

REINFORCEMENT EFFECT OF PLASMA MODIFIED HALLOYSITE NANOTUBES IN A
CARBON BLACK FILLED NATURAL RUBBER-BUTADIENE RUBBER MATRIX

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Presented at the Fall 180th Technical Meeting of the Rubber Division of the American Chemical
Society, Inv. Cleveland, OH

October 10-13, 2011

ISSN: 1547-1977

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ABSTRACT

Rubber composites are generally produced by the direct incorporation of fillers like carbon black and/or silica into the rubber matrix. The incorporation of different types of nanofillers is the subject of recent research with the aim of preparing composites with special compositions and properties. A successful application of such composites depends mainly on the degree of dispersion of the nano-sized fillers.

Recently, a naturally occurring clay mineral, halloysite nanotubes (HNTs), is investigated concerning its suitability for rubber reinforcement. As these nanotubes have geometrical similarity with carbon nanotubes, it is expected that these minerals would impart a significant reinforcement effect on the rubber compounds owing to its high aspect ratios. However, the dispersion of these nanofillers is difficult. In the present work, halloysite nanotubes have been surface-modified by plasma polymerization with different monomers in order to change their surface polarity and chemical nature. These modified nanotubes were used as reinforcing filler in combination with carbon black in a natural rubber (NR)/butadiene rubber (BR) blend system. The aim of the treatment was to improve the dispersion of the fillers and to enhance the compatibility and interaction between HNTs and the rubber matrix. The deposition of the plasma coating was proven by thermo gravimetric analysis, whereas water penetration measurements showed a reduction in surface polarity. The effect of the plasma treatment of the HNTs on dispersion and rubber-filler interaction was investigated by measurement of the Payne effect and mechanical properties.

INTRODUCTION

Carbon black and silica are conventionally used fillers in rubbers, which are characterized by primary particles with dimensions in the nanometer range, and structural reinforcing units with dimensions of a few hundreds of nanometers. In the last few decades, as nanotechnology was explored and implemented, nanofillers have extensively been investigated as fillers for polymers. It was found that they carry many benefits compared to conventional fillers. They have been reported to e.g., increase tensile strength, hardness, modulus, and electrical conductivity¹⁻⁵. Conventional fillers are generally processed by direct incorporation into the rubber matrix, eventually with the help of a coupling agent. However, 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. Among the various nano-fillers clays are the most widely studied nanomaterials used with rubbers. Nanoclays typically are layered silicates, and usually phyllosilicates such as montmorillonite, hectorite and saponite are used. Other kind of clays with tubular structure have also received importance. A plenty of reports could be found where halloysite nanotubes were used as nanofillers⁶⁻¹⁰. Halloysite nanotubes (HNTs) are 1:1 aluminosilicates; it is 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. The outer layer has Si-O groups on the surface and there are aluminiumhydroxide groups on the inner side and edges of the tube.⁴ The OH-groups are known to complicate dispersion of clay materials due to their inter-particle affinity, but the filler-filler interactions are lower with HNTs than with layered silicates. Furthermore, there is no need for exfoliation. Due to the tubular form, HNTs have a higher aspect ratio than other clay materials. The aspect ratio of HNTs 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.

Besides dispersion, the interaction between the rather hydrophobic elastomers and hydrophilic fillers cause a challenge. The compatibility between a hydrophobic polymer and a hydrophilic filler can be improved by changing the polarity of fillers. Different kinds of coupling agents are typically used to change the surface properties of fillers, which are added to the elastomer-filler blend during mixing. The coupling agent has to react with polymer and fillers simultaneously during the mixing step, which requires a certain temperature and time for the reaction to be completed. An alternative could be a pre-treatment of the filler by plasma treatment. Silica has been successfully modified by plasma polymerization treatments ¹¹⁻¹⁴. Halloysite nanotubes 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. 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 the present work, halloysite nanotubes 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 material properties.

EXPERIMENTAL

Materials

Halloysite nanotubes 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. Natural rubber was Standard Malaysian Type (SMR). Butadiene rubber was produced by Dow Chemical Company, Germany. Carbon black N-234 was delivered by Evonik, Germany. The TDAE-oil used in this study was Vivatex 500 produced by Hansen & Rosenthal GmbH, Germany. ZnO was a product from Grillo Zinkoxid GmbH, ceresine wax delivered by Statoil Wax GmbH, stearic acid was from Oleon N.V, sulphur from Solvay Barium Strontium GmbH, and TMQ (2,2,4-trimethyl-1,2-dihydroquinoline), 6PPD (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine) and CBS (Cyclohexyl-2-benzothiazyl sulphonamide) from Lanxess.

Plasma treatment

The plasma polymerization was carried out in a tubular vertical reactor. It consists of a round flask made from Pyrex glass and a long tubular region. The flask is connected to the vacuum pump (DuoSeal, model number 1402 B from Welch vacuum). Above the flask, there is a long cylindrical tube which is surrounded by a copper coil. The coil is connected to a radio frequency generator from MKS/ENI, type ACG-3B-01. At the top of the tube, there are two ports, which are meant as inlet for the monomers and connection for the pressure gauge (MKS Baratron® type 627B). Stirring of the powder was done by a magnetic stirrer. 20 grams of HTNs were placed into the bottom flask where they were treated with the activated monomers. The parameters of the plasma treatment of the different batches are presented in Table I.

TABLE I

Preparation of Nanocomposites

Natural rubber, butadiene rubber, nanofillers and other ingredients such as zinc oxide, stearic acid, carbon black (N-234), wax, oil and antioxidants were mixed in a Krupp Elastomertechnik GK 1.5 E intermeshing mixer (50°C, 70 rpm). CBS and sulphur were added on a mill. Table II shows the composition of the compound and the mixing procedure. In the reference compound, only carbon black (CB) was used as filler in a concentration of 42.5 phr. In the HNT containing compounds, 2.5 phr of CB was replaced by the same amount of HNTs.

TABLE II

Characterization

The deposition of the plasma coating was controlled by thermo gravimetric analysis in a Perkin-Elmer STA 6000 TGA. The heating temperature varied from 25°C to 995°C and the heating rate was 20°C/min; the measurements were done in a nitrogen atmosphere. 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 fillers onto the surface of a solvent; in this case water was used. More quantitative measurements were made by a water penetration test. In this test, 0.02 g of the filler was exposed to water and the change in weight due to absorption of water was measured over time.

The Mooney viscosity of the compounded material was measured in a MV 2000 Mooney Viscometer from Alpha Technologies. The measurement included 1 minute heating time and 4 minutes measuring time at 100°C. Curing studies and Payne effect were performed by using an Advanced Polymer Analyzer 2000 from Alpha Technologies. Curing studies were carried out at 160°C for 60 min and the Payne effect was studied in a strain sweep from 1.51% to 99.82% at 100°C.

Tensile tests of the samples were carried out with a Messphysik Midi 10-20 universal tester according to ISO 37.

RESULTS AND DISCUSSION

Filler Characterisation

To check the hydrophobicity the untreated HNT powder was poured into water and it was found that the powder sank into water immediately. However, after plasma treatment, a part of the material floated on the water for a while: this proves the reduction in polarity of the halloysite nanotubes after plasma treatment. The water absorption results are presented in Figure 1a. It is clear from Figure 1a, that pure HNTs as well as pyrrole and thiophene coated HNTs absorbed water with time and after a certain period an equilibrium level was attained. However, pure HNTs absorbed more water as compared to thiophene and pyrrole coated HNTs indicating a higher hydrophobic nature of plasma treated HNTs. In earlier studies with plasma treated silica, the reduction in water absorption was also observed but the effect was much stronger¹¹. This preliminary investigation indicates that pyrrole and thiophene coated HNTs could be more compatible with a non-polar rubber matrix.

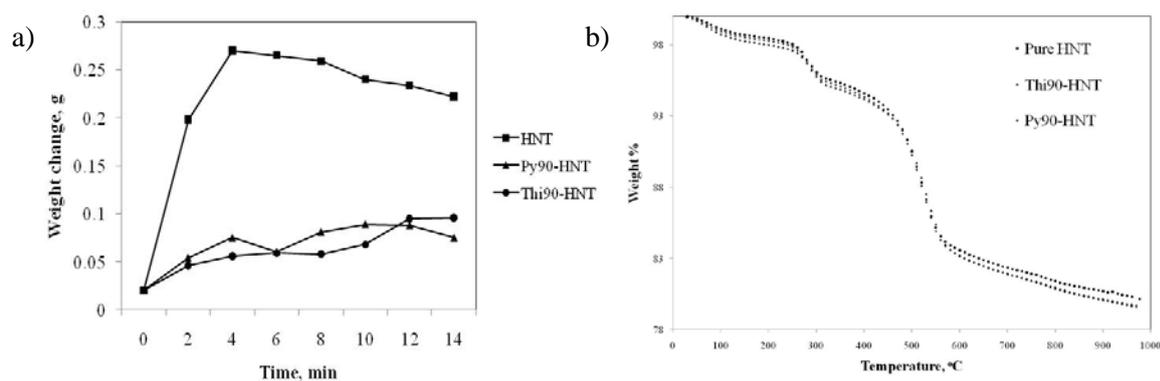


Figure 1. a) Water penetration of the plasma coated HNTs and b) Thermo-gravimetric analysis of the plasma coated HNTs.

The TGA curves of untreated, pyrrole and thiophene polymerized halloysite nanotubes are shown in Figure 1b and a three step degradation mechanisms was found to be operative there. The difference in

weight loss between treated and untreated fillers is the amount of plasma-polymerized film on the surface of filler. According to the measurements, HNTs treated by pyrrole had 0.7 wt% coating whereas HNTs treated by thiophene had 1.0 wt% coating.

Mooney Viscosity and Curing Studies

The Mooney viscosities [ML(1+4), 100°C] of the hybrid composites were determined with the different types of fillers. The Mooney viscosity showed a substantial increase in viscosity for the composite containing HNTs coated with pyrrole; the viscosity of the compound with the thiophene treated filler was slightly lower, but still higher than the viscosity of the material with untreated HNTs and without any HNTs. Untreated HNTs did not affect the viscosity at all (Fig. 2). The increase in viscosity is due to enhanced rubber-filler interactions, as plasma modified HNTs interact with the elastomer chain more firmly and increase the reinforcement.

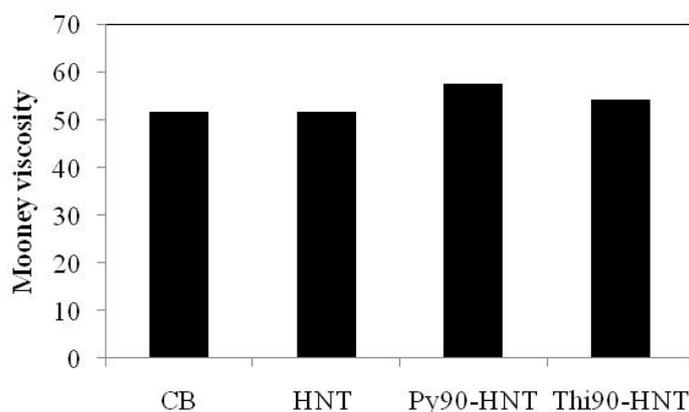


Figure 2. Mooney viscosity of the rubber compounds.

The vulcanization rheograms taken at 160°C are presented in Figure 3a. It is interesting to note that both, compounds with pyrrole and with thiophene coated HNTs, show a plateau in the cure curve whereas carbon black and pure HNTs filled compounds show a decrease in the torque value at a longer period of time. Reversion is a well-known phenomenon for sulphur 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 anti-reversion agents in the rubber compound. At the same time, the maximum rheometric torque increased with both types of plasma coated HNTs, and this increase is more pronounced for the compound containing plasma pyrrole treated HNTs than thiophene treated HNTs. The nitrogen and sulphur present in the molecular structure may influence the crosslinking kinetics, what is reflected in the torque development. A curing study at a relatively high temperature (193°C) showed that reversion can be observed for all compounds in this case, but the extent of reversion is much lower for compounds with plasma treated HNTs than for compounds with untreated HNTs or CB. At both temperatures, the cure curves for the CB and CB/HNT filled compounds are almost similar, indicating that the addition of the HNTs does not influence the curing characteristics.

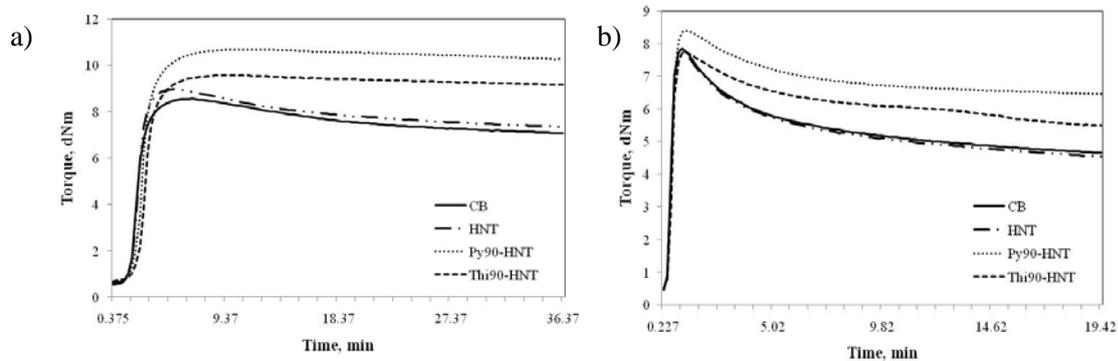


Figure 3. Development of the torque values of the NR/BR compounds filled with carbon black and halloysite nanotubes measured at a) 160°C b) 193°C.

Mechanical Properties

Stress-strain experiments of the NR/BR composites were carried out in order to investigate the effect of the incorporation of the plasma modified HNTs on the mechanical properties. It is evident from table III, that incorporation of pyrrole modified HNTs into the NR/BR matrix increases the 100% modulus 13% and the 300% modulus 12% where as with thiophene the values increase 5% and 7%. It should be remembered here the total amount of fillers in all the cases were kept constant at 42.5 phr. It is expected that minor influence on the modulus values is physically more significant particularly when the total volume fraction of the fillers in the mixed filler system is little bit less as the density of the HNTs are lower than CB used in this case. In terms of tensile strength, the highest value was

found when thiophene modified HNTs were introduced together with the carbon black. In this case also the elongation at break was found to be the highest. This is an effect of the sulphur moieties on the surface of the HNTs, which enables them to crosslink with the polymer and form interpenetrating networks.

Table III

The dynamic properties as a function of strain can help to understand the filler-filler interaction as well as the rubber-filler network of a filled elastomer matrix. Actually, the value of the storage modulus remains unchanged with strain in an unfilled system, while for a filled system a significant decrease can be observed. This non-linear behaviour was also observed in our system. Figure 4 illustrates the strain dependency of the storage modulus of the filled NR/BR matrix measured at 100°C. It is evident from the figure that at very low strain amplitudes ranges the value of G' remains constant up to a certain strain, and then the value is decreasing with further increase of strain. The CB filled NR/BR (Fig. 4) shows the highest G' values compared to the other vulcanizates indicating a stronger filler-filler network in CB filled system. As soon as 2.5 phr CB is replaced by 2.5 phr HNTs, the filler-filler interaction becomes weaker and the dispersion of the filler is improved as a consequence of better rubber-filler interactions.

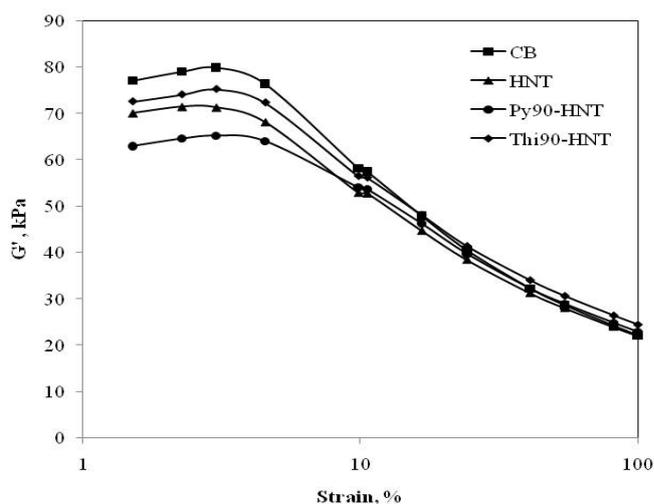


Figure 4. Strain dependence of the storage modulus G' at 100°C for carbon black and HNT filled rubber.

CONCLUSIONS

This study investigates the potential of plasma modification of HNTs in order to overcome the filler-filler interactions and 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. In this way, agglomeration of HNT particles is partially hindered and the dispersion in the polymer matrix improved. The partial replacement of carbon black by 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 a polythiophene coating having the most effect due to the sulphur moieties on the surface of the HNTs and the formation of interpenetrating networks.

ACKNOWLEDGEMENTS

This work has been supported by the Finnish Funding Agency for Technology and Innovation. The authors thank Mrs. S. Pohjonen, Mr. T. Lehtinen from Tampere University of Technology for their technical help. We are also thankful to Department of Elastomer Technology and Engineering, University of Twente for letting use their plasma reactor.

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TABLE I
PARAMETERS OF PLASMA TREATMENT

Monomer	Pressure, Pa	Monomer pressure, Pa	Power, W	Time, min
Pyrrole (Py90)	10	32	150	90
Thiophene (Thi90)	10	50	150	90

TABLE II
FORMULATION OF NR/BR COMPOUNDS AND MIXING PROCEDURE

Ingredients*	Amount, phr	Mixing, minutes
Nanofiller	0/2.5	1
N-234	42.5 / 40.0	
6PPD	2.0	1.5
TMQ	1.0	
ZnO	5.0	
TDAE-oil	8.0	2
Stearic acid	2.0	
Wax	1.5	Mixing: 4
CBS	1.5	
Sulphur	1.5	Mill: 5

*All the ingredients were taken in parts per hundred of rubber. The rubber composition was 80:20 with respect to NR and BR.

TABLE III
PHYSICAL PROPERTIES OF CARBON BLACK AND HNT FILLED RUBBER.

Sample	Tensile strength, MPa	Elongation, %	100% Modulus, MPa	300% Modulus, MPa
CB	20.6	442.8	2.5	12.1
HNT	19.7	380.0	2.7	12.8
Py90-HNT	21.7	410.4	2.8	13.5
Thi90-HNT	23.0	445.4	2.7	13.0

Figure 1. a) Water penetration of the plasma coated HNTs and b) Thermo-gravimetric analysis of the plasma coated HNTs.

Figure 2. Mooney viscosity of the rubber compounds.

Figure 3. Development of the torque values of the NR/BR compounds filled with carbon black and halloysite nanotubes measured at a) 160°C b) 193°C.

Figure 4. Strain dependence of the storage modulus G' at 100°C for carbon black and HNT filled rubber.