

The effect of coupling agents on silicate-based nanofillers/carbon black dual filler systems on the properties of a natural rubber/butadiene rubber compound

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Abstract

Nanofillers have been introduced a few years ago, but their application in elastomers is still a challenge. With the existing rubber processing equipment and constraints of rubber mixing, dispersion of nanofillers is difficult. The processability and performance of compounds containing plate- or tube-like silicates in a blend with conventional fillers, such as carbon black (CB), are investigated, and the effect of surface modification of the nanofillers is studied.

Processing is facilitated by the replacement of CB by the nanofillers, but curing efficiency is reduced. The dispersion of the fillers is improved with the addition of nanofillers. The dynamic properties of the cured composite material are affected, giving the composite material lower hysteresis, while the mechanical properties are merely affected by the addition of nanofillers. Additionally, the filler–polymer interaction is increased. The addition of a compatibilizing and coupling agent, a silane, has only a minor effect and does not improve processing and properties significantly for these combined filler systems.

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Introduction

Carbon black (CB) is widely used as a filler for elastomers due to its reinforcing properties. However, the production of CB causes pollution as it is prepared from petroleum feedstock. The replacement of CB with naturally occurring minerals is one way to reduce this environmental burden, and an alternative are mineral nanofillers, as they show an outstanding reinforcing potential due to their small particle size and high aspect ratio. This allows using a lower filler loading, which also has a positive effect on certain material characteristics, especially dynamic mechanical properties.

Nanoclays are layered silicates (LSs) such as montmorillonite, which is the most intensively studied silicate mineral. They are 2:1 phyllosilicates and consist of octahedral and tetrahedral sheets; octahedral layers of alumina or magnesia are placed between the tetrahedral sheets and they share oxygen atoms.¹ In order to achieve nanosized fillers, these layers need to be intercalated and exfoliated. The thickness of one single layer is approximately 1 nm. LSs are reported to have many benefits over conventional fillers, such as CB and silica; they reduce viscosity and gas permeability and increase strength, hardness, and moduli of the material at small concentrations.^{2–6}

Recent studies^{7–19} were also focused on halloysite nanotubes (HNTs), which are naturally occurring 1:1 aluminosilicates with tubular form. HNTs have silanol groups on the edges of the tubes which make the dispersion more difficult due to their interparticle affinity. Thus, the main challenges with both, LSs and HNTs, is to have good dispersion and polymer–filler interaction.

The most crucial aspect of getting a good property profile of an elastomeric material is interaction and adhesion between the polymer and the filler, especially in the case of nanofillers, with appropriate dispersion. In the special case of silicates, the chemical structure of the filler surface results in high interparticular forces, resulting in aggregation of the filler. This is the case for compounds with only nanofillers but also for filled compounds that contain a blend of conventional fillers and nanofillers, in which the latter in general is the minority component. The small particle size, that is large surface area, and high van der Waals forces between two particles make it difficult to properly disperse and distribute it in the matrix material.

A proven way to overcome the interparticular forces in rubber mixing is the treatment of the filler with a coupling agent such as silane. These coupling agents not only form a bond between the filler and the polymer during vulcanization, but also act as a covering agent. During mixing, they chemically react with the polar groups on the filler surface, resulting in reduced polarity and lower concentration of surface active groups responsible for the filler–filler interaction. This technology was successfully introduced for silica as filler and silane as coupling agent.²⁰ However, in the case of dual filler systems with the silicate as the minor component, dispersion and effective reaction of the compatibilization and coupling agent with the nanofiller is problematic due to its very low concentrations.

Bis(3-triethoxysilylpropyl)tetrasulfide (TESPT) is commonly used as a coupling agent in rubber applications with silica. TESPT is a bifunctional organosilane, which contains sulfur for chemically coupling the filler–silane complex to the polymer. As LSs and HNTs have partly the same chemical moieties on their surface as silica, silanol groups, it can be assumed that TESPT could be used as a coupling agent for these fillers as well. However, the concentration of OH groups on the HNT and silicate surface is lower than the concentration on the surface of silica, which is reported to be four to five silanol groups per square nanometer for precipitated silica.²¹ From these three silicate-based fillers, HNTs have the lowest silanol group density.²² This will result in a lower reaction rate and yield for the surface modification, and it has to be investigated if it still gives sufficient surface modification for improved dispersion and filler–polymer interaction and adhesion. The LS used in this study was activated by sodium (Na^+) ions, which increase the cation-exchange capacity and intergallery distances. The surface modification of these silica layers with silane is expected to improve dispersion, to stabilize the dispersed filler in the rubber matrix, and to provide a coupling between the silicate and the polymer. This should finally result in improved properties of the material. The HNTs are also expected to react with the coupling agent, and thus, to disperse easier and show a better filler–polymer interaction.

In this study, HNTs and LSs were treated with a silane. The effect of a partial replacement of CB by silane-treated nanoclays on the properties of rubber was investigated.

Experimental

Materials

LS used in this study was Nanofill 116 (Rockwood Clay Additives, Germany). This is a Na-modified silicate, which is expected to be easily dispersible compared with untreated LSs. It has a density of 2.6 g/cm^3 and a median particle size of smaller than $20 \text{ }\mu\text{m}$ in the nonexfoliated state. The HNTs were delivered by Sigma-Aldrich (St Louis, Missouri, USA). The diameter of the nanotubes was $30\text{--}70 \text{ nm}$ and the length varied between 1 and $4 \text{ }\mu\text{m}$. The specific surface area of these tubes was $65 \text{ m}^2/\text{g}$. Other compounding ingredients are specified in Table 1.

Test methods

The Mooney viscosity of the compounded material was measured using an MV 2000 Mooney Viscometer from Alpha Technologies (Washington, USA). The measurement included 1 min heating time and 4 min measuring time at 100°C . Curing studies were performed by using an Advanced Polymer Analyzer 2000 from Alpha Technologies (Akron, Ohio, USA). They were carried out at 150°C for 20 min, and the compounds were vulcanized at their respective curing times t_{90} at 150°C .

Tensile tests of the samples were carried out with a midi 10-20 universal tester (Messphysik Materials Testing, Austria) according to ISO 37 standard. Dynamic properties were studied with an Advanced Polymer Analyzer 2000 from Alpha Technologies at 60°C . A frequency of 10 Hz and 3.5% strain were used.

Table 1. Formulation of NR/BR compounds.

Ingredients	Type/producer	Amount of rubber(phr)
NR	SMR10	80
BR	Buna- <i>cis</i> -132/Dow Chemical Company	20
Nanofiller		0/1/2.5/5/7.5
N-234	Evonik	50/49/47.5/45/42.5
6PPD	Lanxess	2.0
TMQ	Lanxess	1.0
ZnO	Grillo Zinkoxid, GmbH	5.0
TDAE oil	Vivatec 500/Hansen & Rosenthal, GmbH	8.0
Stearic acid	Oleon N.V	2.0
Ceresine wax	Statoil wax, GmbH	1.5
CBS	Lanxess	1.5
Sulfur	Solvay Barium Strontium, GmbH	1.5

N-234: carbon black; 6PPD: *N*-(1,3-dimethylbutyl)-*N'*-phenyl-1,4-benzenediamine; TMQ: 2,2,4-trimethyl-1,2-dihydroquinoline; TDAE oil: treated distillate aromatic extract oil; CBS: *N*-cyclohexyl-2-benzothiazolesulfenamide; NR: natural rubber; BR: butadiene rubber; ZnO: zinc oxide.

Bound rubber (BDR) measurements were carried out by dissolving 0.2 g of uncured rubber in toluene for 96 h. Toluene was exchanged every 24 h. After 96 h, the samples were dried and weighed. The BDR content was calculated by the formula:

$$\text{BDR (\%)} = \frac{m_0 - (m_1 - m_2)}{m_0} \times 100,$$

$$m_0 = m_s \times \frac{100}{\text{cpd}}$$

where m_0 is the rubber content in the sample, m_1 is the combined weight of bag and sample, m_2 is the weight of the dried bag and sample, m_s is the weight of the dry sample, and cpd is the total amount of rubber and filler in the compound in parts per hundred.²³

The state of dispersion of the HNT particles in the natural rubber (NR)/butadiene rubber (BR) nanocomposites was investigated by scanning electron microscopy (SEM) using a Philips XL-30 model (Philips, Amsterdam, The Netherlands).

Material preparation

NR, BR, fillers, and other ingredients except curatives were mixed in a Krupp Elasto-merstechnik GK 1.5 E intermeshing mixer (Germany; mixing chamber temperature 50°C and rotor speed 70 rpm). After addition of the ingredients, the temperature was raised to 140°C and mixing was continued for 5 min at constant temperature to complete the silanization reaction. The accelerator and sulfur were added on an open two-roll mill. In the reference compound, only CB was used as filler with a concentration of 50 phr using the same mixing protocol. In the compounds with HNTs and LSSs, a certain amount of CB was substituted by the same amount of silicates/HNTs up to 7.5 phr.

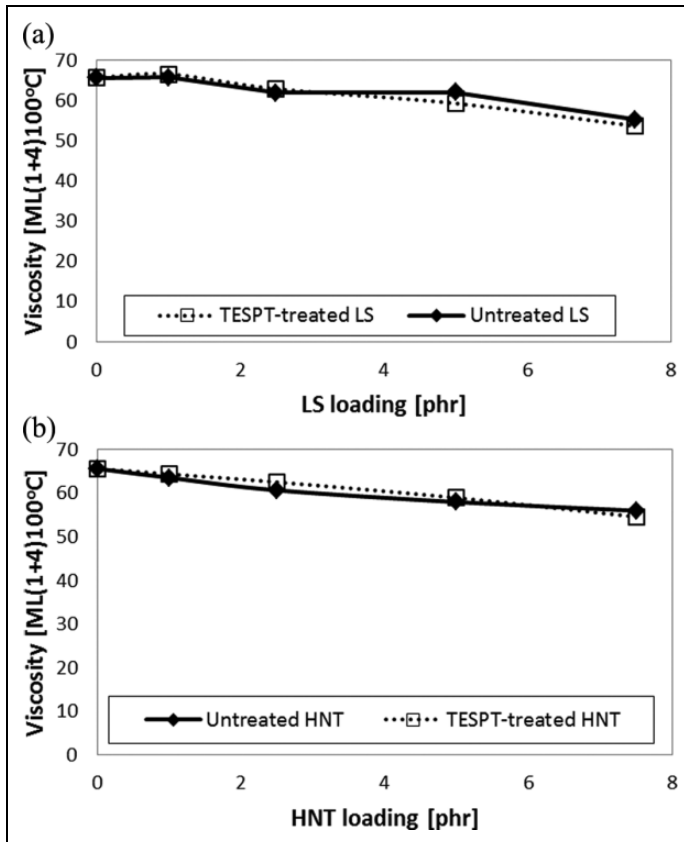


Figure 1. Mooney viscosity of the compounds with increasing amount of nanofillers, without and with silane, for (a) LSs and (b) HNTs. LS: layered silicate; HNT: halloysite nanotube.

Results and discussion

Figure 1(a) and (b) show the Mooney viscosity of the final compounds after the productive mixing step. The viscosity decreases proportionally with the amount of nanofiller added to the compound for both filler types. This might be due to better dispersion of the CB particles.

The curing behavior of the compounds is shown in Figure 2. The final torque of the compounds with just 1 phr of LS is similar to the final torque of the reference compound. Low quantities of LS do not influence cross-linking of the compound nor the final torque by a viscosity effect. For higher quantities, the final torque is lower, the higher the LS concentration, probably due to the viscosity reduction seen earlier.

Again, no difference in final torque is found between compounds with silane-modified and -unmodified LSs. No clear trend can be seen for the scorch time. Ismail and Mathialagan reported the decrease in scorch time when silica and calcium carbonate

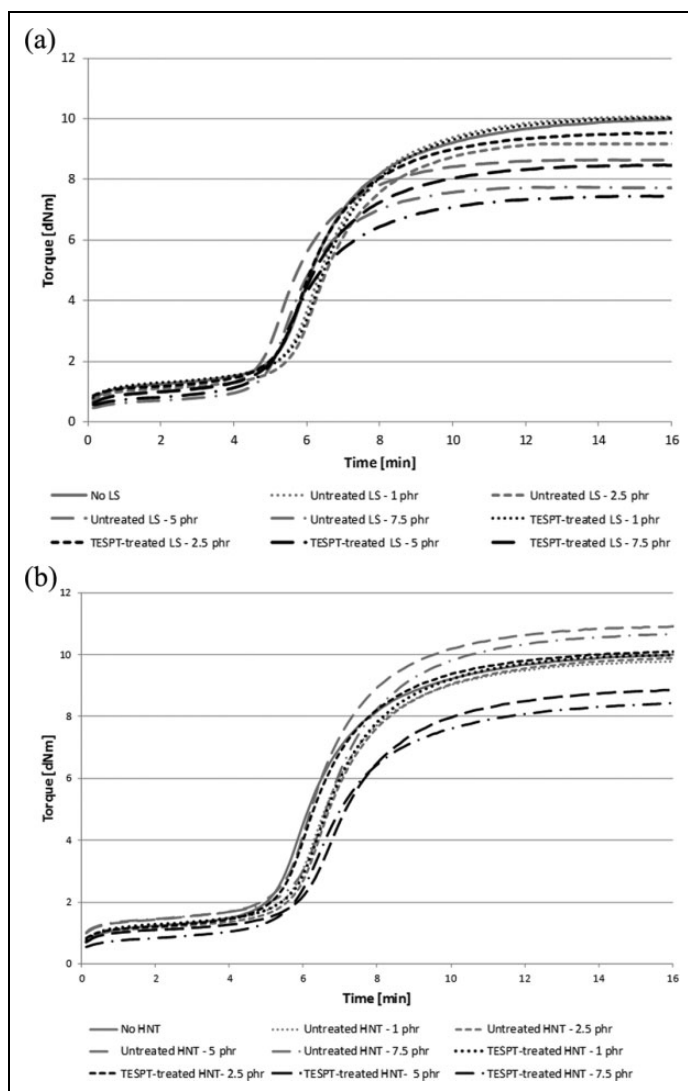


Figure 2. Rheograms of the compounds without and with silane with varying amount of (a) LSs and (b) HNTs. LS: layered silicate; HNT: halloysite nanotube.

were replaced by bentonite as it reduces their tendency to react with accelerators.⁶ Here, CB, which does not absorb accelerators, was used, and the differences in scorch time could not be observed. Kim et al. reported that a compound containing 10 phr organoclays shows reversion, while the compound containing 1 phr silane shows this phenomenon to a lesser extent. This was explained by an antireversion effect of the coupling

agent.⁴ As the curing time and temperature were lower in the present study, the possible antireversion effect could not be seen in this case.

For the compounds with untreated HNTs, the trend is different. An increasing final torque with increasing HNT concentration is observed. For TESPT-treated HNTs, the torque decreases with increasing HNT concentration indicating better filler dispersion. Rooj et al. observed opposite behavior in HNT-filled NR compounds. The torque was higher with TESPT-treated HNTs than with untreated HNTs.⁸ However, they used HNTs as the only filler. In this study, CB was used as primary filler, and addition of HNTs also improved the dispersion of CB which causes the reduction in maximum torque. The scorch time becomes longer with addition of HNTs, which can be explained by inactivation of curing additives due to adsorption. The same effect was observed when HNT-filled NR was studied.⁹ The HNTs appear to be more active than the LS in this sense. However, the influence of HNTs on the final torque was lower than the influence of the LSs; the efficiency of cross-linking is reduced by HNT but to a lesser extent than by LS.

The storage modulus G' as a measurement of the Payne effect, which gives an indication of filler–filler interaction, is shown in Figure 3. A reduced Payne effect expresses a lower degree of filler–filler interaction, which implies better dispersion of the filler. For the compounds with unmodified LS, the Payne effect is reduced. There is a gradual reduction up to 5 phr of LS, and between 5 phr and 7.5 phr of LS an over-proportional reduction occurs. The presence of LS suppresses filler–filler interaction, even of the CB, in the compound. This might be explained by the low interaction between CB and silicates, and the fact that a higher concentration of LS increases the probability that LS particles arrange themselves between the CB particles. Another explanation of the reduction of the moduli can also be the decrease in filler volume fraction when CB is replaced by silicates. Replacing 7.5 phr of CB by LSs or HNTs decreases the total volume fraction of fillers by 4%. The loss modulus G'' is slightly reduced with increasing nanofiller content. In the case of HNTs, both moduli decrease proportionally with increasing concentration of the nanofiller. For both filler systems, the addition of the silane seems not to be effective, as it does not result in significant differences of the moduli. Rooj et al. reported an increase in Payne effect with increased concentration of HNTs in a fluoroelastomer composite.⁷ In this case, the increase can be explained by higher filler concentrations, whereas in the present article the filler concentration was equal and the ratio of CB to nanofiller varied.

As one of the envisaged applications of this material is tire treads, the dynamic properties of the cured material are important. This is in particular true for $\tan \delta$ value, that is, the ratio of the loss modulus to the storage modulus. Responsible for the energy loss expressed in the $\tan \delta$ value is a slippage of the polymer chains over the surface of the filler, which is stronger for higher values of the loss angle, and the interactions and bonds between the polymer chains and the filler surface are weaker. Figure 4 shows the values of the loss angle as a function of the nanofiller concentration at 60°C, the temperature of a tire on the road and thus the temperature for measuring rolling resistance. An increasing amount of nanofillers reduces $\tan \delta$ values, and this indicates that less energy is lost by dissipation. For the application in tire treads, this means that the rolling resistance will be reduced by the addition of these fillers. These results are in line with

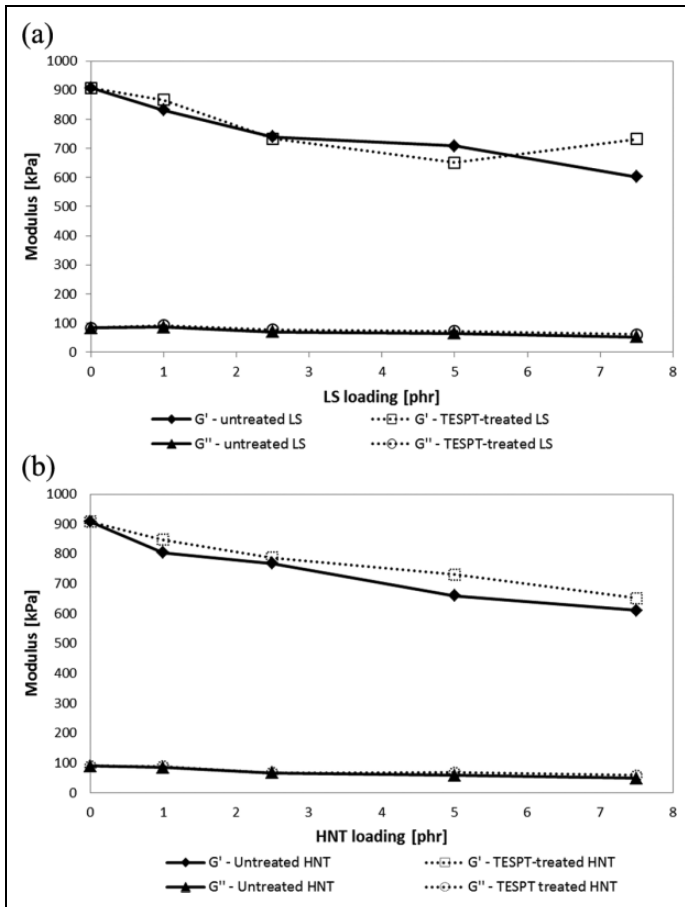


Figure 3. Storage and loss moduli of the compounds without and with silane with increasing amount of (a) LSs or (b) HNTs. LS: layered silicate; HNT: halloysite nanotube.

the results reported by Pasbakhsh et al. for ethylene propylene diene monomer (EPDM)/HNT nanocomposites.¹¹ The influence of the silane is not very conclusive, but it is obvious that the addition of higher concentrations of nanofillers together with silane leads to higher $\tan \delta$ values than the material without silane. A strong coupling between the filler and the polymer in general gives lower $\tan \delta$ values; in this case, this coupling seems not to be effective in that sense. It might very well be that the silane covers the filler by physical adsorption, either the nanofillers or the CB, resulting in more physical interaction between the fillers and the polymer and thus more energy dissipation due to slippage. There is no indication of strong chemical bonds between the polymer and the filler in this system.

Figure 5 shows the results of the stress–strain measurements. The strength of the materials does not change with the replacement of CB by the LS; the reinforcing effect of both nanofillers is comparable with the reinforcing effect of CB, as seen in Figure 5.

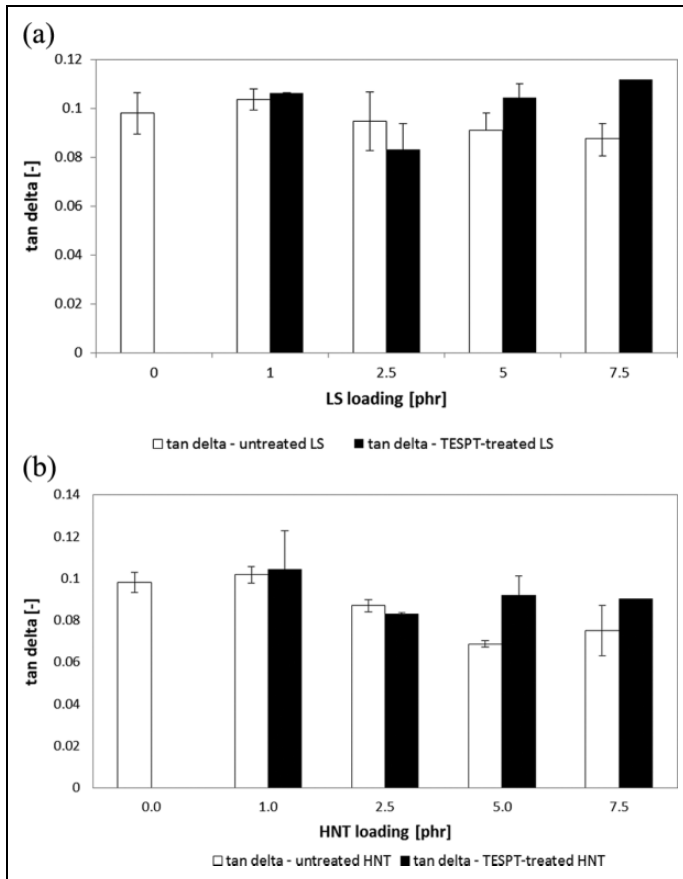


Figure 4. $\tan \delta$ values of the compounds with increasing amount of nanofillers, without and with silane at 60°C, for (a) LSs and (b) HNTs. LS: layered silicate; HNT: halloysite nanotube.

Only for HNTs at higher concentrations, a slight additional reinforcing effect is observed. There is no influence on material strength when silane is added. Elongation at break values show an increasing trend for higher quantities of nanofillers, though the variation is rather high, especially in the case of HNTs.

Ismail et al. observed that tensile strength increases up to 20 phr of HNTs in HNT/NR nanocomposites and a reduction in elongation at break.⁹ When silica and calcium carbonate were partially replaced by bentonite, the tensile strength of the EPDM compounds containing calcium carbonate and bentonite increased generally with increasing bentonite loading, indicating that this filler has a higher reinforcing effect than calcium carbonate. The tensile strength of the compounds containing silica and bentonite increased with the increased bentonite loading up to 15/15 phr loading, respectively, showing a synergistic effect and improved dispersion due to the presence of both fillers.⁶

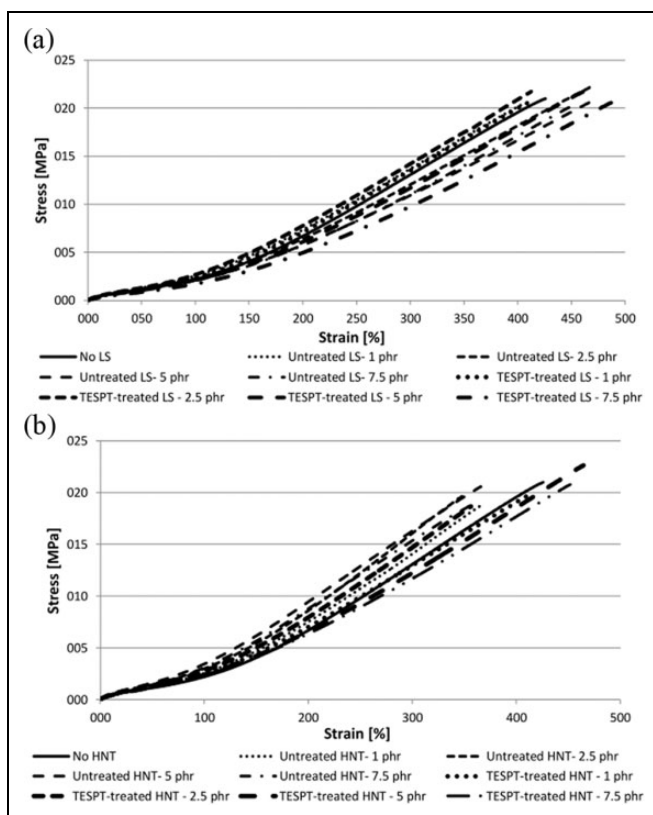


Figure 5. Stress–strain curves of the cured materials without and with silane with increasing amount of (a) LSs and (b) HNTs. LS: layered silicate; HNT: halloysite nanotube.

As in our study, Kim et al. reported that TESPT did not improve the tensile strength and elongation at break of organoclay-filled NR/BR compounds but rather decreased the stress–strain properties.⁴

In terms of moduli, the replacement of CB by LS has a clear effect; when more LS is added, the values are lower. Again, the presence of silane does not make a difference, as seen in Figure 6. Other studies reported that TESPT increased the tensile moduli of organoclay-filled NR/BR compounds,⁴ and an increase in tensile modulus in HNT-filled NR nanocomposites.⁹ According to Rooj et al., the TESPT treatment increased the M300 modulus but decreased tensile strength and elongation at break in HNT-filled NR nanocomposites.⁸ In Figure 6, it is also obvious that the HNT-filled materials do not show a clear trend as the LS-filled compounds do. This might be explained by the more difficult processing behavior of the HNT-compounds, which can result in differences in dispersion of the fillers.

The measurement of the BDR content is a way to directly determine the filler–polymer interaction. In this study, no difference is made between physically and chemically BDR, as the chemical bond between the coupling agents and the nanofiller is

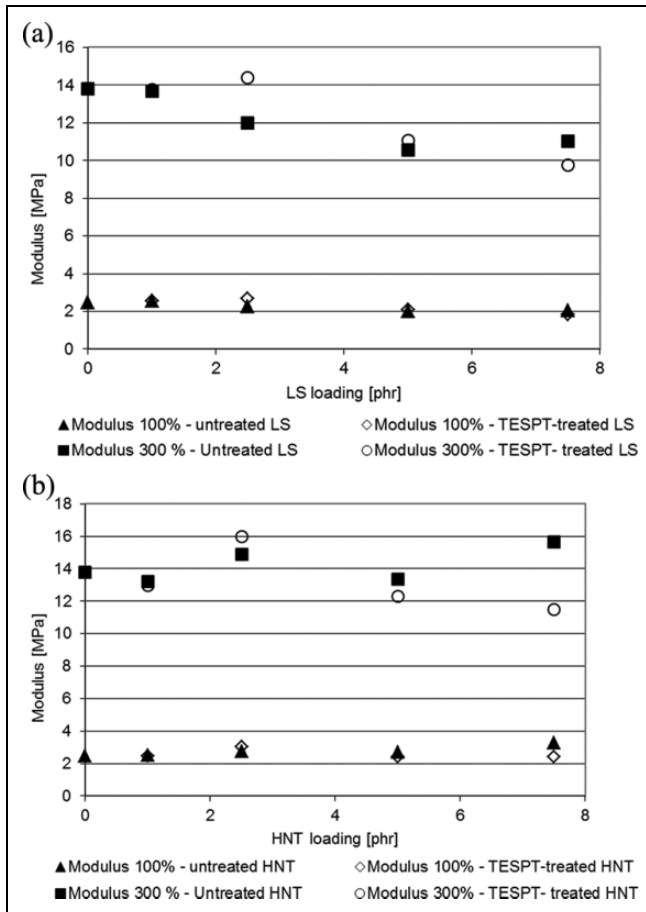


Figure 6. 100% and 300% moduli of the compounds without and with silane with increasing amount of nanofillers for (a) LSs and (b) HNTs. LS: layered silicate; HNT: halloysite nanotube.

expected to be rather low due to the low concentrations of these components. As concluded earlier, there is no structural increase in chemical filler–polymer interaction due to the silanization seen here neither, as seen in Figure 7. The addition of the silane is not effective in these systems. For the compound containing LS, the BDR content is increased when silane is added, showing an improvement of the interaction between the polymer and the filler. However, the difference is rather small. The replacement of CB by LS results in a higher amount of BDR up to a maximum. At high concentrations of LS and without silane, the LSs are less dispersed, and therefore, the polymer chains cannot attach to all the particles in an optimal way.

For HNT-filled rubber, the BDR content increases, as more amount of nanofiller is added. Due to the low compatibility of the polar HNT with the apolar polymer, it is not

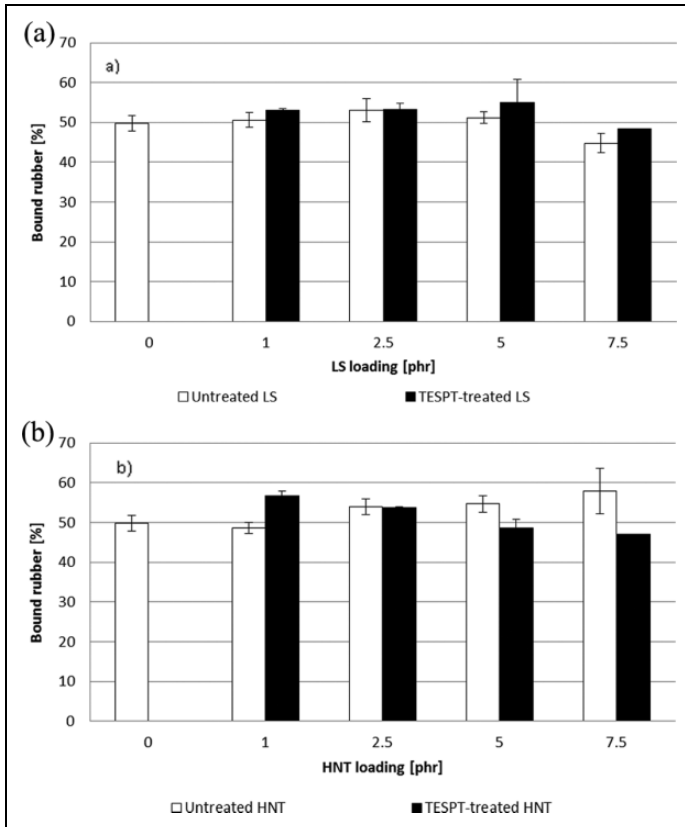


Figure 7. BDR content of the cured compounds without and with silane with increasing amount of (a) LSs and (b) HNTs. BDR: bound rubber; LS: layered silicate; HNT: halloysite nanotube.

very probable that this is the result of an interaction between the nanofiller and the polymer. It might be caused by better dispersion of the CB filler due to the presence of the HNTs, which results in better polymer–filler interaction. The results of the materials containing silanes are rather unexpected. BDR content decreases with increasing nanofiller and silane contents. This is in accordance with the higher $\tan \delta$ values as seen in Figure 4(a) and indicates weaker filler–polymer interaction. An explanation for this effect might be an interaction between the CB and the silane, which reduces the interactions of this filler with the polymer.

Figure 8(a) and (b) shows SEM pictures of the compounds with untreated and TESPT-treated LS at a concentration of 5 phr. In the compound containing untreated LSs, clusters of nanoparticles are visible, and failure of the material took place from the interfaces between rubber and nanofiller. When using TESPT-treated LSs, clusters are not visible, indicating that the dispersion is better. Furthermore, the particles seem to be covered with a rubber layer due to the better bonding of the polymer to the filler. The

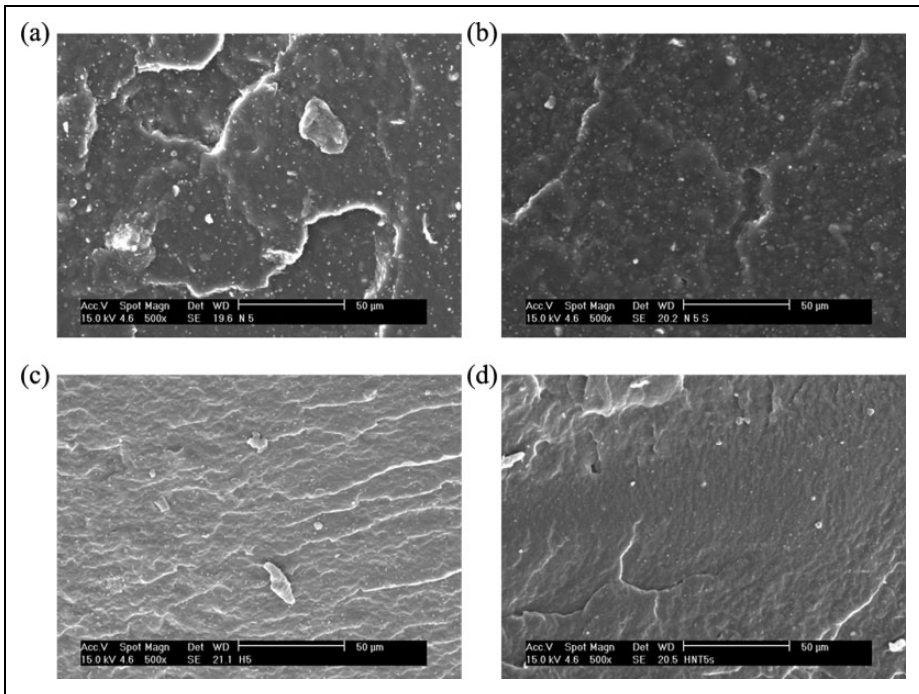


Figure 8. SEM pictures of NR/BR compounds containing 5 phr of nanofiller. (a) Untreated LS, (b) TESPT-treated LS, (c) untreated HNTs, and (d) TESPT-treated HNTs. SEM: scanning electron microscopy; NR: natural rubber; BR: butadiene rubber; LS: layered silicate; TESPT: bis(3-triethoxy-silylpropyl)tetrasulfide; HNT: halloysite nanotube.

same effects can be seen in Figure 8(c) and (d), which illustrate untreated and TESPT-treated HNTs, respectively. The compound containing untreated HNTs shows some agglomerates, but in the case of TESPT-treated HNTs, this kind of clusters is not visible. In the compound containing TESPT-treated HNTs, the particles seem to be smaller than in the compound containing untreated HNTs. This may be due to either better coverage of the particles with rubber or smaller aggregates and thus better dispersion.

Conclusions

The replacement of CB by LSs as well as HNTs facilitates processing, as it reduces the viscosity of the compound. The addition of both nanofillers reduces the efficiency of the curing process resulting in lower final torque values. The dynamic properties are affected by the blend of fillers. The storage and loss modulus are reduced when the amount of HNTs is increased, as is the loss angle. This makes the dual filler systems attractive for tire applications, as lower $\tan \delta$ values result in lower rolling resistance. The strength of the material is merely affected, and the moduli are reduced by the addition of LSs. The

effect of HNTs is not very explicit, which can be explained by the more difficult processing of this material. The BDR values are increased, indicating an effect of the nanofillers on filler–polymer interaction.

The addition of silane does not improve the properties as it does in neat silica-filled compounds. This is probably a consequence of the very low amount of silane that was added, in accordance with the low loading of the silicate filler.

Overall, it can be concluded that the replacement of a small quantity of CB with a silicate results in improved dispersion of the fillers and better dynamic properties. However, a significant increase in mechanical properties could not be observed.

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