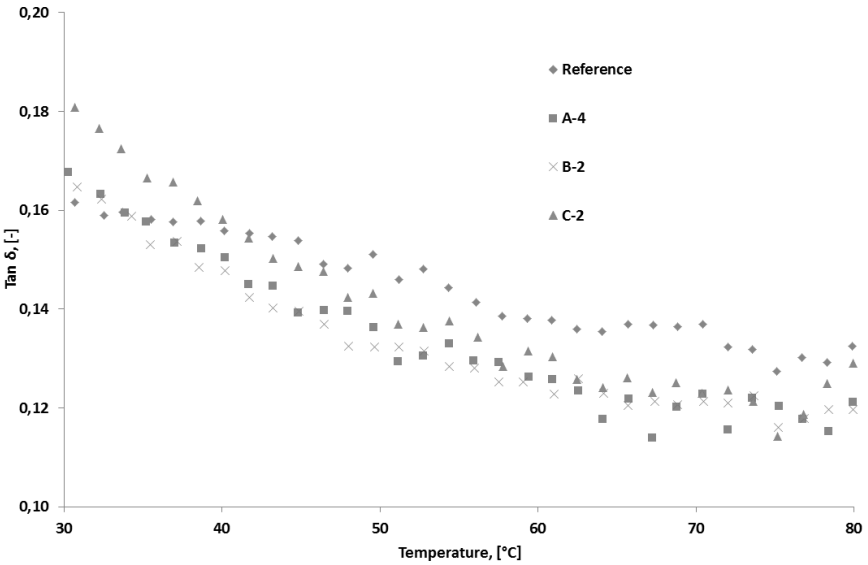

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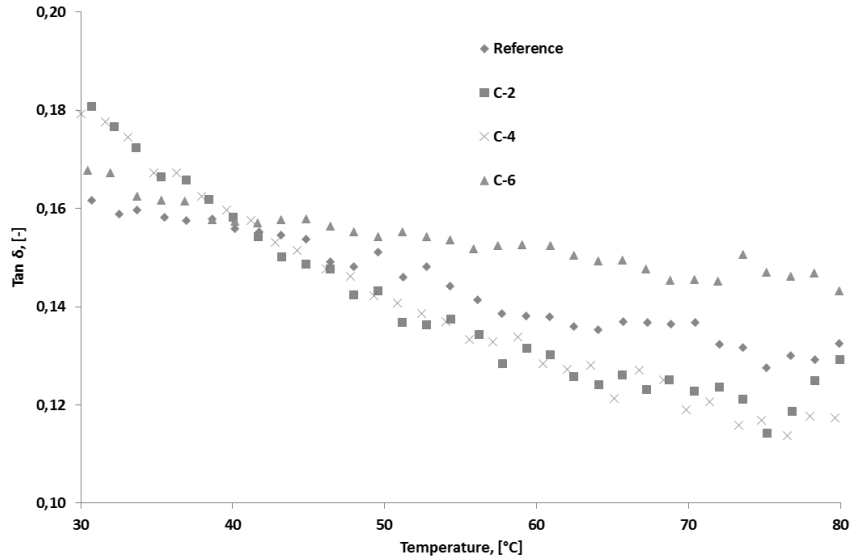
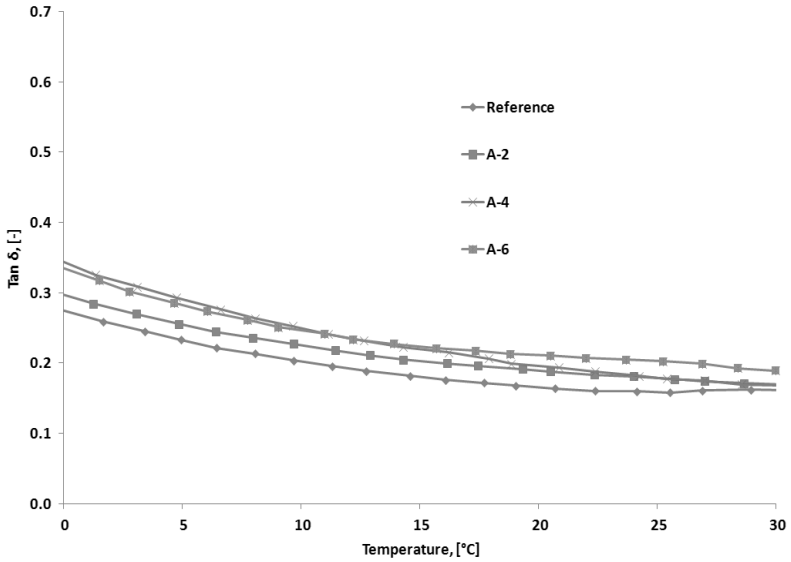


III

Figure 3: Tan δ against temperature in the RR range of 30 – 80 ^{o}C for all compounds



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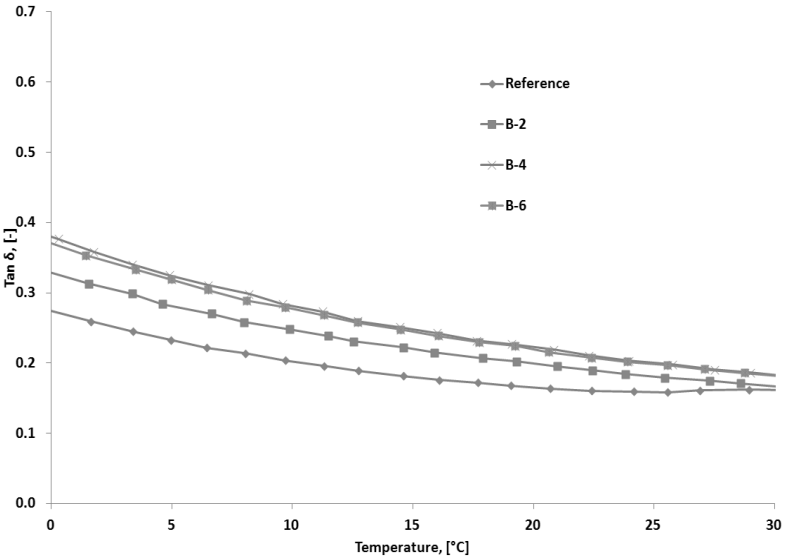

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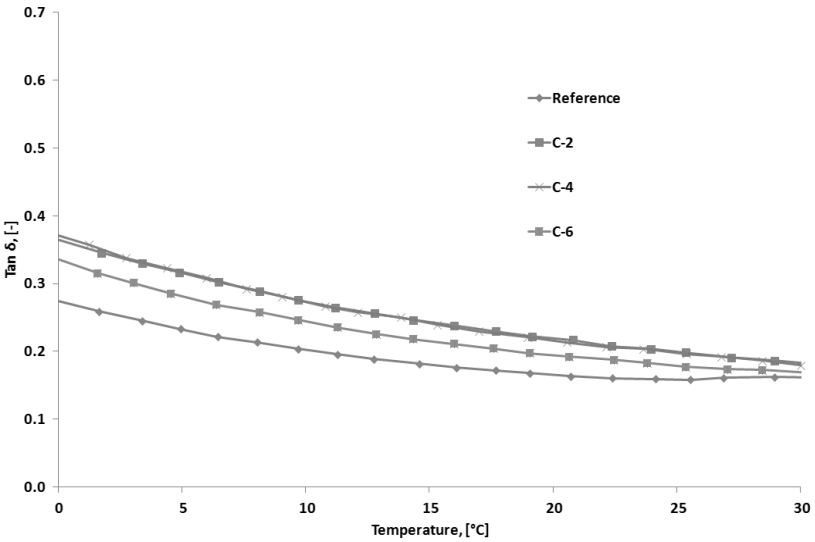
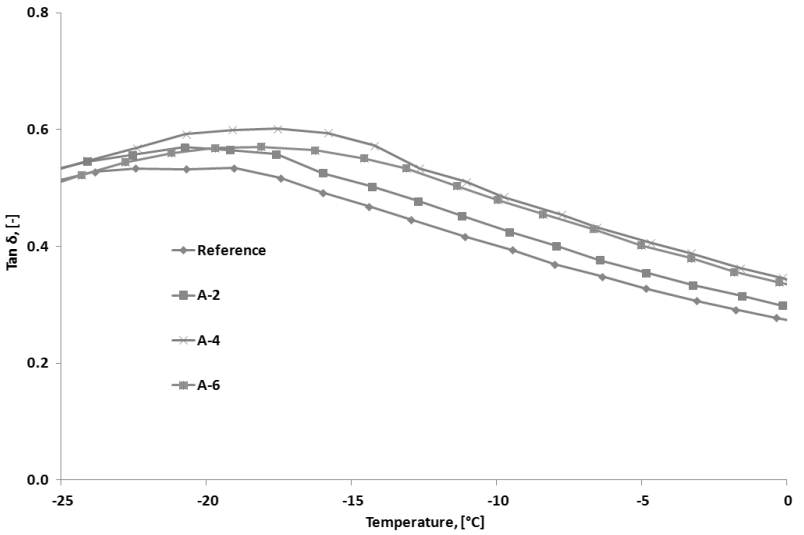


III

Figure 4: Tan δ against temperature in the WSR range for all compounds



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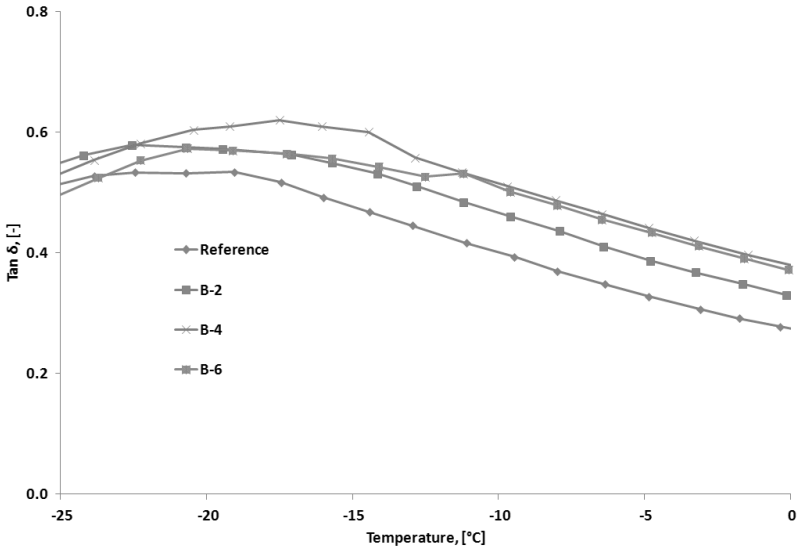

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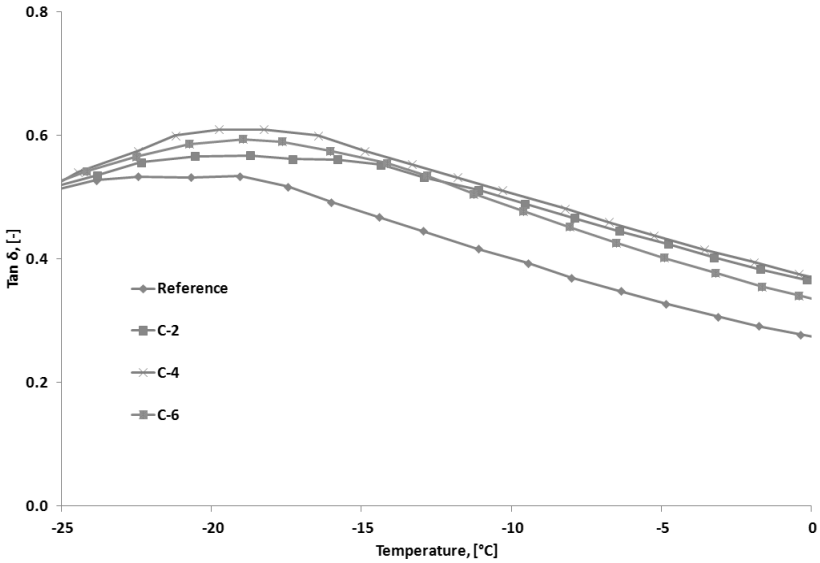

III

Figure 5: Tan δ of resin group A, B and C (10 Hz and 0.1% dynamic strain) in the ice grip temp. range