



Contribution of filler–filler interaction and filler aspect ratio in rubber reinforcement by silica and mica

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Received: 8 February 2020 / Accepted: 22 July 2020
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Abstract

The reinforcement degree offered by silica as a spherical filler with low aspect ratio and high filler–filler interaction was compared with mica as a platelet filler with higher aspect ratio and lower filler–filler interaction. By replacing half of the carbon black with silica or mica in a typical formulation, rubber composites were prepared and their properties were evaluated under two conditions: In the first one, the impact of increasing the amount of a chemical surface modifier, namely silane TESPT (bis triethoxysilylpropyl tetrasulfide), was investigated and in the second one, the increasing amount of a physical modifier namely DPG (diphenyl guanidine) on the performance of the two fillers was explored. The resulting composites were subjected to physico-mechanical experiments including the bound rubber, tensile test, and the dynamic mechanical thermal analysis (DMTA). Results indicated that the greater amount of filler–filler interaction resulting from the higher SiO₂ and hydroxyl content in silica has a dominating role over the aspect ratio of mica which is then led to a remarkable difference in their bound rubber. However, the mica-containing composites were capable of competing with silica when the DPG was used. Nevertheless, the compound only containing carbon black with 19.7 MPa of tensile strength and 24.4 kgf/cm of tear strength showed the best mechanical properties among other fillers, and by replacing 30 phr carbon black, these properties decreased approximately 15 ± 3%. Based on DMTA findings, promising data were obtained for the mica-reinforced rubbers with regard to the tire application.

Keywords Silica · Mica · Carbon black · Bound rubber · Grip · Rolling resistance

Introduction

Unfilled rubbers have such poor toughness and strength that they cannot be used in almost any practical applications [1]. Reinforcing rubbers with fillers in a high volume fraction is a classical method and still the most practical solution. The impact of filler on the rubber reinforcement can be elucidated in principle by one of the following main mechanisms: (1) the stress transferring from the soft matrix to the stiff particles, (2) the substitution of a portion of the rubber

matrix with the stiffer filler and (3) the reduced segmental immobilization caused by the interaction of polymer chains with the filler surface [2]. The correlation of reinforcement to the structure and chemistry of fillers can accordingly be anticipated. For instance, when compared to a spherical filler, layered shape fillers having aspect ratios higher than 1 are capable of providing stronger stress transfer.

The microstructure of such fillers, if properly dispersed, can be converted from the micro-assembled layers to a “house of cards” morphology, which by consequence leads to an enhanced segmental immobilization of rubbers [3]. Similarly, filler–filler interaction which is a function of the surface energy and the polarity of chemical groups existing on the filler surface affects the rubber reinforcement through the modification of chain immobilization, particularly at high filler loading [4, 5]. Therefore, depending on the chemical and structural characters of the fillers, their reinforcing potential may be competing with each other, and experimental practices are required to find out the dominating role. While carbon black is the most common filler of rubbers,

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recent trends for green tire applications have shifted the academic and industrial attention to other mineral alternatives such as precipitated silica [6–8]. The precipitated silica has been traditionally used as a reinforcing filler in rubber applications where a high degree of tear resistance was required. When used with suitable surface modifiers (i.e., silanes), silica can decrease the heat build-up and viscoelastic energy dissipation, when compared to carbon black-filled rubbers. This has led to its indispensable role in green tire technology [9, 10]. However, there are some ever-existing challenges with the use of silica including (1) poor processability, (2) low electrical conductivity, and (3) high cost, mainly attributed to the expense of the silane coupling agent [11]. This has paved the way for evaluating the performance of many other mineral fillers including mica for tire applications. It has been suggested in the literature that exfoliating layered particles such as clays, mica, and graphite have a remarkable reinforcing potential, even at loading lower than those used in the case of solid particles such as carbon black and silica [12–14].

The interaction of silica or other silicate fillers such as kaolin and mica (which contain silanol and siloxane groups, usually found as SiO_2 in the manufacturer's data sheet) with rubbers is very weak due to the relatively high filler–filler interactions resulting from the existence of abundant hydroxyl groups on their surfaces [9, 15, 16]. Increasing levels of filler–filler interaction and the polar nature of filler adversely influence the final properties through at least two mechanisms: First, it reduces the cross-linking density by adsorbing and deactivating the curing accelerators on their acidic surfaces. Second, it forms a poorly dispersed morphology with large aggregates and agglomerates which by consequence deteriorates the engineering aspects of rubber properties [17–19]. Treatment of silica surface by either physical modifiers such as diethylene glycol (DEG), polyethylene glycol (PEG), and DPG or the chemical modifiers such as the silane-coupling agent TESPT are among the recommended solutions. It is worthwhile to note that the DPG, in addition to the role as a surface modifier, is an amine-type accelerator that has a synergistic effect on the performance of the sulfenamide accelerators [20–22].

The treatment of silica by surface modifiers though improves the filler dispersion and the rubber curing, reduces the filler–filler interaction and thus leads to a loss in its maximum reinforcing ability [23].

The present contribution aims to understand whether or not the higher aspect ratio of the silicate fillers can balance its lower content of filler–filler interaction at a level that could be competed with the reinforcing characters of the treated silica. The aim of this study is to evaluate the possibility of replacing the half of carbon black in a conventional tire tread compound with silica and mica, by assessing the mechanical and dynamic properties of the two composites.

Silica with its high filler–filler interaction and mica with a non-spherical shape have distinct features to compete with each other with regard to the reinforcing capabilities. The comparison of the two reinforcing fillers is made by a systematic increase of two types of surface modifiers: covalent type (i.e., TESPT) and a physical one (i.e., DPG). Based on DMTA results, the replacement of half of the carbon black content by silica or mica can show similar wet grip and rolling resistance properties.

Experimental

Materials and preparation of compounds

All materials were combined according to Table 1 and mixed in three steps as Table 2. Mica was supplied from Narmkooban Co., (Iran) and its sieve residue on mesh No.200 (0.074 mm) measured according to ISO 787-2 was reported less than 0.1%. Ultrasil VN3 as precipitated silica was supplied from Evonik Industries AG (Germany) and its sieve residue on mesh No. 230 (0.063 mm) measured according to ISO 787-2 was reported less than 0.1% and its specific surface area measured according to ISO 9277 was reported $180 \text{ m}^2/\text{g}$.

The first and second stages were performed in an internal mixer with a fill factor of 0.7 and a rotor speed of 60 rpm with an initial temperature of $80 \text{ }^\circ\text{C}$ and a dump temperature of $145 \pm 5 \text{ }^\circ\text{C}$. Then, the third step after 24 h of resting was done on a two-roll mill.

With the exception of the control sample which contained 60 phr N330 carbon black, the rest contained 30 phr N330 and 30 phr silica or mica.

The amounts of TESPT and DPG used in this formulation were based on the CTAB specific surface area of the silica according to Eqs. 1 and 2 as suggested by Guy et al. [10] respectively:

$$\text{TESPT (phr)} = 5.3 \times 10^{-4} \times \text{specific surface area of silica (m}^2/\text{g)} \\ \times \text{silica amount (phr)}, \quad (1)$$

$$\text{DPG (phr)} = 1.2 \times 10^{-4} \times \text{specific surface area of silica (m}^2/\text{g)} \\ \times \text{silica amount (phr)}. \quad (2)$$

Hence, the optimal values of TESPT and DPG for 30 phr Ultrasil VN3 were calculated as 2.6 and 0.6, respectively. Since the percentage of SiO_2 in mica was about half of the SiO_2 in silica, other amounts of TESPT and DPG were selected as 1.3 phr and 0.3 phr, respectively. The range of filler–polymer interaction was extended in silica-containing rubbers using new values of TESPT (3.9 and 1.3 phr) and

Table 1 Formulation of compounds in this research

	Designation	supplier	Co	CB	SiT13	SiT39	SiD3	SiD6/SiT26	SiD9	MIT13	MIT39	MI D3	MI D6/MI T26	MI D9
SBR1502	Bandar Imam Petrochemical Co., Iran			100	100	100	100	100	100	100	100	100	100	100
N330	Iran Carbon, Iran			60	30	30	30	30	30	30	30	30	30	30
Ultrasil VN3	Evonik, Germany			0	30	30	30	30	30	0	0	0	0	0
Mica	Narmkooban, Iran			0	0	0	0	0	0	30	30	30	30	30
Si69	Shin-Etsu Chemical Co., Japan			0	1.3	3.9	2.6	2.6	2.6	1.3	3.9	2.6	2.6	2.6
ZnO	Pars Neko Co., Iran			3	3	3	3	3	3	3	3	3	3	3
St.A	Persian Gulf, Indonesia			1	1	1	1	1	1	1	1	1	1	1
TMQ	Rongcheng, China			1	1	1	1	1	1	1	1	1	1	1
Sulfur	Parto Googerd Asia, Iran			1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CBS	Taizhou, China			2	2	2	2.3	2	1.7	2	2	2.3	2	1.7
DPG	Taizhou, China			0.6	0.6	0.6	0.3	0.6	0.9	0.6	0.6	0.3	0.6	0.9
AR-29	Iranol, Iran			10	10	10	10	10	10	10	10	10	10	10

DPG (0.9 and 0.3 phr). The corresponding modification was also applied for the mica case.

To eliminate the effect of curative on the cure characterization and mechanical properties, all curative quantities were kept constant in all composites. Therefore, by enhancing the DPG level, the amount of co-accelerator (CBS) was declined.

Methods for characterization

Mooney viscosity (ASTM D1646) and cure characterization (ASTM D2084) were measured by the Monsanto rheometer (Gomplast Machinery, Inc., USA) at 100 °C and 160 °C, respectively.

The mechanical properties were obtained by a Universal Testing Machine (Hiwa200, Hiwa, Iran). To evaluate the tensile strength and tear strength, dumb-bell (ASTM D412) and die C (ASTM D624) specimens were punched out from the molded sheets, respectively. The tests were repeated three times and the average values of the tensile strength, elongation-at-break, and tear strength were reported.

Dynamic mechanical thermal analysis was performed with Tritec 2000 (Triton, England) in a single cantilever bending mode with a frequency of 10 Hz, a strain of 0.15% and a temperature range of –100 °C–100 °C with a heating rate of 5 °C/min (ASTM E-1640).

The scanning electron microscopy (SEM) images were taken from the gold-coated surface of samples which cut in liquid nitrogen, using the Phenom-ProX Netherlands microscope with 15 kV voltage and 1000× and 10,000× magnification.

DMTA and SEM were compared only for compounds containing 2.6 phr TESPT and 0.6 phr DPG.

To determine the SiO₂ content of silica and mica powder, X-ray fluorescence (XRF) test was performed with Philips PW2404. XRF results showed that the SiO₂ contents of silica and mica were 98.1% and 55.8%, respectively. Also, it is reported that Ultrasil VN3 silica has about 98% SiO₂ [24].

To measure the percentage of bound rubber, 0.5 g of a sample having no curatives (the specimens obtained at the end of the second stage) was cut into small pieces and loosely packed in a steel cage (mesh size 400). Then the cage was immersed in 50 mL toluene solvent at ambient temperature for 7 days. Next, it was placed in the *n*-hexane solvent for 24 h and finally dried at ambient temperature for 2 days to constant weight. The initial sample and sample after dissolution were weighed. The percentage of bound rubber was calculated according to Eq. 3.

$$\text{Bound rubber(\%)} = \left[W_{fg} - W \left(\frac{m_f}{m_f + m_p} \right) \right] / W \left(\frac{m_p}{m_f + m_p} \right) \times 100, \quad (3)$$

where W is the initial sample weight, W_{fg} is the carbon black load and gel, m_f is the filler mass in the compound, and m_p is the polymer mass in the compound [25–27].

Results and discussion

Reinforcement

Cure characteristics

Part of the reinforcing ability of a filler in a rubber composite is due to the impact of fillers on the cure characteristics. Also, from a mechanistic point of view, the Mooney viscosity and the minimum torque (ML) are excellent measures of the degree of filler–filler and filler–polymer interactions. They may also reflect the possible impact by premature cross-linking, filler re-aggregation, and shortening the length of the polymer chain due to the shear force

during mixing, as secondary factors. At various levels of TESPT and DPG, the main attributes of vulcanization are listed in Tables 3 and 4, respectively. The highest values of the Mooney viscosity and the minimum torque are for the silica-containing rubber, which is then followed by the CB and mica-containing fillers. Such a trend is a result of strong filler–filler interactions in silica, lower filler–filler but rather higher filler–polymer interaction in CB, and finally reduced filler–filler and filler–polymer interactions in mica-containing rubbers. As an early finding, it seems that the higher aspect ratio of mica has not been sufficient to provide the same level of filler–polymer interaction in CB. The addition of coupling agent TESPT and DPG to both silica and mica on one side reduces the filler–filler interaction but enhances the filler–polymer interaction on the other. The net effect can readily be found by comparing the Mooney viscosity and the minimum torques of the samples, as similarly conducted elsewhere [28]. In the

Table 2 Mixing procedure

Step 1		Step 2		Step 3
Time	Action	Time	Action	Action
0.00	Add rubber	0.00	Add master batch	All curatives (DPG, CBS, and S) were mixed on a two-roll mill
1.00	Add white filler, TESPT	1.00	Add ZnO	
3.00	Add carbon black, stearic acid, TMQ, oil	5.00	Dump	
5.00	Sweep			
8.00	Dump			

Table 3 TESPT effects on cure characteristics

Properties	Unit	SBR/CB	SBR/silica TESPT (1.3)	SBR/silica TESPT (2.6)	SBR/silica TESPT (3.9)	SBR/mica TESPT (1.3)	SBR/mica TESPT (2.6)	SBR/mica TESPT (3.9)
ML (1+4)@100 °C	MU	84.1	94.2	95.7	94.6	52.5	50.1	52.4
Minimum torque (ML)	dNm	14.5	15.0	18.0	16.0	12.0	11.5	10.0
Maximum torque (MH)	dNm	79.0	72.0	86.0	72.0	71.0	75.0	66.0
MH–ML	dNm	64.5	57	68	56	59	63.5	56
ts2	min	3.4	4.8	4.2	4.6	4.0	3.9	3.8
t90	min	6.0	8.8	7.5	8.1	6.6	7.0	6.8
Cure rate index	%	76.92	50.00	60.61	57.14	76.92	64.52	66.67

Table 4 DPG effects on cure characteristics

Properties	Unit	SBR/CB	SBR/silica DPG (0.3)	SBR/silica DPG (0.6)	SBR/silica DPG (0.9)	SBR/mica DPG (0.3)	SBR/mica DPG (0.6)	SBR/mica DPG (0.9)
Minimum torque	dNm	14.5	20.0	18.0	19.0	11.5	11.5	11.0
Maximum torque	dNm	79.0	86.0	86.0	83.5	78.0	75.0	72.0
MH–ML	dNm	64.5	66	68	64.5	66.5	63.5	61
ts2	min	3.4	4.4	4.2	4.2	4.1	3.9	3.6
t90	min	6.0	7.5	7.5	7.0	7.2	7.50	6.8
Cure rate index	%	76.92	64.52	60.61	71.43	64.52	64.52	62.50

compounds containing silica, with increasing TESPT up to 2.6 phr, the minimum torque increased, but with addition to 3.9 phr in both compounds containing silica and mica, the minimum torque decreased.

At the cure temperature, silica re-agglomeration (i.e., flocculation) also takes place and this phenomenon, depending on its rate, alters the maximum torques (MH). The maximum torque has the previous filler impacts in addition to the contributions resulting from the filler re-agglomeration, and rubber crosslinking.

Comparing the MH–ML values for all types of composites, one may have a rough approximation of the degree of the crosslinking. This factor does not vary much among the composites and thus the mechanical properties of the composites may be compared with no definite impact from the difference in crosslinking densities. Interestingly, for the DPG-modified systems such interference may further be excluded in the interpretation of the results due to the closer values of MH–ML for all composites.

When compared to the CB-filled rubber, the time for the start of curing and the optimum curing time (i.e., t_{s2} and t_{90} , respectively) have prolonged for both of the silica- and mica-containing rubbers. These are traditionally related to the acidic nature of the fillers. It is believed that intrinsic polarity and the free silanol groups can absorb basic curatives and delay the vulcanization process. The use of TESPT helps to reduce these groups through the silanization reactions, so it accelerates the cure time. Also, increasing the amount of TESPT from 1.3 to 3.9 phr, decreases the scorch time.

Stiffness and bound rubber

The concept of the “bound rubber” and the volume of the rubber that has experienced mobility restriction has long been regarded as an acceptable criteria of the rubber stiffness. As stated previously in the literature [4], various mechanisms contribute to the formation of bound rubber including “shell”, “occluded” and “trapped” rubber depending on the filler volume fraction, filler structure, filler–filler as well as filler–polymer interaction. At low filler loading, a thin layer of rubber with restricted mobility is formed around the filler as a result of filler–polymer interaction. The total available surface area of the filler will determine the amount of shell rubber. For high “structure” fillers, new portions of rubber may be occluded and prevented from routine movement within the fractal shape of a filler aggregate (known as occluded rubber). At high filler volume fraction or at severe filler–filler interaction, the entrapment of large content of rubbers inside the filler aggregates (which is known as trapped rubber) also gives rise to the formation of bound rubber. As shown in Fig. 1 and in accord with the results of Mooney viscosity and minimum torque, the percentage of bound rubber in the compound containing silica is higher

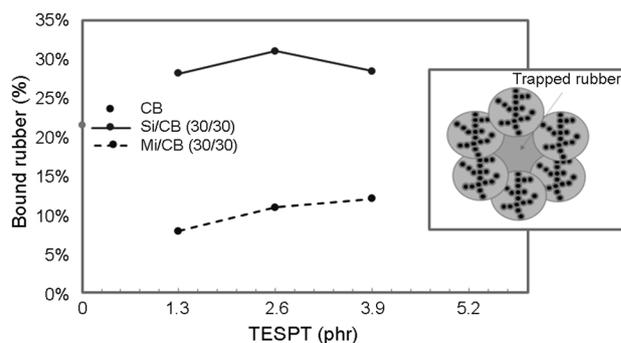


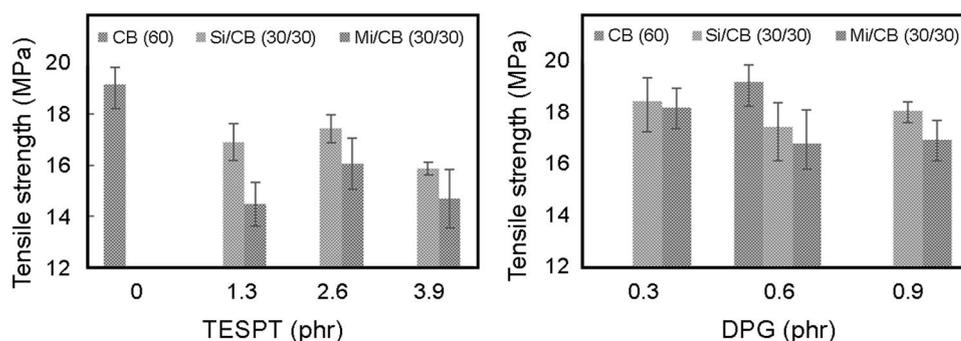
Fig. 1 Effect of TESPT on bound rubber percentage of silica- and mica-containing composites

than that in other samples. Filler–filler interaction, resulting from the higher amounts of hydroxyl groups existing on the silica surface, traps a larger amount of rubbers within the aggregates. It was expected earlier that mica with the higher aspect ratio may lead to an enhanced amount of shell rubber that could compete with the higher filler–filler interaction and trap the rubber obtained from the silica. It is realized that for such high filler rubber composite (60 phr filled rubber), it is the trapped rubber that has dominated the bound rubber over the shell rubber. With the increase of TESPT, the filler–polymer interaction is enhanced and the filler–filler interaction is reduced which leads to the observation of a peak for the moderate amounts of silane. For the mica system, it seems that the reduction of filler–filler interaction due to the addition of TESPT is rather minor and the continuous improvement of filler–polymer interaction is the possible cause of the monotonic improvement in the bound rubber. The enhanced degree of the polymer–filler interaction in silica by the addition of silane might be of physical hydrophobic–hydrophobic interaction, or, in a less probable state, of the chemical bonding type that may be formed between the filler and rubber during the high temperature mixing process.

Strength properties

The results of the TESPT as a chemical modifier and DPG as a physical modifier on the tensile strength of both silica- and mica-containing rubbers are investigated in Fig. 2. The tensile strength of the composites is dictated by the combinatory impacts of the composite stiffness (i.e., modulus) and the resistance-to-fracture (crack nucleation and growth). Fracture by itself is defined by the quality of filler dispersion and the viscoelastic energy dissipations. It is rather accepted that the composites with higher bound rubber commonly have higher values of both the stiffness and the energy dissipation. There is no doubt, as bound rubber results imply, both the modulus and the viscoelastic dissipation would be

Fig. 2 Effect of TESPT and DPG on tensile strength of the composites



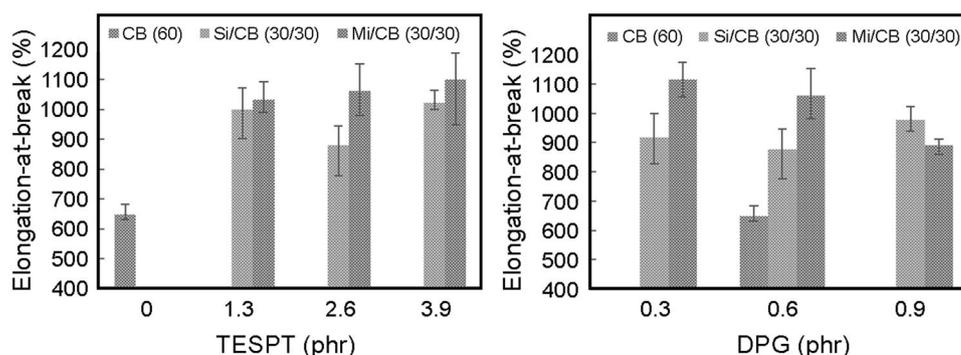
the highest among all silica-containing composites. It is then the good quality of filler dispersion that has led to the highest values of tensile strength for CB composite, even though the bound rubber of this composite has produced a moderate value. The mica-containing rubber has the lowest tensile strength, due to the lowest bound rubber content and the improper filler dispersion which is expected from its inorganic nature. Again there is a clear manifestation of the fact that the role of filler–filler interaction in bound rubber formation (stiffness and dissipation) cannot be simply surpassed by the higher aspect ratio of the filler.

By improving the filler–polymer interaction using silane TESPT or DPG, two different trends can be found depending on the type of surface modifier. In TESPT-containing composite, the trend is similar to the bound rubber described earlier, except for the mica that lost its dispersion at higher TESPT loading. Such a large amount of TESPT provides numerous covalent bonding at the interface that would drop the dissipation and thus the fracture resistance. The interesting result can be seen when the DPG has been used as a physical modifier instead of TESPT. Here, the mica can compete in tensile strength with silica, particularly at lower DPG values where filler–filler interaction in mica can still contribute to the bound rubber and stiffness. For DPG systems, the loss in filler–filler interaction of silica is more significant than the gain of filler–polymer interaction. Therefore, although the filler–filler interaction of silica is reduced by the surface treatment, the covalent bonding formed at the

interface by the use of TESPT improves the stress transferring mechanism and maintains both the stiffness and strength at an acceptable level. As long as the TESPT is replaced by the DPG, there would be a possibility to find similar strength and stiffness properties for both silica and mica systems.

The elongation-at-break has some indications of the fracture resistance of the materials and thus it can be related to the filler dispersion, the agglomeration of the filler particles, and the filler–rubber interactions. Muniandy et al. [29] associated the reduction of elongation-at-break with the agglomeration and reduction of the filler–rubber interactions, while Ismail et al. [30] reported that the reduction of elongation-at-break is due to the improvement of the filler dispersion and the adhesion of filler–matrix interface. As observed in Fig. 3, with increasing TESPT, elongation-at-break increased for the mica-based compound, while with increasing DPG, elongation-at-break decreased. In the silica-based compound, elongation-at-break was obtained in the lowest value when TESPT and DPG were used according to suggested Guy formula. Due to the low modulus of mica and its lower amount of bound rubber, the resulting composite has the least modulus and the highest extensibility and elongation-at-break. By emphasizing that the low modulus and the high extensibility are of the fundamental requirements of any practical rubber article, the mica seems to be a promising candidate for reinforcement of rubbers. The competition between mica and silica is very close with regard to the elongation-at-break and there are particular cases with

Fig. 3 Effect of TESPT and DPG on elongation-at-break of the composites



similar behavior for both the systems with TESPT and DPG modifiers.

The M300/M100 values as a reinforcement index are plotted in Fig. 4. As observed, the reinforcement index is improved when TESPT is increased especially for mica-containing rubbers. These results are consistent with bound rubber results. Also, the enhancement of the reinforcement index with TESPT adding was reported by Sengloyluan [28]. On the other hand, the reinforcement index of mica-filled samples increased by DPG adding. It might be due to this fact that DPG promotes the silanization reaction.

The tear strength which manifests the resistance to cut growth is again defined by the energy dissipation and the filler dispersion as tensile strength (Fig. 5). In contrast, however, the stochastic nature of crack nucleation is avoided here and only resistance to growth is measured. In DPG-treated systems, the existence of a crossing point in the behavior of the mica and silica with regard to the tear strength can again be found. For TESPT systems, very close values can be observed, especially at extreme levels of the silane used.

SEM results

To find out whether or not the speculations regarding the filler dispersion in the previous section are valid, SEM images of the compounds were taken at two magnifications as shown in Fig. 6 (a, c, e: $\times 1000$; b, d, f: $\times 10,000$). The TESPT and DPG are constant in SEM images of compounds containing silica or mica (2.6 phr TESPT and 0.6 phr DPG). The carbon black-containing rubber reveals the excellent state of the filler distribution and dispersion. The grooved

lines at the fracture surface of the control sample proved that considerable levels of stress are needed to break this sample. For this reason, the control sample which only contains carbon black has exhibited the highest tensile strength. The silica system has also shown a more uniform fracture surface than mica. Also, grooved lines with less intensity are observed in some areas of the fracture surface of the compound containing silica. However, at the fracture surface of the compound containing silica, spherical microporous and agglomerations are observed, which suggests that in spite of using the TESPT coupling agent, defect-containing filler networks were formed. In the case of mica, the filler–filler interaction is lower than silica but due to their layered structure, the uniform dispersion of the filler is more challenging.

DMTA and prediction of tire tread performance

To predict the performance of a tire tread, $\tan\delta$ (or loss factor) measurements of the tread compound at 10 Hz frequency as a measure of the ice grip about -10°C , wet grip about 0°C , dry grip about 25°C , rolling resistance about 60°C and heat build-up about 100°C , are common [31–33].

The loss factor which is a ratio of the loss modulus or viscous modulus to storage modulus or elastic modulus is related to the molecular movement. Therefore, $\tan\delta$ value may disclose the interface interaction between the rubber and the filler. The loss modulus can be due to the friction of the filler–filler interfaces, where the particles hold each other in the form of weak aggregations; or the friction of the filler–polymer interface, where there is no adhesion in the interface [34]. In other words, decreasing the height of the

Fig. 4 Effect of TESPT and DPG on reinforcement index (M300/M100)

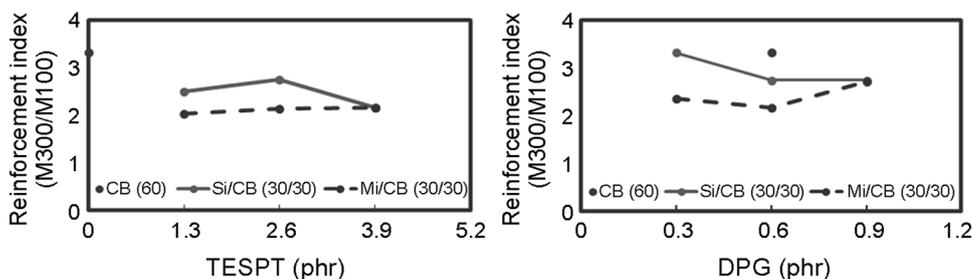
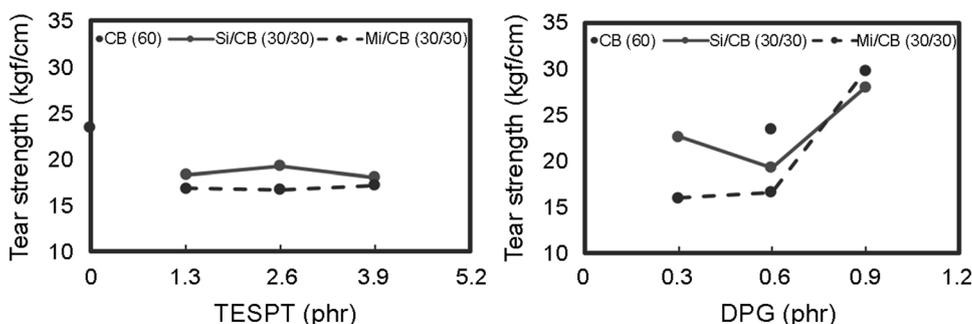


Fig. 5 Effect of TESPT and DPG on tear strength of the composites



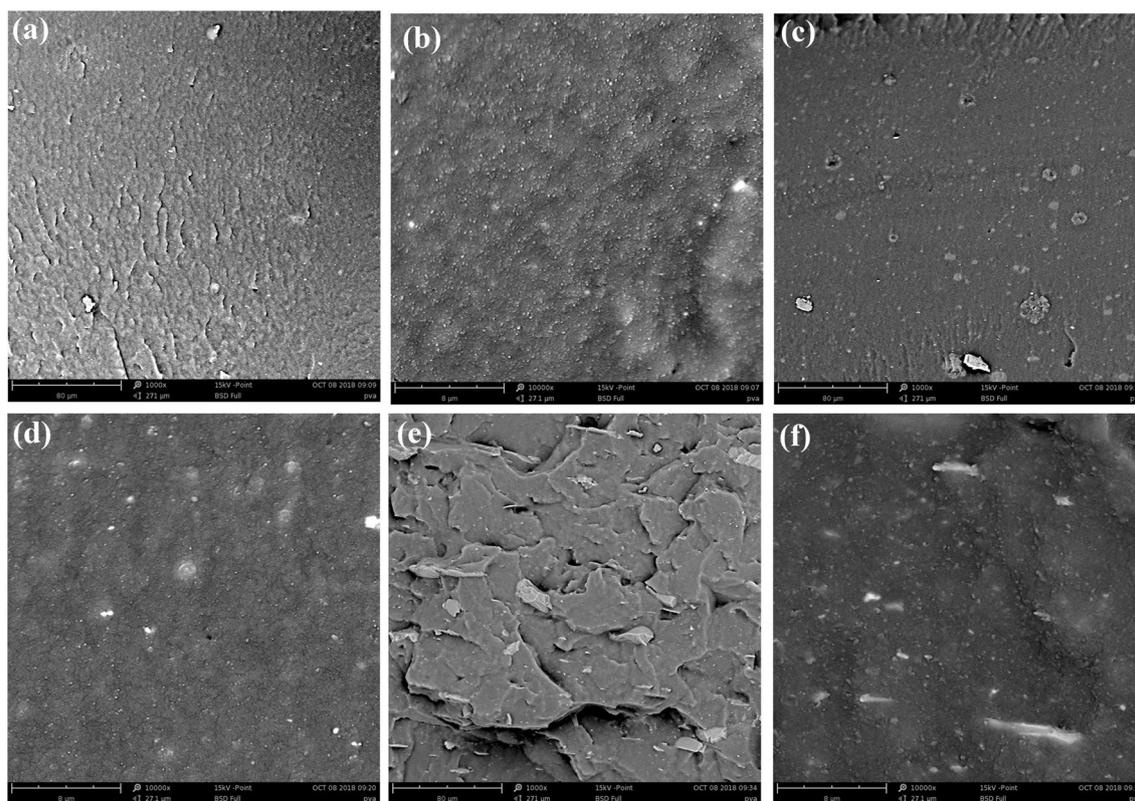


Fig. 6 SEM images of compounds containing various fillers (all samples containing 2.6 phr TESPT and 0.6 phr DPG): C (a, b) B (60 phr), (c, d) Si/CB (30/30), (e, f) Mi/CB (30/30) (up: $\times 1000$, down: $\times 10,000$)

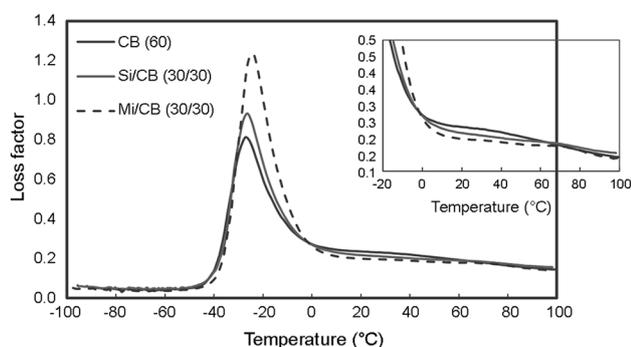


Fig. 7 Temperature-dependent functions of loss factor for compounds containing various fillers (all samples containing 2.6 phr TESPT and 0.6 phr DPG)

$\tan\delta$ peak is due to the restriction of polymer chain movement as a result of the physical and chemical absorption of the rubber molecules on the filler surface [30, 35]. Therefore, the control sample and the sample containing silica with a minimum $\tan\delta$ at T_g temperature exhibited greater reinforcement effect (Fig. 7).

For temperatures above -10°C , the $\tan\delta$ values of the composites are very close to each other as only 30 phr of

carbon black has been replaced with silica or mica. Nevertheless, it is perceived that the direction of ice grip improvement (the $\tan\delta$ value at -10°C) is in the order: mica > silica > carbon black compound. Also, the $\tan\delta$ value at 0°C for compounds containing different fillers are approximately the same, while at 25°C is the greatest for the control sample and the lowest for the mica-based compound. In the case of rolling resistance or $\tan\delta$ value at 60°C , the results are in the order: silica \approx carbon black > mica.

Conclusion

When the silica surface is treated by a bifunctional silane such as TESPT, the filler–filler interaction is reduced and part of the reinforcing ability that is rooted in filler–filler interaction has vanished. However, the formation of the covalent bonding at the interface imparts a new possibility for stress transferring mechanism. The mica with its lower filler–filler interaction but a higher aspect ratio cannot simply compete with silica when such a stress transferring mechanism is operating. However, if the silica surface is treated by a physical modifier, new opportunities are developed for mica and the reinforcing potential of these

two fillers becomes comparable. Considering the extensibility and elongation-at-break, as two of the most important engineering properties of rubbers, mica composites perform even better than silica. The DMTA results, which reflect a measure of the performance properties of a tire, indicate that the replacement of 30 phr carbon black by silica or mica can show a similar wet grip and rolling resistance. Ice grip was predicted to be greater for mica-containing tire tread composite.

References

- Liu J, Wang S, Tang Z, Huang J, Guo B, Huang G (2016) Bioinspired engineering of two different types of sacrificial bonds into chemically cross-linked cis-1,4-polyisoprene toward a high-performance elastomer. *Macromolecules* 49:8593–8604
- Kalfus J, Jancar J (2008) Reinforcing mechanisms in amorphous polymer nano-composites. *Compos Sci Technol* 68:3444–3447
- Mittal V (2009) Optimization of polymer nanocomposite properties. Wiley, New York
- Kohls DJ, Beaucage G (2002) Rational design of reinforced rubber. *Curr Opin Solid State Mater Sci* 6:183–194
- Gheller J Jr, Ellwanger MV, Oliveira V (2016) Polymer–filler interactions in a tire compound reinforced with silica. *J Elastomers Plast* 48:217–226
- Ahmed NM, El-Sabbagh SH (2014) The influence of kaolin and calcined kaolin on SBR composite properties. *Polym Compos* 35:570–580
- Ahmadi SJ, G'Sell C, Huang Y, Ren N, Mohaddespour A, Hiver JM (2009) Mechanical properties of NBR/clay nanocomposites by using a novel testing system. *Compos Sci Technol* 69:2566–2572
- Lagazzo A, Lenzi S, Botter R, Cirillo P, Demicheli F, Beruto DT (2010) A rheological method for selecting nano-kaolin powder as filler in SBR rubber. *Particuology* 8:245–250
- Liu Q, Zhang Y, Xu H (2008) Properties of vulcanized rubber nanocomposites filled with nanokaolin and precipitated silica. *Appl Clay Sci* 42:232–237
- Guy L, Daudey S, Cochet P, Bomal Y (2009) New insights in the dynamic properties of precipitated silica filled rubber using a new high surface silica. *Kautsch Gummi Kunstst* 62:383–391
- Mouri H, Akutagawa K (1999) Improved tire wet traction through the use of mineral fillers. *Rubber Chem Technol* 72:960–968
- Mark J, Ngai K, Graessley W, Mandelkern L, Samulski E, Wignall G, Koenig J (2004) Physical properties of polymers. Cambridge University, Cambridge
- Kamal MM, Clarke J, Ahmad MA (2009) Comparison of properties of natural rubber compounds with various fillers. *J Rubber Res* 12:27–44
- Leblanc JL (2002) Rubber–filler interactions and rheological properties in filled compounds. *Prog Polym Sci* 27:627–687
- Wu W, Tian L (2013) Formulation and morphology of kaolin-filled rubber composites. *Appl Clay Sci* 80:93–97
- Zhang Q, Liu Q, Zhang Y, Cheng H, Lu Y (2012) Silane-grafted silica-covered kaolinite as filler of styrene butadiene rubber. *Appl Clay Sci* 65:134–138
- Kaewsakul W (2013) Silica-reinforced natural rubber for low rolling resistance, energy-saving tires: aspects of mixing, formulation and compatibilization. University of Twente, Enschede
- Sattayanurak S, Noordermeer JWM, Sahakaro K, Kaewsakul W, Dierkes WK, Blume A (2019) Silica-reinforced natural rubber: synergistic effects by addition of small amounts of secondary fillers to silica-reinforced natural rubber tire tread compounds. *Adv Mater Sci Eng*. <https://doi.org/10.1155/2019/5891051>
- Dierkes WK (2005) Economic mixing of silica-rubber compounds: interaction between the chemistry of the silica-silane reaction and the physics of mixing. University of Twente, Enschede
- Hewitt N, Ciullo P (2007) Compounding precipitated silica in elastomers: theory and practice. William Andrew, New Jersey
- Issel H, Steger L, Bischoff A (2005) Application of dithiophosphates in silica reinforced elastomer compounds. *Kautsch Gummi Kunstst* 58:529
- Vilmin F, Bottero I, Travert A, Malicki N, Gaboriaud F, Trivella A, Thibault-Starzyk F (2014) Reactivity of bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT) silane coupling agent over hydrated silica: operando IR spectroscopy and chemometrics study. *J Phys Chem C* 118:4056–4071
- Mihara S (2009) Reactive processing of silica-reinforced tire rubber: new insight into the time- and temperature-dependence of silica rubber interaction. University of Twente, Enschede
- Ash M (2007) Handbook of fillers, extenders, and diluents, 2nd edn. Synapse Information Resources Inc.
- Choi SS, Im SH, Nah C (2012) Influence of solvent swell and bound rubber on wax solubility of carbon black-reinforced NR composite. *J Appl Polym Sci* 125(S1):E342–E347
- Choi SS, Ko E (2014) Novel test method to estimate bound rubber formation of silica-filled solution styrene-butadiene rubber compounds. *Polym Test* 40:170–177
- Berspacher M, Nikiel L, Yang HH, O Farrel PO, Schwartz GA (2002) Flocculation in carbon black filled rubber compounds. *Kautsch Gummi Kunstst* 55:596–604
- Sengloyluan K (2015) Silica-reinforced natural rubber: use of natural rubber grafted with chemical functionalities as compatibilizer. University of Twente, Enschede
- Muniandy K, Ismail H, Othman N (2012) Effects of partial replacement of rattan powder by commercial fillers on the properties of natural rubber composites. *BioResources* 7:4640–4657
- Ismail H, Ishak S, Hamid ZAA (2014) Effect of silane coupling agent on the curing, tensile, thermal, and swelling properties of ethylene-propylene-diene monomer rubber (EPDM)/mica composites. *J Vinyl Addit Technol* 20:116–121
- Ezzoddin S, Abbasian A, Aman-Alikhani M, Ganjali ST (2013) The influence of non-carcinogenic petroleum-based process oils on tire compounds' performance. *Iran Polym J* 22:697–707
- Maghami S (2016) Silica-filled tire tread compounds: an investigation into the viscoelastic properties of the rubber compounds and their relation to tire performance. University of Twente, Enschede
- Kashani MR (2009) Aramid-short-fiber reinforced rubber as a tire tread composite. *J Appl Polym Sci* 113:1355–1363
- Hamdan S, Hasihim DMA, Yusop M (2004) Dynamic mechanical thermal analysis (DMTA) of thermoplastic natural rubber (TPNR) barium ferrite (BaFe₁₂O₁₉) composites. *ASEAN J Sci Technol Dev* 21:69–79
- Malas A, Das CK (2012) Carbon black–clay hybrid nanocomposites based upon EPDM elastomer. *J Mater Sci* 47:2016–2024