Kombinationen aus Naturkautschuk und Fällungskieselsäure für die Laufflächen von Lkw-Reifen mit geringem Rollwiderstand
Natural Rubber – Silica Combinations for Low Rolling Resistance Truck Tyre Treads

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Introduction

The highly-dispersible silica technology, as it is used today, employs mainly solution-polymerised synthetic rubber[1], and is still not commercially feasible with Natural Rubber (NR)[2]. It was postulated that non-rubber constituents contained in NR such as proteins compete with the coupling agent for reaction with the silica during mixing, so disturbing its reinforcement action.

NR derived from *Hevea Brasiliensis* latex contains about 3-5% of non-rubber constituents[3], essentially proteins and phospholipids[4]. The structure of a linear NR chain consists of a long sequence of 1000-3000 cis-1,4 isoprene units, two trans-1,4 isoprene units, with α- and ω-chain ends[5-6]. The α- and ω-terminals are associated with proteins and phospholipids respectively[7], and are presumed to play a part in the branching and gel formation in NR[8-10].

The thermal history particularly the mixing dump temperature is an important parameter in mixing silica and rubber in presence of a coupling agent in order to achieve proper silanisation of silica and to avoid premature reactions[11-13]. In the present paper, the influence of mixing dump temperature on the properties of silica reinforced compounds in natural rubber with varying protein content are investigated. Filler-filler, rubber to filler interactions and physical properties of compounds are discussed.

Experimental

Mixing. The compound ingredients as shown in Table 1, except the curatives, were mixed in a Brabender Plasticorder 350S internal mixer with 60 rpm rotor speed and 70% fill factor.

The starting temperature was varied from 70 to 120 to obtain variable temperature histories and dump temperatures. The curatives were added on a two-roll mill.

NR's with different protein contents were compared in this study as shown in Table 2. For skim rubber the formulation was adjusted to 112 phr to take into account the high protein content.

Ingredient	phr
NR (various types)	100
Silica Ultrasil 7005	55
Silane TESPT[a]	5
Zinc oxide	2.5
Stearic acid	1
TDAE oil	8
TMQ[b]	2
Sulphur	1.4
Accelerator (CBS[c])	1.7
Diphenyl guanidine (DPG)	2

a. bis-(triethoxysilylpropyl) tetrasulphide
b. 2,2,4-trimethyl-1,2-dihydroquinoline
c. N-cyclohexyl-2-benzothiazol sulphenamide

Tab. 1: Compound Formulation

NR type	Protein content, %
NR (SMR 20)	1.31
DPNR (Deproteinised NR)	0.44
Skim Rubber	12.9

Tab. 2: Protein Content of NR's used

Mooney viscosity. Mooney viscosity was measured at 100 °C with a Mooney viscometer 2000E (Alpha Technologies) using a large rotor for compounds and small rotor for masterbatches.

Payne effect. The Payne effect was measured prior and after cure in a Rubber Process Analyser (RPA) 2000 (Alpha Technologies). Before cure the sample was heated to 100 °C in the RPA and subsequently subjected to a strain sweep at 0.5 Hz. The Payne effect was calculated as the difference between the storage modulus, G' at 0.56% and G' at 100.04% strain. The Payne effect after cure was measured after vulcanization in the RPA at 150 °C for 10 minutes and subsequent cooling to 100 °C, making use of the same strain sweep conditions.

Bound Rubber Content (BRC). The BRC measurements were performed on unvulcanised samples by extracting the unbound rubber with toluene at room temperature for seven days in both normal and ammonia environment. The ammonia treatment of BRC was done to obtain the chemically BRC as ammonia cleaves the physical linkages between rubber and silica[14–15]. The amount of BRC (g/g filler) was calculated by:

$$BRC(g/g\ filler) = \frac{w_{dry} - w_{insolubles}}{w_o \times \dfrac{w_{filler,phr}}{w_{total,phr}}}$$

<div align="right">eq.1</div>

Where w_o is the initial weight of the sample, w_{dry} is the dry weight of the extracted sample, $w_{insolubles}$ is the weight of insolubles (mainly filler) in the sample, $w_{filler,\ phr}$ is the total filler weight in phr and $w_{total,\ phr}$ is the total compound weight in phr. The physically BRC was taken as the difference between untreated BRC and ammonia treated BRC.

Vulcanization. Curing curves were measured using a RPA 2000 at 150 °C, under condition of 0.833 Hz and 2.79% strain. The vulcanisates were prepared by curing the compounds for their respective t_{95} at 150 °C using a Wickert laboratory press WLP 1600/5*4/3 at 100 bar.

Physical properties. Tensile properties of the vulcanisates were measured using a Zwick Z020 tensile tester according to ISO-37. The hardness of the cured samples was determined according to DIN-53505. The tan delta (G''/G') at 60 °C was measured using the RPA by applying a frequency sweep at 3.49% strain after first curing in the RPA at 150 °C.

Results and discussion

Compound Viscosities. A comparison of the Mooney viscosities of silica-filled NR with silica-filled DPNR and silica-filled skim rubber as a function of dump temperature is shown in Figure 1. The viscosities of NR and DPNR masterbatches are comparable, where they increase with increasing dump temperature up to 150 °C and afterwards slowly start to decrease. The Mooney viscosities of the skim rubber masterbatches are lower than for the NR and DPNR, also show an increase with dump temperature and level off at dump temperatures above 150 °C.
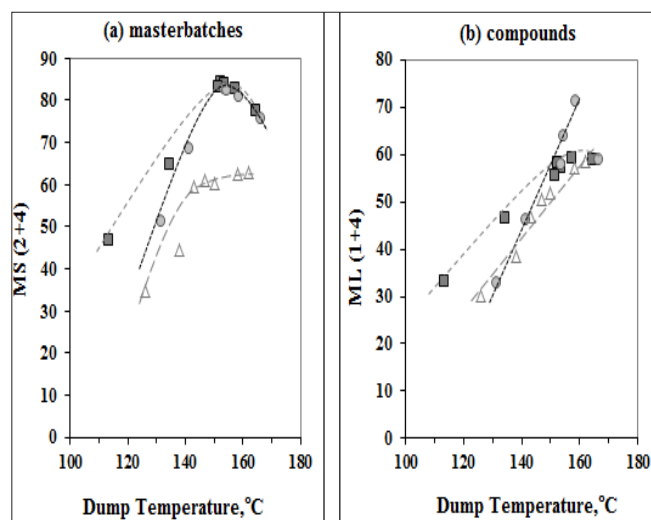
Once the curatives are added to the compounds, the viscosities drop to acceptable levels, mainly due to the re-milling step. The Mooney viscosity of the NR compound is seen to increase with increasing dump temperature up till 150 °C and becomes constant afterwards. For the DPNR compounds, a linear increase in Mooney viscosity is observed with increasing dump temperature to a maximum for 160 °C, and the values are also higher than those of NR. The skim rubber compound also shows a linear trend with increasing dump temperature. In spite of the overall lower Mooney viscosities of the skim rubber masterbatches after the first mixing step, the Mooney viscosities with curative included by mill mixing are almost comparable with those of the NR and DPNR compounds.

Payne effect. Filler-filler interaction is commonly measured by the so-called Payne effect. The storage modulus of filled rubber drastically decreases as the strain increases as the result of breakage of physical bonds between filler particles, for example van der Waals, hydrogen bonds and London forces.

A comparison of filler-filler interaction in NR-silica compounds is demonstrated in Figure 2. The Payne effect of NR- and DPNR-silica compounds decreases sharply with increasing dump temperature, as is also seen in synthetic rubber / silica compounds and taken as a sign of reaction and consequent hydrophobation of the silica by the silane coupling agent[11]. No effect of mixing temperature is perceived on filler-filler interaction for the skim rubber compound. This suggests a strong interference of the proteins in skim rubber with the silica-silica network.
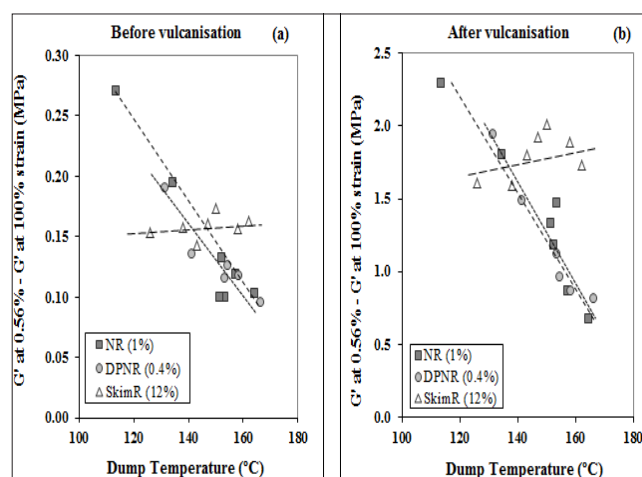
Fig. 2: Payne effect of silica compounds with silane TESPT at varying protein contents in NR: (a) unvulcanised samples; (b) vulcanised samples.

Fig. 1: Mooney viscosity of: (a) masterbatches after 1st mixing, and (b) compounds after 2nd mill mixing of silica-filled NR at varying protein contents: (●): 0.4% (DPNR); (■): 1% (NR); (Δ): 12% (SkimRubber).

The same trend is observed for the unvulcanised as well as for the vulcanised compounds. This indicates that the silica-silica network is not influenced for skim rubber even at high dump temperature because silanisation is hindered. The non-rubber components or proteins in the

skim rubber prevent modification of the silica surface by the silane coupling agent. The logical explanation is that the interaction between silica and proteins overrule the coupling agent and that proteins are shielding the silica surface.

Bound Rubber Content. The filler-to-rubber interaction of silica-filled NR with varying protein contents can also be judged on basis of the chemically and physically bound rubber content as illustrated in Figure 3. The chemically bound rubber of the NR compound increases with increasing dump temperature up to 150 °C, but above 150 °C it stabilizes. This can be explained by a higher rate of silanisation. At 150 °C, there is saturation in the amount of TESPT which has reacted and the surface of silica covered. Hence, there is no increase in chemically bound rubber above 150 °C. The low protein DPNR compound also shows an increase in chemically bound rubber with increasing dump temperature but has an optimum at 155 °C dump temperature. The skim rubber compound has no chemically bound rubber at low dump temperature, below 140 °C. This clearly indicates that no silanisation occurs and the interaction of protein and silica in skim rubber is purely physical of nature. Above 150 °C the skim rubber compound has a constant, and high chemically bound rubber content comparable to DPNR. At high dump temperature, the chemically bound rubber for regular NR compound is somewhat lower than for the DPNR and the skim rubber compounds.
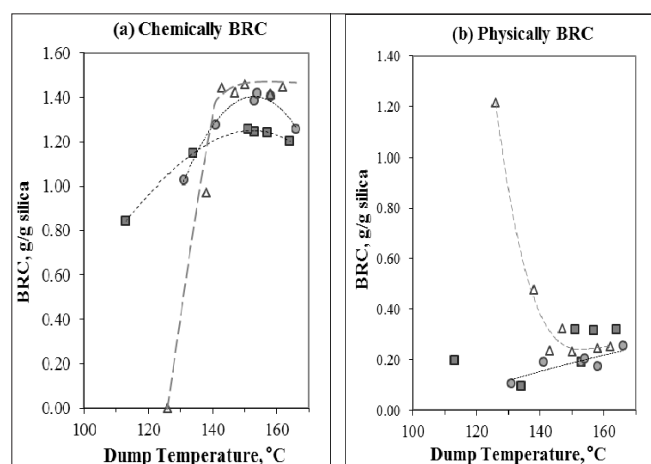

Fig. 3: Comparison of: (a) chemically and (b) physically bound rubber content of silica compounds with varying protein contents. (●): 0.4% (DPNR); (■): 1% (NR);(Δ): 12% (SkimRubber).

An increase in physically bound rubber of the NR-silica compound at higher dump temperature can be explained by the saturation of silica-TESPT coupling. Additional interactions above 150 °C between the non-hydrophobized silica surfaces and rubber are physical of nature, which originate from remaining silica-protein interactions. This corresponds with the observation, that for the low protein content DPNR compound, the physically bound rubber is

lowest throughout the whole dump temperature range, but also still shows a slight tendency to grow at higher dump temperatures. Further, a strong interaction between protein and silica can be seen in the high physically bound rubber for the skim rubber at low dump temperatures.

The trends seen in chemically bound rubber correlate surprisingly well with the Mooney viscosities of the masterbatches: Figure 1(a). Apparently, when more chemically bound rubber is formed, the molecular motion of the rubber chains is restricted and this results in higher Mooney viscosity. This emphasizes the importance of chemical coupling of the rubber to the silica surface.

Physical properties. – The effect of protein content in the NR on the physical properties of vulcanisates at varying dump temperatures is depicted in Figure 4. The tensile strength of the NR-silica vulcanisates seems to drop somewhat at dump temperatures above 150 °C. This shows that mixing temperature is of importance for the NR-silica compound. However, this reduction in tensile strength at high dump temperature is not seen for the low protein DPNR-silica vulcanisates. For the high protein skim rubber vulcanisate, the tensile strength is inferior to NR and DPNR vulcanisates. The tensile strength of skim rubber is observed to have a slight improvement with increasing dump temperature. NR and DPNR vulcanisates have comparable hardness and show quite a decrease in hardness with increasing dump temperature. Skim rubber vulcanisates, however show a constant hardness and are not affected by the mixing temperature.
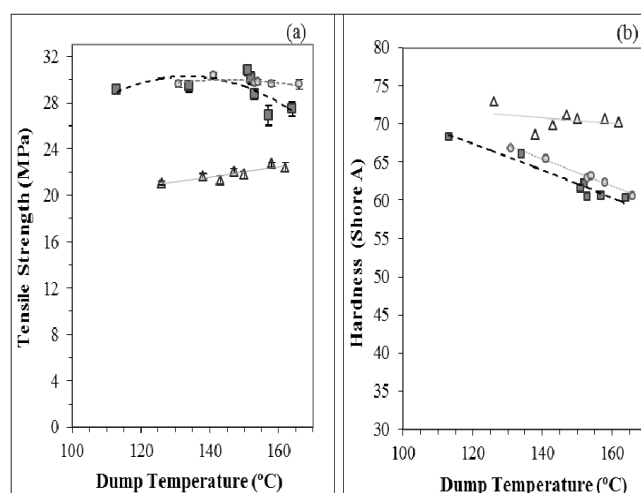

Fig. 4: Physical properties of silica-filled NR vulcanisates with different amounts of protein contents: (●): 0.4% (DPNR); (■): 1% (NR); (Δ): 12% (SkimRubber); (a) Tensile strength, (b) Hardness.

Commonly, two characteristic properties of cured compounds are employed as indications for the rolling resistance of tyres made thereof: the reinforcement index M300/M100 and the loss tan δ at 60 °C. The higher M300/

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M100 or the lower tan δ at 60 °C, the lower the rolling resistance expected in real tyre performance. Figure 5 illustrates both indications of rolling resistance of the silica-filled vulcanisates. Both NR-silica and DPNR-silica have a superior reinforcement index as compared to skim rubber-silica vulcanisates. With increasing mixing temperature, the reinforcement index of the NR vulcanisate is somewhat improved. The processing conditions have no influence on the reinforcement index (M300/M100) of DPNR and skim rubber vulcanisates, where skim rubber is substantially lower than NR and DPNR.
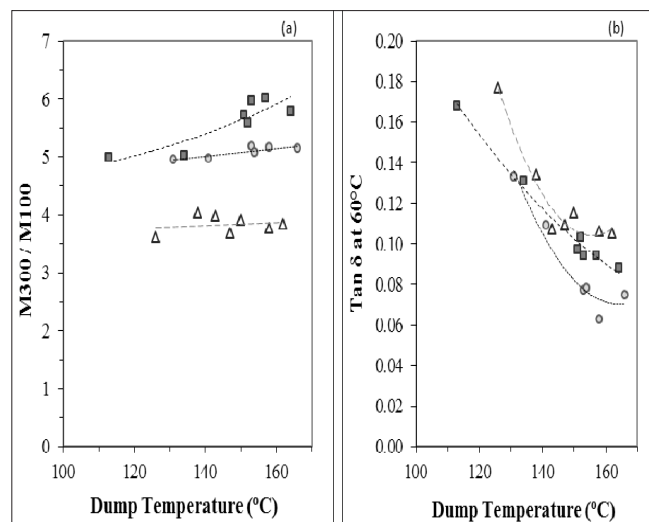

Fig. 5: Comparison of : (a) reinforcement index (M300/M100) and (b) tan δ at 60 °C for natural rubber vulcanisates with varying protein content: (●): 0.4% (DPNR); (■): 1% (NR); (Δ): 12% (SkimRubber).

These data seem to indicate that mixing temperature history has little effect on the rolling resistance, except for NR itself. However, all natural rubber vulcanisates show a strong decrease in tan δ at 60 °C with increasing dump temperature regardless of the amount of protein in the rubber. Improvement in tan δ at 60 °C can still be achieved with higher mixing temperature, like with synthetic rubber. This must obviously be the result of more coupling of silica to the rubber with greater silanisation efficiency at high temperatures. With low protein content, the DPNR vulcanisates exhibit the lowest tan δ at 60 °C at high dump temperature. This actually relates well with a higher chemically bound rubber content of DPNR than of the NR compound. Still with all the protein contained in skim rubber, the tan δ at 60 °C is significantly lowered by mixing temperature history and only marginally worse than for NR and DPNR. It is quite surprising that the reinforcement index and tan δ at 60 °C show opposite behaviour in the present NR systems, compared to synthetic rubber based silica-filled compounds[16].

Conclusions

Mixing temperature is a parameter of great importance for NR-silica compounds as it has an effect on final properties. Silica-silica interaction is reduced with establishment of silica-silane-rubber linkages through silanisation at high mixing temperatures. This is clearly the case for NR and low protein content rubber DPNR. However, mixing temperature has little influence on the properties of a high protein-content skim rubber compound. When high amounts of proteins are present in the rubber, the Payne effect and filler structure parameter are unaffected by dump temperature. Consequently, the hydrophobation of the silica surface by silane is partially hindered due to silica-protein interactions. NR-silica vulcanisates mixed at high dump temperature exhibit somewhat lower tensile properties. On the other hand, DPNR-silica vulcanisates show slightly more constant physical properties. The skim rubber vulcanisates perform overall much worse compared to NR and DPNR in physical properties, due to lack of sufficient silica-rubber coupling. A lower tan δ at 60 °C is obtained for all NR-silica vulcanisates at high dump temperature, indicating that improvement in the rolling resistance of all NR vulcanisates can be achieved if applied in tyre treads with higher silanisation efficiency.

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