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Colloquium

SILICA REINFORCED NATURAL RUBBER: SYNERGISTIC EFFECTS BY ADDITION OF SMALL AMOUNTS OF SECONDARY FILLERS TO SILICA- REINFORCED NATURAL RUBBER TIRE TREAD COMPOUNDS

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Abstract

Modern fuel-saving tire treads are commonly reinforced by silica due to the fact that this leads to lower rolling resistance and higher wet grip compared to carbon black-filled alternatives. The introduction of secondary fillers into the silica-reinforced tread compounds, often named hybrid fillers, may have the potential to improve tire performance further. In the present work, two secondary fillers: organoclay nanofiller and N134 carbon black were added to silica-based natural rubber compounds at a proportion of silica/secondary filler of 45/10 phr. The compounds were prepared with variable mixing temperatures based on the mixing procedure commonly in use for silica-filled NR systems. The results of Mooney viscosity, Payne effect, cure behavior and mechanical properties imply that the silica hydrophobation and coupling reaction of the silane coupling agent with silica and elastomer are significantly influenced by organoclay due to an effect of its modifier: an organic ammonium derivative. This has an effect on scorch safety and cure rate. The compounds where carbon black was added as a secondary filler do not show this behavior. They give inferior filler dispersion compared to the pure silica-filled compound, attributed to an inappropriate high mixing temperature and the high specific surface area of the carbon black used. The dynamic properties indicate that there is a potential to improve wet traction and rolling resistance of a tire tread when using organoclay as secondary filler, while the combination of carbon black in silica-filled NR does not change these properties.

Introduction

Tire compounds generally contain about 30% by weight of active fillers like carbon black and silica [1]. Carbon black is conventionally used as reinforcing filler for tire tread compounds because it can effectively improve mechanical properties such as tensile strength, modulus, tear strength, flex fatigue and abrasion resistance as well as providing good skid resistance. The reinforcing effect of carbon black is normally controlled by particle size, structure, specific surface area and surface chemistry [2]. Replacement of carbon black with silica in tire tread compounds, after the patent of Michelin [3], offers tires with lower rolling resistance and higher wet grip [4], so less fuel consumption and better safety. The other compound properties also can improve by using silica such as tensile strength, tear strength, heat build-up, cut-, chip-, and chunking-resistance [5]. However, the use of silica in rubber compounds has some shortcomings such as incompatibility with non-polar tire rubbers, poor dispersion and distribution in the rubber matrix, and poor filler-rubber interaction [6]. In order to overcome those limitations, sulfur containing silane coupling agents such as bis-(3-TriEthoxySilylPropyl) Tetrasulfide (TESPT) are commonly applied in such compounds. The mixing of silica with silane in rubber involves a chemical reaction, so called silanization, and the extent of this reaction has a dramatic effect on the resulting compound properties [7-8]. Due to the nature of

TESPT as sulfur donor, to ensure scorch safety during processing, bis-(3-TriEthoxySilylPropyl) Disulfide (TESPD) may be used [9].

A recent study on silica-reinforced natural rubber (NR) tire tread compounds has shown that, under optimal conditions and formulation, silica can effectively reinforce NR as shown by mechanical and dynamic properties [8]. However, there remains a question regarding the performance of such tire treads in terms of abrasion or wear resistance. The abrasion mechanism of rubber vulcanizates is very complex involving multiple factors, and fillers have a major influence on this property [10]. The filler particle size, structure, surface activity and filler-rubber interaction all have an impact on the abrasion performance. Nowadays, in addition to carbon black and silica, there is a new generation of reinforcing fillers available, especially nano-fillers that can be also applied for tire compounds. One of the most widely studied nanofillers is organo-modified clay or shortly organoclay (OC) which has been modified by cation exchange with ammonium salts or phosphonium salts in order to obtain the hydrophobic structure that is compatible with non-polar rubbers [11,12]. OC-elastomer composites with low nanofiller contents (usually 10 phr or less) show improved mechanical properties, thermal stability, gas permeability and wear resistance [13].

To reinforce the rubber, either a single or dual filler system is utilized. A combination of silica and carbon black attracts interests as to combine the advantages of each filler in the rubber compounds. Investigations on silica and carbon black reinforced NR-based truck tread compounds demonstrated that, when N220 Carbon Black (N220 CB) was progressively replaced by TESPT-modified silica, the complete replacement of carbon black by the TESPT-silica resulted in 30% improvement in the rolling resistance with little change in the treadwear index (abrasion resistance) and wet traction [14]. The retraction behavior of NR vulcanizates as influenced by silica-N220 CB mixed fillers in the presence and absence of a silane coupling agent was studied [15], in which the vulcanizates containing the silane coupling agent showed faster recovery rates compared to those without due to the polymer-filler interactions, crosslinks between the rubber and silica, and increased crosslink densities. With increasing the silica proportion, the vulcanizates with and without the silane showed a decrease in hardness and modulus. Based on the mechanical properties of NR reinforced with various ratios of N330 CB/silica hybrid fillers, it was reported that vulcanizates containing 20 and 30 phr of silica with a total mixed filler content of 50 phr exhibited the best overall mechanical properties [16]. The partial substitution of CB with silica/silane improved tear strength and crack growth but had a negative effect on abrasion resistance [17]. Composites of Solution-SBR rubber/Silica/CB showed better filler dispersion, lower Payne effect and a synergistic effect in mechanical properties compared to the compound with single filler. In this case, the SiO₂/CB ratio of 20/50 showed the best overall properties in which a good balance of rolling resistance, wet skid resistance and wear resistance was obtained. With increasing silica content, the optimum cure time was prolonged and the surface and volume resistivity was increased [18]. The addition of small amounts of silica into SBR/N330 CB compounds, such as by the use of a CB/silica ratio of 45/5 phr, decreased the filler cluster branching and increased the reinforcement efficiency. The depressed filler networking and more homogeneous filler dispersion resulted in better abrasion resistance, lower rolling resistance and better wet skid resistance. However, when the silica proportion was high, filler cluster branching increased quickly and deteriorated the properties [19]. The use of Semi-Reinforcing Furnace (SRF) CB/silica hybrid filler in Nitrile Rubber compounds showed that the replacement of carbon black with silica decreased the material's stiffness, tensile strength, compressive strength, tear strength and modulus, but increased elongation at break and rebound resilience [20].

A combination of silica and clay has also been studied. The physico-mechanical properties of silica/China clay-filled NR for a heavy-duty truck tire tread formulation [21] showed the best balance of properties in heat build-up and abrasion resistance at a silica/clay ratio of 60/20. The use of Precipitated Silica (PS)/Montmorillonite (MMT) in peroxide cured Silicone Rubber (SR) nanocomposites resulted in the improved maximum stress compared to unreinforced Silicone Rubber [22]. The use of MMT (Cloisite 20A) and silica with Si69 (=TESPT) as silane coupling agent in SBR/BR tread compounds improved tensile strength, elongation and traction properties at low Si69 content while enhancing modulus, hardness, wear resistance, dry handling and rolling resistance at high Si69 content [23]. Hybrid filler systems consisting of precipitated silica and kaolin

modified with a Sodium salt of Rubber Seed Oil (SRSO) in NR/BR blends demonstrated that a substitution of 5-10 phr of silica with SRSO modified kaolin resulted in lower Mooney viscosity, higher cure rate, increased chemical crosslink density index and bound rubber content [24], indicating a higher extent of rubber-rubber and rubber-filler interactions. This resulted in enhanced mechanical properties such as abrasion resistance, compression set, tensile- and tear strength and elongation at break of the blend vulcanizates. The vulcanizate containing silica/SRSO hybrid filler also showed enhancement of dynamic properties, beneficial for tire tread applications. The reduction of filler networking in silica based elastomeric nanocomposites with exfoliated organo-montmorillonite resulted in improved mechanical reinforcement and reduced energy dissipation and thus fuel consumption and carbon footprint [25].

The present work aims at a synergistic effect of silica with different additional fillers in order to shift tire performance with respect to wet grip and rolling resistance for fuel savings, respectively towards a better abrasion resistance, all characterized by the dynamic mechanical properties of the vulcanized compounds. The use of a secondary filler that has different filler characteristics in combination with silica, a so-called hybrid filler system, may lead to better filler dispersion, filler-rubber interaction and consequently a better balance of performance characteristics.

As to silica-reinforced NR compounds, the dump/discharge temperature after mixing is a crucial parameter that needs to be controlled as it has a strong influence on both processing and vulcanizate properties [8]. Therefore, the influence of initial mixer temperature setting was investigated in this work in order to determine an optimal condition for the best possible properties of the compounds.

Experimental

Compound preparation

The rubber formulations used in this study are shown in Table 1. The compounds were prepared using a two-step mixing procedure: the first was to prepare a masterbatch of rubber and fillers, and the second to prepare the final compounds including the curatives. For the first step, an internal mixer Brabender Plasticoder 350 ml was used, operated at a rotor speed of 60 rpm, fill factor of 70%, and varied initial temperature settings of 60, 80, 100 and 120°C. The

Table 1. Compound formulations used for this study.

Ingredients	Dosage (phr)	
	Silica reference	Silica/secondary filler
Natural rubber (RSS)	100.0	100.0
Silica (Ultrasil 7005)	55.0	45.0
Secondary filler *)	-	10.0
TESPD	5.0	4.1
TDAE oil	8.0	8.0
ZnO	3.0	3.0
Stearic acid	1.0	1.0
TMQ, stabilizer	1.0	1.0
DPG	1.1	0.9
CBS	1.5	1.5
Sulfur	1.5	1.5

*) Carbon black N134 (CB) or organoclay Dellite 67G (OC).

secondary fillers carbon black or organoclay, were added together with the first half of silica, the first half of bis(Tri-EthoxySilyl-Propyl)-Disulfide (TESPD) and DiPhenyl-Guanidine (DPG) secondary accelerator in order to obtain good dispersion. The other halves of silica and TESPD were added later on in the first mixing step, together with Treated Distillate Aromatic Extract (TDAE) extender oil. The second step was for the addition and mixing of the other half of DPG, N-Cyclohexyl Benzothiazyl Sulfenamide (CBS) primary accelerator, and sulfur at a rotor speed of 30 rpm, fill factor of 70%, and an initial temperature setting of the internal mixer of 70°C. The two-step mixing procedure is summarized in Figure 1.

Sample characterizations

Mixing data were derived from the real-time monitoring program coupled with the internal mixer.

Mooney viscosity, ML(1+4)100°C.- was tested using a Mooney viscometer (MV200VS, Alpha Technologies) according to ASTM D1646.

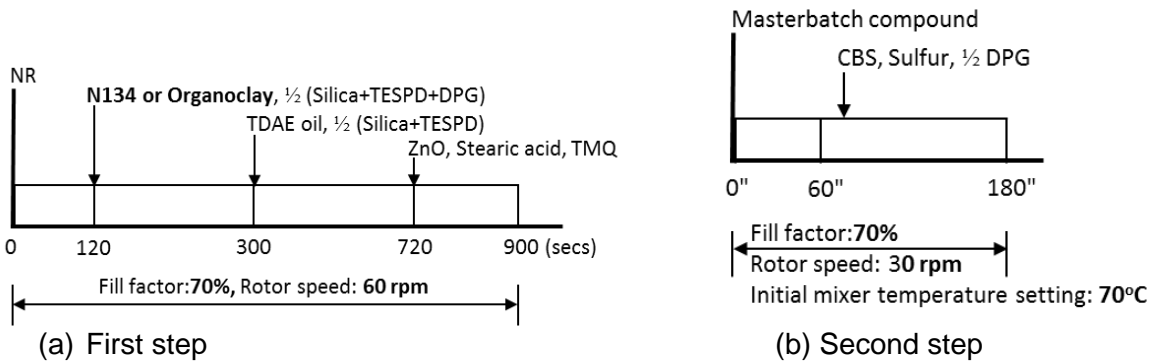


Figure 1. Two-step mixing procedure for preparing the compounds in this study.

Payne effects.– the Payne effects or filler-filler interactions of still uncured silica-filled NR compounds with curatives were studied using a Rubber Process Analyzer (RPA2000, Alpha Technologies) at 100°C, frequency 0.5 Hz and varying strains in the range of 0.56 to 100%.

Cure characteristics.– the cure properties of the compounds were studied using the RPA at 150°C, frequency 0.83 Hz and 2.79% strain for 30 mins.

Tensile properties.– the compounds were vulcanized to their optimum cure times ($t_{c,90}$) using a Wickert WLP 1600 laboratory compression press at 150°C and 100 bars into 2 mm thick sheets. Type 2 dumbbell test specimens were die-cut from the press-cured sheets and tensile tests carried out with a Zwick tensile tester (model Z1.0/TH1S) at a crosshead speed of 500 mm/min according to ASTM D412.

Dynamic properties.– the tan delta at -20 °C and 0°C of the vulcanizates were determined using a Dynamic Mechanical Analyzer (Metravib DMA) with temperature dependence analysis in tension mode at a strain of 0.1% and frequency 10 Hz. For the mechanical loss angle tan delta at 60°C, the RPA was employed with conditions set at: temperature at 60°C, strain 3.49%, and varying frequency sweeps in the range of 0.05-33.00 Hz. Prior to these measurements the samples were cured in the same RPA chamber at 150°C to their optimum cure times before being cooled down to 60°C and tested.

Results and discussion

Figure 2(a) shows that the dump/discharge temperature increases with raising the initial mixer temperature setting for both secondary fillers. The final torque of silica/CB compounds mixed at various temperatures significantly increases and then levels off at 80°C temperature setting, which is attributed to a higher degree of silanization that results in a better filler-rubber interaction. On the other side, silica/OC compounds show a slight decrease in final mixing torque with increasing dump or discharge temperature. This must be due to the effect of the modifying agent, an organic ammonium derivative [3], within the organoclay which remarkably reduces the mutual filler-filler interaction of silica, as is also confirmed by the Mooney viscosities and Payne effect results depicted in Figure 2(b).

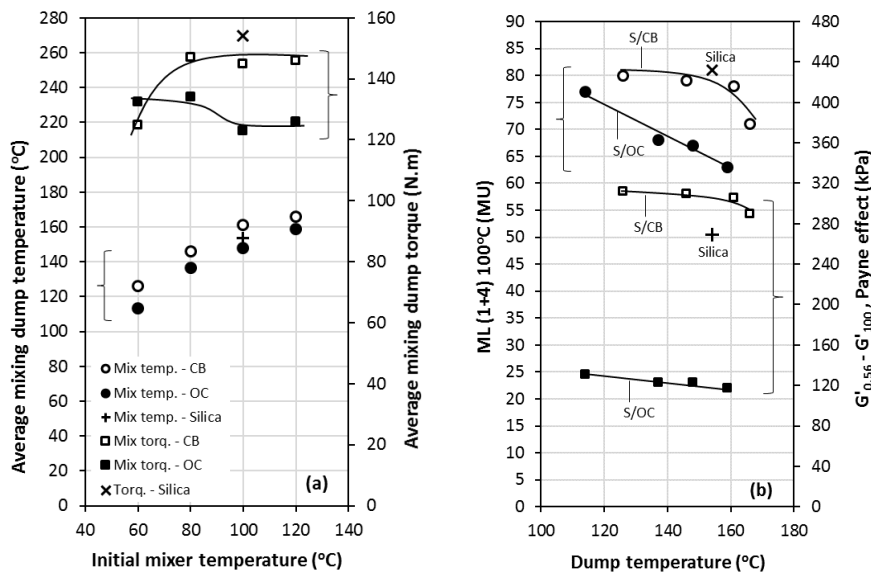


Figure 2. Average mixer dump/discharge temperature and torque at the final stage of mixing in the internal mixer as a function of initial mixer temperature setting. Influence of dump temperature on viscosity and Payne effect of silica-filled NR compounds with different secondary fillers: (a) carbon black and (b) organoclay.

A higher mixer temperature setting and consequent dump temperature results in a lower Mooney viscosity (at 100°C) of the compounds due to increased silanization and consequent decreased filler-filler interactions. However, the higher temperature causes also breakdown of NR molecules by oxidative reactions under shear forces [26], a factor not to be overlooked for NR. Organoclay shows a more substantial drop in Mooney viscosity than carbon black, which must be attributed to influence of the modifier of the clay, as stated before.

The Payne effects of the silica/CB-filled and silica/OC-filled NR compounds decrease with increasing dump temperature due to better silanization at higher mixing temperatures. This clearly confirms the explanation for the mixing data and corresponding compound Mooney viscosities. The Payne effects of the silica/CB-filled NR is higher than for the silica-filled NR reference compound. This is due to the smaller inter-aggregate distance of the strongly reinforcing carbon black that gives a higher possibility for the formation of a strong filler-filler network. On the other side, the Payne effects of the silica/OC-filled NR are much lower than for the silica-filled NR reference compound, due to lower filler-filler interactions as well as the lower Mooney viscosities, which may be ascribed again to the clay-modifier.

Based on cure curves in Figure 3, the scorch times of silica-filled NR compounds with carbon black and organoclay as secondary fillers decrease, when compared with the reference compound with silica alone. It is well known that free silanol groups on the silica surface interfere with vulcanization due to their acidic nature and their tendency to adsorb vulcanization accelerators, and so retard the vulcanization [16]. Only about 30% of the silanol groups on silica are reacting with the coupling agent, so 70% remains unreacted. The role of the secondary accelerator, in particular the alkaline DPG, is to shield these remaining silanol groups. In the present case, the organoclay-containing compounds show by far the largest decrease in scorch time, again the result of the alkaline modifying agent of the organoclay, an organic ammonium derivative [27]. Interestingly, the organoclay containing compounds also show a considerable decrease in torque increment: Fig. 3(b). The main reason must again be the effect of the modifying agent of the organoclay that might play an extra role in further modification of the silica surface over DPG, leading to a lowered extent of hydrogen bonding between the silica particles and so a reduced Payne effect or filler-filler interactions as seen in Fig. 2(b). These results mutually confirm each other.

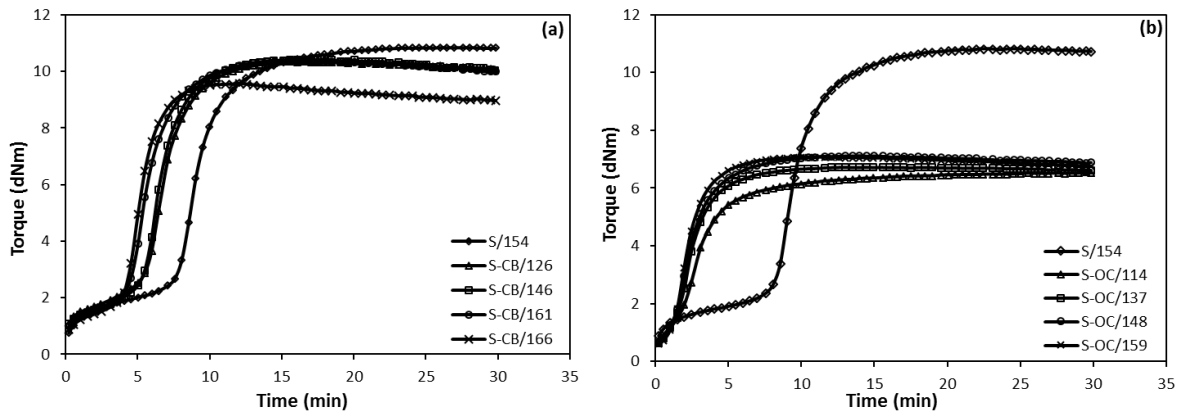


Figure 3. Effect of secondary fillers on cure characteristics of silica-filled NR compounds: (a) carbon black, and (b) organoclay. Dump temperatures indicated in curve designations.

Figure 4 shows the mechanical properties of the corresponding vulcanizates. At various dump temperatures, the tensile strength, elongation at break, 100% and 300% moduli of NR filled with silica/CB (Fig. 4a) slightly increase until 160°C and then decrease when the dump temperature surpasses 166°C. Natural rubber degradation at higher temperatures can be the primary reason that causes that drop in tensile strength. On the other hand, the tensile strength and elongation at break of NR filled with silica/OC remain almost on the same levels. The moduli at 100% and 300% strain of NR filled with silica/OC (Fig. 4b) increase with raising dump temperature until 151°C and then slightly decrease. This is again due to degradation of NR at higher temperatures. The moduli are significantly lower than for the reference silica and silica/CB compounds, which corresponds with the much lower torque differences seen in the cure curves (Fig. 3) for these compounds. However, interestingly the tensile strengths and elongations at break do not differ much from those for the reference silica and silica/OC compounds.

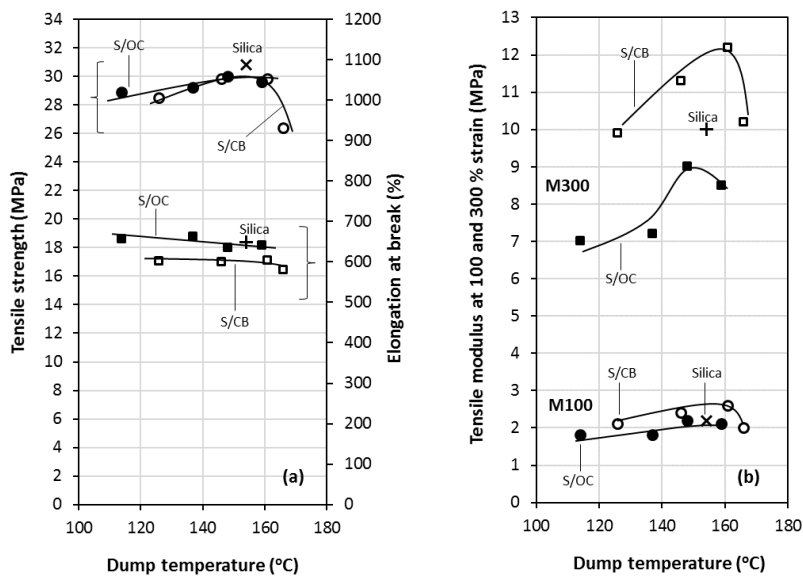


Figure 4. Influence of dump temperature on: (a): tensile strength and elongation at break; and (b): tensile moduli of the silica-filled NR compounds containing different secondary fillers: carbon black or organoclay.

Figure 5 shows the DMA results of tan delta at -20°C and 0°C for silica-filled NR with the hybrid fillers. The tan delta at -20°C to +20°C measured on laboratory scale is often considered to predict the wet traction of a tire equipped with a tread based on the same compound [6], respectively the value at -20°C as a first indication of wear resistance. The tan delta at -20°C of the silica/CB-filled NR as well as the silica/OC-filled NR rises with increasing dump temperature. This is again due to the better silanization at higher dump temperatures as also demonstrated in the lower Payne effects

in Figure 2b. The tan delta at -20 and 0°C of the silica/OC-filled with NR is substantially higher than for the silica/CB as well as for the pure silica compounds. This indicates that there is a potential to improve wet traction and wear performance of a tire tread by using a small amount of organoclay in combination with silica.

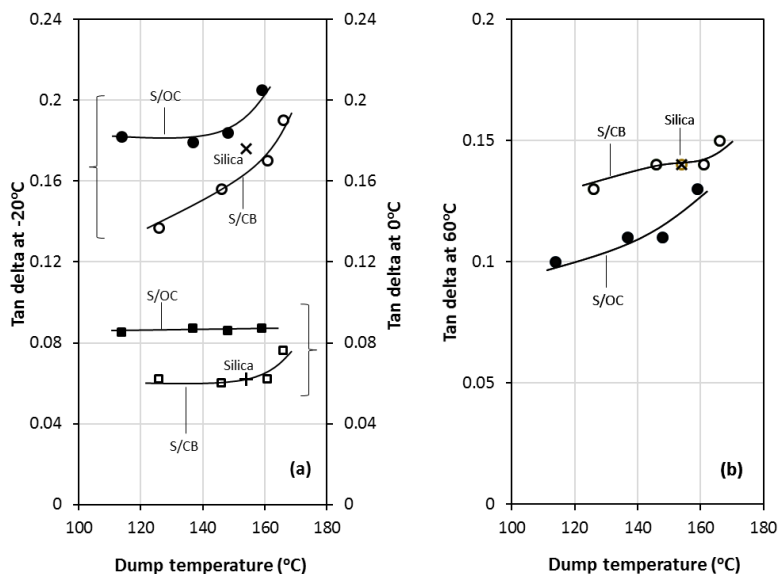


Figure 5. Influence of dump temperature on: (a): tan delta at -20 and 0°C from DMA; and (b) tan delta at 60°C from RPA of silica-filled NR compounds containing different secondary fillers: carbon black or organoclay.

The tan delta at 60°C of the vulcanizates indicates the energy loss by hysteresis under dynamic deformation, related to tire rolling resistance, commonly used to indicate rolling resistance on laboratory scale [28]. When comparing the results of tan delta at 60°C of the reference silica-filled NR, silica/CB-filled NR and silica/OC-filled NR at the given mixer dump temperatures, the results for the silica/CB compounds are comparable with the reference silica-filled NR. So, the replacement of a little silica by carbon black would not change the level of rolling resistance of a tire. On the other hand, the organoclay gives a significantly lower tan delta at 60°C compared to the reference silica-compound, pointing at a large decrease/improvement of the rolling resistance for tires with some organoclay applied next to silica.

Conclusions

- An increased dump temperature for silica-filled NR compounds with the secondary fillers leads to a better silanization reaction between the silica and the coupling agent TESPD, but NR degradation can occur at too high mixing temperatures.
- The silica/CB-filled NR shows a higher cure rate and tensile moduli, while maintaining similar ultimate tensile properties and tan delta at 60°C compared to a pure silica-filled system.
- The silica/OC-filled NR shows a lower Payne effect, higher cure rate, lower moduli combined with similar ultimate tensile properties to silica or silica/CB, higher tan delta at -20°C and 0°C, indication better wear and wet grip performance, respectively a lower tan delta at 60°C compared to the silica-filled system, indicative for reduced rolling resistance.
- The use of hybrid fillers, small amounts of secondary fillers as carbon black and in particular organoclay next to silica in NR, therefore offers the potential of further improvement in wear resistance, wet traction and rolling resistance of tire treads.

Acknowledgments

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