

Synergistic Effect of Plasma-Modified Halloysite Nanotubes and Carbon Black in Natural Rubber—Butadiene Rubber Blend

Minna Poikelispää,¹ Amit Das,^{1,2} Wilma Dierkes,^{1,3} Jyrki Vuorinen¹

¹Plastics and Elastomer Technology, Department of Materials Science, Tampere University of Technology, P.O. Box 589, FI-33101 Tampere, Finland

²Composite Materials, Leipzig Institute of Polymer Research Dresden, D-01069, Germany

³Elastomer Technology and Engineering, University of Twente, NL-7522 AE Enschede, The Netherlands

Correspondence to: M. Poikelispää (E-mail: minna.poikelispaa@tut.fi)

ABSTRACT: Halloysite nanotubes (HNTs) were investigated concerning their suitability for rubber reinforcement. As they have geometrical similarity with carbon nanotubes, they were expected to impart a significant reinforcement effect on the rubber compounds but the dispersion of the nanofillers is difficult. In this work, HNTs were surface-modified by plasma polymerization to change their surface polarity and chemistry and used in a natural rubber/butadiene rubber blend in the presence of carbon black. The aim of the treatment was to improve the rubber–filler interaction and the dispersion of the fillers. A thiophene modification of HNTs improved stress–strain properties more than a pyrrole treatment. The surface modification resulted in a higher bound rubber content and lower Payne effect indicating better filler–polymer interaction. Scanning electron microscopy measurements showed an increased compatibility of elastomers and fillers. As visualized by transmission electron microscopy, the thiophene-modified HNTs formed a special type of clusters with carbon black particles, which was ultimately reflected in the final mechanical properties of the nanocomposites. The addition of HNTs increased loss angle. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: plasma polymerization; polymer–filler interactions; nanocomposites; halloysite

Received 11 January 2012; accepted 17 May 2012; published online

DOI: 10.1002/app.38080

INTRODUCTION

Carbon black and silica are conventionally used fillers in rubbers. Their primary particles have dimensions in the nanometer range, and structural reinforcing units have dimensions of a few hundreds of nanometers. In the last decade, in which nanotechnology has been developed and implemented, nanofillers have extensively been investigated as fillers for polymers. They have been found to carry many benefits compared to conventional fillers: They have been reported to, for example, reduce viscosity and increase tensile strength, hardness, modulus, abrasion resistance, electrical conductivity as well as chemical resistance.^{1–11} Nanoclays are widely studied materials used with rubbers. Typically, they are layered silicates, and usually phyllosilicates such as montmorillonite, hectorite, and saponite are used.

Recent studies^{1,2,12–14} have focused on halloysite nanotubes (HNTs), which are 1 : 1 aluminosilicates, a naturally occurring clay mineral with the empirical formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$. HNTs have a double layered crystalline structure. There are Si—O groups on the surface of the outer layer and $\text{Al}(\text{OH})_3$ -groups on the inner side and edges of the tube.¹³ The OH-

groups have interparticle affinity which complicates dispersion of clay materials, but the filler–filler interactions are lower with HNTs than with layered silicates.¹³ Furthermore, HNTs do not require exfoliation. Because of the tubular form, HNTs have a higher aspect ratio than other clay materials. The aspect ratio of HNT can vary between 10 and 130 depending on the dimensions of the tubes. The high aspect ratio and surface area of HNTs is expected to result in a special reinforcing effect on the polymer matrix.

Conventional fillers are generally processed by direct incorporation into the rubber matrix, eventually with the help of a coupling agent. The incorporation of nanofillers is more challenging, and it is difficult to achieve a good dispersion by direct incorporation. Therefore, a successful application of nanofillers depends mainly on a good dispersion of the fillers.

Besides dispersion, the interaction between rather hydrophobic polymers and hydrophilic fillers cause a challenge. The compatibility can be improved by changing the polarity of the fillers. Different kinds of coupling agents, such as silanes, are typically used to change the surface properties of the fillers. The coupling agents

Table I. Formulation of NR/BR Compounds and Mixing Procedure

Ingredients	Type/producer	Amount (phr)	Mixing (min)
NR	SMR10	80	0
BR	Buna-cis-132/ Dow Chemical Company	20	
Nanofiller		0/2.5	1
N-234	Evonik	42.5/40.0	1.5
6PPD	Lanxess	2.0	
TMQ	Lanxess	1.0	
ZnO	Grillo Zinkoxid GmbH	5.0	
TDAE-oil	Vivatec 500/ Hansen & Rosenthal GmbH	8.0	2
Stearic acid	Oleon N.V	2.0	
Ceresine wax	Statoil Wax GmbH	1.5	Mixing: 4
CBS	Lanxess	1.5	Mill: 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.

are typically added to the blend during mixing. The reaction between the coupling agent and the filler requires a certain temperature and time for the silanization reaction to be completed.

An alternative could be a pretreatment of the filler by plasma treatment. Silica has been successfully modified by plasma polymerization treatments.^{15–19} HNTs have a comparable surface chemistry to silica; therefore, it is expected that the surface of HNTs can also be modified by plasma polymerization. By choosing the appropriate monomer, the following effects can be expected:

- The polarity of the HNT surface can be reduced.
- The functional groups on the surface, mainly hydroxyl groups, can be shielded.
- The chemical composition of the surface can be changed to hydrocarbons.
- Functional groups can be created in the surface.

The creation of functional groups which can react with the polymer during curing might result in interpenetrating networks: Besides the polymer–polymer network, a strong covalent filler–polymer network can be build up during vulcanization. Furthermore, the sulfur and nitrogen moieties in the plasma polymers can contribute to the crosslinking reaction. This will influence the properties of the final material.

In the plasma polymerization process, the plasma is generated by electric discharge. With the help of plasma energy, the monomer gases, which continuously float into the reactor, are activated and form electrons, ions, and radicals. They are able to polymerize and form a deposit on the surface of the filler. This surface coating consists of a two-dimensional network of the monomer in question, it is very adherent and it preserves the structural characteristics of the nanotubes.

In this work, HNTs were surface-modified by plasma polymerized pyrrole and thiophene. The effect of the surface coating on surface polarity and chemistry was investigated, as well as the effect of this filler on the rubber properties.

EXPERIMENTAL

Materials

HNTs were delivered by Sigma–Aldrich. The diameter of the nanotubes was 30–70 nm and the length varied between 1 and 4 μm . The specific surface area of these tubes was 65 m^2/g . Pyrrole (py) and thiophene (thi), both from Sigma–Aldrich, were used as monomers in the plasma polymerization process. The other materials used are presented in Table I.

Plasma Treatment

The plasma polymerization was performed in a tubular vertical reactor. It consists of a round flask made from Pyrex glass, which is connected to the vacuum pump (Duo Seal, model number 1402 B from Welch vacuum), and a long cylindrical tube which is surrounded by a copper coil. The coil is connected to a radiofrequency generator from MKS/ENI, type ACG-3B-01. At the top of the tube, there are ports for the inlet of monomers and the connection of pressure gauge (MKS Baratron® type 627B). No carrying gas was used in the modification process. Stirring of the powder was done by a magnetic stirrer. About 20 g of HNTs were placed into the flask where they were treated with the activated monomers. The parameters of the plasma treatment of the different batches are presented in Table II.

Table II. Parameters of Plasma Treatment

Monomer	Initial pressure ^a (Pa)	Monomer pressure ^b (Pa)	Power (W)	Time (min)
Pyrrole (Py90)	10	22	150	90
Thiophene (Thi90)	10	40	150	90

^aPressure in the reactor before monomer is applied.

^bMonomer inlet pressure.

Characterization of the Treated Fillers

The deposition of the plasma coating was quantified by thermogravimetric analysis in a Perkin-Elmer STA 6000 thermogravimetric analysis (TGA). The heating temperature changed from 25°C to 995°C and the heating rate was 20°C/min; a nitrogen atmosphere was used. The total weight loss within this temperature window was taken into consideration.

Changes in surface polarity were studied by an immersion test. The test was done by pouring a small amount of filler onto the surface of a solvent; in this case, water was used. The original HNTs sink immediately due to their hydrophilic surface, whereas the treated fillers should float longer as they are less hydrophilic. More quantitative measurements were made by a water penetration test. In this test, 0.02 g of filler was placed into a glass column and the opening was sealed with two layers of a hydrophobic filter (pore size 0.2 μm). The column was placed in water and the change in weight due to absorption of water was measured over time.

Preparation of Nanocomposites

Natural rubber (NR), butadiene rubber (BR), nanofillers, and other ingredients presented in Table I were mixed in a Krupp Elastomertechnik GK 1.5 E intermeshing mixer (50°C, 70 rpm). Then, *N*-cyclohexyl-2-benzothiazolesulfenamide (CBS) and sulfur were added on an open two-roll mixing mill. In the reference compound, only carbon black (CB) was used as filler in a concentration of 42.5 phr. In the HNTs containing compounds, 2.5 phr of CB was replaced by the same amount of HNTs. The total mixing time was nearly 15 min.

The Mooney viscosity of the compounded material was measured in a MV 2000 Mooney Viscometer from Alpha Technologies. The measurement included 1 min heating time and 4 min measuring time at 100°C. Curing studies and Payne effect measurements were performed using an Advanced Polymer Analyzer 2000 from Alpha Technologies. Curing studies were carried out at 160°C for 60 min and 193°C for 30 min. The compounds were vulcanized at their respective curing time at 160°C. The Payne effect was studied in a strain sweep from 0.28 to 100% at 100°C.

Swelling behavior was studied by soaking vulcanized circular test pieces in toluene until equilibrium swelling (72 h). The diameter of the test pieces was 12 mm and thickness 2 mm. The swelling degree *Q* of the rubber was calculated by the equation:

$$Q = \frac{W_t - W_0}{W_0}$$

W_0 is the initial weight of sample and W_t is the weight at time t .

Tensile tests of the samples were performed with a Messphysik Midi 10–20 universal tester according to ISO 37. Dynamic properties were studied with a GABO Eplexor 2000N, operating in tension mode. The vulcanized sheet with a thickness of 2 mm was cut into rectangles of 35 × 10 mm². Storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) were recorded at a heating rate 10°C/min from –80 to +80°C. The frequency

used in these measurements was 10 Hz with a dynamic load at 0.5% strain and static load at 1% strain, which was kept constant through the measurement.

Bound rubber (BDR) measurements were performed 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:

$$\text{BDR}\% = \frac{m_0 - (m_2 - m_3)}{m_0} \times 100$$

with

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

where m_0 is the weight of the rubber content in the sample, m_2 is the combined weight of the bag and sample, m_3 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 phr.²⁰

The state of dispersion of the HNT particles in the NR/BR nanocomposites was investigated by scanning electron microscopy (SEM) using a Philips XL-30, and by transmission electron microscopy (TEM) using a JEM 2010 model. Cross-section samples were used for the SEM measurements. For TEM samples, the ultrathin section of the samples was cut by an ultramicrotome (Leica Ultracut UCT) at –100°C with a thickness of ~ 80–100 nm. Because of the very low amount of halloysites compared to CB, it was very difficult to locate the halloysite particles. Both fillers showed the same contrast in bright field images, only the shape of the two fillers was different. Hence, for detection of the HNTs, TEM investigations were performed at an energy loss of 0 eV (= bright field image) and 180 eV for each region. By comparing the two images, it was possible to distinguish between CB and HNT.

RESULTS AND DISCUSSION

Filler Characterization

To check the changes in hydrophobicity, the water immersion test was performed: As expected, the untreated HNT powder sank in water immediately; after treatment, a part of the material floated on water for a certain period. This proves the reduction in polarity of the HNTs after plasma treatment, although it also indicates an inhomogeneous coating, which could be caused by filler aggregates in the reactor during the plasma treatment. The water absorption results are presented in Figure 1. Pure HNTs as well as pyrrole- and thiophene-coated HNTs absorbed water over time and after a certain period an equilibrium level was attained. However, pure HNTs absorbed more water than plasma-treated HNTs, indicating a more hydrophobic nature of plasma-treated HNTs. In earlier studies with plasma-treated silica, such a reduction in water absorption was also observed, but the effect was a lot stronger.¹⁵ This preliminary investigation indicated that pyrrole- and thiophene-coated HNTs are more hydrophobic and less polar than the untreated

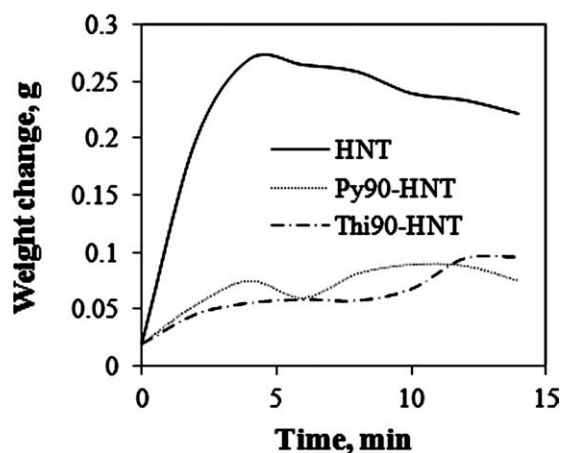


Figure 1. Water absorption of the plasma-coated HNTs.

filler, and they could be more compatible with a nonpolar rubber matrix.

The TGA curves of untreated, pyrrole and thiophene polymerized HNTs are shown in Figure 2. The difference in weight loss between treated and untreated fillers at the final temperature of 995°C is the amount of the plasma-polymerized film on the surface of the filler. The decomposition of the pyrrole and thiophene start around 200°C. In this area, the difference in the TGA curves can be observed. According to repeated measurements, HNTs treated with pyrrole had 0.7 wt % coating on average, whereas HNTs treated with thiophene had 1.0 wt % coating on average.

Mooney Viscosity and Curing Studies

The Mooney viscosities of the composites with the different types of fillers were determined. The composites showed a substantial increase in viscosity for the composite containing pyrrole-coated HNTs (Figure 3). The viscosity of the compound with the thiophene-treated HNTs was slightly lower, but still higher than the viscosity of the compound with untreated HNTs and without any HNTs. Untreated HNTs did not affect the viscosity at all. The increase in viscosity is due to enhanced

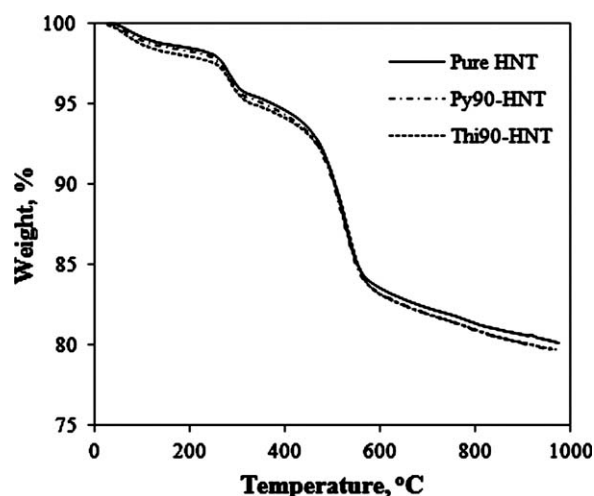


Figure 2. Thermogravimetric analysis of the plasma-coated HNTs.

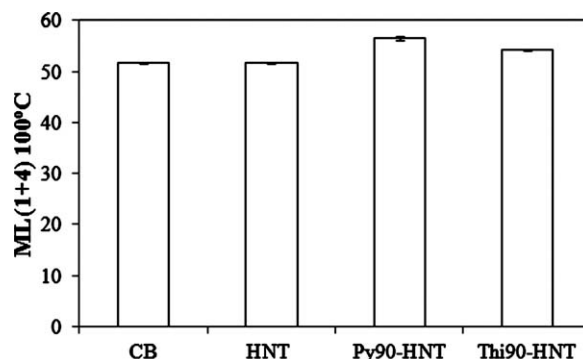


Figure 3. Mooney viscosity of the NR/BR compounds.

polymer–filler interactions, as plasma-modified HNTs interact with the elastomer chains more firmly and increase the reinforcement.

The rheograms taken at 160°C are presented in Figure 4(a). It is interesting to note that both, compounds with plasma-treated HNTs, showed a plateau in the cure curve, whereas carbon black and pure HNT-filled compounds showed a decrease in the torque values after the optimum curing time. Reversion is a well-known phenomenon for sulfur-cured diene rubbers, especially when cured at higher temperatures, and this ultimately affects properties and performance of the material. Here, the plasma-coated HNTs seem to stabilize the network and suppress the reversion; they act as antireversion agents in the rubber compound. At the same time, the maximum rheometric torque increases with the addition of both types of plasma-coated HNTs, and it is higher for the compound containing plasma-pyrrole-treated HNTs than for the compound containing thiophene-treated HNTs. The increase in torque may be due to crosslinking density. To see if the extent of curing or the degree of crosslinking were influenced by the modifier of the HNTs swelling degree was calculated. The swelling data (Table III) indicates that the extent of overall crosslinking was marginally higher for all HNT-filled samples compared with carbon black sample. Thus, HNTs are giving more rubber–filler interactions as a result of improvement of total crosslinking density coming from chemical and physical crosslinking of the rubber chains. A minor effect can be found if the HNTs are modified by plasma coating.

As can be seen from Figure 4(b), at high temperature (193°C), the reversion can be observed for all compounds in this case, but the extent to which it occurs is much lower for compounds with plasma-treated HNTs than for compounds with untreated HNTs or CB. The plasma polymers seem to either result in a more stable network or it prevents rearrangement of the crosslinks at higher temperatures.

At both temperatures, the cure curves for the CB and CB/HNT-filled compounds are almost similar, indicating that the addition of untreated HNTs has only a minor influence in the curing characteristics in practice even if the cure rate index presented in Table III is higher for the compound containing untreated HNTs.

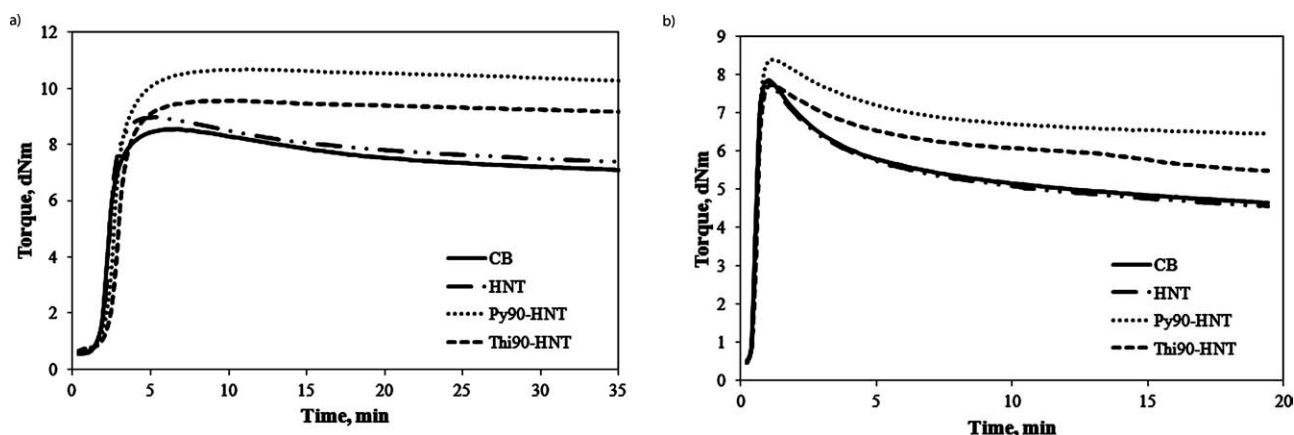


Figure 4. Development of the torque values of the NR/BR compounds filled with carbon black and HNTs measured at (a) 160°C and (b) 193°C.

Morphology

To visualize the dispersion of the HNTs in the rubber matrix, the morphology of the materials was investigated by SEM and TEM. The image of pristine HNTs is shown in Figure 5(a), showing the tube-like dimension and the agglomerated nature of the tubes. Owing to the high surface area of these very small particles, the tubes themselves remain aggregated. In Figure 5(b), both carbon black as well as the relatively smaller unmodified HNT particles are clearly visible. The carbon black particles form a spherical aggregated structure, whereas the unmodified HNTs are homogeneously dispersed through the rubber matrix. It is interesting to note in Figure 5(c,d) that in the presence of modified HNTs, the aggregated structure of CB becomes smaller compared to Figure 5(b). These investigations indicate that the compatibility between the two elastomers and carbon black is facilitated by modified HNT. The plasma polymer coatings reduce the hydrophilic character of the filler surface making it more compatible with the polymers and their chemical structure resembles the chemical structure of the polymers and also increase the compatibility to carbon black due to the presence of carbon-carbon double bonds which are also present on the carbon black surfaces. Very similar observations were also reported for plasma-modified silica as filler in elastomer blends: a remarkable improvement of the dispersion of the silica and filler polymer interaction was found.¹⁵ However, this work was based on a 100% replacement of pristine silica by the plasma-treated filler. The results of this investigation show that it might be sufficient to add a small percentage of surface-modified filler. Another proof of this compatibilization effect is the Payne effect, which is reduced by the addition of HNTs. The Payne effect is the decrease of the storage modulus G' with increasing

strain, as the interparticle forces between the filler particles are effective only over small distances between them. The higher the interparticle forces, the higher the Payne effect. In general, the value of the storage modulus remains unchanged with strain for an unfilled system, whereas for a filled system, a significant decrease can be observed. This nonlinear behavior was also observed in this study. Figure 6 illustrates the strain dependency of the storage modulus of the filled NR/BR matrix measured at 100°C. It can be observed that at very low strain amplitude ranges the value of G' remains constant up to a certain strain, and then the values decrease with further increase of strain. The CB-filled NR/BR have the highest Payne effect indicating the strongest filler-filler network. When 2.5 phr CB is replaced by 2.5 phr HNTs, the filler-filler interactions become weaker and the dispersion of the main filler is improved as a consequence of better rubber-filler compatibility. The fact that the thiophene-treated HNTs have a higher Payne effect than the other two HNT-containing samples might be caused by a HNT-CB interaction due to the peculiar coating on the HNT surface. Moreover, the plasma-modified HNT particles show a good dispersion in the rubber matrix, whereas the untreated HNTs are preferably located at the interface between the continuous and discontinuous phases.

Figure 7 shows TEM images of the composites. It is observed from Figure 7(a), that the unmodified HNTs remain as agglomerations in the matrix, whereas the modified HNTs are found to be well dispersed up to the level of single particles [Figure 7(b,c)]. The high surface polarity of the HNT particles favors their tendency to remain in the agglomerated form due to a significant contribution of filler-filler interactions together with the lack of interactions between the filler and the elastomer

Table III. Curing Characteristics Measured at 160°C and Swelling Degree of Nr/Br Compounds

	CB	HNT	Py90-HNT	Thi90-HNT
Scorch time T_{s2} (min)	2.1	2.2	2.3	2.5
Optimum curing time T_{90} (min)	3.5	3.4	4.3	4.2
Cure rate index (min^{-1})	71	83	50	59
Swelling degree	1.70 ± 0.05	1.62 ± 0.02	1.58 ± 0.04	1.61 ± 0.03

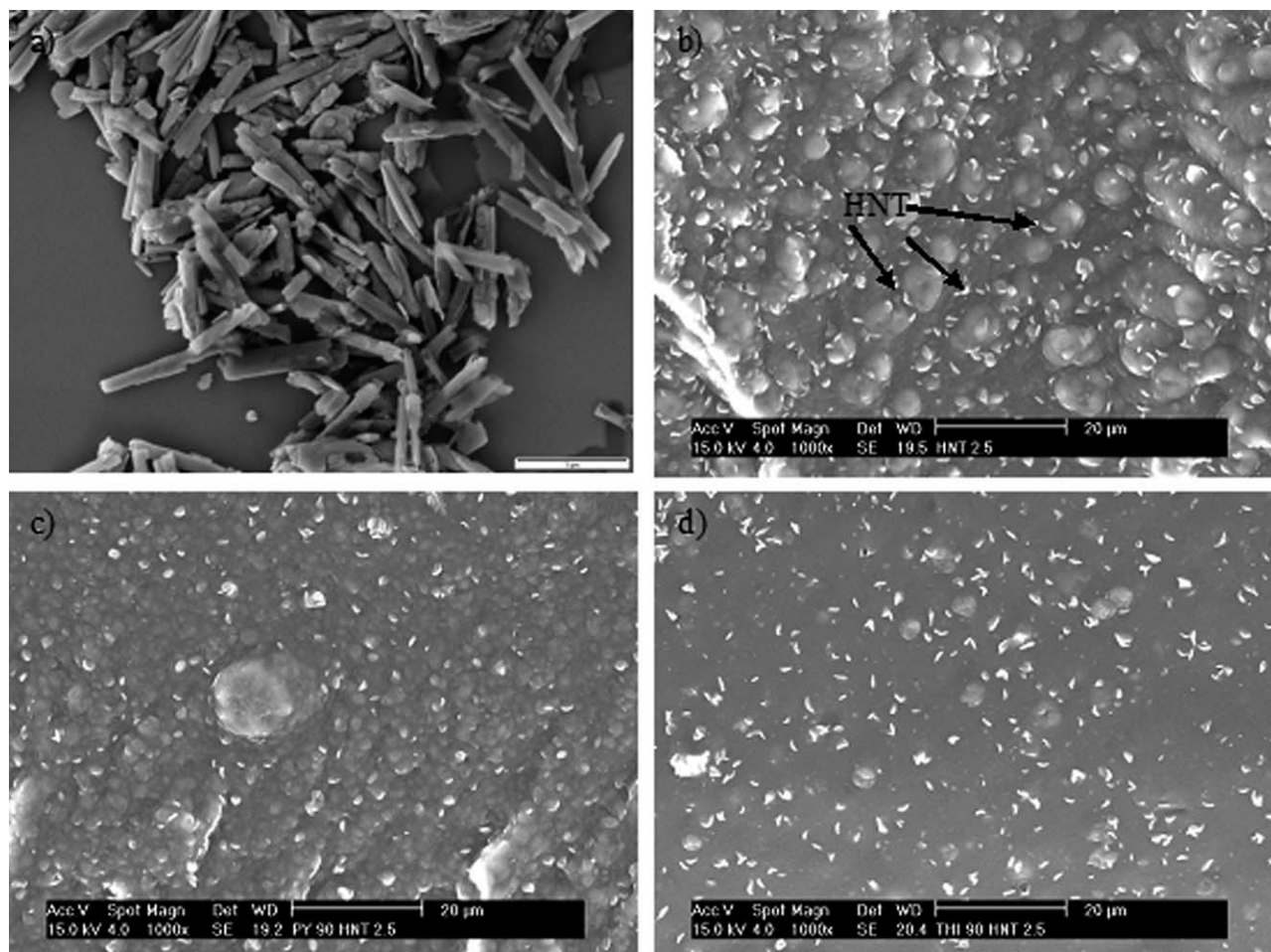


Figure 5. Scanning electron microscopic images of (a) pristine HNTs, and NR/BR compounds filled with carbon black and, (b) untreated, (c) pyrrole-modified and (d) thiophene-modified HNTs.

matrix. The plasma modification with pyrrole and thiophene leads to a decrease of the surface polarity and improves the dispersion of the HNTs. However, the HNT particles in the rubber matrix are found to be smaller in length as compared to the pristine particles shown in Figure 5(a): They are most probably ruptured during shear mixing and thus transformed into smaller particles. This reduces the aspect ratio and might result in a lower reinforcing activity. The breakage of the nanotubes is expected to result in easier dispersion of this filler but it is not influencing the filler–polymer interaction, as this is a surface effect and not depending on the shape and size of the particles.

Bound Rubber

The BDR value describes the amount of polymer which is physically or chemically bound to the filler. Figure 8 shows the BDR content values of compounds with untreated and plasma-modified HNTs. The compounds with plasma-pyrrole treated HNTs show the highest BDR content. This indicates a stronger polymer–filler interaction for the compounds including plasma-treated HNTs.

Mechanical Properties

Stress–strain measurements of the NR/BR composites were performed to investigate the effect of the plasma-modified HNTs

on the physical properties. It is evident from Table IV, that incorporation of pyrrole-modified HNTs into the NR/BR matrix increased the 100% modulus by 13% and the 300% modulus by

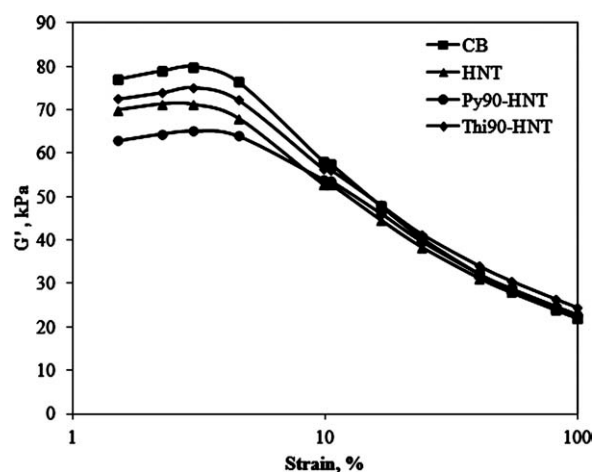


Figure 6. Strain dependence of the storage modulus G' at 100°C for carbon black and HNT filled rubber.

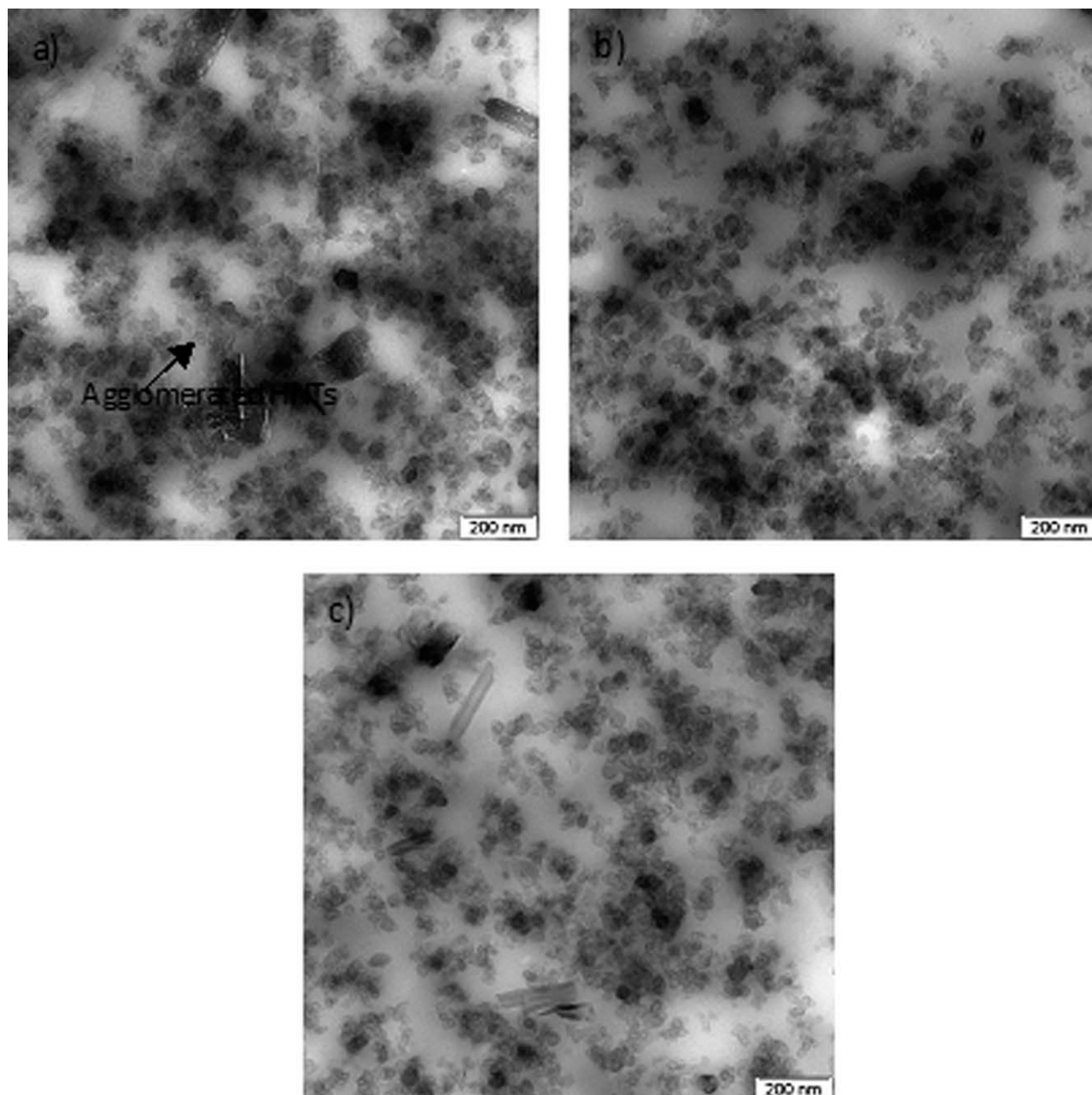


Figure 7. Transmission electron microscopic images of NR/BR filled with carbon black and (a) untreated HNTs, (b) pyrrole-modified HNTs, and (c) thiophene-modified HNTs.

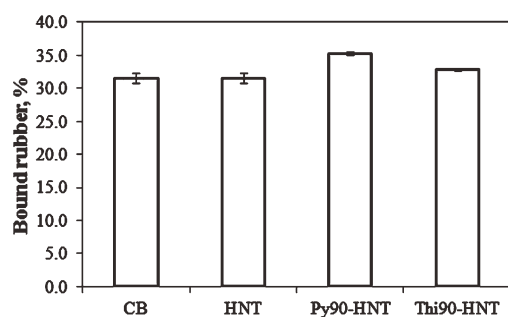


Figure 8. BDR content of the NR/BR compounds filled with carbon black and HNTs.

Table IV. Physical Properties of Carbon Black and HNT-Filled Rubber

Sample	Tensile strength (MPa)	Elongation (%)	100% Modulus (MPa)	300% Modulus (MPa)
CB	20.6	443	2.5	12.1
HNT	19.7	380	2.7	12.8
Py90-HNT	21.7	410	2.8	13.5
Thi90-HNT	23.0	445	2.6	13.0

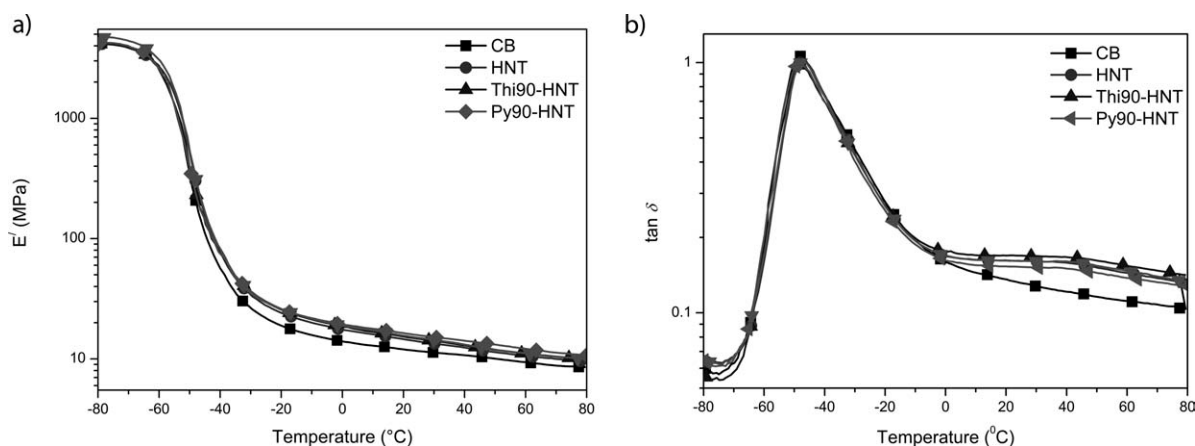


Figure 9. Temperature dependence of the (a) storage modulus (E') and (b) loss tangent ($\tan \delta$) of the crosslinked rubber.

12%, whereas the thiophene modification resulted in an increase of 5 and 7%, respectively. It is important to keep in mind that the total amount of filler on a weight-basis in all cases was kept constant at 42.5 phr. As the modulus is directly related to the volume fraction of the fillers, a lower volume fraction of the total amount of the fillers in the hybrid filler system would lead to inferior moduli value, particularly, when there is a considerable difference in density. In terms of tensile strength, the highest value was found when thiophene-modified HNTs were introduced together with the carbon black. This compound also showed the highest elongation at break value. This is an effect of the sulfur moieties on the surface of the HNTs, which enables them to crosslink with the polymer and form interpenetrating networks.

Figure 9 shows dynamic mechanical analysis (DMA) plots of the E' and $\tan \delta$ values for the vulcanizates. As reference, the pure carbon black compound is also shown. From these measurements, it becomes clear that all HNT containing vulcanizates show higher storage moduli in the whole temperature region as compared to vulcanizates filled with 42.5 phr carbon black. It shows that the replacement of 2.5 phr of carbon black by modified HNTs enhances the rubber–filler interaction and that the material becomes less elastic. This observation also corroborates with the stress–strain data as discussed previously. At lower temperatures, a peak in the loss tangent appears around -48°C , which is the glass transition temperature of the rubber. As the position of the peak does not change, the addition of HNTs do not affect the glass transition temperature of the rubber matrix. Interestingly, at higher temperatures, an additional broad relaxation phenomenon is observed when the elastomer is filled with both, modified and unmodified HNTs. A higher $\tan \delta$ in the temperature range just above 0°C is an indication for a better wet grip when used as tire tread material.²¹ However, the $\tan \delta$ at a temperature around 60°C is also higher compared to the carbon black filled material, and that indicates a higher rolling resistance. These differences in the loss modulus are a consequence of changes in the interaction between elastomer chains and fillers, as well as the morphology of the mate-

rial. The addition of HNTs results in increased energy dissipation under these circumstances.

CONCLUSIONS

This study focused on the potential of surface modification of HNTs by plasma polymerization to overcome filler–filler interactions and to establish rubber–filler interactions.

HNTs can be surface coated by a plasma polymer film based on pyrrole or thiophene as monomers. This modification reduces the polarity of the filler and improves the compatibility of the system. As a consequence, agglomeration of HNT particles is hindered and dispersion in the polymer matrix is improved. The extent, to which the dispersion can be improved, depends on the monomer which is chosen for the plasma polymerization process.

The partial replacement of carbon black by modified HNTs influences the curing characteristics of the compound; it reduces reversion over a wide temperature range. Mechanical properties of the composite material are improved by the plasma treatment, with the polythiophene coating having the most effect due to the sulfur moieties on the surface of the HNTs, which can promote sulfur bridge to the rubber molecules. These improvements in rheological and mechanical properties clearly demonstrate the potential of HNTs with a tailored surface chemistry. In terms of dynamic properties, the addition of HNTs results in higher values of the loss angle, which means more energy dissipation. This is an indication for better wet skid resistance, however, at the same time for a higher rolling resistance.

ACKNOWLEDGMENTS

This work has been supported by the Finnish Funding Agency for Technology and Innovation (TEKES Grant No 40352/08). The authors thank S. Pohjonen and T. Lehtinen from the Tampere University of Technology for their technical help. We are also thankful to R. Boldt, Leibniz-Institute for Polymer Research, Dresden, for the TEM images. We are also thankful to Department of Elastomer

Technology and Engineering, University of Twente for allowing using their plasma reactor.

REFERENCES

1. Rooj, S.; Das, A.; Heinrich, G. *Eur. Polym. J.* **2011**, *47*, 1746.
2. Rooj, S.; Das, A.; Thakur, V.; Mahaling, R. N.; Bhowmick, A. K.; Heinrich, G. *Mater. Des.* **2010**, *31*, 2151.
3. Subramaniam, K.; Das, A.; Heinrich, G. *Comp. Sci. Technol.* **2011**, *71*, 1441.
4. Das, A.; Wang, D.-Y.; Leuteritz, A.; Subramaniam, K.; Greenwell, H. C.; Wagenknecht, U.; Heinrich, G. *J. Mater. Chem.* **2011**, *21*, 7194.
5. Das, A.; Stöckelhuber, K. W.; Wang, D.-Y.; Jurk, R.; Fritzsche, J.; Lorenz, H.; Klüppel, M.; Heinrich, G. *Adv. Polym. Sci.* **2011**, *239*, 85.
6. Bokobza, L.; Rahmani, M.; Belin, C.; Bruneel, J.-L.; El Bouinia, N.-E. *J. Polym. Sci.* **2008**, *46*, 1939.
7. Xu, D.; Sridhar, V.; Mahapatra, S. P.; Kim, J. K. *Appl. Polym. Sci.* **2009**, *111*, 1358.
8. Arroyo, M.; Lopéz-Manchado, M. A.; Herrero, B. *Polymer* **2003**, *44*, 2447.
9. Jia, Q.-X.; Wu, Y.-P.; Wang, Y.-Q.; Lu, M.; Zhang, L.-Q. *Compos. Sci. Technol.* **2008**, *68*, 1050.
10. Kim, M.-S.; Kim, G.-H.; Chowdhury, S. R. *Polym. Eng. Sci.* **2007**, *47*, 308.
11. Rooj, S.; Das, A.; Heinrich, G. *Polym. J.* **2011**, *43*, 285.
12. Ismail, H.; Pasbakhsh, P.; Ahmad Fauzi, M. N. *Polym. Test.* **2008**, *27*, 841.
13. Paskbakhsh, P.; Ismail, H.; Ahmad Fauzi, M. N.; Abu Bakar, A. *Polym. Test.* **2009**, *28*, 548.
14. Paskbakhsh, P.; Ismail, H.; Ahmad Fauzi, M. N.; Abu Bakar, A. *J. Appl. Polym. Sci.* **2009**, *113*, 3910.
15. Tiwari, M.; Noordermeer, J. W. M.; van Ooij, W. J.; Dierkes, W. K. *Polym. Adv. Technol.* **2008**, *19*, 1672.
16. Tiwari, M.; Noordermeer, J. W. M.; van Ooij, W. J.; Dierkes, W. K. *Chem. Technol.* **2008**, *81*, 276.
17. Tiwari, M.; Dierkes, W. K.; Datta, R. N.; Talma, A. G.; Noordermeer, J. W. M. *Rubber Chem. Technol.* **2009**, *82*, 473.
18. Nah, C.; Huh, M.-Y.; Rhee, J. M.; Yoon, T.-H.; *Polym. Int.* **2002**, *51*, 510.
19. Mathew, G.; Huh, M.-Y.; Rhee, J. M.; Lee, M.-H.; Nah, C. *Polym. Adv. Technol.* **2004**, *15*, 400.
20. Leblanc, J. L.; Hardy, P. *Kautsch. Gummi Kunstst.* **1991**, *44*, 1119.
21. Nordsiek, K. H. *Kautsch. Gummi Kunstst.* **1985**, *38*, 178.