

# UTILIZATION OF ORGANOCLAY AS SECONDARY FILLER IN SILICA-REINFORCED NATURAL RUBBER TIRE TREAD COMPOUNDS

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## ABSTRACT

Silica-reinforced Natural Rubber (NR) truck tire tread compounds are investigated using organoclay (OC) as secondary filler. By varying mixer temperature settings at silica/OC ratio of 45/10 phr, dump temperatures are reached of approximately 120, 140, 150 and 160°C. The increased dump temperature leads to a better silanization reaction to result in lower mixing torque, Mooney viscosity and Payne effect. The optimum mixing dump temperature was found to be around 150°C. By varying the loadings of OC in the silica-filled NR compounds from 0 to 36 wt% relative to total filler amount, the increased OC loadings decrease the Payne effect and compound viscosities, significantly shorten scorch and cure times and raise the tan delta at -20°C and 0°C as indications for ice traction and wet skid resistance of tire treads made thereof. The optimum loading of OC of 18 wt% relative to total filler content shows better Payne effect, cure rate index, tan delta at -20°C and 60°C indicative for rolling resistance, and DIN abrasion resistance index. The results indicate that the use of this hybrid filler may provide tires with better wet traction, lower rolling resistance and wear resistance compared to the pure silica-filled system.

Keywords: silica; organoclay; hybrid filler; natural rubber; tire tread

## INTRODUCTION

Natural rubber (NR) is widely used in all types of tires especially for heavy trucks and aircrafts in order to obtain low heat build-up. Many components of passenger car tires are also made from NR such as bead filler, sidewall and tread compounds, because it provides low heat build-up, good flex-fatigue and excellent mechanical properties. Particulate reinforcing fillers such as carbon black and silica are most commonly used in combination with NR for tire tread applications. Carbon black was the first reinforcing filler for rubber compounds to improve tensile strength, modulus, tear strength, abrasion resistance, skid resistance as well as other properties. Replacement of carbon black with silica, after the patent of Michelin [1] for passenger car tires, offers tire compounds with lower rolling resistance and higher wet grip [2], so less fuel consumption and better driving safety. However, the successful use of silica in rubber compounds requires sufficient bonding and/or interaction between the silica and the elastomer because of differences in polarity of silica and rubbers. Sulfur-containing silane coupling agents such as bis-(3-triethoxysilylpropyl)tetrasulfide (TESPT) is commonly applied in such compounds vulcanized with a sulfur system. For better scorch safety, bis-(3-triethoxysilylpropyl)disulfide (TESPD) can be used but when compared to TESPT, compounds with lower filler-rubber interactions, dispersion stability, tensile strength, and tear resistance were observed [3]. The mixing of silica with silane in rubber involves a chemical reaction, called silanization. The mixing temperature has a more dominant effect than mixing time on the silica-silane reaction [4]. The effect of mixing temperature for the silica-silane (TESPT) technology has been studied in different types of elastomers such as a styrene-butadiene rubber (SBR) blend with butadiene rubber (BR) [5-6], isoprene rubber (IR) [7] and NR [7-8]. The silanization reaction between silica and silane coupling agent increases with increasing mixing dump temperature, as indicated by a reduction of filler-filler interactions monitored by the Payne effect, and increased filler-elastomer interactions as evidenced by higher chemically bound rubber content. The extent of silanization has a dramatic effect on the resulting compound properties [8-9]. Therefore, the effect of mixing dump temperature for hybrid fillers of silica and organoclay (OC) in NR compounds must be investigated. Even with small parts of silica replaced by OC a significantly improved balance of properties may be achieved.

New reinforcing fillers for rubber products have been introduced and one of the most widely studied is nanoclay. To enhance compatibility with tire elastomers, organo-modified clay or shortly organoclay which has been modified by cation exchange with ammonium salts or phosphonium salts to promote its hydrophobicity, is generally used [10]. The organoclay

has a dimension on the nanometer level and may be dispersed in single platelets or small silicate stacks with a high aspect ratio of 50-1000 [11]. Organoclay-elastomer composites with low nanofiller contents (usually 10 phr or less) show an improvement in mechanical properties, thermal stability, wear resistance and gas permeability. Recently, there is an increasing interest in hybrid fillers or combinations of silica and OC in order to achieve synergistic effects in rubber properties from each filler. A combination of silica and China clay in NR for a heavy-duty truck tire tread formulation was studied and the best balance of heat build-up and abrasion resistance was found at a silica/clay ratio of 60/20 [12]. Hybrid fillers of precipitated silica/MontMorillonite (MMT) in peroxide cured silicone rubber nanocomposites resulted in the improvement of tensile strength, Young's modulus, moduli at 100% and 300% strain (M100 and M300), elongation at break, hardness and crosslink density [13]. A SBR/silica/OC nanocomposite prepared by a latex mixing method with replacement of silica by 7 phr of OC was investigated in comparison with the use of pure silica at 60 phr loading. This work reported that the silica/OC gave an indication for better skid and rolling resistance with high 100% and 300% modulus [14]. The use of MMT and silica with TESPT as silane coupling agent in solution-SBR (SSBR)/BR tread compounds improved tensile strength, elongation at break and traction properties at low TESPT content while enhancing modulus, hardness, wear resistance, dry handling and rolling resistance at high TESPT content [15]. 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 [16], 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 of fuel consumption and carbon footprint of tires made thereof [17].

In a previous study, the effect of mixing temperature in the masterbatch stage on a hybrid filler system of silica/OC-filled NR with bis-(3-triethoxysilylpropyl)disulfide (TESPD) as coupling agent was investigated in a preliminary manner [18]. In the present work, the effect of loading levels of OC on the hybrid filler system, still in combination with mixing temperature is fully explored. The cure characteristics, filler-filler interactions, filler-rubber

interactions, tensile and tear properties, DIN abrasion resistance index, dynamic mechanical properties and morphology in terms of clay dispersion of such silica/OC-filled NR compounds are studied.

## EXPERIMENTAL

### MATERIALS

Natural rubber (Ribbed Smoked Sheet No.3, RSS3) was provided by Sri Trang Agro-Industry, Thailand. Silica ULTRASIL 7005 and silane coupling agent bis-(3-triethoxysilylpropyl)disulfide (TESPD) were obtained from Evonik, Germany. Organoclay Dellite 67G, functionalized with 47 wt% of dimethyl dihydrogenated tallow ammonium chloride (2HT), 115 meq/100 g of cation exchange capacity and interlayer distance of 34.3 Å was provided by Laviosa Chimica Mineraria S.p.A, Italy. The other ingredients: Treated Distillate Aromatic Extract oil (TDAE) (Vivatec 500) (Hansen & Rosenthal, Germany); diphenyl guanidine (DPG), N-cyclohexyl-2-benzothiazyl sulfenamide (CBS), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) (all from Flexys, Belgium); zinc oxide (ZnO), stearic acid and sulfur were all commercial grades for the rubber industry.

### PREPARATION OF RUBBER COMPOUNDS

The compound formulations employed are given in Table I. The compounds were prepared using a two-step mixing procedure: the first was to prepare a masterbatch of rubber and fillers, and the second was to prepare the final compounds including the curatives. For the first step, an internal mixer Brabender Plasticorder 350 ml was used, operated at a rotor speed of 60 rpm and fill factor of 70%. The OC as secondary filler was added together with the first half of silica, TESPd and DPG secondary accelerator in order to obtain a good dispersion. The other half of silica and TESPd were added later on in the first mixing step, together with TDAE extender oil. The second step was used for the addition and mixing of the other half of DPG, 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 Scheme 1. A study of the influence of dump temperature was first executed in order to determine the optimal condition for the best possible properties of the silica/OC-filled NR compounds using a silica/OC ratio at 45/10 phr. Therefore, the initial mixer temperature setting for the first step mixing was varied at 60, 80, 100 and 120°C. A reference mix with

silica only was also prepared using an initial mixer temperature setting at 100°C according to a previous report [8]. In the second part of this study, based on the optimum temperature setting found, the OC content was varied at 0, 2.5, 5, 7.5, 10, 15 and 20 phr or 0, 5, 9, 14, 18, 27 and 36 wt% relative to total filler amount, and the silica amount reduced accordingly.

Table I  
Formulations of silica-filled NR compounds with organoclay as a secondary filler.

Ingredients	Amount (phr)	
	Silica Reference	Silica/Secondary filler
Natural rubber (RSS3)	100.0	100.0
ULTRASIL 7005	55.0	45.0 (or variable) <sup>a</sup>
Dellite 67G (OC)	-	10.0 (or variable) <sup>a</sup>
TESPD <sup>b</sup>	5.0	4.1
TDAE oil	8.0	8.0
ZnO	3.0	3.0
Stearic acid	1.0	1.0
TMQ	1.0	1.0
DPG <sup>b</sup>	1.1	0.9
CBS	1.5	1.5
Sulfur	1.5	1.5

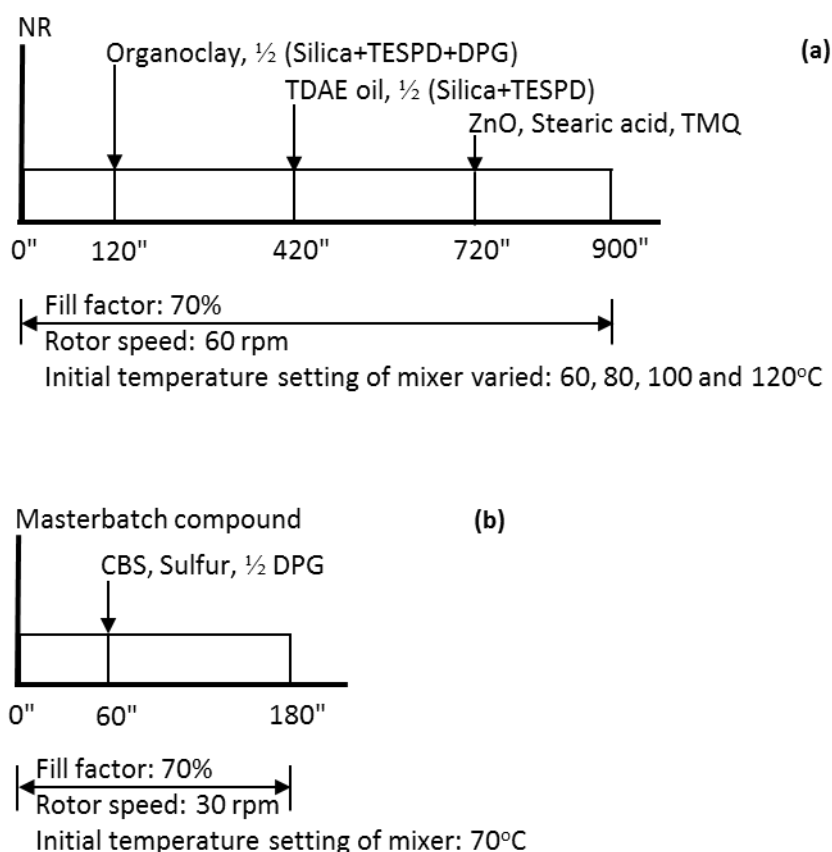
<sup>a</sup>Loadings of silica/OC were varied at 55/0, 52.5/2.5, 50/5, 47.5/7.5, 45/10, 40/15 and 35/20 phr/phr, or equal to 0, 5, 9, 14, 18, 27 and 36 wt% of OC relative to total fillers, respectively.

<sup>b</sup>Amounts of TESPD and DPG were added according to the following equations [19]:

$$\text{TESPD (phr)} = 0.00053 \times Q \times A \quad (1)$$

$$\text{DPG (phr)} = 0.00012 \times Q \times A \quad (2)$$

where Q is the amount of silica (phr) and A is the CTAB surface area of the silica (171 m<sup>2</sup>/g).



SCHEME 1. Two-step mixing procedure for compound preparation: for masterbatch (a), and final compounds (b).

## MATERIAL CHARACTERIZATIONS; UNCURED COMPOUNDS

*Mooney viscosity* – Mooney viscosity, ML(1+4), 100°C was tested using a Mooney viscometer (MV2000VS, Alpha Technologies, Akron, USA) according to ASTM D1646.

*Bound Rubber Content (BRC)* – An amount of 0.25 g of uncured compound (without curatives) was immersed in 40 ml of toluene for 7 days at room temperature. Then the sample was removed from toluene, dried at 80°C in a vacuum oven for 24 h and weighed. The bound rubber content was calculated using the following equation.

$$BRC(\%) = \frac{(m - m_s)}{m_r} \times 100 \quad (3)$$

where  $m$  is the weight of sample after extraction,  $m_s$  and  $m_r$  are the weights of filler and rubber in the original sample respectively.

*Payne effect* – The storage shear moduli ( $G'$ ) of the rubber compounds with curatives were evaluated by using a Rubber Process Analyzer RPA 2000 (Alpha Technologies) at a temperature of 100°C, frequency of 0.5 Hz and varying strains in the range of 0.56-100%. The

Payne effect was taken as the difference in storage shear moduli at low strain (0.56%) and high strain (100%).

*Cure characteristics* – The cure characteristics of the compounds were measured by using the RPA 2000 at a temperature of 150°C, frequency 0.833 Hz and 2.79% strain. The Cure Rate Index (CRI) was calculated as  $[100/(\text{optimum cure time} - \text{scorch time})]$ , the optimum cure time defined as  $t_{c90}$  and scorch time as  $t_{s2}$ .

## MATERIAL CHARACTERIZATIONS; RUBBER VULCANIZATES

*Apparent crosslink density* – Vulcanizate samples with a dimension of 3 x 5 x 2 mm<sup>3</sup> were immersed in toluene at room temperature for 7 days. Thereafter, the swollen samples were taken out and blotted lightly with paper to remove excess toluene from the surface. The weights of the rubbers before and after swelling were measured and the swelling ratio (Q) was calculated according to the following equation:

$$\text{Swelling ratio } (Q) = (M_t - M_0)/M_0 \quad (4)$$

where  $M_0$  and  $M_t$  are the weights of the samples before and after swelling, respectively. The apparent crosslink density was calculated from the reciprocal of swelling ratio (i.e. 1/Q) [20], because the real crosslink density by for example the Flory-Rehner approach [21] is not feasible to acquire with the varying filler loadings.

*Tensile and tear properties* – The compounds were vulcanized to their optimum cure time ( $t_{c90}$ ) by using a Wickert WLP 1600 laboratory compression press at 150°C and 100 bars into 2 mm thick sheets. For tensile properties, Type 2 dumb-bell test specimens were die-cut from the press-cured sheets and tests were carried out with a Zwick tensile tester Model Z1.0/TH1S (Zwick Roell Group, Ulm, Germany) at a crosshead speed of 500 mm/min according to ASTM D412. For tear strength, the vulcanized rubber was tested at room temperature using Delft-type specimens with the same machine and crosshead speed as applied for tensile tests according to ISO 34-2.

*DIN abrasion resistance index and its abraded surface* – DIN abrasion resistance index (ARI) was tested using a DIN abrader (Abrasion tester 564C, Karl Frank GmbH, Germany) according to method A of DIN 53516. The test specimen has a diameter of  $16 \pm 2$  mm with a minimum thickness of 6 mm. The silica-filled NR was used as reference rubber. The ARI was calculated according to the following equation:

$$ARI = \left( \frac{\Delta m_r \cdot d_t}{\Delta m_t \cdot d_r} \right) \cdot 100 \quad (5)$$

where  $\Delta m_r$  is mass loss of the reference rubber (g),  $d_r$  is density of the reference rubber ( $\text{g/cm}^3$ ),  $\Delta m_t$  is mass loss of the test rubber (g), and  $d_t$  is density of the test rubber ( $\text{g/cm}^3$ ).

The DIN abraded surface was characterized by scanning electron microscopy (SEM, Quanta 400, FEI Company, the Netherlands). The surface was coated with gold prior to being analyzed.

*X-ray diffraction analysis* – The interlayer spacing (d-spacing) of the organoclay layers was determined by an X-ray diffractometer (Empyrean, PANalytical, Netherlands) with a  $\text{CuK}\alpha$  radiation source ( $\lambda=0.15406$  nm). The operating voltage and current of the X-ray emitting tube were 40 kV and 30 mA, respectively. The test was performed at room temperature with angular range from  $1^\circ$  to  $10^\circ$  ( $2\theta$ ) and a scan speed of  $0.022^\circ/\text{min}$ .

*Dynamic mechanical properties* – The loss tangent or tan delta at  $60^\circ\text{C}$  of the vulcanizates was determined using the RPA at strain 3.49% with varying frequencies in the range of 0.05-33.00 Hz. The samples were cured in the RPA chamber at  $150^\circ\text{C}$  to reach their optimum cure times prior to being tested for loss tangent. In addition, the dynamic mechanical properties of the filled NR vulcanizates under a temperature sweep from  $-80^\circ\text{C}$  to  $80^\circ\text{C}$  were characterized by using a Metravib Viscoanalyzer VA 2000. Samples of dimensions of  $6 \times 4 \times 2$  mm<sup>3</sup> were tested in tension at a frequency of 10 Hz and 0.1% strain. Tan delta values at  $-20^\circ\text{C}$ ,  $0^\circ\text{C}$  are used as indicative for ice traction and wet grip respectively, and tan delta at  $60^\circ\text{C}$  is to indicate rolling resistance of tire treads.

## RESULTS AND DISCUSSION

### OPTIMIZING THE DUMP TEMPERATURE FOR SILICA/ORGANOCLAY-FILLED RUBBER COMPOUNDS

#### MIXING BEHAVIOR

The properties of rubber compounds are strongly influenced by mixing quality, especially for silica-reinforced mixes, for which the extent of the silanization reaction needs to be sufficient during mixing inside the internal mixer. It has been well established that the dump or discharge temperature is the key governing factor [5-9]. In this present work, even though only small parts of silica were replaced by OC aiming to improve dispersion and thus properties, the effect of mixing dump temperature on this hybrid filler is still worth to



investigate in order to be able to obtain the best possible balance of properties. For that reason a preliminary optimization study was done towards the effect of the dump temperature, making use of the silica/OC compound at 45/10 phr and the compound with pure silica as reference. By varying the initial mixer temperature settings at 60, 80, 100 and 120°C, the dump torques and dump temperatures are shown in Figure 1 in comparison with the reference with silica only that was mixed using an initial mixer temperature setting of 100°C.

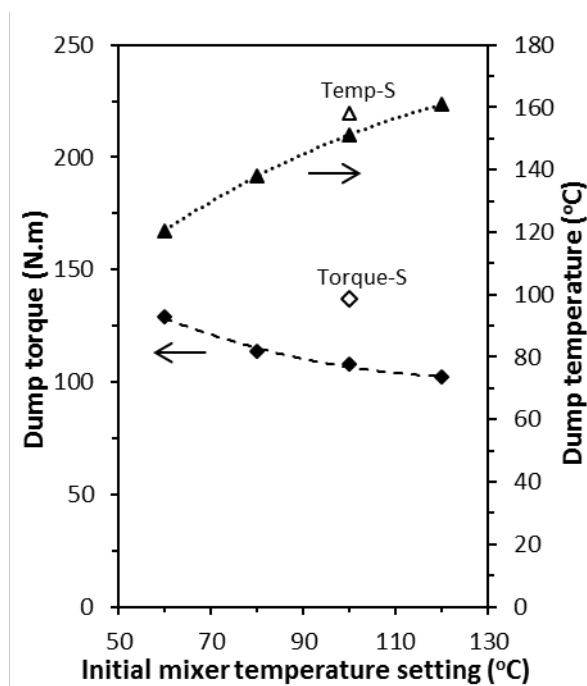


FIG. 1. — Dump torques and dump temperatures of silica/OC-filled NR compounds with varying initial temperature settings of the internal mixer. Closed symbols = 45/10 phr silica/OC; open symbols 55 phr silica only, also marked as S.

With increasing initial mixer temperature settings from 60, 80, 100 and 120°C, the dump temperatures of silica/OC-filled NR reach 121, 138, 151 and 161°C, respectively, and the dump torques gradually decrease. At the same mixer temperature setting of 100°C, both pure silica- and silica/OC-filled NR compounds show similar dump temperatures, but a clear difference in dump torque. The decrease of mixing torque with increasing temperature is due to lower viscosity in the mixer and additionally a better silanization that causes less filler networking or lower filler-filler interaction and so better filler dispersion, also adding to a lower viscosity. Interestingly, the presence of OC reduces the mixing torque compared to the silica only system which would indicate a better dispersion of the fillers. This can be due to reduction of the silica network by OC and/or influence of the modifying agent in OC that provides a plasticizing effect in the rubber compounds, as supported by the Payne effect results shown

below. The long tail structure of dihydrogenated tallow in such modifying agent can plasticize the system causing an increasing free volume between the high molecular weight rubber chains to facilitate the flow. Moreover, the polar functional groups that are present in the modifying agent (C=O, C-O and -N=) can interact with the left-over free silanol groups on the silica surface after the silanization reaction, providing a shielding effect that promotes hydrophobicity and interfacial compatibility between rubber and filler.

#### FILLER-FILLER AND FILLER-RUBBER INTERACTIONS

Non-linear viscoelastic behaviors of the filled rubber compounds can be observed in a change of storage modulus with strain as seen in Figure 2(a). By increasing the strain, the storage modulus sharply decreases due to a breakdown of the filler network, i.e. a reduction of filler-filler interactions, and the difference between the modulus at low strain and high strain can be used to indicate the level of filler-filler interaction, called Payne effect [22]. This Payne effect may also be considered an indirect indication for microdispersion of fillers within the rubber matrix. Figure 2(a) shows that the Payne effect of silica-filled NR is much higher than for the silica/OC-filled NR compounds mixed at different temperature settings, and among the silica/OC mixes the increasing dump temperatures reduce the Payne effect. The decrease of filler-filler interaction in the silica/OC-filled NR compounds with increasing dump temperature is clearly due to a better silanization at higher mixing temperature [6-9]. The remarkable drop in filler-filler interactions or Payne effect in the silica/OC systems compared to the pure silica compound indicates a potential of OC to suppress filler networking. The hybrid filler system of silica/OC that led to reduction of filler networking has previously been reported by Galimberti et al. [17] for blends of IR/SBR with constant 70 phr of silica and the amount of OC changed. It was discussed that the lipophilic ammonium cation of the modifying agent of OC acts as a plasticizer that results in a reduction of the storage modulus of the matrix both at low and at large strains. Moreover, when the organically modified clay was below the threshold required to establish a hybrid OC-silica filler network, reduction in filler networking was still observed [17].

Bound Rubber Content (BRC) is the measurements for filler-elastomer interactions [23]. A higher bound rubber content means a stronger filler-elastomer interaction. The increase of dump temperature for the silica/OC-filled NR compounds up to 151°C increases the total bound rubber content which is a combination of both physical and chemical interactions due to the better silanization. However, too high mixing dump temperature at 161°C causes a drop

in total bound rubber content, as seen in Figure 2(b). This has been observed before and can be ascribed to degradation of natural rubber that yields lower molecular weight material which can dissolve easier in toluene [8]. The bound rubber content of the pure silica-silane system is very much higher compared to the system with OC at every dump temperature. Its higher Payne effect seen in Figure 2(a), i.e. more filler network, leads to more occluded or trapped rubber. Moreover, the silanization efficiency in this system may be better as there is no interference from OC and its modifier. Both may explain the higher bound rubber.

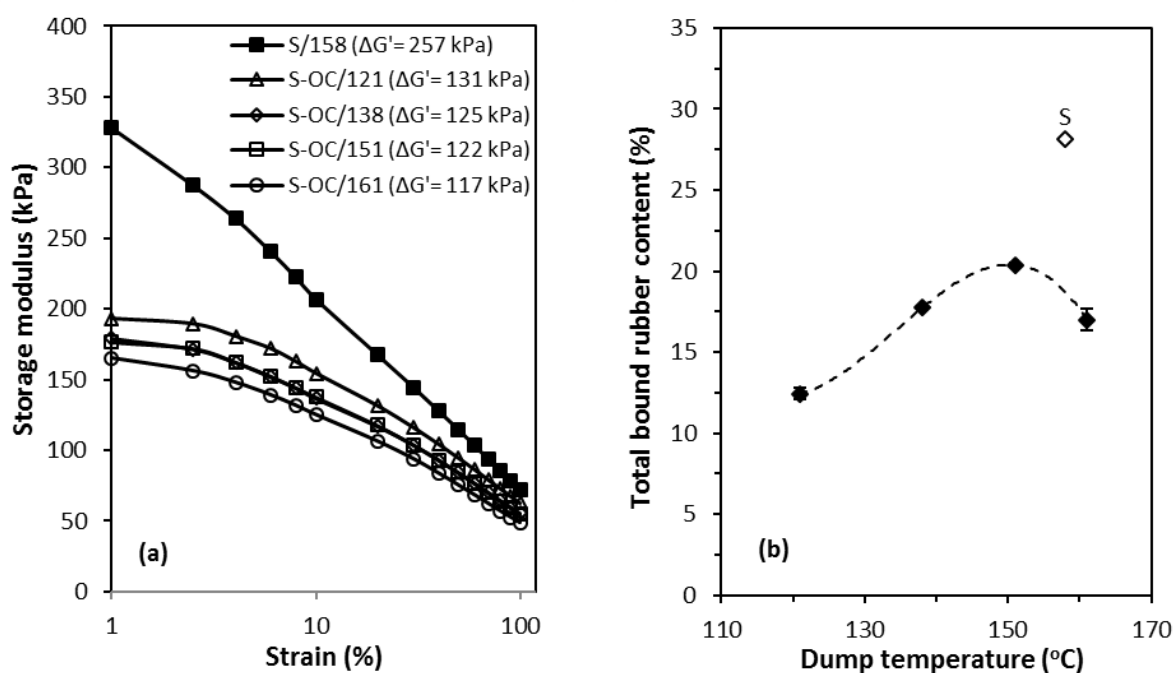


FIG. 2. — Effect of dump temperature on storage modulus as a function of strain (a) and total bound rubber content (b) of silica/OC-filled NR compounds in comparison with pure silica-filled NR (S).

## VISCOSITY AND CURE PROPERTIES

The effect of mixing dump temperature on the cure characteristics and Mooney viscosities of silica/OC-filled NR compounds in comparison with pure silica-filled NR compounds are shown in the Table II. The minimum torques ( $M_L$ ) and Mooney viscosities of the NR compound filled with silica/OC and mixed till different dump temperatures in the first mixing step show the same trend as seen in Table II and Figure 3(a) and both properties are clearly lower than the values for the reference compound with silica only, in accordance with the previous observations [17,24]. Both  $M_L$  and Mooney viscosity are indicative of rubber compound viscosity or its flowability. The lower viscosity means an improvement in

processability. The results are in accordance with the mixing dump torque (Figure 1) and the level of filler-filler interaction (Figure 2a). The decreased Payne effect or less filler networking, the better the filler dispersion as a result of better silanization at higher dump temperature, as well as the plasticizing effect caused by 2HT modifying agent for the organoclay, all contribute to the lower viscosities of the silica/OC-filled system. On the other hand, the pure silica-filled reference compound is only affected by the silanization reaction. So, it shows a higher Mooney viscosity and minimum torque than the system with the OC-silica combination. It should also be noted that natural rubber is prone to degradation at high temperature [25], so it is inevitable to include molecular chain breakdown that also reduces the viscosity.

The maximum torques ( $M_H$ ) and cure torque differences ( $M_H-M_L$ ) of silica/OC-filled NR compounds with various mixing dump temperatures are shown in Table II in comparison with the reference pure silica-filled NR.  $M_H$  or even better  $M_H-M_L$ , indicate the stiffness of the rubber compounds influenced by chemical crosslinks, both chemical and physical interactions and the filler network. Both  $M_H$  and  $M_H-M_L$  values of the pure silica-filled NR compound are distinctly higher than that of the silica/OC-filled ones which is in agreement with their viscosities, total bound rubber content and level of filler network. Among the silica/OC compounds mixed at different temperatures, the  $M_H$  and  $M_H-M_L$  values increase with increasing dump temperature. This can again be ascribed to the effect of the better silanization reaction at higher temperatures that results in better filler-rubber interaction.

Table II

Cure characteristics and Mooney viscosity of silica/OC-filled NR compounds, in comparison with pure silica-filled NR (S).

<b>Compound/Dump temperature (°C)</b>	<b><math>M_L</math> (dN.m)</b>	<b><math>M_H</math> (dN.m)</b>	<b><math>M_H-M_L</math> (dN.m)</b>	<b><math>t_{s2}</math> (min)</b>	<b><math>t_{c90}</math> (min)</b>	<b>CRI (<math>\text{min}^{-1}</math>)</b>	<b>ML(1+4) 100°C (MU)</b>
S/158	0.76	10.8	10.1	8.2	13.1	20	82.6
S-OC/121	0.68	6.5	5.9	1.7	7.8	16	77.1
S-OC/138	0.63	6.7	6.1	2.0	5.2	32	67.5
S-OC/151	0.64	7.1	6.5	1.9	4.9	33	66.7
S-OC/161	0.59	7.1	6.5	1.8	4.5	36	63.0

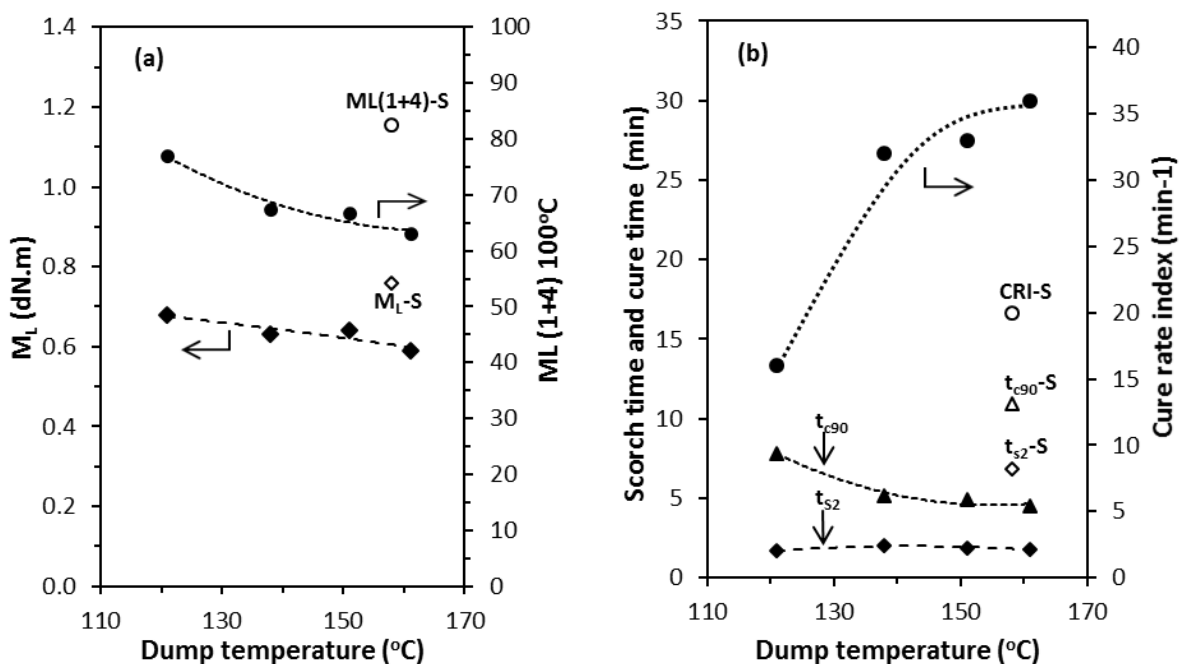


FIG. 3. — Effect of dump temperature on minimum cure torque, Mooney viscosity (a) scorch time, optimum cure time and cure rate index (b) of silica/OC-filled NR compounds, in comparison with pure silica-filled NR (S).

Increase of the dump temperature reduces the optimum cure time ( $t_{c90}$ ) and increases the cure rate index (CRI) of silica/OC-filled NR significantly, while scorch time ( $t_{s2}$ ) remains at a similar level. For dump temperatures above 135 °C, the silica/OC-filled system shows a faster cure rate than the pure silica-filled NR, as seen in Table II and Figures 3(b). It is well known that the silanol-groups on the silica surface retard the vulcanization reaction due to their acidic nature [26] and their hydrogen bonding with polar cure accelerators, The greater extent of silanization as promoted by the higher mixing temperature results in less free silanol groups and so the cure rate index is raised by increasing dump temperature. However, as has been reported based on a model compound study that only approximately 25% of the Si-OH groups are able to react with the silane coupling agent due to limited accessibility of these silanol-groups for incoming silane molecules [27], the presence of small molecules such as amines, especially aliphatic amines [28] can provide a further shielding effect to increase the hydrophobation of the silica surface that is beneficial for the vulcanization reaction and interfacial compatibility. In the silica/OC system, as the OC employed was modified by 2HT modifier content of 47 wt%, these compounds have an additional effect from the ammonium-based modifying agent. This agrees with what was reported previously for synthetic rubber and OC added to a fixed amount of silica, that modified clay accelerates the vulcanization reaction

of the elastomer and decreases the activation energy ( $E_a$ ) of the vulcanization process [17,29]. The amine groups of the organic modifying agent on OC promote the faster curing reaction [30-35], i.e. higher CRI. So the presence of OC can be beneficial from a processing aspect, as it can increase the productivity and reduce the energy required for vulcanization.

## MECHANICAL AND DYNAMIC PROPERTIES

The tensile properties, i.e. tensile strength, elongation at break, 100% modulus (M100), 300% modulus (M300) and reinforcement index (M300/M100) of the silica/OC-filled NR compounds at different dump temperatures compared to the pure silica-filled NR reference are displayed in Figure 4. Tensile strength, elongation at break and reinforcement index show only small changes with dump temperature variation, in which tensile strength and reinforcement index marginally increase while elongation at break slightly decreases. When compared at the same dump temperature, tensile strength and moduli at 100% and 300% elongations of the silica/OC-filled NR are marginally higher than that of the pure silica-filled compound. Modulus at 300% shows dependence on the dump temperature as the values are increased until 151°C and thereafter decrease, most likely due to degradation again of the natural rubber at high temperature as mentioned previously. The change of M300 with dump temperature has the same pattern as that of the total bound rubber content (Figure 2b), as the increase of the interactions within the material restricts the deformation.

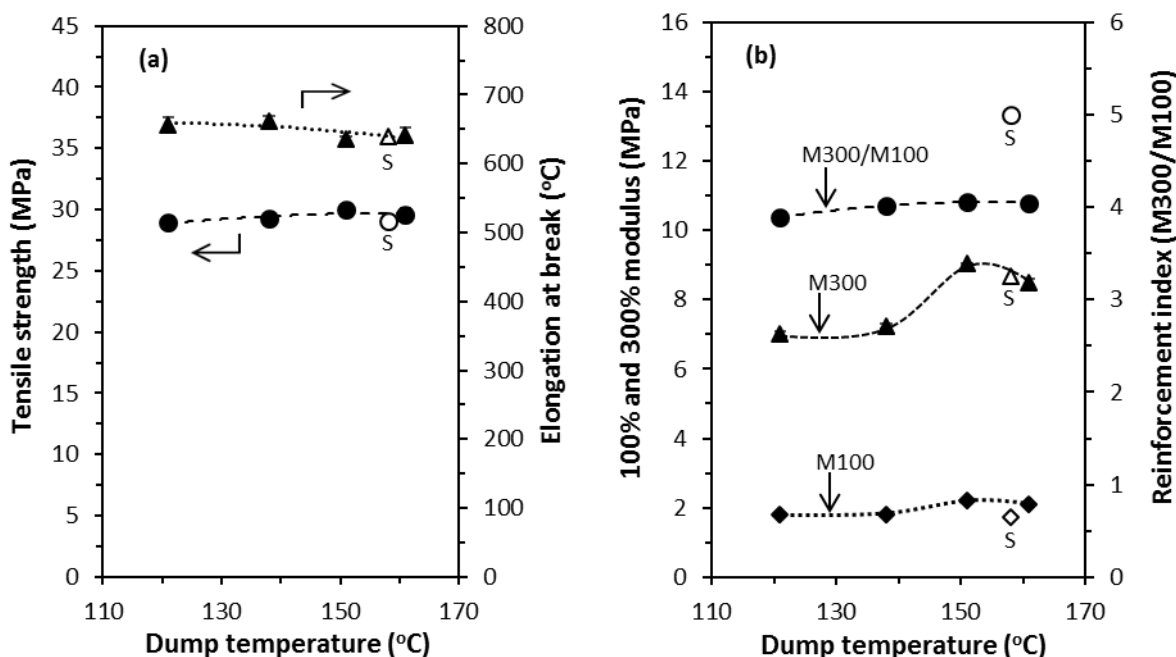


FIG. 4. — Effect of dump temperature on tensile strength and elongation at break (a) and moduli (b) of silica/OC-filled NR compounds, in comparison with pure silica-filled NR (S).

Tear strength and apparent crosslink density (Figure 5a) of silica/OC-filled NR are enhanced with increasing dump temperature to the optimum at 151°C, and thereafter decrease in accordance with the result of modulus (Figure 4b) and total bound rubber contents (Figure 2b). At its optimum, the silica/OC-filled NR compound shows the same level of tear strength but lower apparent crosslink density compared to the reference pure silica-filled one. The increase of dump temperature enhances the silanization reaction that results in more filler-rubber interactions and higher resistance to tear and deformation. The decrease of properties when the dump temperature reached 161°C confirms the oxidative degradation of NR at high temperature. The mixing of silica or silica/OC with NR therefore needs to avoid excessive heat input to have a good balance between the maximized silanization reaction and minimized NR degradation.

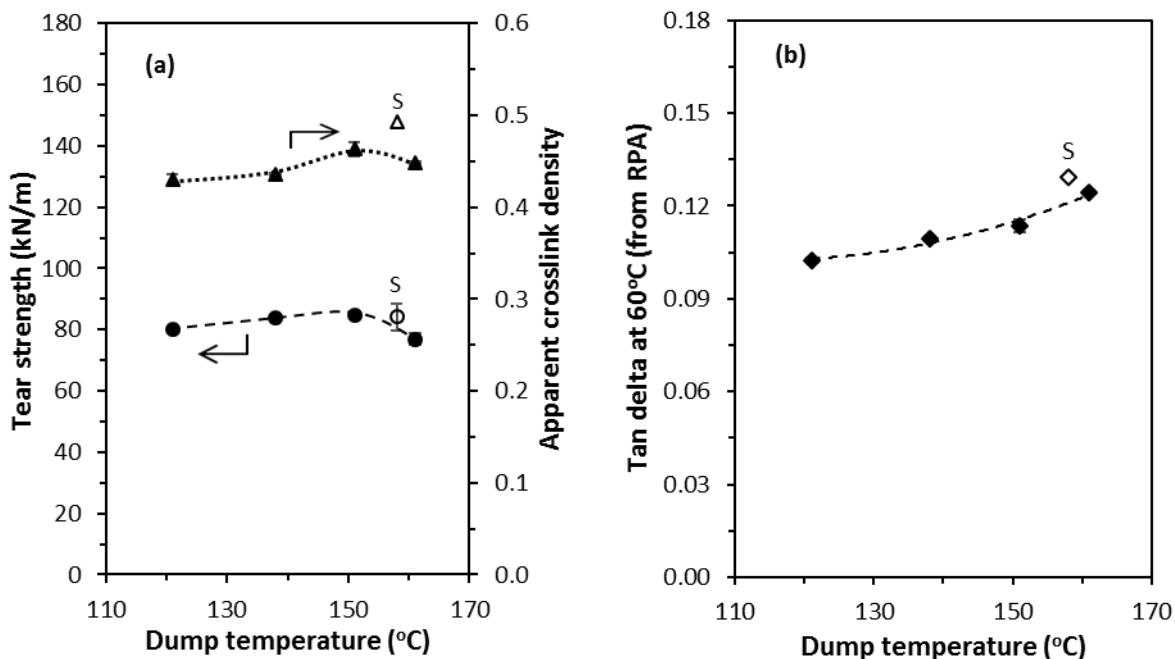


FIG. 5. — Effect of dump temperature on tear strength and apparent crosslink density (a) and tan delta at 60°C (b) of silica/OC-filled NR compounds in comparison with pure silica-filled NR (S).

Figure 5(b) shows the results of tan delta at 60°C of the rubber vulcanizates as tested by the RPA, useful to indicate tire rolling resistance on a laboratory scale [36]. Surprisingly, the tan delta values at 60°C of NR filled with silica/OC increase with increasing dump temperatures. The results are in contrast with the pure silica-filled NR compounds with various dump temperatures as reported by Kaewsakul et al. [8] where the increase of dump temperature reduced tan delta at 60°C. By considering the changes of compound viscosities, the increased dump temperatures increased the viscosities of the silica-filled NR compounds [8], but in the present work decreased the viscosities of the silica/OC system. The lower viscosity during mixing generated less shearing forces to disperse the filler. Even though a lower Payne effect generally used to indicate the filler-filler interaction was observed (Figure 2a), the presence of OC with high amount of modifying agent affects the storage modulus and plasticizes the system that results in a poorer elastic response and higher energy loss in the silica/OC-compounds compared to the pure silica-filled reference. However, at every dump temperature the silica/OC-filled compounds show lower tan delta at 60°C than the silica filled one, indicating its potential to be applied for decreased rolling resistance tires. Overall it can be concluded that a dump temperature of 150°C is best for the OC/silica compounds, just like observed before for pure silica compounds [8].



## EFFECT OF ORGANOCLAY LOADINGS ON THE PROPERTIES OF SILICA/ORGANOCLAY-FILLED RUBBER COMPOUNDS

By taking the initial mixer temperature setting of 100°C that results in the dump temperature of approximate 150°C as the optimum, the silica/OC-filled NR compounds with different loading levels of OC were prepared and the properties were evaluated in comparison with pure silica-filled NR compounds.

### MIXING BEHAVIOR

The dump torques and dump temperatures of the NR compounds filled with silica/OC hybrid filler with different loading levels of OC are given in Figure 6. The mixing torques after the addition of the second half of filler and the dump torques of silica/OC-filled compounds decrease sharply with the first loading of OC which can be due to a combination of different phenomena, to include the plasticizing effect derived from the organic modifying agent in the OC and the reduced silica network in the presence of the secondary filler. However, the increase of OC loading has no significant effect anymore on the dump temperature, as seen in Figure 6.

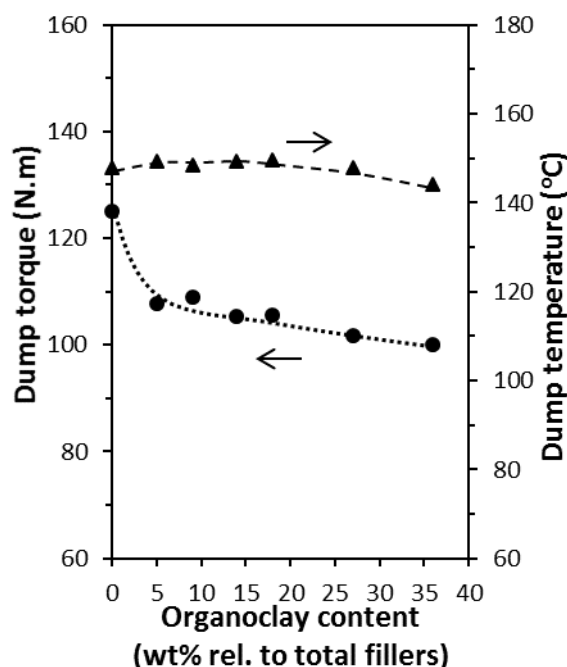


FIG. 6. — Dump torque and dump temperature of silica-filled NR compounds with varying loadings of organoclay (OC).

## FILLER-FILLER INTERACTION

The influence of OC loadings on the filler-filler interactions and the filler network can be derived from the change of storage modulus with strain as shown in Figure 7(a). From determining the difference of storage moduli values at low and high strains, i.e.  $G'$  0.56% and 100% respectively, the Payne effect is shown in Figures 7(b). The incorporation of OC remarkably reduces the storage modulus at low strain of the silica-filled compounds, especially in the range of 0-9 wt% relative to total filler amount; thereafter only a small reduction is observed when the OC amount is increased. The reduction of  $G'$ -modulus and  $\Delta G'$  by the modifying agent 2HT is in accordance with a previous observation [17] that described the effect of this lipophilic ammonium cation type as plasticizer, resulting in reduction of the modulus of the matrix. In addition to the reduced modulus of the rubber matrix as observed in the high strain range after the breakdown of the filler network, the presence of this modifying agent in the silica-filled compounds also remarkably reduces filler-filler interactions at low strain which can be due to a better silanization and additional shielding effect. Moreover, the presence of OC as secondary filler may interrupt the silica-silica network too. A large decrease is observed when the OC loading is increased to 9 wt% relative to the total filler level or at the ratio of silica/OC of 50/5 phr, thereafter the Payne effect decreases only slightly.

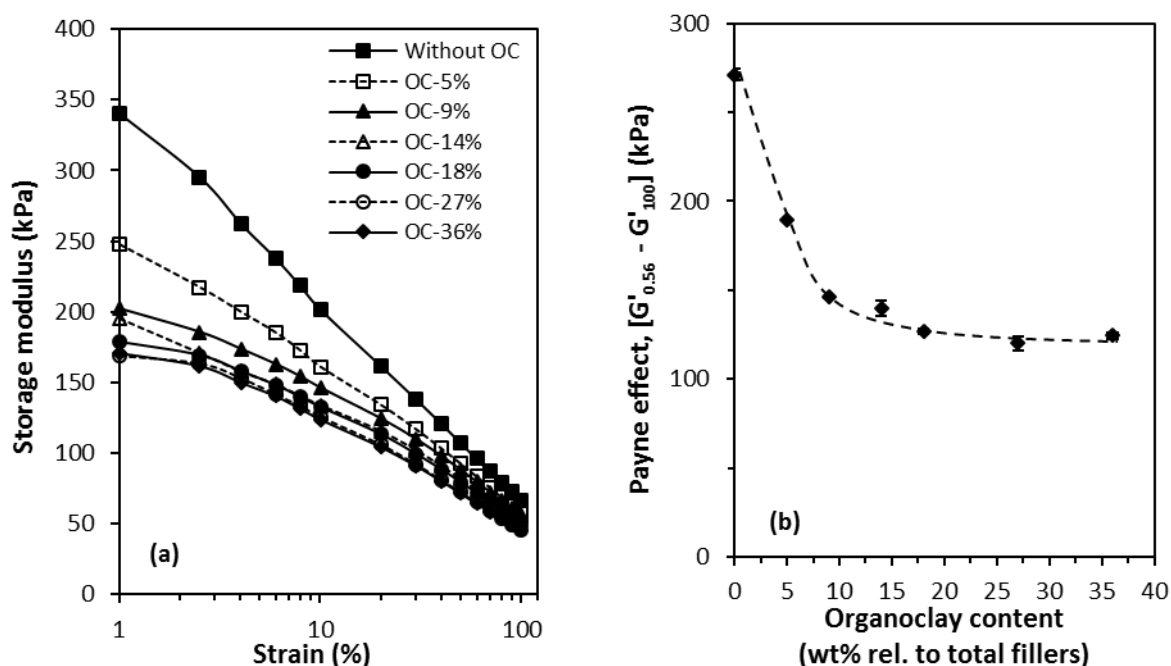


FIG. 7. — Storage modulus as a function of strain (a) and Payne effect (b) of silica-filled NR compounds with varying loadings of OC.

## COMPOUND VISCOSITY AND CURE PROPERTIES

The minimum cure torques ( $M_L$ ) and Mooney viscosities of NR filled with silica/OC decrease with increasing OC contents as shown in Figure 8(a) in line with the mixing torques as displayed in Figure 6. The suppression of the Payne effect by OC in silica/OC-filled rubber compounds in Figure 7 means that there is less filler network to obstruct flow and that the molecular chain mobility is enhanced. This again can be attributed to the effect of the modifying agent in OC as described in the previous part of this manuscript.

With regard to cure characteristics, the maximum cure torques ( $M_H$ ) and cure torque differences ( $M_H - M_L$ ) of the silica-filled NR compounds with different OC loadings are shown in Figure 8(b), and the scorch times ( $t_{s2}$ ), cure times ( $t_{c90}$ ) and cure rate indices (CRI) in Figure 9. The changes of  $M_H$  and  $M_H - M_L$  of the silica-filled NR compounds with increasing OC content resemble the change of compound viscosities. As stated in the first part of this study, the levels of  $M_H$  and  $M_H - M_L$  indicate the vulcanizate stiffness influenced by several contributions: chemical crosslinks by the vulcanization reaction, filler-rubber interactions and filler-filler interactions. The diminished filler-filler interactions as shown by the Payne effect in Figure 7(b) by the presence of OC play the most significant role in reducing the maximum cure torques.

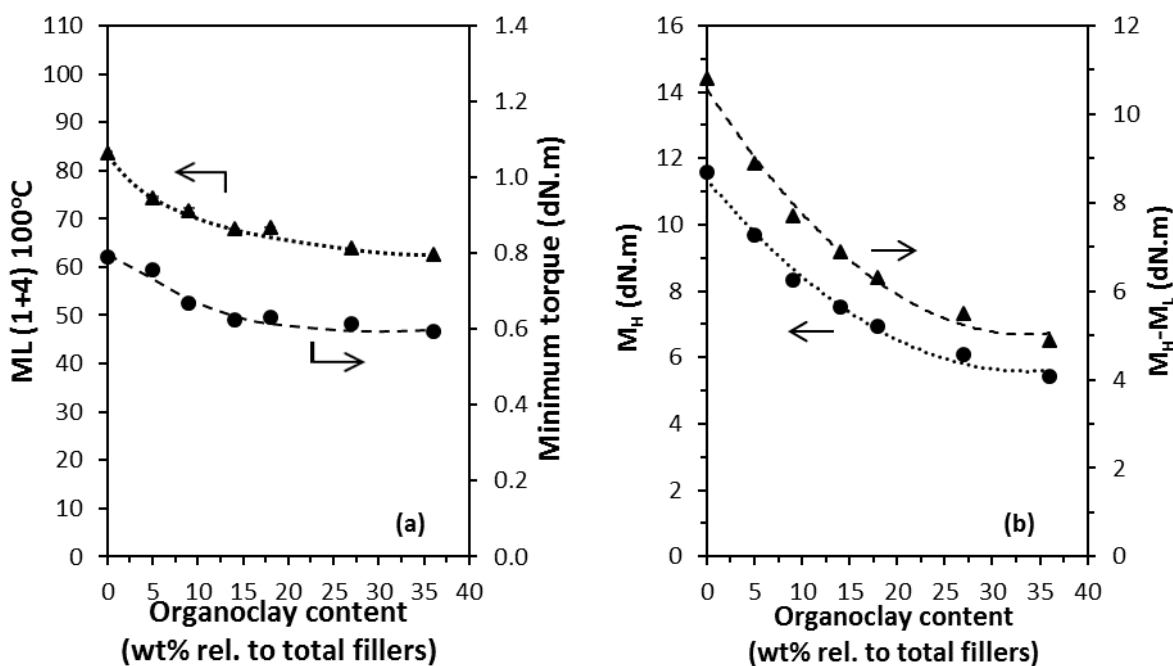


FIG. 8. — Mooney viscosity and minimum torque (a) and maximum torque and cure torque different (b) of silica-filled NR compounds with varying loadings of OC.

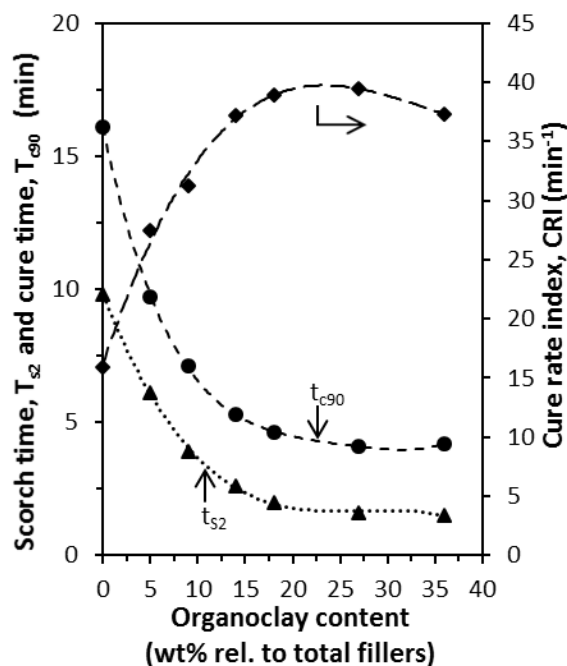


FIG. 9. — Scorch time ( $t_{s2}$ ), cure time ( $t_{c90}$ ) and cure rate index (CRI) of silica-filled NR compounds with varying loadings of OC.

The increasing loadings of OC significantly shorten both scorch and optimum cure times of the silica/OC-filled NR compounds due to an alkalinity of the organic modifying agent that accelerates the curing reactions resulting in the increase of CRI. The effect of organoclay on accelerating the curing reactions has previously been documented, but mainly for pure OC [30-35,37-39].

For the silica-filled NR compound, even though a silane coupling agent was utilized there are still some left-over silanol groups available, so accelerator adsorption and interference in the vulcanization reaction can still take place resulting in the longest scorch- and cure times. Galimberti et al. [17] indicated that the interaction between the cation and the sulfur based crosslinking system most likely via amine formation, was to promote higher interface crosslinking density.

#### MECHANICAL PROPERTIES AND APPARENT CROSSLINK DENSITY

Tensile properties of the NR compounds reinforced with silica/OC combinations are shown in Figure 10. Tensile strength, elongation at break and 100% modulus change marginally with increased loading of OC, but the 300% modulus (M300) shows a sharp drop

when the OC content is higher than 14 wt% relative to total fillers content: Figure 10b. With high OC content the plasticizing effect due to its modifying agent becomes dominant and so the rubber vulcanizates show less resistance to deformation at moderate 300% elongation. The reinforcement index ( $M_{300}/M_{100}$ ) of the silica/OC-filled NR compound consequently also tends to drop at higher loadings of OC.

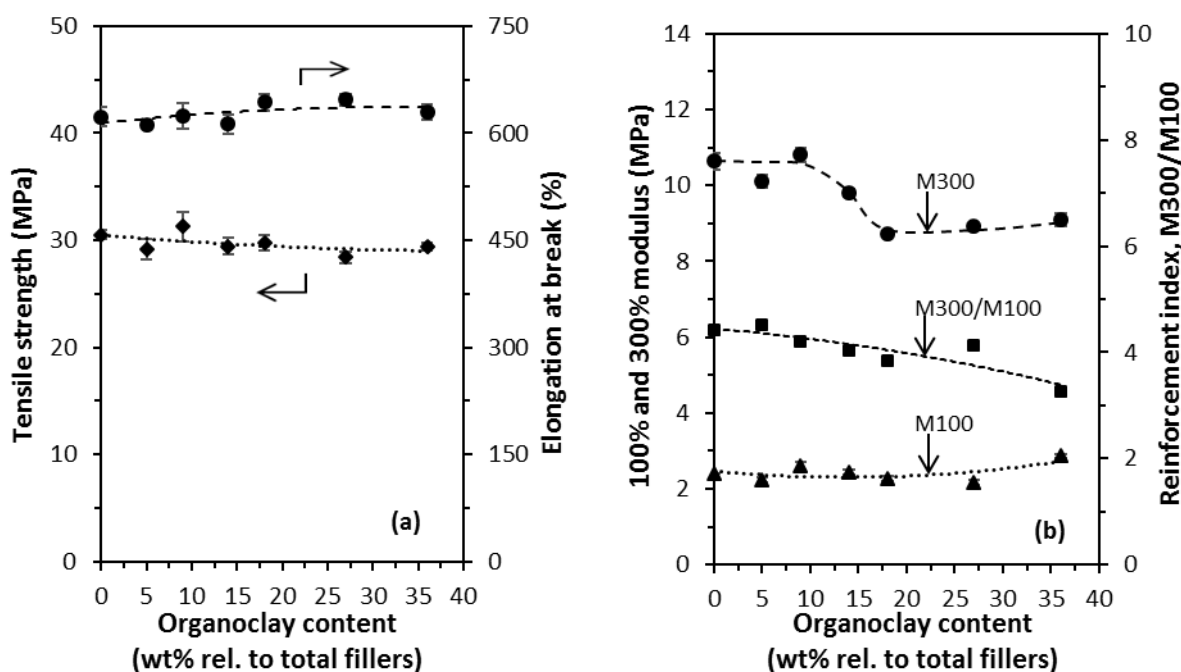


FIG. 10. — Tensile strength and elongation at break (a) and 100% modulus, 300% modulus and reinforcement index (b) of silica-filled NR compounds with varying loadings of OC.

The silica/OC hybrid filler shows a clear impact on tear strength, apparent crosslink density, abrasion resistance and Shore A hardness, as shown in Figure 11(a)-(b). The apparent crosslink density values are decreased with increasing contents of OC, in correspondence with the values of maximum cure torque ( $M_H$ ) and torque difference ( $M_H - M_L$ ) in Figure 8(b). Tear strength and DIN abrasion resistance index show a similar trend when the OC ratio is increased in the silica/OC-hybrid filled blends, with almost unchanged hardness level. Both properties are initially increased when the OC content is raised to 9 wt% relative to total fillers content or at 50/5 phr of silica/OC, and then decrease. Both sharply decrease when the loading of OC exceeds 18 wt% relative to total fillers amount. As the presence of OC in silica-filled compounds suppresses the filler network and reduces the apparent crosslink density, the excess amount of OC leads to a reduction of tearing energy and wear resistance. Moreover, as the modifying agent in OC plasticizes the system and causes a reduction in shearing force and

compound viscosity during mixing, some re-agglomeration of OC can also have taken place at high loading of OC resulting in deterioration of the present properties.

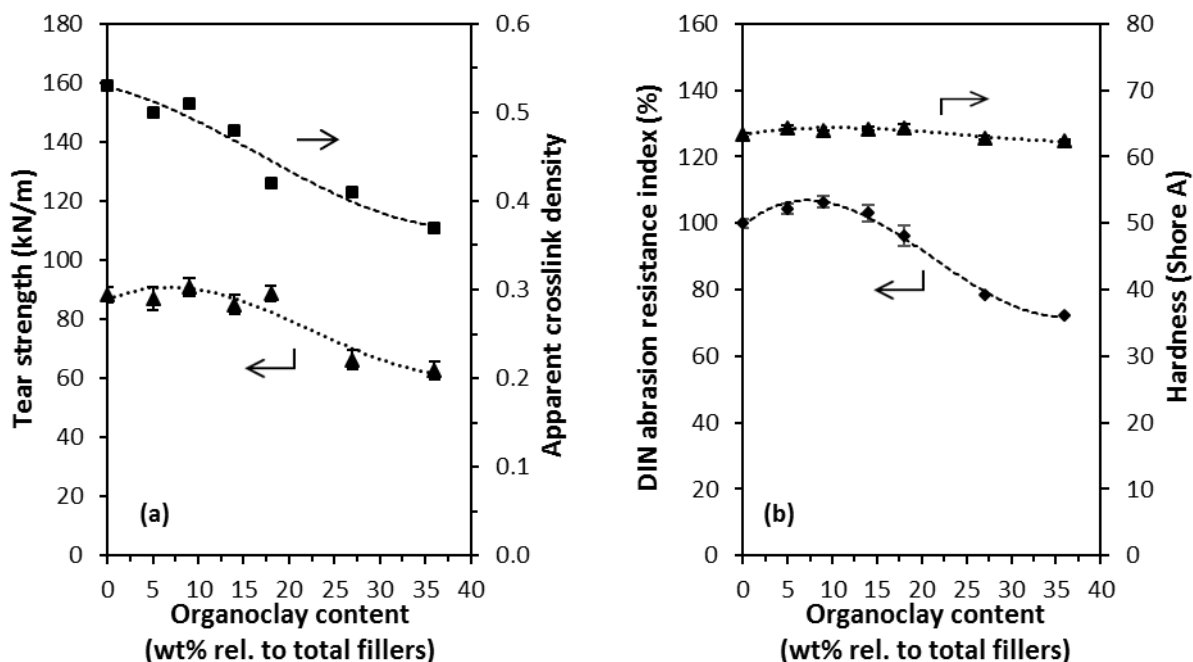


FIG. 11. — Tear strength and apparent crosslink density (a) and DIN abrasion resistance index (b) of silica-filled NR compounds with varying loadings of OC.

### SEM IMAGES AND DIN ABRADED SURFACES

Based on the slight improvement in abrasion resistance at low loading of OC, i.e. at silica/OC of 50/5 or at 9 wt% of OC relative to total fillers content, and the clear deterioration of this property at high OC loadings, it is of interest to look at the abrasion pattern of the surfaces. The SEM images of the DIN abraded samples of silica/OC-filled NR compounds with OC 9, 18 and 36 wt% relative to total fillers contents are shown in comparison with that of the pure silica-filled one, as shown in Figure 12. The abrasion patterns on the DIN abraded surfaces agree well with the abrasion resistance index. The compound with 9 wt% of OC relative to total fillers content that shows the best abrasion resistance demonstrates a smoother abraded surface with only small asperities. The ones with OC at higher contents, i.e. at 18 and 36 wt% relative to total fillers with poorer abrasion resistance, show larger asperities and a rougher surface in accordance with their inferior tear strength. The abrasion patterns indicate that the asperities for the weaker materials with higher loadings of OC can be torn off easier. So that, in order to achieve positive mechanical reinforcement, OC should be used in low amount,

below a certain threshold content [17]. It was reported earlier for 70 phr of silica-reinforced synthetic IR/SBR blends with the addition of Dellite 67G on top, that the threshold content of OC required to establish a hybrid OC-silica filler network was at about 7 phr, like found in the present study.

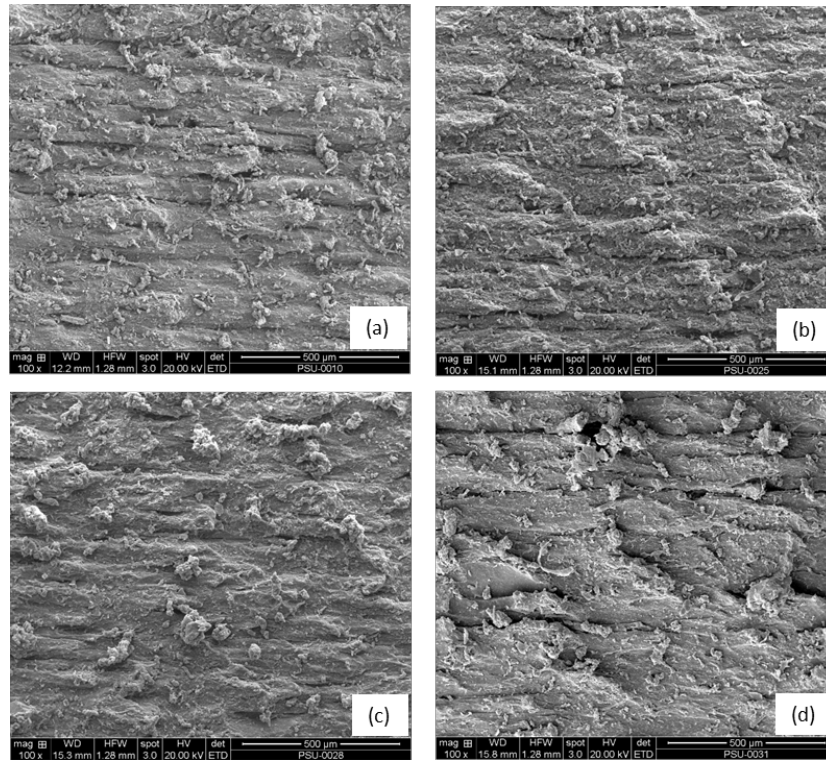


FIG. 12. – SEM photographs of DIN abraded surfaces of silica-filled NR compounds with various loadings of OC (a= 0%, b= 9%, c= 18% and d= 36%).

#### MORPHOLOGY OF ORGANOCLAY IN RUBBER MATRIX AS CHARACTERIZED BY X-RAY DIFFRACTION (XRD)

As discussed earlier that at high loading of OC re-agglomeration may occur, X-ray diffraction patterns of the compounds with 9, 18 and 36 wt% of OC relative to total fillers content were therefore characterized. The results are shown in comparison with the XRD pattern of OC (Dellite 67G) itself in Figure 13.

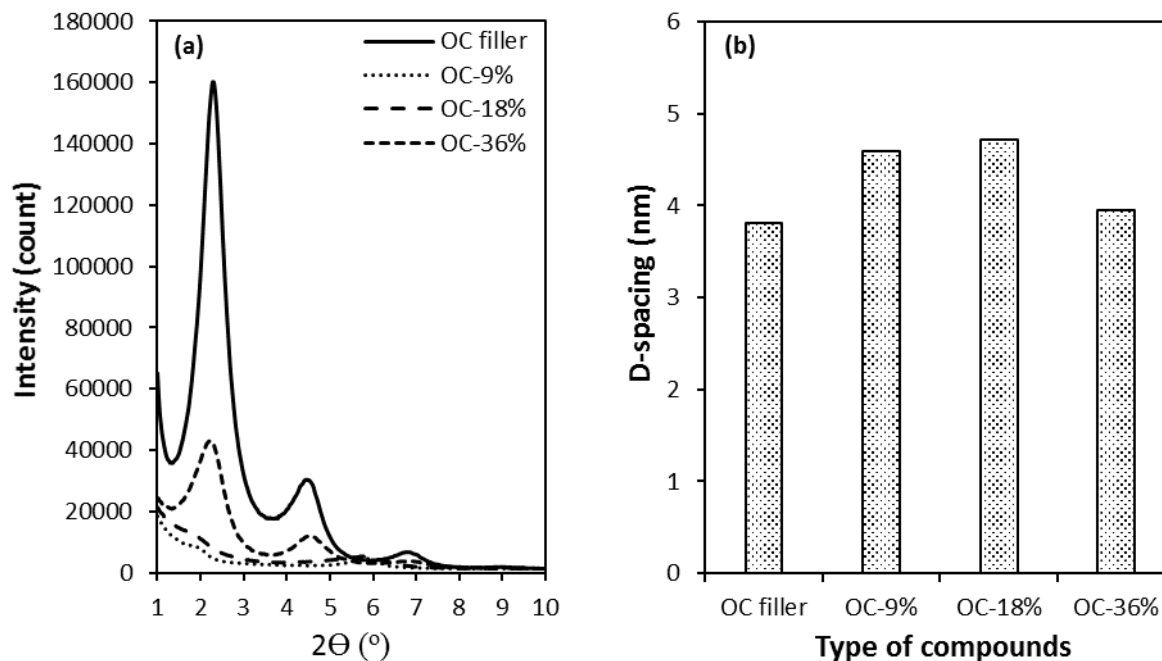


FIG. 13. — X-ray diffraction patterns (a) and d-spacing (b) of silica-filled NR compounds with various loadings of OC.

By applying Brag's law, d-spacing of the clay platelets can be determined. As shown in Figure 13(a), the rubber specimens with OC of 9 and 18 wt% relative to total fillers, show a very small trace of diffraction peaks with the  $2\theta$  values that can be converted to interlayer d-spacing as shown in Figure 13(b). An increased d-spacing is observed where the XRD pattern indicates that the OC is well intercalated in the NR matrix. However, at 36 wt% of OC relative to total fillers, the interlayer distance is slightly decreased again and the characteristic peaks of OC can be clearly observed, indicating re-agglomeration of the OC. The previous work on organomodified clay (Cloisite 20A)-filled natural rubber reported that nearly an exfoliated structure was observed at an OC concentration of 5 phr [38].

#### DYNAMIC MECHANICAL PROPERTIES

To further evaluate potential use of silica/OC systems to reinforce NR tire tread compounds, tan delta or the loss tangent values of the rubber vulcanizates are given in Figure 14. The tan delta at 60°C, indicative of tire rolling resistance, obtained from both RPA and DMA analysis (Figure 14a) shows a minimum value in the range of 9-14 wt% of OC relative to total fillers, i.e. 5-7.5 phr of OC. Thereafter, the tan delta at 60°C tends to increase with increasing the OC content, especially after exceed 18 wt% relative to total fillers. The poorer elastic response at high loading of OC is in accordance with the poorer mechanical properties



ascribed to the re-agglomeration of OC, the plasticizing effect by the modifying agent, and the silica-OC network beyond the threshold content. The reduced tan delta at 60°C of the compound with 5 phr of OC indicates that there is a potential to decrease rolling resistance of a tire when a suitable content of OC is used with silica.

Figure 14(b) shows the values of tan delta at -20°C and 0°C, indicative of ice and wet traction of the rubber vulcanizates respectively, as evaluated on the laboratory testing scale [36]. The tan delta at -20°C shows an optimum point at about 14 and 18 wt% relative to total fillers, i.e. at 7.5-10 phr of OC, whereas the tan delta at 0°C is increased with increasing the OC loading and the values are higher than that of the pure silica reinforced NR compound. This result also favors tire wet grip in addition to the better rolling resistance as indicated by tan delta at 60°C.

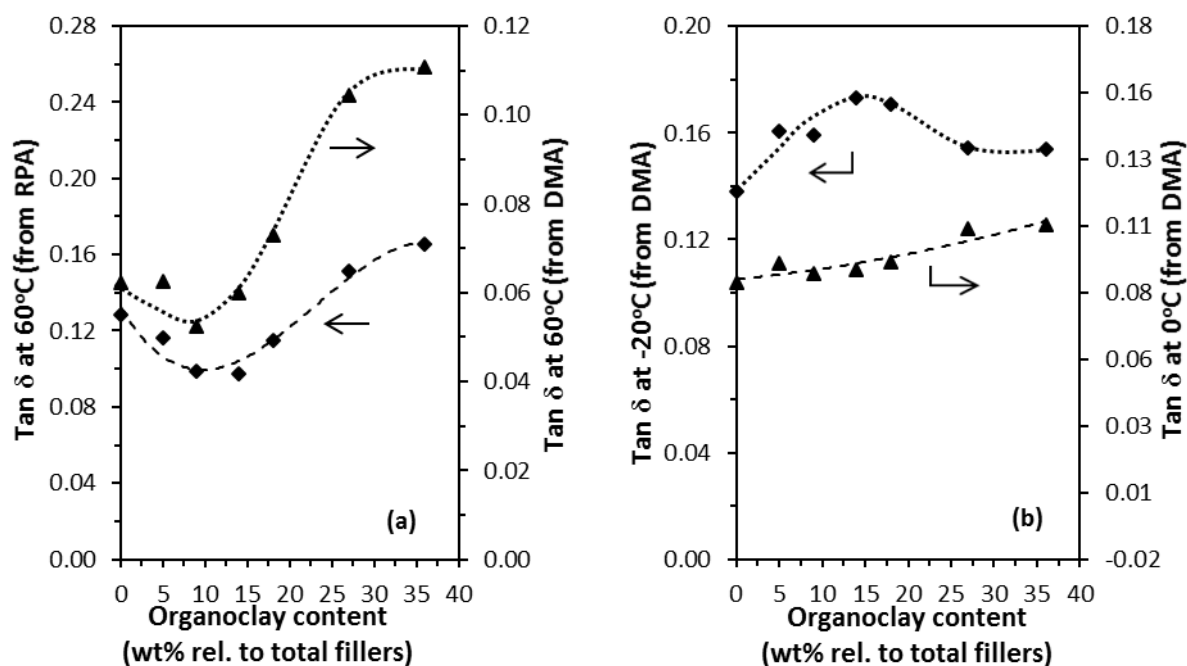


FIG. 14. — Tan delta at 60°C (a) and tan delta at -20°C and 0°C (b) of silica-filled NR compounds with various loadings of OC.

## CONCLUSIONS

The properties of pure silica and silica/OC (45/10)-filled NR compounds are affected by the mixing temperature. Increasing dump temperatures from 121 to 151°C improves the properties of both compounds and vulcanizates, but at 161° the properties are deteriorated due to natural rubber degradation. Based on the optimum initial mixer temperature setting at 100°C

to achieve a dump temperature at around 151°C, a comparison between silica-filled NR and the silica/OC-filled NR compound shows faster cure, lower Mooney viscosity, much less Payne effect and similar tensile and tear properties. For the silica/OC variant, when the loadings of OC were varied from 0-20 phr or from 0 to 36 wt% relative to total fillers content, the presence of OC only in small amounts, i.e. in the range of 2.5-7.5 phr or 5-14 wt% relative to total fillers results in a remarkable decrease in compound viscosity, Payne effect and scorch and cure times. The optimum silica/OC ratio is at 50/5 phr or at 9 wt% relative total fillers where the compound shows overall the best balance of properties. When compared to the pure silica-reinforced NR reference compound, the silica/OC combination provides compounds with lower Payne effect, higher cure rate index, similar tensile properties (modulus, tensile strength and elongation at break), and somewhat improved tear strength, DIN abrasion resistance index, and tan delta at 60°C. The silica/OC-filled NR compounds enable therefore overall processing benefits from easier flow and shorter cycle time, and by judicious incorporation of OC in combination with silica at the optimum ratio, i.e. at silica/OC ratio of 50/5 phr, the compounds show enhanced wear, rolling resistance, ice traction and wet grip, which are favored for tire applications.

## ACKNOWLEDGEMENTS

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