

Hybrid filler benefits

Improving silica-reinforced natural rubber based tire treads with hybrid fillers

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Replacement of carbon black with silica in tire tread compounds gives modern tires lower rolling resistance and higher wet grip, and therefore lower fuel consumption and better safety for vehicles. Michelin was a pioneer of this technology with the launch of its Energy Saver tire in 1992.¹ Other compound properties can also be improved by using silica, such as tensile strength, tear strength, heat build-up and cut-, chip- and chunking resistance. A recent study on silica-reinforced natural rubber (NR) tire tread compounds has shown that, under optimal conditions and with a proper formulation, silica can effectively reinforce NR as shown by mechanical and dynamic properties.² 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.

Nowadays a new generation of reinforcing fillers is available, notably nanofillers, which can also be applied in tire compounds. Combining silica and nanofillers to gain the advantages of both fillers in rubber compounds has attracted interest. The use of a secondary filler with different filler characteristics in combination with silica – a so-called hybrid filler – may lead to better filler dispersion, filler-rubber interaction, and consequently a better balance of performance characteristics.

The present work aims to achieve a synergistic effect of silica with different fillers to alter tire performance with respect to wet grip and rolling resistance, aiming at better abrasion resistance, all characterized by the dynamic mechanical properties of the vulcanized compounds. The dump/discharge temperature after mixing turns out to be a crucial parameter

Figure 1: Magic triangle of tire performance with a further attempt to improve abrasion resistance of a tire based on silica-filled NR tread compounds

Figure 2: Payne effects and Mooney viscosities as a function of dump temperatures of silica-filled NR compounds with different secondary fillers: CB and OC

since it has a strong influence on both processing and vulcanizate properties. This was therefore investigated to determine optimal conditions 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 step was to prepare a masterbatch of rubber and fillers, and the second was to prepare the final compounds including curatives. A Brabender Plasticorder 350ml internal mixer

was used, operated at a rotor speed of 60rpm, fill factor of 70%, and initial temperature settings of 60°C, 80°C, 100°C and 120°C.

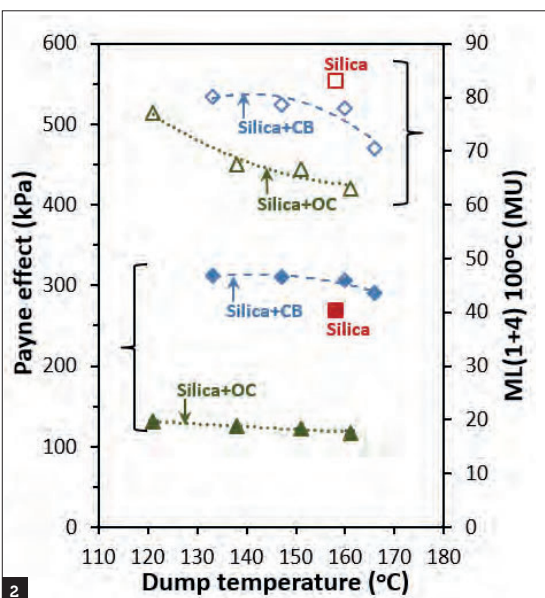
NR was first mixed for two minutes. The secondary fillers – carbon black N134 or organoclay Dellite 67G – were added together with the first half of silica, the first half of bis(3-triethoxysilylpropyl) disulfide (TESPD) and diphenylguanidine (DPG) secondary accelerator, and mixed for five minutes to obtain good dispersion. The other halves of silica and TESP were added later in the first mixing step, together with treated distillate aromatic extract (TDAE) oil and mixed for five minutes. Zinc oxide (ZnO), stearic acid and antioxidant were finally added and mixed for three minutes. The second step was the addition and mixing of the other half of the DPG, N-cyclohexyl-2-benzothiazole sulfenamide (CBS) primary accelerator, and sulfur at a rotor speed of 30rpm, fill factor of 70%, and an initial temperature setting of the internal mixer of 70°C. The mixing time was three minutes in total for this step.

Measurements of Mooney viscosity, cure characteristics and Payne effect

ML(1+4) 100°C was tested using a Mooney viscometer (MV200VS, Alpha Technologies) according to ASTM D1646. The cure properties of the compounds were studied using a rubber process analyzer (RPA2000, Alpha Technologies) at 150°C, a frequency of 0.83Hz, and 2.79% strain for 30 minutes. The Payne effect, or filler-filler interactions, of still uncured silica-filled NR compounds with curatives were studied using the RPA at 100°C, a frequency of 0.5Hz and varying strains in the range 0.56% to 100%.

Determination of mechanical properties

The compounds were vulcanized for their optimum cure times (t_{c90})



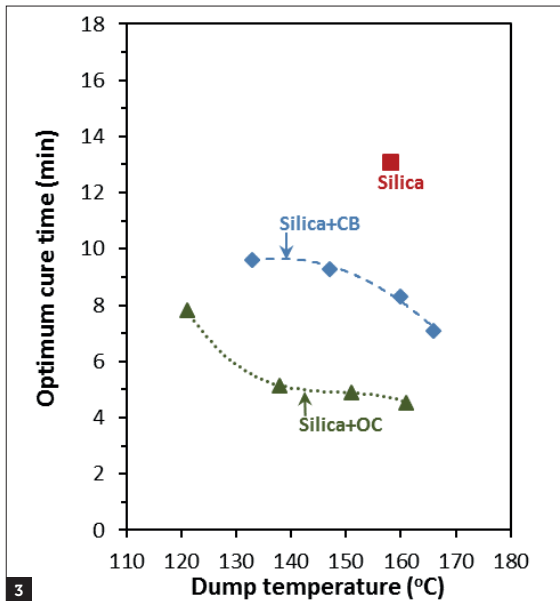
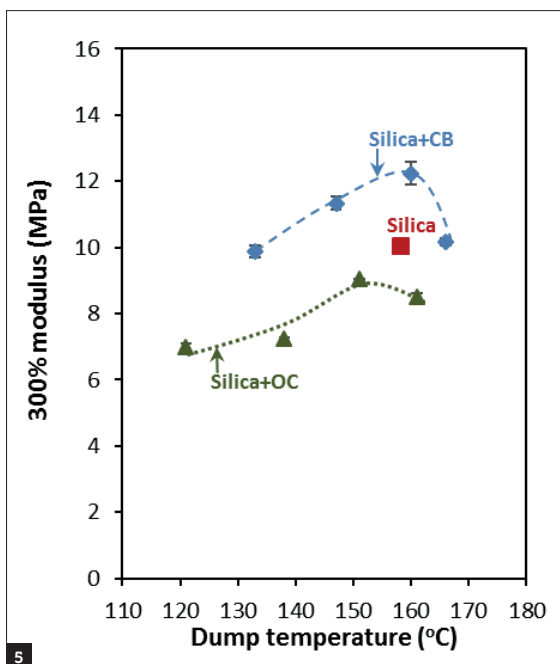
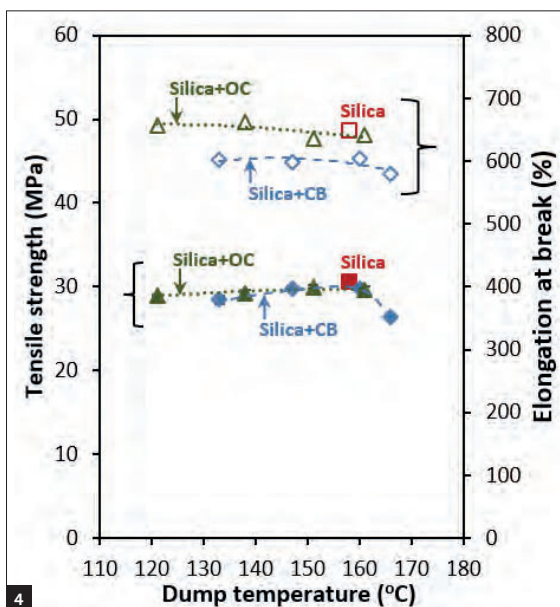


Figure 3: Influence of dump temperature on optimum cure time of silica-filled NR compounds containing different secondary fillers: CB and OC

Figure 4: Tensile strength and elongation at break as a function of dump temperatures of silica-filled NR compounds with different secondary fillers: CB and OC

Figure 5: Influence of dump temperature on 300% modulus of silica-filled NR compounds with different secondary fillers: CB and OC



using a Wickert WLP 1600 laboratory compression press at 150°C and 100 bar into 2mm-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/THIS) at a crosshead speed of 500mm/min according to ASTM D412.

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

Results and discussion – Filler-filler interaction and compound viscosity

The Payne effects ($G'_{0.56\%} - G'_{100\%}$), or filler-filler interactions, depicted in Figure 2 were derived from the difference between storage moduli at 0.56% and 100% strain. The Payne effects of the silica/carbon black (CB)-filled and silica/organoclay (OC)-filled NR compounds decrease with increasing dump temperature due to better silanization at higher mixing temperatures. This clearly confirms the corresponding Mooney viscosities. A higher dump

temperature results in a lower Mooney viscosity of the compounds (at 100°C) due to increased silanization and consequential decreased filler-filler interactions. The Payne effect of the silica/CB-filled NR is higher than for the silica-filled NR reference compound. This is due to the smaller interaggregate distance of the strongly reinforcing carbon black, which 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 to the effect of the modifier used in the clay – an organic ammonium derivative.

Cure time

Figure 3 shows that the optimum cure times of silica-filled NR compounds with carbon black and organoclay as secondary fillers considerably 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 tendency to adsorb vulcanization accelerators, thus retarding the vulcanization. Only about 30% of the silanol group on silica react with the coupling agent, so 70% remains unreacted. For silica/CB compounds, 18wt% of silica was replaced by carbon black, resulting in less adsorption of accelerators by silica, and so increasing the

Table 1: Compound formulations

Ingredients	Dosage (phr)	
	Silica reference	Silica/secondary filler
Natural rubber (RSS#3)	100.0	100.0
Silica (Ultrasil 7005)	55.0	45.0
Secondary filler ^a	-	10.0
TESPD ^b	5.0	4.1
TDAE oil		8.0
Zinc oxide		3.0
Stearic acid		1.0
TMQ		1.0
DPG ^b		1.1
CBS		1.5
Sulfur		1.5

^aSecondary fillers are carbon black N134 (CB), or organoclay Dellite 67G (OC)

^bAmounts of TESPD and DPG were calculated following the optimizing equations suggested by Guy, et al.³

vulcanization rate. Interestingly the organoclay-containing compounds show by far the largest decrease in optimum cure time, which must again be the result of the alkaline modifying agent in the organoclay. This agent might play an extra role in further modification of the silica surface over the alkaline DPG, leading to an increased cure speed. An increase in dump temperature reduces the optimum cure time of the silica/CB and silica/OC compounds, due to a better hydrophobation on the silica surface, as shown in Figure 2.

Mechanical properties

Figures 4 and 5 illustrate the mechanical properties of the corresponding vulcanizates. At various dump temperatures, the tensile strength, elongation at break, and 300% modulus of NR filled with silica/CB slightly increase until about 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 at the same levels. The modulus at 300% strain of NR filled with silica/OC increases with raising dump temperature until 151°C and then slightly decreases. This is again due to degradation of NR at higher temperatures. Interestingly the tensile strengths and elongations at break do not differ much from those of the reference silica compounds.

Indications of tire performance

The tan delta at -20°C to 20°C and 60°C measured on a laboratory scale are often considered to predict the wet traction and rolling resistance of a tire equipped with a tread based on the same compound, with the value at -20°C being a first indication of wear resistance. The tan delta at -20°C, shown in Figure 6, 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 2. The tan delta at -20°C of the silica/OC-filled with NR is substantially higher than for the silica/CB, as well as for the pure silica compounds.

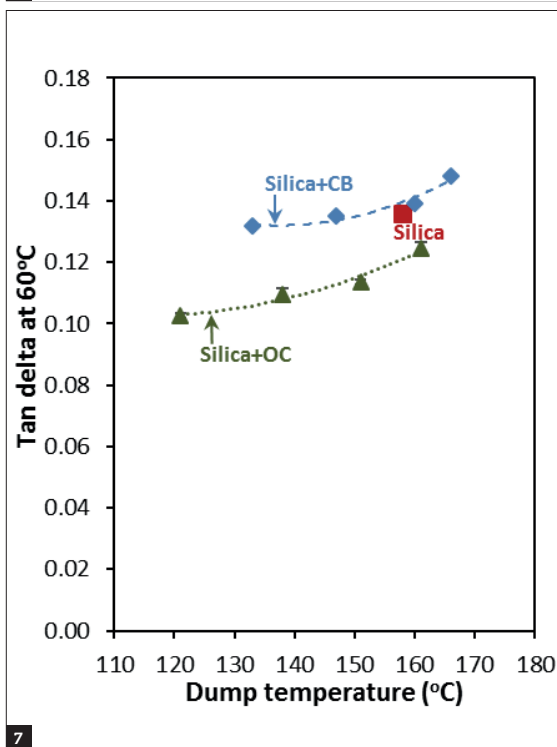
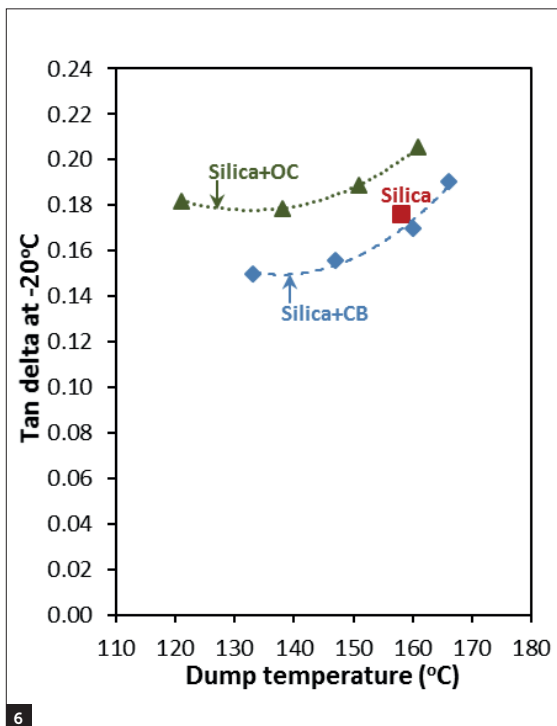


Figure 6: Tan delta at -20°C from DMA as a function of dump temperatures of silica-filled NR compounds with different secondary fillers: CB and OC

Figure 7: Effect of dump temperature on tan delta at 60°C from RPA of silica-filled NR compounds with different secondary fillers: CB and OC

This indicates that there is potential to improve wet traction and wear performance of a tire tread by using a small amount of organoclay in combination with silica. The results of tan delta at 60°C (Figure 7) for the silica/CB compounds are comparable with the reference silica-filled NR. On the other hand, the organoclay gives a significantly lower tan delta at 60°C compared with the reference

silica compound, pointing to a large decrease in the rolling resistance for tires with some organoclay applied next to silica.

Conclusion

The introduction of secondary fillers into the silica-reinforced NR tread compounds may have the potential to improve tire performance further. 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 optimum cure time.

The compounds where carbon black was added as a secondary filler do not show this behavior. They give inferior filler dispersion compared with 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 potential to improve wet traction and rolling resistance of a tire tread when using organoclay as a secondary filler, while the combination of carbon black in silica-filled NR does not change these properties. **tire**

Acknowledgements

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