

MORPHOLOGY, INTERFACIAL INTERACTION AND PROPERTIES OF STYRENE-BUTADIENE RUBBER/MODIFIED HALLOYSITE NANOTUBE NANOCOMPOSITES*

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Abstract A natural nanotubular material, halloysite nanotubes (HNTs), was introduced to prepare styrene-butadiene rubber/modified halloysite nanotube (SBR/m-HNT) nanocomposites. Complex of resorcinol and hexamethylenetetramine (RH) was used as the interfacial modifier. The structure, morphology and mechanical properties of SBR/m-HNT nanocomposites, especially the interfacial interactions, were investigated. SEM and TEM observations showed that RH can not only facilitate the dispersion and orientation of HNTs in SBR matrix at nanometer scale, but also enhance the interfacial combination between HNTs and rubber matrix. FTIR and XPS investigations confirmed that a number of hydrogen bonds were formed between the phenol hydroxyl groups in resorcinol-formaldehyde resin derived from RH and the oxygen atoms in Si—O bonds or hydroxyl groups on HNTs surfaces. The m-HNTs modified with RH have significant reinforcing effect on SBR vulcanizates. RH as a good interfacial modifier can remarkably improve mechanical properties of SBR/HNT composites. The substantial improvement of comprehensive properties for SBR/m-HNT nanocomposites can be attributed to good dispersion and orientation of HNTs in SBR matrix at nanometer scale and the enhanced interfacial interaction between HNTs and rubber matrix.

Keywords: Styrene-butadiene rubber; Halloysite nanotubes; Complex of resorcinol and hexamethylenetetramine; Nanocomposites; Hydrogen bond.

INTRODUCTION

It is well known that inorganic fillers have been widely used in rubber industry. However, most of those fillers have no reinforcing effect on rubber except carbon black and silica. This is due to the micrometer dimensions of the filler particles, inferior compatibility and weak interfacial combination between fillers and rubber matrices. In the past two decades, the application of inorganic fillers with nanometer sizes has attracted great attention in rubber field^[1–3]. Among these nanometer fillers, layered silicate^[4–8], nano silica^[9–12], nano calcium carbonate^[13–15] and carbon nanotubes^[16] have been widely investigated. Generally, good dispersion at nanoscale and strong interfacial interaction are the prerequisites for the rubber/inorganics nanocomposites with excellent properties.

Halloysite nanotubes (HNTs) are a type of natural silicates with nanotubular structure, which have the same chemical composition as kaolinite. The nanotubular structure was evolved from kaolinite by rolling up the layers under natural conditions. Most of halloysite nanotubes are multi-wall nanotubes. Typically the outer diameters, inner diameters and lengths of the nanotubes are about 10–50 nm, 5–20 nm and 2–4 μm , respectively^[17]. Due to the special chemical structure, geometry shape and surface property, HNTs have been widely applied in many fields such as ceramics, cosmetics, drug delivery and catalyst carriers^[18–22]. Recently, our research group first introduced HNTs to polymer materials as a nanometer filler and found that the natural inorganic nanotubes had

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significant reinforcement and flame retardant effect on nylon, polypropylene, epoxy resin, linear low density polyethylene, natural rubber and other polymers^[23–28]. The authors have briefly reported in a rapid communication^[28] the reinforcing effect of HNTs on styrene-butadiene rubber (SBR) in the presence of coupling agent Si69. However, the SBR/HNT nanocomposites modified with other interfacial modifier have not yet been reported.

Due to low compatibility with rubber macromolecules, HNTs without surface modification show inferior dispersion and weak interfacial combination in rubber matrices^[29–31]. Consequently, their reinforcement effect on rubber is discounted. To improve the dispersion of HNTs in rubber matrices and the interfacial interactions between HNTs and rubber matrices, the surface modification of HNTs should be executed.

Complex of resorcinol and hexamethylenetetramine (RH) is generally used as the adhesive in rubber industry. Liu and Jia *et al.*^[32] introduced RH to nitrile-butadiene rubber-organomontmorillonite (NBR-HMMT) nanocomposites as an interfacial modifier. The results showed that the mechanical properties of the NBR-RH-HMMT nanocomposites were far superior to those of NBR-HMMT composites. RH could enhance the interface combination between the rubber and the organoclay through the interactions of RH with NBR and modified clay.

Syrene-butadiene rubber (SBR) is the most important and widely used synthetic rubber. The researches on the nanocomposites of SBR and HNTs have theoretical and practical significance. The key of these researches is the surface modification of HNTs or interfacial modification of the composites. In this paper, RH was used as the interfacial modifier of HNTs to prepare modified HNTs (m-HNTs) and SBR/m-HNT nanocomposites. The structure and morphology of SBR/m-HNT nanocomposites, especially the interfacial hydrogen bond interaction between m-HNTs and SBR, were characterized. The effects of m-HNTs and RH on mechanical properties and dynamic mechanical properties of the nanocomposites were investigated. It was found that RH can facilitate the dispersion and orientation of HNTs in SBR matrix at nanometer scale and enhance the interfacial combination between HNTs and rubber matrix through forming interfacial hydrogen bonds. Consequently the obtained SBR/m-HNT nanocomposites possess substantially improved properties.

EXPERIMENTAL

Materials

Butadiene-styrene rubber (SBR 1502) is a commercial product of Jilin Chemical Industrial Co., Ltd. Halloysite nanotubes (HNTs) were mined from Hubei province, China. Its specific surface area is 50.45 m²/g. The chemical compositions are as follows (wt%): SiO₂ 58.9, Al₂O₃ 40.4, P₂O₅ 0.138, Fe₂O₃ 0.275, TiO₂ 0.07, others 0.217. RH was provided by Guangzhou Pearl River Rubber Tire Co., Ltd. The molar ratio of resorcinol and hexamethylenetetramine is 1:1. Other ingredients were all commercial products and used as received.

Surface Modification of HNTs

A certain amount of RH and HNTs were added to a flask and stirred vigorously for about 30 min at room temperature, then heated for 4 h at 60°C to obtain modified HNTs (m-HNTs). Typical RH/HNTs mass ratio was 6/100.

Preparation of SBR/m-HNT Nanocomposites

SBR and m-HNTs were compounded by using a ϕ 160 two-roll mill and then compounded with other ingredients. The compounds were compression molded and vulcanized at 150°C. The curing characteristics of the compounds were determined at 150°C by U-CAN UR-2030 vulcameter.

The basic formulation is as follows (mass parts): SBR 100, HNTs 0–50, RH 0–10, stearic acid 2, zinc oxide 5, accelerating agent CZ 1.5, accelerating agent DM 0.5, anti-ager 4010NA 1.5, sulfur 1.5.

Scanning Electron Microscopy (SEM)

SEM observation was carried out by using an SM1530VP Scanning Electron Microscope. Fracture surfaces of frozen specimens in liquid nitrogen were coated with gold thin films before the observations.

Transmission Electron Microscopy (TEM)

TEM observation was conducted by using a JEM-100CXII transmission electron microscope with an accelerating voltage of 100 kV. An ultrathin section was prepared by a Leica EM UC6 ultramicrotome in liquid nitrogen.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was conducted on a Netzsch 242C DMA equipment. The tensile mode was selected. The heating rate was set at 10 K/min and the frequency at 5 Hz.

Fourier Transform Infrared Spectroscopy (FTIR)

The HNTs powder or HNTs/RH (m-HNTs) powder was compression molded with potassium bromide into a round specimen with 10 mm in diameter and 2 mm in thickness. FTIR analysis of the specimen was carried out by using a MAGNA 760 FTIR spectrometer.

X-ray Photoelectron Spectroscopy (XPS)

XPS spectra of RH and HNTs coated with RH were recorded by using an X-ray Photoelectron Spectrometer (Kratos Axis Ultra DLD) with an aluminum (mono) $K\alpha$ source (1486.6 eV). The aluminum $K\alpha$ source was operated at 15 kV and 10 mA.

Mechanical Properties

Tensile tests were performed following ISO standard 37-2005 at room temperature. Tensile strength, modulus and elongation at break were measured using an U-CAN UT-2060 instrument (Taiwan). Shore A hardness was performed following ISO standard 7619-1986 by a XY-1 sclerometer (Shanghai).

RESULTS AND DISCUSSION**Effect of RH on the Morphology of SBR/HNT Composites**

The SEM photographs of SBR/HNT (100/50) and SBR/m-HNT (100/50) composites are shown in Fig. 1. It can be seen from Figs. 1(a) and 1(c) that a certain amount of agglomerates of HNTs are observed in SBR/HNT composites. Moreover, the interfaces between halloysite nanotubes and rubber matrix are clear, and many debonded nanotubes pulled out from SBR matrix are observed. This suggests that there may exist a weak interfacial combination between HNTs and rubber matrix. As contrasted with SBR/HNT composite, for the SBR/m-HNT composites shown in Figs. 1(b) and 1(d) the agglomerates are obviously less than the former and most of HNTs particles are uniformly dispersed at nanometer scale in rubber matrix. It is also observed that the interfaces between HNTs and rubber matrix are blurry and nearly no debonded HNTs. These results suggest that RH can not only facilitate the dispersion of HNTs, but also increase the interfacial combination ability between HNTs and rubber matrix.

Figure 2 shows the TEM photographs of SBR/HNT and SBR/m-HNT composites. In SBR/HNT composite the dispersion of HNTs particles is irregular, and many HNTs particles are obviously formed with agglomerates. In SBR/m-HNT composites, however, the agglomeration of HNTs particles is reduced due to the effect of interfacial modifier RH, and the orientation of the particles is obviously improved. It is indicated that RH can facilitate the dispersion and orientation of HNTs particles in SBR matrix, and the SBR/m-HNT composites possess the characteristics of nanocomposites. The TEM results are consistent with those of SEM observations described above.

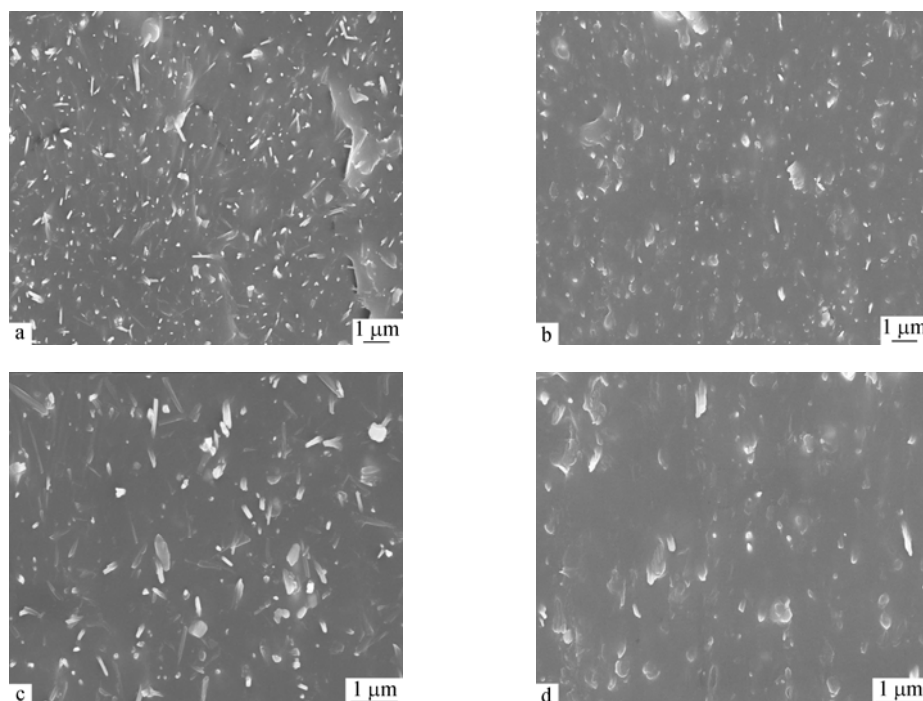


Fig. 1 SEM photographs of SBR/HNT (a, c) and SBR/m-HNT (b, d) composites
a) SBR/HNT (100/50), Mag. = 5K; b) SBR/m-HNT (100/50), Mag. = 5K; c) SBR/HNT (100/50), Mag. = 10K; d) SBR/m-HNT (100/50), Mag. = 10K

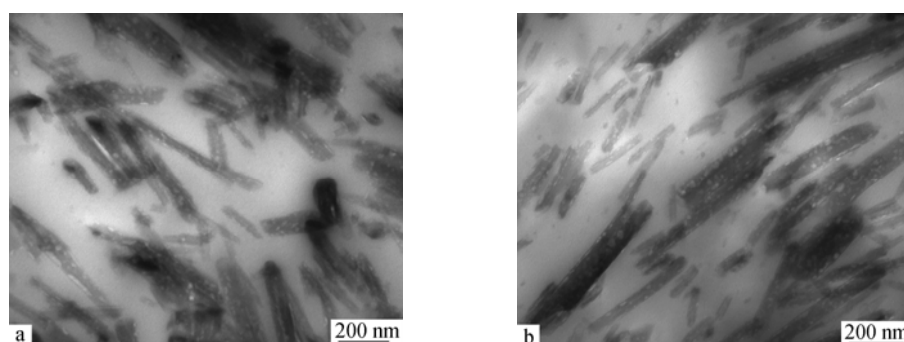


Fig. 2 TEM photographs of SBR/HNT (a) and SBR/m-HNT (b) composites
a) SBR/HNT (100/50); b) SBR/m-HNT (100/50)

Dynamic Mechanical Analyses of SBR/HNT and SBR/m-HNT Composites

Figure 3 shows the DMA spectra for SBR/HNT and SBR/m-HNT composites. It can be seen that the glass transition temperatures (T_g) of SBR/HNT and SBR/m-HNT composites are -30.4°C and -27.8°C , respectively. This indicates that the modification of SBR/HNT composite by RH causes the increase of the T_g of the composites. It can be explained that in the SBR/HNT composite the interfacial interaction between unmodified HNTs and SBR matrix is relatively weak, whereas for the SBR/m-HNT nanocomposite some chemical or physical interactions between HNTs and rubber matrix can be formed, and the interfacial interaction can be enhanced by the incorporation of RH. This will result in a certain limitation on the segmental motion of rubber molecules and hence cause the increase of the T_g .

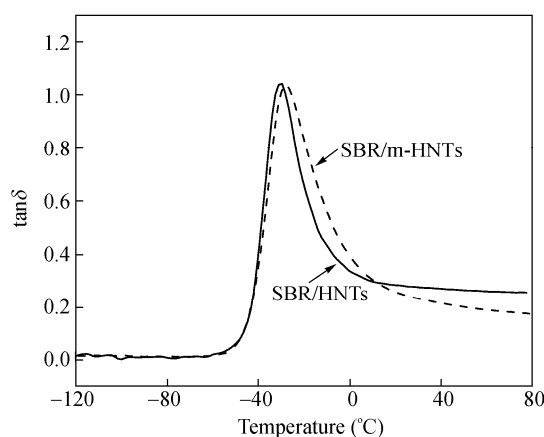


Fig. 3 DMA curves of SBR/HNT and SBR/m-HNT composites

It is known that the $\tan\delta$ values at different temperatures or at different frequencies in DMA spectra correspond to wet grip and rolling resistance of the vulcanizates^[33–35]. Generally, the $\tan\delta$ values at about room temperature and at about 60°C represent the wet grip and the rolling resistance of the vulcanizates, respectively. Figure 3 shows that the $\tan\delta$ values of SBR/m-HNT nanocomposites at about 0°C are higher than those of unmodified SBR/HNT composites, whereas the $\tan\delta$ values of SBR/m-HNT nanocomposites in the vicinity of 60°C are obviously lower than those of SBR/HNT composites. This indicates that the addition of RH can improve the wet grip and reduce the rolling resistance of SBR/HNT vulcanizates simultaneously, which is advantageous for green tires. The reduction of rolling resistance of the filled vulcanizates relates to the interfacial combination between filler and rubber. The DMA results suggest that the interfacial combination in SBR/HNT composites is relatively weak, and in SBR/m-HNT nanocomposites the interfacial combination between m-HNTs and rubber matrix is obviously strengthened by the addition of interfacial modifier RH.

Characterization of Hydrogen Bond Interaction between HNTs and RH

To investigate the nature of interfacial combination between HNTs and SBR, FTIR and XPS analyses were conducted. Under the curing conditions, hexamethylenetetramine in RH will decompose to produce activated methylenes, which can react with resorcinol and form resorcinol formaldehyde resin. The resorcinol formaldehyde resin can react with SBR macromolecular chains to form co-cured networks by the addition reaction of double bonds in butadiene units or by the substitution reaction of α -hydrogen atoms of butadiene units in SBR macromolecular chains^[32]. At the same time, a large number of phenol hydroxyl groups contained in the formed resorcinol formaldehyde resin can form hydrogen bonds with oxygen atoms of Si—O bonds or hydroxyl groups on the surfaces of HNTs. These hydrogen bonds can increase the interfacial interaction between HNTs and resorcinol formaldehyde resin combined with SBR macromolecules. Consequently the interfacial modifier RH can remarkably enhance interfacial combination between HNTs and SBR.

In order to investigate the interfacial hydrogen bond interaction in the nanocomposites, the HNTs and the mixture of HNTs/RH (m-HNTs) as a model system were compression molded into the specimens for FTIR analysis respectively. The FTIR spectra are shown in Fig. 4. In Fig. 4(a) the strong characteristic peaks at 1029 and 1096 cm^{-1} in HNTs spectrum are assigned to the stretching vibration of Si—O bonds on HNTs surfaces. It is observed that the corresponding absorption peaks in HNTs/RH system are shifted to 1019 and 1086 cm^{-1} , respectively. In Fig. 4(b) the strong absorption peak at 3694 cm^{-1} in HNTs spectrum is assigned to the absorption of external hydroxyl groups on HNTs surfaces. The corresponding absorption peak in HNTs/RH system is shifted to 3698 cm^{-1} . It is believed that the shifts of FTIR absorption peaks are resulted from the formation of hydrogen bonds between the oxygen atoms of Si—O bonds or hydroxyl groups on the surfaces of HNTs and the phenol hydroxyl groups of resorcinol in RH.

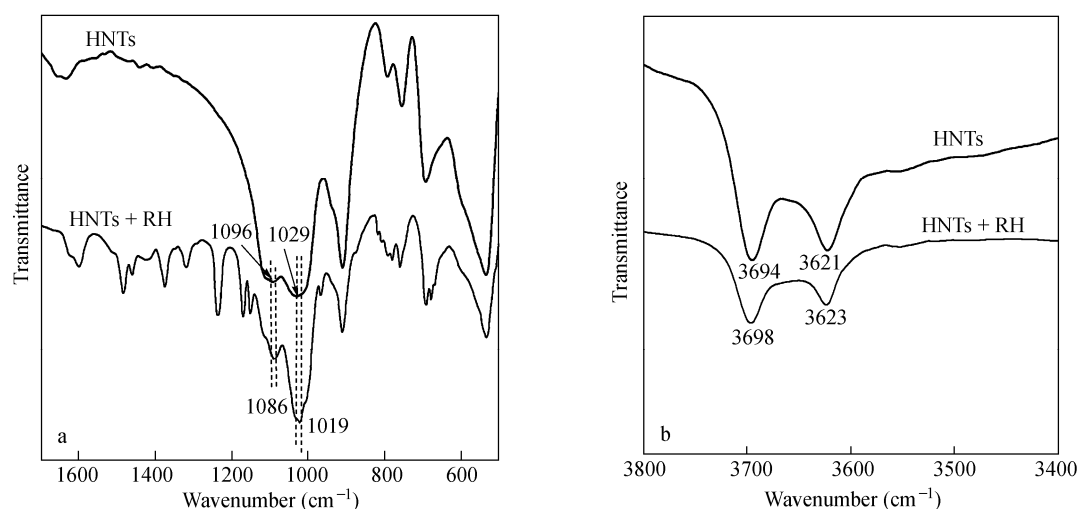


Fig. 4 FTIR spectra of HNTs and HNTs/RH mixture

The formation of hydrogen bonds will cause the change of chemical environment around atoms forming hydrogen bonds and hence lead to the change of binding energy of the atoms^[36–38]. Therefore, X-ray photoelectron spectroscopy (XPS) can be used as an effective method to characterize the formation of hydrogen bonds. The survey-scan XPS spectra and O1s high resolution XPS spectra of RH and RH/HNTs mixture are showed in Fig. 5 and Fig. 6, respectively.

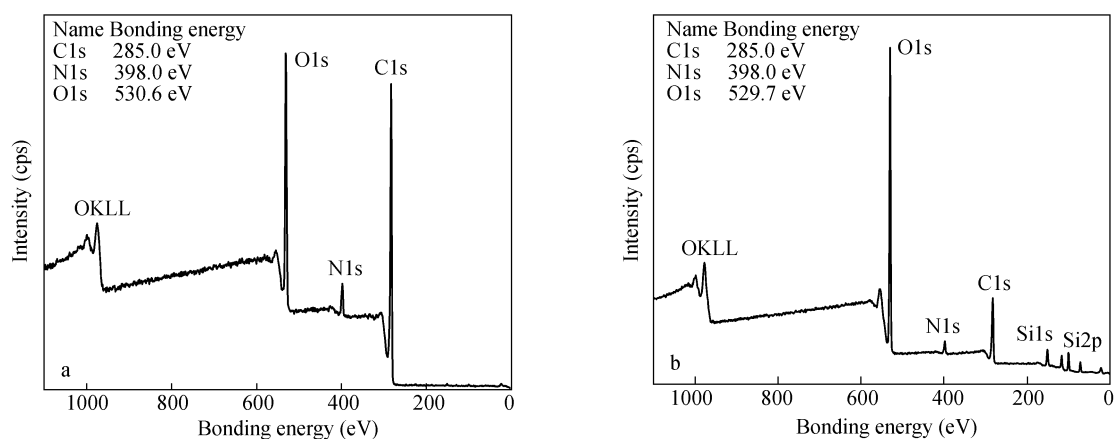


Fig. 5 Survey-scan XPS spectra of RH (a) and RH/HNTs mixture (b)

From the survey-scan XPS spectra shown in Fig. 5 it is indicated that there is no difference in the binding energies for C atoms and N atoms between RH and RH/HNTs systems, while obvious change occurs in the O1s binding energy. O1s XPS spectra, as shown in Fig. 6, show that the O1s binding energy in RH molecules is 530.5 eV, while the O1s binding energy in RH/HNTs system (marked by 1O1s) is changed to 529.5 eV. These results indicate that the chemical environment of O atom has been changed in RH/HNTs system, and it is believed that the change is caused by the formation of hydrogen bonds.

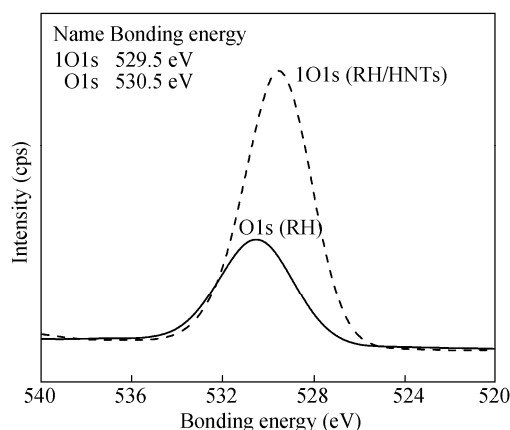


Fig. 6 O1s XPS spectra of RH and RH/HNTs mixture

Mechanical Properties of SBR/m-HNT Nanocomposites

Table 1 summarizes the effects of m-HNTs content on the mechanical properties of SBR/m-HNT nanocomposites. It is found that the modulus, tensile strength, tear strength and hardness of the nanocomposites are gradually increased with increasing the content of HNTs. The results indicate that m-HNTs modified with RH have significant reinforcing effect on SBR vulcanizates.

Table 1. Effects of m-HNTs content on the mechanical properties of SBR/m-HNT nanocomposites*

m-HNTs content (phr ^{**})	Modulus at 300% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)	Permanent set (%)	Tear strength (kN/m)	Shore A hardness
0	1.33	2.4	610	4	11.3	42
10	2.27	3.4	580	6	16.9	48
20	3.02	4.7	590	8	24.6	52
30	3.57	6.6	600	16	29.3	56
40	5.09	8.4	580	20	37.1	61
50	4.81	9.3	600	30	37.7	64

* RH/HNTs mass ratio is 3/50 in m-HNTs; ** Parts per hundred rubber

Table 2 shows the effects of RH content on the mechanical properties of SBR/m-HNT nanocomposites. The modulus, tensile strength, tear strength and hardness of the nanocomposites are considerably increased with increasing RH contents, whereas the permanent set and the elongation at break of the nanocomposites are reduced with the increase of RH contents. The results indicate that RH is a good interfacial modifier of SBR/HNT composites, and it can remarkably improve the mechanical properties of SBR/HNT composites.

Table 2. Effects of RH content on the mechanical properties of SBR/m-HNT (100/50) nanocomposites

RH content (phr)	Modulus at 300% elongation (MPa)	Tensile strength (MPa)	Elongation at break (%)	Permanent set (%)	Tear strength (kN/m)	Hardness, shore A
0	3.04	10.3	680	62	30.0	61
2	4.43	10.5	610	40	36.5	64
4	5.84	11.4	610	34	43.4	66
6	7.71	12.5	580	32	50.7	68
8	8.12	13.9	600	40	54.0	69
10	8.69	13.4	540	40	53.8	71

CONCLUSIONS

SBR/m-HNT nanocomposites can be prepared by using RH as the interfacial modifier in mixing and vulcanizing processes. RH not only can facilitate the dispersion and orientation of HNTs in SBR matrix at nanometer scale, but also strengthen the interfacial combination between HNTs and rubber matrix. Under the curing conditions, a

number of hydrogen bonds are formed between the phenol hydroxyl groups in resorcinol-formaldehyde resin derived from RH and the oxygen atoms in Si—O bonds or hydroxyl groups on HNTs surfaces. These hydrogen bonds can enhance the interfacial combination between HNTs and SBR matrix. The m-HNTs modified by RH have significant reinforcing effect on SBR vulcanizates. RH as a good interfacial modifier can remarkably improve mechanical properties of SBR/HNT composites. It is believed that the substantial improvement of comprehensive properties for SBR/m-HNT nanocomposites can be attributed to good dispersion at nanometer scale and orientation of HNTs in SBR matrix and enhanced interfacial interaction between HNTs and rubber matrix.

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