

Elucidating the role of clay-modifier on the properties of silica- and silica/nanoclay-reinforced natural rubber tire compounds

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Abstract. Organoclay (OC) is one of the potential secondary fillers to be applied in silica-reinforced rubber compounds for tire applications. Commercial OC contains a large proportion of surface modifier, *i.e.*, dimethyl dihydrogenated tallow ammonium chloride (2HT) type, that has an influence on the compound properties. To elucidate the effect of 2HT on the properties of silica-Natural Rubber (NR) compounds, a silica-only system, silica/OC, and silica/montmorillonite (MMT)/2HT added *in situ* during mixing, were comparatively studied. Irrespective in which form 2HT is added, it has potential to further enhance the performance of silica-NR compounds. Incorporation of 2HT suppresses filler flocculation and improves processability. Overall, the silica-only filled compound shows better mechanical properties than the silica/clay dual filler systems. The use of a small amount (2.4–4.7 phr) of 2HT improves 300% modulus, tear strength and abrasion resistance. The silica/OC gives better mechanical properties than the silica/MMT/2HT. With the optimum content of 2HT, a higher $\tan \delta$ at -20°C and lower $\tan \delta$ at 60°C can be achieved, all showing the beneficial potential of utilization of the modifying agent to improve wet traction and rolling resistance of silica-based tire tread compounds.

Keywords: reinforcement, rubber, nanoclay, surface modifying agent, silica

1. Introduction

Tires with better energy saving, safety and durability are required to meet more stringent customer's requirement as well as new legislations/regulations. Reinforcement materials such as carbon black (CB) and silica are added to rubber compounds to improve some basic requirement in properties such as modulus, hardness, tensile strength and tear resistance. Moreover, key tire tread performances which include wet traction, rolling resistance and wear need to be optimized. Tires generally contain 30–35% of CB of several grades that are used for different parts [1]. After 1992

when Michelin first introduced silica for passenger car tire tread compounds [2] showing that it could reduce rolling resistance and enhance wet grip, silica-reinforced tire treads became the subject of investigations worldwide in order to produce tires with better energy savings and driving safety [3]. However, mixing of silica into tire rubbers faces several difficulties such as poor dispersion and distribution in the rubber matrix, incompatibility with non-polar rubbers and poor filler-rubber interaction. To overcome those problems, silane coupling agents that contain sulfur in the structure such as bis-(3-triethoxysilylpropyl)tetrasulfide

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(TESPT) are generally used in silica-reinforced rubber compounds to promote silica-rubber interaction, better silica dispersion and also to suppress accelerator adsorption on the silica surface. As TESPT has some drawbacks like short scorch time and premature crosslinking in a rubber compound [4], so a silane coupling agent with lower sulfur rank like bis-(3-triethoxysilylpropyl)disulfide (TESPD) can be applied to provide better scorch safety. By mixing rubber with silica-TESPT or -TESPD silane coupling agents, the silanization reaction takes place during mixing and the extent of reaction is mainly governed by the mixing temperature [5–10]. The silanization reaction between silica and the silane coupling agent increases with increasing mixing discharge or dump temperature, as indicated by a reduction of filler-filler interactions, and an increase of filler-elastomer interactions. The optimum dump temperature for silica-reinforced NR compounds is in the range of 135–150 °C [9]. The extent of the silanization has a dramatic effect on the resulting compound properties [6, 7, 9]. The optimum mixing dump temperature for hybrid fillers of silica/OC and silica/CB (N134) in natural rubber (NR) compounds at 45/10 phr was recently reported [11]. Based on basic mathematical models and response surface methodology applied for styrene-butadiene rubber (SBR)/organoclay nanocomposites, the predicted and experimental data agreed that by increasing temperature and mixing time a better organoclay dispersion and tensile property was achieved [12]. Additionally, compatibilization between silica and NR by means of epoxidized natural rubber (ENR) as compatibilizer has been investigated. The results showed a reduction in Payne effect, enhancement of filler-rubber interaction and better silica dispersion by adding either ENR [13] or epoxidized low molecular weight natural rubber (ELMWR) [14] as compatibilizer when compared to the compound without ENR. Similar results were reported for the effect of silane-grafted NR as compatibilizer in silica-filled rubber tire compounds [15].

Nowadays, nanofillers attract a lot of interests for material development including rubber compounds for high performance products. This is due to their potential to improve compound properties at lower content used (usually less than 10 phr) as compared to conventional reinforcing fillers like CB and silica (usually higher than 30 phr) [16–18]. The large specific surface area of nanofillers provides larger contact

spots between polymer and filler. If the interfacial interaction between nanofiller and polymer is strong enough, an efficient stress transfer from the matrix to filler will be obtained. Nanoclay has been widely studied in rubber compounds because it has the potential to offer a very high degree of reinforcement, high thermal stability, improved impermeability to gases and liquids, good optical clarity, and enhanced flame retardancy [19]. The commonly used nanoclay layered silicates are 2:1 phyllosilicates including hectorite, saponite, montmorillonite, and synthetic mica. Montmorillonite (MMT) has been widely investigated due to its low cost, abundance in nature, high surface area, high aspect ratio, and good surface reactivity [19]. However, original MMT appears in the form of stacks of clay platelets with hydrophilic silicate surfaces. So, it is incompatible with tire rubbers like NR, styrene butadiene rubber (SBR), butadiene rubber (BR). To enhance the dispersion and promote intercalation/exfoliation of clay in the rubber matrix, cation exchange with ammonium salts or phosphonium salts is the most commonly used technique to alter the hydrophilic to hydrophobic surface. The obtained material is called organically modified clay or shortly organoclay (OC) [20]. The OC may be dispersed in single platelets or small silicate stacks with a high aspect ratio of 50–1000 [21]. The use of OC as a single filler in elastomers shows an improvement in mechanical properties, thermal stability, wear resistance and gas impermeability. A study on microstructural evolution of rubber/clay nanocomposites during the vulcanization process showed that the intercalated structure of OC changed throughout the whole curing process, and the spatial distribution of OC was much better in a polar rubber matrix than in a non-polar rubber matrix [22].

The use of nanofillers alone cannot meet the requirements for most of high performance rubber products, especially for tire applications, that require a certain modulus and hardness level. A combination of nanofiller with conventional fillers either CB or silica is therefore an alternative. The idea is to obtain a synergistic reinforcing effect from each filler type. Hybrid fillers of silica with different types of fillers have been investigated such as silica/CB [23–28], silica/kaolin or China clay [29], silica/MMT [30, 31], silica/organomodified kaolin [32] and silica/OC [11, 33, 34]. The utilization of silica/kaolin clay hybrid fillers for a heavy-duty truck tire tread formulation based on NR [29] revealed that the best balance of

heat build-up and abrasion resistance was observed at the ratio of silica/clay at 60/20. The use of silica/MMT with TESPT in SSBR/BR tread compounds improved tensile strength and traction properties at low TESPT content while enhanced modulus, hardness, wear resistance and rolling resistance at high TESPT content [31]. Substitution of 5–10 phr of silica with the sodium salt of rubber seed oil modified kaolin in NR/BR blends [32] resulted in lower Mooney viscosity, higher cure rate, increased chemical crosslink density index and bound rubber content, indicating a higher extent of rubber-rubber and filler-rubber interactions. Moreover, the mechanical properties such as abrasion resistance, compression set, tensile- and tear strength of the blend vulcanizates were enhanced, as well as the dynamic properties that are beneficial for tire tread applications. A comparison between the use of silica 60 phr and silica/OC nanocomposite with a replacement of silica by 7 phr of OC in SBR showed that the silica/OC system gave better skid and rolling resistance with higher 100 and 300% moduli [33]. The reduction of filler networking in silica-based elastomeric nanocomposites with exfoliated OC resulted in improved mechanical reinforcement and reduced energy dissipation [34]. Our own recent work on a hybrid filler system of silica/ OC-filled NR at 45/10 phr [11] revealed several positive effects when compared to reference pure silica-NR compounds, as the hybrid filler gave lower Payne effect (*i.e.* lower silica networking), higher cure rate index (*i.e.* better productivity in terms of reduced product cycle time), higher $\tan \delta$ at -20°C (*i.e.* better ice traction), and lower $\tan \delta$ at 60°C (*i.e.* reduced rolling resistance).

The OC contains an organic modifying agent or cationic surfactant that is used to increase the *d*-spacing between clay layers and to change the clay surface characteristic to be more hydrophobic. The most important end groups of cationic surfactants are primary-, secondary- and tertiary-amino groups, and quaternary ammonium groups. The presence of this active surfactant in the rubber compounds also plays a role on the properties. The loading of a diamine salt of fatty acid, called a multifunctional additive, on a silica-filled NR compound [35] improved mechanical properties due to better silica dispersion and crosslink density. Modification of silica by cyclohexylamine [36] resulted in improvement of filler dispersion and mechanical properties, lower $\tan \delta$ value at 60°C , and higher crosslink density of silica-filled

NR. The use of alkanolamide at the optimum loading (5.0 phr) for silica-reinforced NR [37] resulted in faster vulcanization and better cure torque differences, tensile strength, 100 and 300% moduli, hardness and crosslink density. An application of a multifunctional additive, *N*-phenyl-*N'*-(gamma-triethoxysilane)-propyl thiourea (STU), in NR-silica composites resulted in a fine-dispersed structure of silica in the rubber matrix and enhanced tensile properties [38]. Based on the modification of MMT with different concentrations of octadecylamine (OCT) as organic modifying agent [39], an optimum OCT content was observed at 1.5 times the cation-exchange capacity of MMT as determined by a larger *d*-spacing of the clay and a higher degree of OC dispersion in the NR matrix that led to improved mechanical properties of the NR/OC nanocomposites. By varying the loadings of *N,N*-dimethyl- dodecylamine for MMT modification [40] for SBR-OC nanocomposites prepared by the latex mixing method that was later used to mix with silica to obtain hybrid filler compounds of silica/OC at 20/5 phr, with increasing the modifier content in SBR the scorch time and cure time decreased while the cure torque differences, tensile strength and wear resistance increased due to the increase of crosslink density and improved dispersion of the silicate layers in the SBR matrix.

Even though there are a large number of reports related to organoclay-rubber nanocomposites available, there is no previous work that extensively discusses the role of the nanoclay surface modifying agent on the silica-reinforced NR tire tread compounds. To fully explore and better understand the influence of the modifying agent in the OC that affects the rubber compound properties of a silica/OC dual system, this present work employs dimethyl dihydrogenated tallow ammonium chloride (2HT) which is a quaternary ammonium type of surfactant. The effect of modifying agent loadings on three different compound types: silica-filled NR, silica/OC-filled NR with the 2HT already included in the OC, and silica/MMT-filled NR compounds, which contain TESP as coupling agent, are investigated in comparison with a silica-only compound without modifying agent as reference. This is to comparatively elucidate the beneficial effect of the modifying agent when it is used for pretreated MMT (*i.e.* OC) or for *in situ* mixing of MMT in rubber, or as surface modifier for the silica-rubber matrix. The mixes are subjected to characterization in terms of cure characteristics, filler-filler

interactions, filler-rubber interactions, tensile and tear properties, DIN abrasion resistance, dynamic mechanical properties and morphology.

2. Experimental

2.1. Materials

The NR (Ribbed Smoked Sheet, RSS3) was locally produced in Thailand. Silica ULTRASIL 7005 and silane coupling agent TESPD were obtained from Evonik, Germany. Organoclay Dellite 67G, functionalized with 47 wt% of 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, Livorno LI, Italy. Montmorillonite clay was provided by Thai Nippon Chemical Industry, Thailand. 2HT was purchased from Sigma Aldrich. The other ingredients: treated distillate aromatic extract

oil (TDAE oil), diphenylguanidine (DPG), *N*-cyclohexyl-2-benzothiazyl sulfenamide (CBS), 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), zinc oxide (ZnO), stearic acid and sulfur were of commercial grade quality for the rubber industry.

2.2. Compound preparation

The NR based truck tire tread compounds were prepared using the formulations as shown in Tables 1–3. The amounts of TESPD and DPG were adjusted according to the silica content (Equations (1) and (2) [41]):

$$\text{TESPD [phr]} = 0.00053 \cdot Q \cdot A \quad (1)$$

$$\text{DPG [phr]} = 0.00012 \cdot Q \cdot A \quad (2)$$

Table 1. Formulations of silica-filled NR compounds with varying amount of modifying agent.

Ingredients ¹	Amount [phr]						
	Reference	1	2	3	4	5	6
ULTRASIL 7005	55.0	55.0	55.0	55.0	55.0	55.0	55.0
2HT	–	1.2	2.4	3.5	4.7	7.1	9.5
TESPD	5.0	5.0	5.0	5.0	5.0	5.0	5.0
DPG	1.1	1.1	1.1	1.1	1.1	1.1	1.1

¹Remark: All formulations are with NR 100 phr, TDAE oil 8.0 phr, ZnO 3.0 phr, stearic acid 1.0 phr, TMQ 1.0 phr, CBS 1.5 phr and sulfur 1.5 phr.

Table 2. Formulations of silica-filled NR compounds with organoclay as secondary filler.

Ingredients ¹	Amount [phr]						
	Reference	1	2	3	4	5	6
ULTRASIL 7005	55.0	52.5	50.0	47.5	45.0	40.0	35.0
Dellite 67G	–	2.5	5.0	7.5	10.0	15.0	20.0
TESPD	5.0	4.8	4.5	4.3	4.1	3.6	3.2
DPG	1.1	1.1	1.0	1.0	0.9	0.8	0.7

¹Remark: All formulations are with NR 100 phr, TDAE oil 8.0 phr, ZnO 3.0 phr, stearic acid 1.0 phr, TMQ 1.0 phr, CBS 1.5 phr and sulfur 1.5 phr.

Table 3. Formulations of silica/MMT-filled NR compounds with varying amount of modifying agent.

Ingredients ¹	Amount [phr]						
	Reference	1	2	3	4	5	6
ULTRASIL 7005	55.0	52.5	50.0	47.5	45.0	40.0	35.0
MMT	–	2.5	5.0	7.5	10.0	15.0	20.0
2HT	–	1.2	2.4	3.5	4.7	7.1	9.5
TESPD	5.0	4.8	4.5	4.3	4.1	3.6	3.2
DPG	1.1	1.1	1.0	1.0	0.9	0.8	0.7

¹Remark: All formulations are with NR 100 phr, TDAE oil 8.0 phr, ZnO 3.0 phr, stearic acid 1.0 phr, TMQ 1.0 phr, CBS 1.5 phr and sulfur 1.5 phr.

where Q is the amount of silica [phr] and A is the cetyl-trimethyl-ammonium-bromide (CTAB) specific surface area of the silica ($171 \text{ m}^2/\text{g}$).

The two-step mixing procedure is displayed in Figure 1. The first step was executed by using an internal mixer, Brabender[®] 50EHT, (Brabender[®] GmbH & Co.KG, Germany) with a mixing chamber volume of 70 ml, at a rotor speed of 60 rpm, fill factor of 70% and initial mixer temperature setting of 120°C in order to reach a dump temperature in the range of $135\text{--}150^\circ\text{C}$, as suggested in previous reports [9, 11]. For silica-filled NR and silica/MMT-filled NR, all of the modifying agents were added together with the first halves of silica, TESP and DPG. For silica/OC-filled NR, the OC was added with the first half of silica. The other halves of silica and TESP were later added together with TDAE oil in the second interval of the first mixing step. The second step was for the preparation of the reactive or final compounds by mixing the obtained masterbatches with the other halves of DPG, CBS primary accelerator, and sulfur by using the same instrument operated at a rotor speed of 30 rpm, fill factor of 70%, and an initial mixer temperature setting of 70°C . The OC loadings were varied at 0–20 phr at incremental steps, which possessed modifying agent contents from 0–9.5 phr, respectively. By taking the amounts of surface modifying agent in the OC as references, 2HT

was added to the silica-filled NR and silica/pristine MMT-filled compounds.

2.3. Sample characterizations

Characterization of filler-filler interaction: Payne effect

The storage shear modulus (G') of the unvulcanized rubber compounds with curatives were evaluated using a Dynamic Rubber Process Analyzer (D-RPA 3000, MonTech Rubber Testing Solutions, Germany) 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 calculated from the difference in G' at low strain (0.56%) and high strain (100%).

Characterization of bound rubber content (BRC)

An amount of 0.25 g of uncured compound (without curatives) was put into a metal cage and immersed in 40 ml of toluene for 7 days at room temperature, while the toluene was renewed every day. Then the sample was removed from the toluene, dried at 105°C in an oven for 24 h and weighed. The bound rubber content was calculated using Equation (3):

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

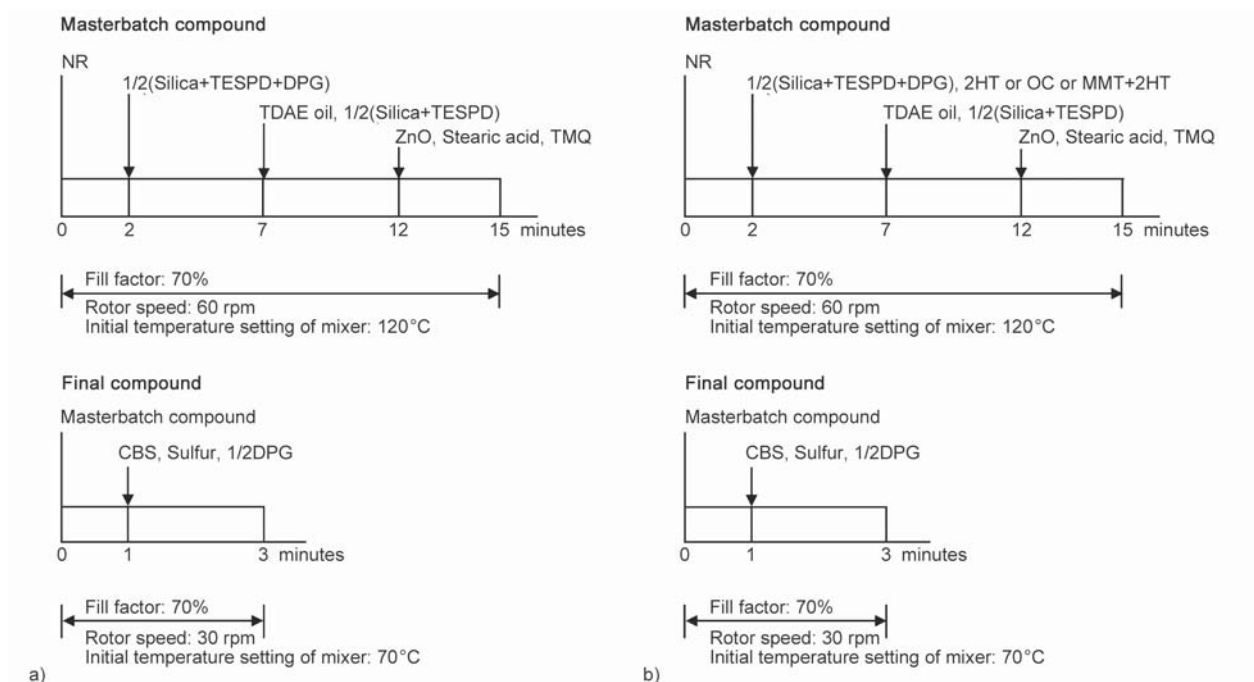


Figure 1. Two-step mixing procedures for compound preparations: (a) NR/silica without clay MMT or OC, nor 2HT; (b) NR/silica+2HT, NR/silica+OC and NR/silica+MMT+2HT compounds.

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.

Cure characteristics

The compounds were measured by using the D-RPA 3000, at a temperature of 150 °C, frequency 0.833 Hz and 2.79% strain for 30 minutes. The CRI was calculated to equal $[100/(\text{optimum cure time } (t_{c90}) - \text{scorch time } (ts2))]$.

Tensile and tear properties

The compounds were vulcanized for their optimum cure times (t_{c90}) by using a compression molding press (CT Compression Machine, Charoen Tut Co, Ltd, Samut Sakhon, Thailand) 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 tensile tester (Hounsfield Test Equipment Co., Ltd., Surrey, England) at a crosshead speed of 500 mm/min according to ISO 37. For tear strength, the vulcanized rubbers were tested at room temperature using Delft-type specimens with a Zwick tensile tester Model Z1.0/TH1S (Zwick Roell Group, Ulm, Germany) and the same crosshead speed as applied for tensile tests according to ISO 34-2.

Apparent crosslink density

Vulcanizate samples with a dimension of $3 \times 5 \times 2 \text{ mm}^3$ 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 Equation (4):

$$Q = \frac{M_t - M_0}{M_0} \quad (4)$$

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.* $1/Q$) [42], because the real crosslink density by for example the Flory-Rehner approach [43] is not feasible to acquire with the varying filler loadings.

DIN abrasion resistance index (ARI) and its abraded surface

The ARI was tested using a DIN abrader (GOTECH Testing Machines Inc, Taichung, Taiwan) according to method A of ISO 4649. The test specimens had a diameter of $16 \pm 2 \text{ mm}$ with a minimum thickness of 6 mm. The pure silica-filled NR without 2HT was used as reference rubber. The ARI was calculated according to Equation (5):

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

where Δm_r is mass loss of the reference rubber [g], d_r is density of the reference rubber [g/cm^3], Δm_t is mass loss of the test rubber [g], and d_t is density of the test rubber [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.

Dynamic mechanical properties

The loss tangent or $\tan \delta$ at 60 °C of the vulcanizates was determined using the D-RPA 3000 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 °C to reach their optimum cure times before being tested. In addition, dynamic mechanical properties of silica-filled NR vulcanizates under a temperature sweep from –80 to 80 °C were characterized by using a Metravib Viscoanalyzer VA 2000. The samples of a dimension of $6 \times 4 \times 2 \text{ mm}^3$ were tested in tension mode at a frequency of 10 Hz and 0.1% strain. $\tan \delta$ values at –20, 0 °C are used as indicative for ice traction and wet grip respectively, and $\tan \delta$ at 60 °C is to indicate rolling resistance of a tire tread.

3. Results and discussion

3.1. Filler-filler and filler-rubber interaction

The difference between the values of the storage modulus at low strain (0.56%) and high strain (100%) indicates the Payne effect that reflects the level of filler-filler interaction [44] as shown in Figure 2a. The increase of the modifying agents greatly reduces the Payne effect of all types of compounds to similar levels indicating a further reduction of filler networking

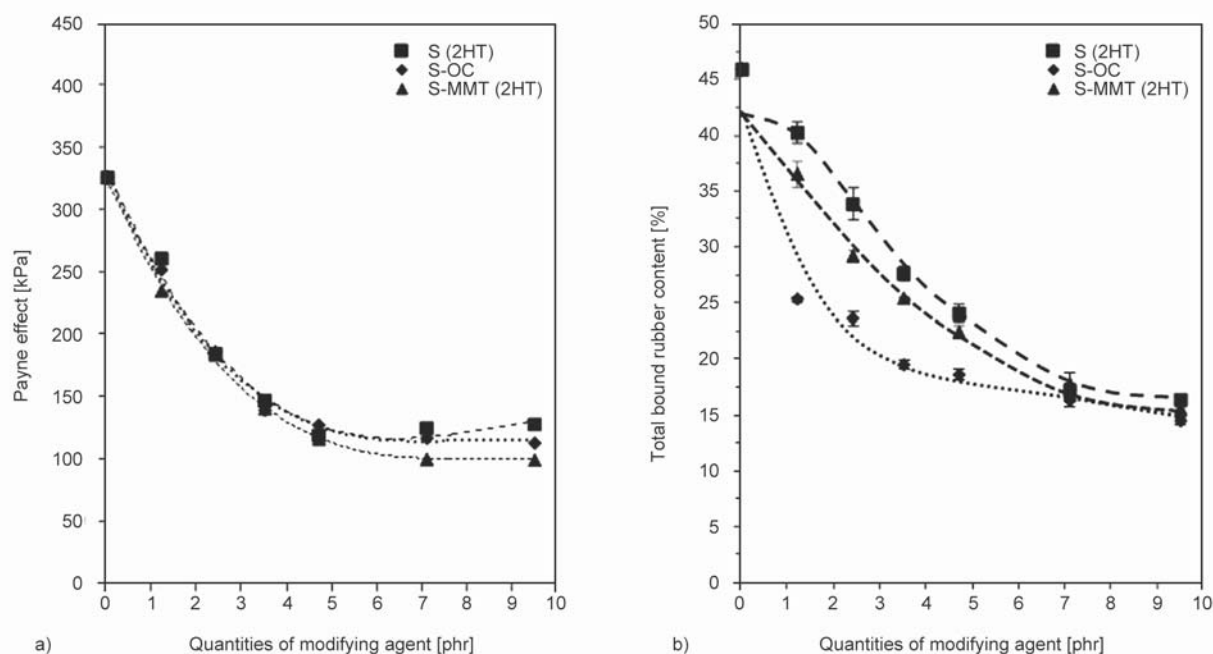


Figure 2. Payne effect (a) and bound rubber content (b) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

by the presence of 2HT, in addition to the effect of the silanization reaction between the alkoxy groups of TESPd and the silanol groups of the silica. As only a portion of the silanol groups could react with the silane due to the limited accessibility after the first silane molecules are grafted on to the silica surface, it has been reported that the availability of alcohols or amines to shield and increase the hydrophobization of the silica surface is helpful [45, 46]. By the incorporation of 2HT into the compounds, better hydrophobization and filler dispersion in the rubber matrix is obtained. Moreover, this 2HT may also enhance the silanization because of its basicity. The Payne effect of all the compounds decreases sharply with increasing modifying agent loadings up to 4.7 phr and thereafter tends to level off. This reduction in filler networking by the modifying agent is in accordance with work reported by Galimberti and co-workers for silica-based nanocomposites [34]. The presence of the quaternary ammonium salt also plasticizes the system and results in the reduction of the modulus of the filled-rubber, as observed in the range of high strain after the breakdown of the filler network.

The decrease of filler-rubber interaction is also reflected in the reduction of bound rubber content [47] as shown in Figure 2b. The sharp drop in bound rubber content with increasing modifying agent is in accordance with the fall in Payne effect in Figure 2a.

These results together indicate that the incorporation of 2HT as surface modifying agent contributes to physical interactions rather than chemical interactions. When comparing the bound rubber contents of the three systems, the silica-filled NR shows a higher bound rubber content than silica/MMT and silica/OC-filled NR. This indicates that the silica-filled NR with silane coupling agent has a higher filler-rubber interaction than the mixes with dual fillers of silica/MMT or OC. The reduction of bound rubber content was also observed in a carbon black/OC system due to the influence of the clay surface modifying agent [48].

3.2. Cure properties

Based on the cure characteristics shown in Figure 3 for all compound types, the incorporation of modifying agent clearly suppresses filler flocculation before the onset of vulcanization when compared to the pure silica without 2HT in which the flocculation is noticeably observed despite the use of TESPd in combination with silica. This filler flocculation manifests itself by the initial hub in the curing curve, before real vulcanization takes over. The addition of modifying agent has a strong influence on both cure torques and times. The minimum cure torque (M_L) indicates compound viscosity which is generally related to molecular chain entanglements of the polymer and filler-related parameters like type, amount,

filler-rubber interaction and filler-filler interaction or the filler network. When the filler content is increased and the formation of the filler network is enhanced, the M_L increases [49]. With increasing the modifying agent content in the silica-filled compounds, the M_L gradually reduces. As seen in Figure 2a, the Payne effect is greatly reduced by the addition of 2HT, so the filler-filler interaction is disrupted. In addition, the bound rubber content is also decreased with increasing the 2HT content. So, there is less obstruction to flow. Moreover, the modifying agent has a long tail structure of dihydrogenated tallow that can plasticize the system, causing increasing free volume between the high molecular weight elastomer chains to facilitate flow. Meanwhile, 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. For these various reasons, the rubber compound viscosities of every filler system: *i.e.* silica, silica/OC and silica/MMT, are remarkably decreased with increasing the modifying agent loading causing improved processability. It has been reported before that by substituting silica with OC, the compound viscosity was similarly affected [34, 50]. After vulcanization, the cure torque differences ($M_H - M_L$) of the silica-, silica/OC- and silica/MMT-filled NR compounds with different modifying agent

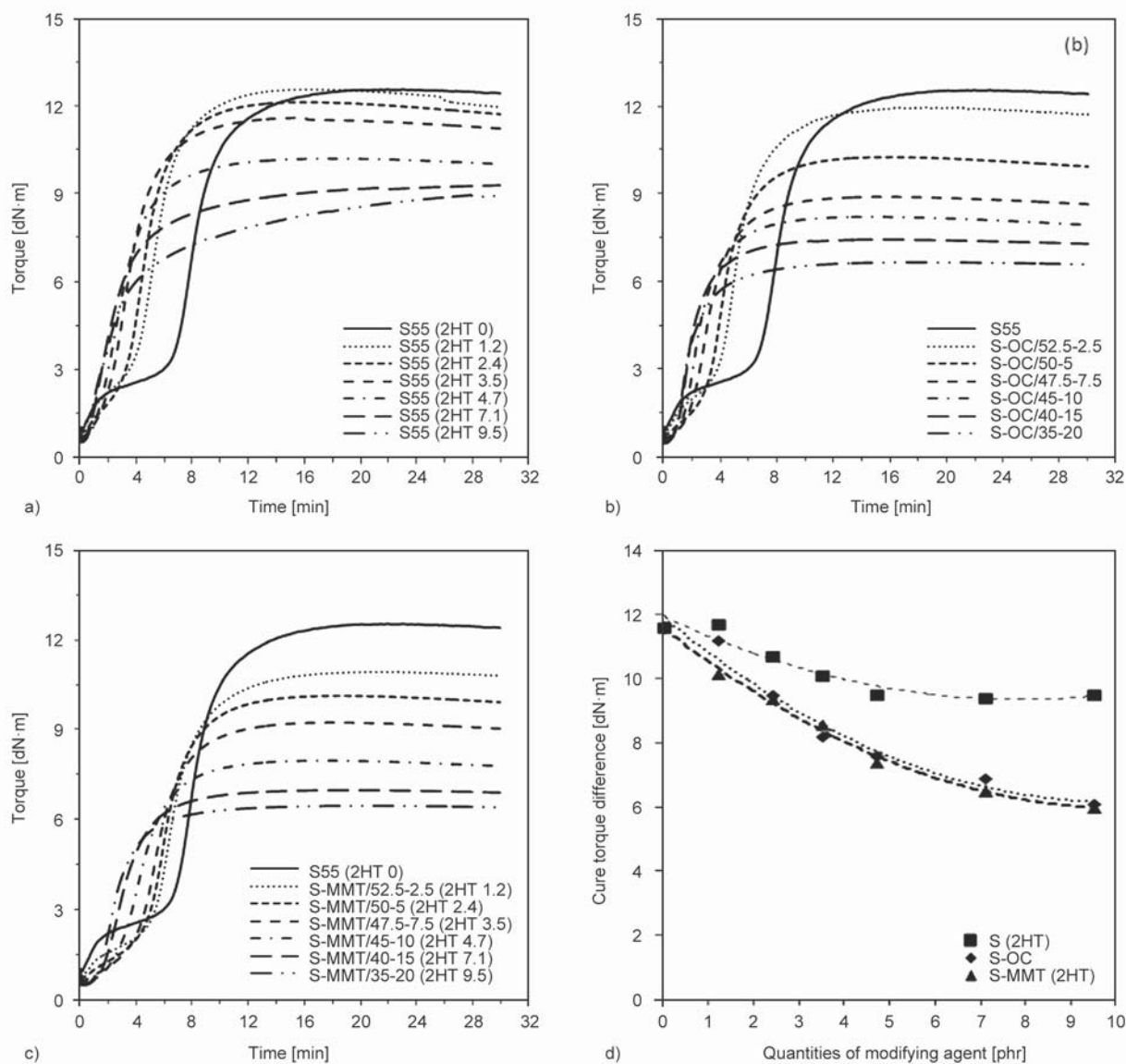


Figure 3. The effect of loadings of modifying agent (2HT) on the cure profiles of silica-filled NR (a), silica/OC-filled NR (b), and silica/MMT-filled NR (c) compounds, with varying loadings of modifying agent 2HT; and their cure torque differences (d).

loadings are shown in Figure 3d. Since the rheometer torque increases by formation of crosslinks, the cure torque difference or delta torque is related to the crosslink density. However, the levels of $M_H - M_L$ which indicate the vulcanizate stiffness are also influenced by several additional factors, combining contributions from chemical crosslinks by the vulcanization reaction, filler-rubber interactions and filler-filler interactions. As displayed in Figure 3d, the $M_H - M_L$ of all the compound types decrease when the modifying agent content is increased, but to different levels. The silica/OC-filled and silica/MMT-filled NR compounds show similar behaviors and the reduction in $M_H - M_L$ is much larger compared with the pure silica-filled NR. As the filler-filler interactions or Payne effect (Figure 2a) and filler-rubber interactions as indicated by bound rubber contents (Figure 2b) are not much different, the clear difference in $M_H - M_L$ of silica only-filled NR when compared to the mixes with OC and MMT is most likely derived from the filler network reformed due to flocculation, as distinctively displayed on the cure curves (Figure 3). The reduction of the cure torque difference when the modifying agent loading is raised, in addition to the reduced filler-filler and filler-rubber interaction with excess amount of the modifying agent, means that the crosslink density may be reduced as a result of diluting effects and interference with the polar curatives.

As the modifying agent is an amino-based compound composed of an ammonium salt, it has an accelerating effect on the vulcanization reaction, that can be beneficial by reducing the required processing cycle time. The increasing loadings of modifying agent progressively shorten scorch time of all the compound types studied, but a different behavior is observed for the cure time. For the silica/OC- and silica/MMT-filled NR compounds, the cure times are gradually reduced with increasing the modifying agent content, but for silica-filled NR the cure time decreases to reach a minimum at the 2HT content of 3.5 phr and thereafter increases again. As observed in Figure 3, the cure curves of silica-filled NR with the addition of 2HT start to show marching modulus torques when the modifying agent loading reaches 4.7 phr and marching is more pronounced at 7.1 and 9.5 phr of 2HT. In this pure silica system wherein the optimum content of silane coupling agent is used, the addition of the polar compound like the modifying agent in excess amounts may cause interference

with the vulcanization reaction, possibly due to interactions between the modifying agents and accelerators. For the compounds containing silica and OC or MMT, the delaminated clay introduces more polar functional groups on the edges that the modifying agent needs to shield. So, in these systems, there will be less free modifying agent to interrupt the vulcanization reaction. Comparing among the three systems, the use of silica/OC results in the shortest scorch time and cure time as the surface of pretreated OC should be most efficiently protected by the modifying agent. The effect of modifying agent in OC on accelerating the curing reactions has been previously documented by various authors [40, 51–58]. Overall, the benefit of adding 2HT in either form is that it substantially reduces the scorch time and optimum cure time, which otherwise are comparatively long in comparison with silica reinforced compounds. This greatly improves the vulcanization processability of pure silica reinforced compounds [59].

3.3. Mechanical properties and apparent crosslink density

The effect of modifying agent loadings on tensile and tear properties of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds are shown in Figure 4. The 100% moduli of all the compound types are quite similar with a tendency to reduce slightly with increasing modifying agent content. However, the modulus values at 300% elongation are different (Figure 4a). The silica/MMT-filled NR shows the lowest 300% modulus which decreases with increase of the modifying agent loading. While the 300% modulus of silica-filled NR and silica/OC-filled NR compounds show optimum values. The addition of small amounts of modifying agent increases the 300% modulus first but soon reaches a maximum and thereafter reduces. Optimum values are observed for 3.5 and 2.4 phr of 2HT for silica-filled- and silica/OC-filled NR compounds, respectively. For the silica/OC system, the optimum of 300% modulus is observed at a loading of OC of 5 phr which corresponds to 2.4 phr of modifying agent. The lowest modulus overall of the silica/MMT-filled system indicates poorest compatibility with the rubber matrix. The lower reinforcement effect of silica/MMT hybrid filler in rubber compounds compared to conventional silica was previously observed [30, 31] and interpreted as a result of hydrogen bonding between the silica and the polar surface of MMT

that lowers the compatibility between MMT and the non-polar rubber [20]. At higher content of modifying agent, a plasticizing effect becomes dominant and so the rubber vulcanizates show less resistance to deformation at moderate 300% elongation. It should be noted that for the filled systems, in addition to crosslink density, more complications arise from filler-rubber interactions, filler networking and interfacial adhesion between filler and the rubber

phase. The properties therefore can vary depending on the dominant factor in that compound. Tensile strength of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds increases slightly or remains at a similar level when the amount of modifying agent added is low as shown in Figure 4b. But this property starts to drop clearly after the modifying agent loading exceeds 4.7 phr as a result of a plasticizing effect and lower bound rubber

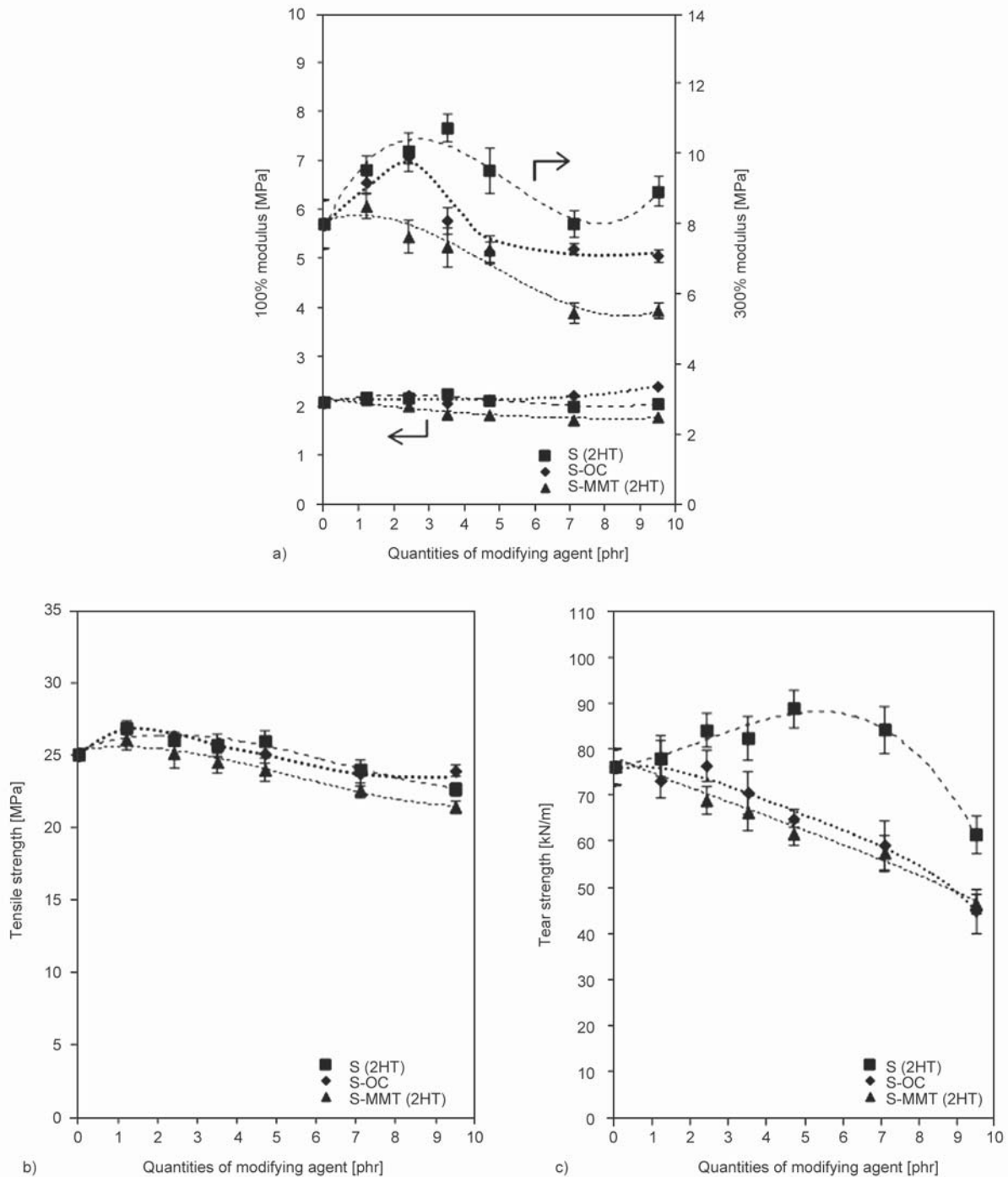


Figure 4. Modulus at 100 and 300% strains (a), tensile strength (b) and tear strength (c) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

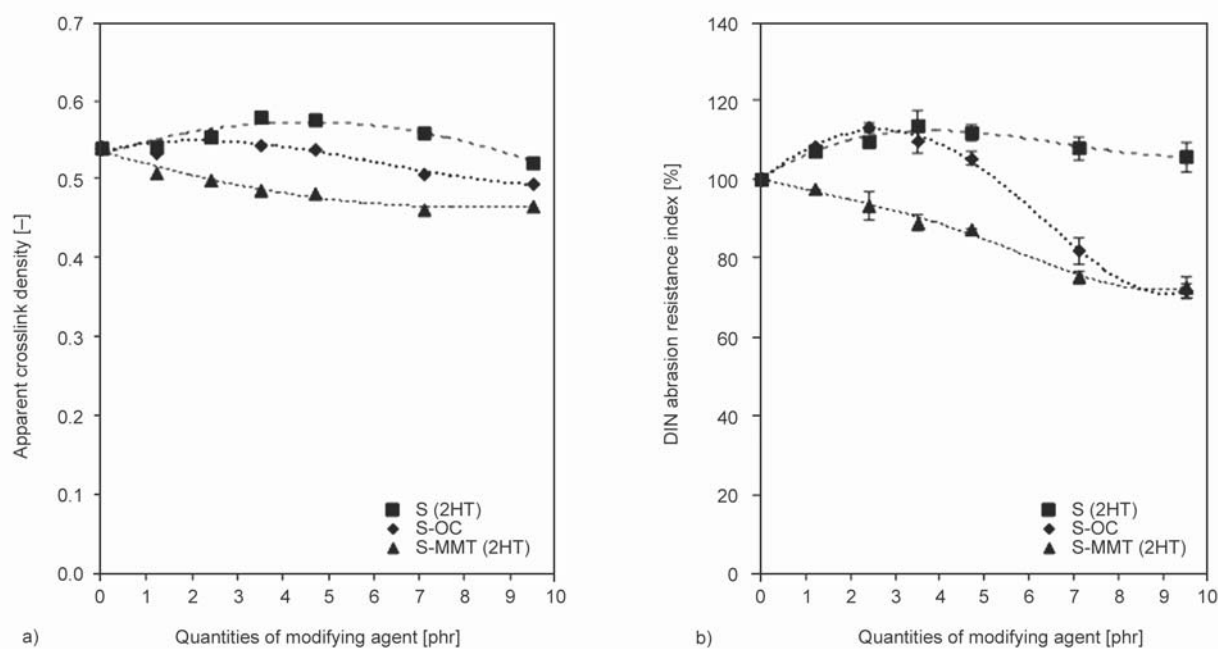


Figure 5. Apparent crosslink density (a) and DIN abrasion resistance index (b) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

content, in correspondence with a reduction of the apparent crosslink density as shown in Figure 5a. Tear strength (Figure 4c) shows a different response, to increase with the modifying agent loading in the compounds of silica-filled NR. It shows enhanced tear strength with increasing modifying agent loading up to 4.7 phr and thereafter decreases, whilst the silica/OC- and silica/MMT-filled vulcanizates show a continuous drop in tear strength. The loadings of modifying agent also have an influence on DIN abrasion resistance index as shown in Figure 5b. Silica-filled NR has the highest abrasion resistance and the incorporation of 2HT improves this property when compared with the one without. The silica/OC-filled NR shows an optimal DIN abrasion resistance index at 2.4 phr of modifying agent or at 5 phr for OC. But for silica/MMT-filled compounds, the DIN abrasion resistance index drops gradually with increasing amount of modifying agent.

3.4. SEM images of DIN abraded surfaces

The SEM images of the DIN abraded samples of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds containing different loadings of modifying agent are analyzed in comparison with that of pure silica-filled NR without modifying agent, as shown in Figure 6. The abrasion patterns of the DIN abraded surfaces agree well with the DIN abrasion resistance indices. The silica-filled compounds that have a higher DIN abrasion resistance index

show smoother abraded surfaces when compared to the silica/OC- and silica/MMT-filled compounds. The silica-filled NR with 9.5 phr of modifying agent in which the abrasion resistance starts to decrease shows more tear lines and larger asperities. For the silica/OC-filled NR compound that shows optimum abrasion resistance at the modifying agent of 2.4 phr, the abraded surface is clearly smoother than those with 4.7 and 9.5 phr of modifying agent. The lowest abrasion resistance of silica/MMT-filled NR compounds results in abraded surfaces with larger asperities and rougher surfaces. The asperities of the weaker material with higher loading of modifying agent can be torn off easier and become more visible on the abrasion patterns. The results are corresponding with their mechanical properties as tensile strength, 300% modulus, tear strength and apparent crosslink density. Overall, the silica only-filled NR compound shows better mechanical properties than the silica/clay dual filler systems. The use of silica/TESPD as silane coupling agent with a small amount (2.4–4.7 phr) of 2HT further improves the mechanical properties, *i.e.* 300% modulus, tear strength and abrasion resistance, as this modifying agent could provide an additional shielding effect on the silica surface. For silica/clay-filled compounds, the silica/OC gives better mechanical properties than the silica/MMT. The pre-modified OC gives a higher apparent crosslink density that is derived from better filler-rubber interaction compared to the use of pristine MMT with modifying

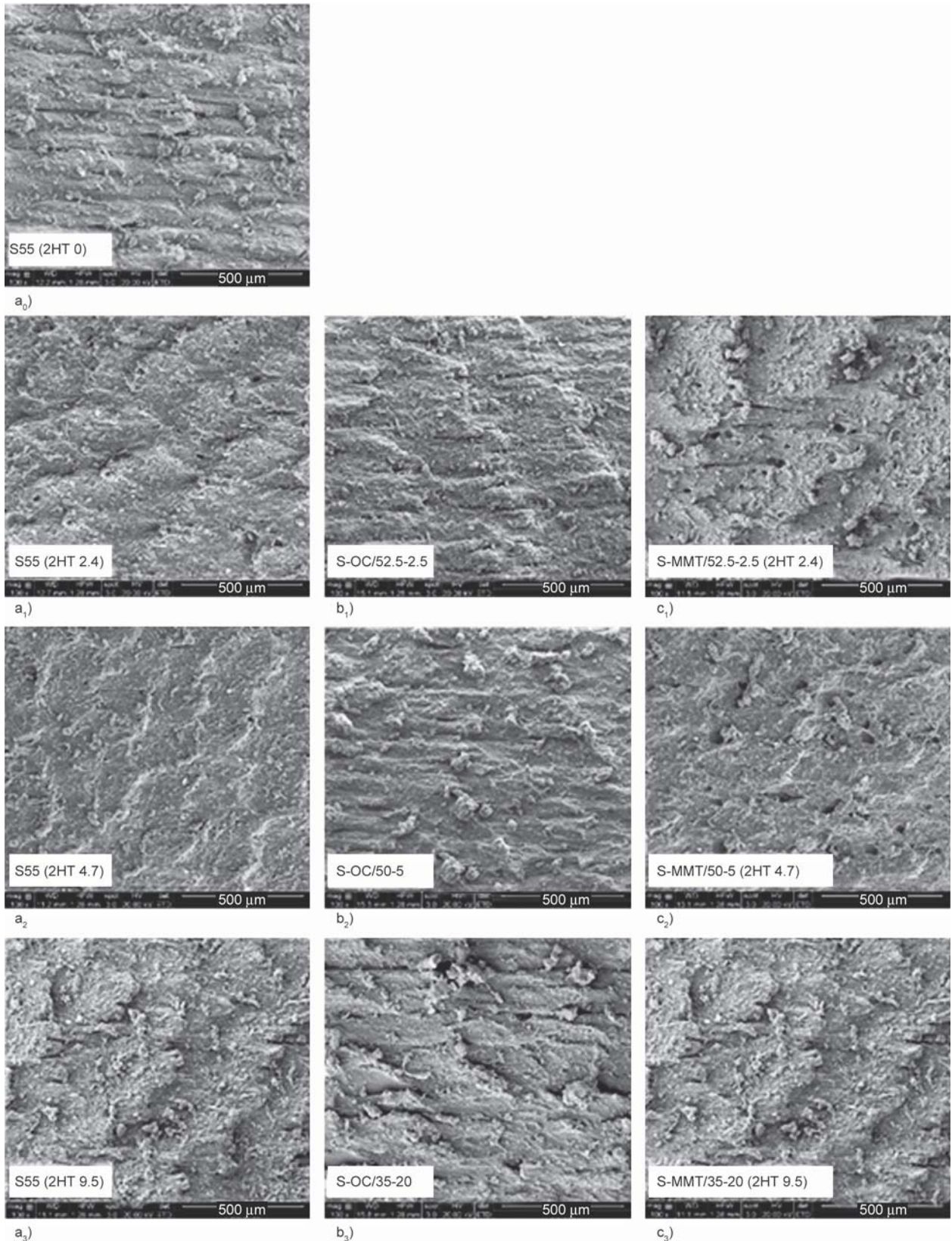


Figure 6. SEM photographs of DIN abraded surfaces of silica-filled NR (a), silica/OC-filled NR (b) and silica/MMT-filled NR (c) compounds with varying loadings of modifying agent 2HT (0–3).

agent added *in situ* during mixing. The optimum properties of silica/OC-filled NR are observed at 5 phr of OC that contains 2.4 of modifying agent.

3.5. X-ray diffraction (XRD)

Figure 7a shows the X-ray diffraction (XRD) patterns of Na-MMT and 2HT-modified Na-MMT

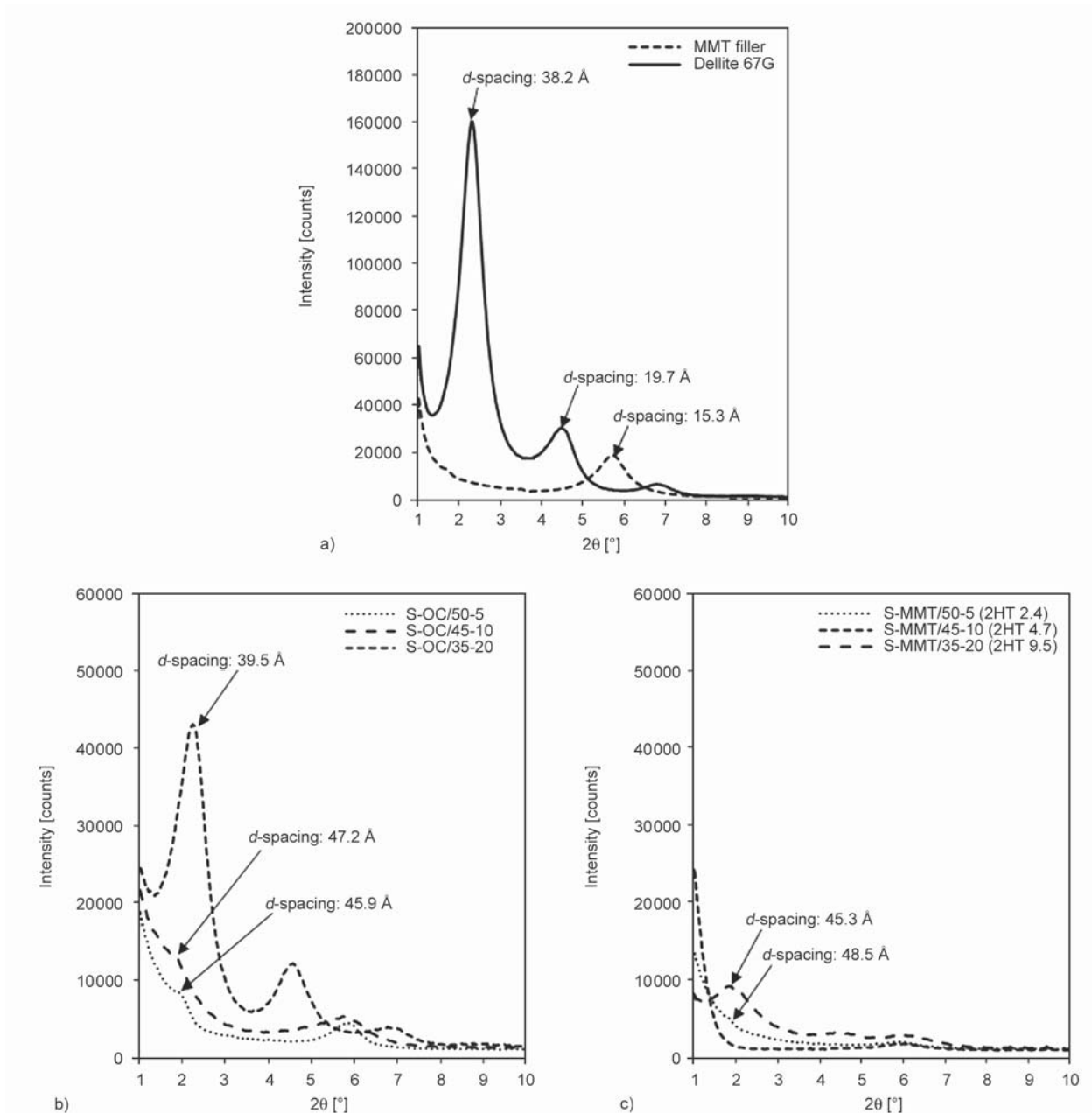


Figure 7. X-ray diffraction patterns and interlayer spacing of unmodified MMT and organically modified clay (a), silica/OC-filled NR (b), and silica/MMT-filled NR (c) compounds with varying loadings of modifying agent 2HT.

(OC). By applying Bragg's law, the interlayer spacing, called d -spacing, of the clay platelets can be determined. The maximum peaks of OC are shifted towards smaller 2θ angles than for the unmodified Na-MMT, indicating a larger d -spacing. The XRD pattern of Na-MMT shows a single peak of 2θ at 5.7° which corresponds to a d -spacing of 15.4 Å. The OC shows three peaks of 2θ , of which the two larger ones are at 2.3 and 4.5° that correspond to d -spacings at 38.2 and 19.7 Å, respectively. The larger d -spacing corresponding to the highest peak for OC is caused by the insertion of modifying agent molecules into the galleries of the pristine clay platelets. It was shown

previously that the OC with intercalated organic layers was due only to low molecular mass substances, essentially the ammonium cation, and no evidences for intercalation of polymer chains between two consecutive layers were observed [60, 61].

The XRD patterns of silica/OC-filled NR and silica/MMT-filled NR compounds with different amounts of modifying agent are shown in Figures 7b, 7c. Figure 7b shows the rubber specimens that contain modifying agent at 2.4, 4.7 and 9.5 phr or 5, 10 and 20 phr of the OC. An increased d -spacing is observed for 2.4 and 4.7 phr of modifying agent in the OC and the XRD patterns indicate that the OC is well intercalated

in the NR matrix because the peak at 2θ around 2° is only vaguely visible. However, at 9.5 phr of modifying agent or 20 phr of OC, the characteristic peaks of OC are clearly visible again with a d -spacing of 39.5 Å which is almost the same value as that of the pure OC (Figure 7a), indicating improper dispersion of the OC at such high concentration. It has been reported previously for organomodified clay (Cloisite 20A)-filled NR that an exfoliated structure was obtained at an OC concentration of 5 phr [57]. It remains a point of discussion whether the vague visibility of the OC-peaks at low loadings is a sign of exfoliation, or just a too low concentration to be able to be properly visible. The silica/MMT-filled NR compounds with varied loadings of modifying agent show different XRD patterns compared to that of silica/OC. The results in Figure 7c show that the materials having MMT of 5 and 10 phr, or with 2.4 and 4.7 phr of modifying agent, respectively, show no clear characteristic peaks of clay, which is often claimed to be an indication of exfoliation, but in the present case must be due to a too low concentration of the clay to be clearly visible [34]. However, at higher loading of MMT and modifying agent, *i.e.* at 20 phr of MMT and 9.5 phr of modifying agent, the silica/MMT-filled NR displays a clear peak again at the interlayer distance at 45.3 Å, indicating improper dispersion again of MMT in the NR matrix at high concentration as observed also in the case of silica/OC.

3.6. Dynamic mechanical properties

Figure 8 compares the values of $\tan \delta$ at -20 , 0 and 60°C of the silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR vulcanizates with varying loadings of modifying agent, taken from dynamic mechanical analysis in the temperature range from -80 to 80°C , at a frequency of 10 Hz and 0.1% strain. The viscoelastic properties of a tread rubber are temperature dependence [62]. For laboratory scale verification of tire tread compound performance, $\tan \delta$ values obtained from dynamic mechanical analysis (DMA) are commonly used. The $\tan \delta$ values between 0 and -40°C are used as indicators for wet and winter traction [63], whereas the $\tan \delta$ value at 60°C is indicative for rolling resistance [64, 65]. A positive correlation between the rolling power loss captured by the rolling resistance testing machine with $\tan \delta$ values obtained from DMA or RPA had been recently confirmed for NR composites [65].

Figure 8 are indicative of ice and wet traction of tire tread rubber vulcanizates respectively, as evaluated on laboratory testing scale [62, 63]. The $\tan \delta$ at -20°C shows some improvement with the addition of modifying agent but has no clear trend. The silica-filled NR and silica/MMT-filled NR compounds show optimum $\tan \delta$ values at -20°C at modifying agent content of 4.7 phr. However, there is no improvement of $\tan \delta$ at 0°C . The silica/OC-filled NR shows an optimum $\tan \delta$ at -20°C at 2.4 phr of modifying agent, or at 5 phr of OC loading, and then clearly drops at higher loadings of OC due to the re-agglomeration of clay platelets as shown by the XRD results in Figure 7b, while the $\tan \delta$ at 0°C shows comparable results as that of the pure silica-filled NR compound.

The $\tan \delta$ at 60°C is indicative of tire rolling resistance on a laboratory scale [62, 64, 65] in which a lower $\tan \delta$ value at a temperature of 60°C indicates a reduced tire rolling resistance. These results obtained from both RPA and DMA analysis are shown in Figures 8c, 8d. The $\tan \delta$ at 60°C of silica-filled NR is generally reduced with increasing modifying agent, while the silica/MMT-filled NR compound shows an optimum point at 4.7 phr of modifying agent content and the silica/OC-filled NR compound shows an optimum point at 2.4 phr of modifying agent or at 5.0 phr of OC loadings. With optimum loadings of modifying agent, lower $\tan \delta$ at 60°C can be obtained indicating the feasibility to reduce tire rolling resistance.

These combined results are summarized in the radar charts hereunder. Figure 9 shows the radar charts covering cure properties, Payne effects and mechanical properties of the compounds (Figure 9a), and tire performance lab-indicators (Figure 9b). The first chart is based on relative values versus the reference. While the chart concerning tire performance is based on index-values: the higher the better.

4. Conclusions

Overall, the addition of modifying agent to silica-reinforced rubber, either in the form of pre-modified MMT, or in combination with MMT or even added in pristine form to silica compounds, provides many benefits. Dependent on the properties of choice, different amounts of modifying agent need to be employed. The incorporation of modifying agent in a range of 0 to 9.5 phr in silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds

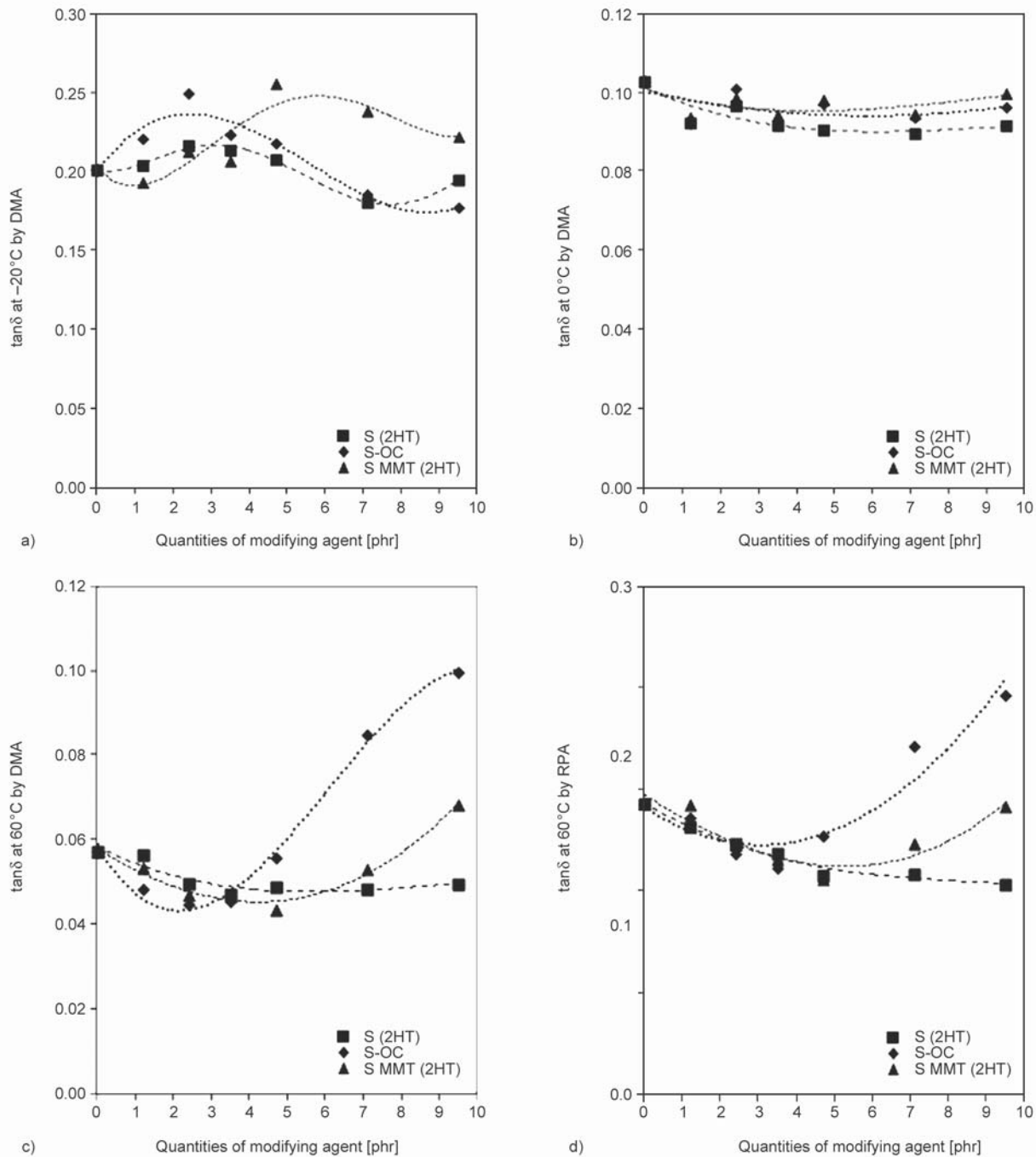


Figure 8. $\tan \delta$ at -20°C (a), $\tan \delta$ at 0°C (b), $\tan \delta$ at 60°C from DMA (c), and $\tan \delta$ at 60°C from RPA (d) of silica-filled NR, silica/OC-filled NR and silica/MMT-filled NR compounds with varying loadings of modifying agent 2HT.

results in a decrease of compound viscosity, Payne effects and scorch times. The optimum amount of modifying agent for silica-filled and silica/MMT-filled NR compounds are observed at 4.7 phr as seen in the best balance of properties, *i.e.* lower Payne effects, higher tensile properties (tensile strength, 300% modulus, tear strength), higher DIN abrasion resistance index, higher apparent crosslink density, higher $\tan \delta$ at -20°C and lower $\tan \delta$ at 60°C . For silica/OC-filled, an optimum loading of modifying

agent is observed at 2.4 phr or at 5.0 phr of OC where lower Payne effect, higher cure rate index, higher tensile properties and tear strength, higher DIN abrasion resistance index, higher apparent crosslink density, higher $\tan \delta$ at -20°C and lower $\tan \delta$ at 60°C are obtained. The shorter scorch time, lower compound viscosities respectively particularly indicate better productivity by reduced cycle times for vulcanization and better processability. The lower $\tan \delta$ at 60°C is an indication of improved rolling resistance

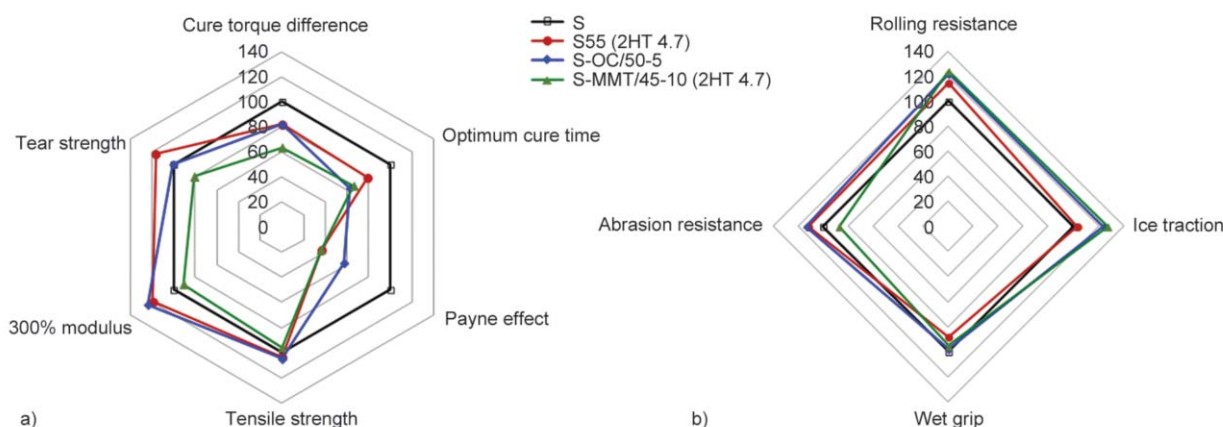


Figure 9. Radar charts comparing cure properties, Payne effect, tensile properties and tear strength (a), and key tire performances indicated by lab-indicators (b) of the NR compound filled with 55 phr silica without organoclay as secondary filler: reference (S), the 55 phr silica-filled NR compound with clay-modifier at an optimum amount of 4.7 phr (S55 (2HT 4.7)), the NR compound filled with 50 phr silica and 5 phr organoclay as secondary filler (S-OC/50-5), and the NR compound filled with 45 phr silica and 10 phr unmodified nanoclay plus clay-modifier at 4.7 phr (S-MMT/45-10 (2HT 4.7)).

which can be achieved with tire treads based on such compounds. Also the higher $\tan \delta$ at -20°C and DIN abrasion resistance index are indications for enhanced ice traction and wear resistance, which are favored for tire applications. So, irrespective in which form the modifying agent is added: included in OC or added separately, it has great potential to further improve NR/silica reinforced tire technology.

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