Composites: Part A 84 (2016) 344–353

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa

Wrapping of polyrhodanine onto tubular clay and its prominent effects on the reinforcement of the clay for rubber

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ARTICLE INFO

Article history:
Received 26 October 2015
Received in revised form 1 February 2016
Accepted 16 February 2016
Available online 23 February 2016

Keywords:
A. Nanocomposites
B. Interface
B. Strength
B. Mechanical properties

ABSTRACT

Polyrhodanine (PRd) was wrapped onto the surface of halloysite nanotubes (HNTs) through the oxidative polymerization of rhodanine on Fe^{3+}-impregnated-HNTs. The wrapping mechanisms were disclosed. The PRd-HNTs exhibited a prominent reinforcing effect for rubber. With the incorporation of 30 phr of PRd-HNTs, the tensile strength was increased by almost 8-fold, and the modulus (at 300% strain) was increased by 257% compared to neat SBR. More strikingly, with only 2.9 wt.% of PRd (relative to HNTs), the tensile strength and modulus of the composite were enhanced by 117% and 87%, respectively, suggesting the high efficiency of the modification. Such profound changes in the reinforcement were attributed to the formation of covalent linkages between PRd-HNTs and rubber through the participation of PRd-HNTs in curing process. In view of the versatility of PRd-wrapping procedure, this method offers significant insight into the interfacial design of rubber nanocomposites consisting of nonpolar matrices and inorganic reinforcements.

1. Introduction

Halloysite nanotubes (HNTs) [1], naturally occurring tubular clays, were formed by rolling kaolinite sheets into multi-walled structure under natural conditions. HNTs are therefore chemically similar to kaolinite. The siloxane and silanols are located outside of the tubes, and the aluminols are mainly located at the ends and inner side of the tubes [2]. Compared to synthetic nanotubes, such as carbon nanotubes (CNTs), HNTs possess many advantages [1,3], easier functionalization due to the presence of the surface groups, better processability due to the weaker inter-tube interactions and entanglement-free nature, natural abundance, low cost, etc. With these attributes, HNTs have attracted extensive attention for use in polymer-based composites [4]. Nanocomposites of polymer/HNTs were found to exhibit many interesting properties, such as much improved mechanical properties [5], enhanced thermal stability [6], controlled release [7] and tailored crystallization [8].

For rubber/HNTs composites, HNTs have been reported to be effective in improving mechanical properties [9], thermal stability [10], abrasion resistance [11] and aging performance [12], etc. Diverse HNTs composites with rubbery matrices such as polar rubber [13] and nonpolar rubbers [14] have been reported.

Dispersion and interfacial interaction are two critical factors in determining the ultimate mechanical performances of the rubber nanocomposites. Therefore, although some success in rubber/HNTs composites has been achieved in some polar rubber [13,15], the reinforcement of nonpolar rubber by HNTs is not adequate due to the high polarity and hydrophilic nature of pristine HNTs; as a result, interfacial modification is always necessary. Various substances have been used as interfacial modifiers in rubber/HNTs composites, such as thiol-containing ionic liquids [16], methacrylic acid [17], sorbic acid [18], silane [19], bis-phenol A [15] and so on. Enhanced reinforcing capabilities of HNTs in SBR/HNT composites, NR/HNTs composites [20] and EPDM/HNTs composites [21,22] have been found. However, one must face an awkward situation: despite the above-mentioned modification practices, the reinforcing effect of HNTs is greatly inferior to that of its inorganic counterpart, nanosilica, which is widely used in rubber industry. That is, the interfacial properties of SBR/HNTs composites remain to be optimized.

Rhodanine (Rd), generally used as an adsorbent [23], possesses an excellent adsorption effect on heavy metal ions. During the adsorption process, rhodanine itself undergoes polymerization to form polyrhodanine (PRd) through the electron transfer effect [24]. During the 1950–1960 s, Rd was used as an accelerator for rubber vulcanization. During the vulcanization, the intermediate containing rhodanine moieties can stabilize the polysulfides; therefore, the polysulfides are difficult to release. As a

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http://dx.doi.org/10.1016/j.compositesa.2016.02.015
1359-835X/

consequence, low accelerating efficiency and low curing rate have been found in the rubber compounds with Rd as the accelerator. Thus, the use of Rd in the rubber industry eventually stopped due to the establishment of a wide variety of alternative accelerators with much higher accelerating effects. However, the lower accelerating effect offers opportunity in the interfacial design if Rd is anchored onto the filler as the formed linkage between the rhodanine intermediate, and the rubber chain may be able to survive.

The oxidative polymerization of Rd by metal ions, such as ferric ions and silver ions, has already been reported [25]. In Jang's work [26], Fe(III) ions were adsorbed on the surface of silica through electrostatic interaction. The polymerization of Rd then occurred preferentially on the surface of the silica nanoparticles through a charge transferring reaction. After the polymerization, PRd was wrapped on the surface of silica, so silica/polyrhodanine core/shell nanoparticles were produced. Due to the negatively charged surface of HNTs, in the present study, Fe(III) ions were anchored onto the surface of the HNTs through electrostatic interaction. Next, the oxidative polymerization of Rd into PRd was conducted on Fe^{3+}-treated HNTs. Accordingly, PRd-wrapped HNTs were prepared. The modified HNTs were incorporated into SBR via two-roll milling to form the rubber/HNTs composites. The wrapping mechanism of PRd onto HNTs was investigated. The mechanical properties and the interface property were evaluated. The prominent effects of the interfacial modification on the reinforcement were found and correlated to the formation of a unique interfacial structure.

2. Experimental section

2.1. Raw materials

Rhodanine was purchased from Innochem. Styrene butadiene rubber (SBR), with the trade name SBR1502 (styrene content 23.5 wt.%), was manufactured by Jilin Chemical Industry Company, China. The HNTs were mined from Yichang, Hubei, China. Other chemicals, including hexane and $FeCl_3$, were analytically pure and used as received. The rubber additives were industrial grade and used as received.

2.2. Preparation of PRd-HNTs compounds

HNTs were purified according to our previously reported procedure [27]. Next, the purified HNTs were vacuum-dried at 60 °C for 8 h. Subsequently, a certain amount of HNTs were dispersed in aqueous solution, followed by the addition of $FeCl_3$ (HNTs/$FeCl_3$ weight ratio of 8:1) under vigorous stirring. The impregnation lasted for 8 h at room temperature. The excess Fe(III) ions were removed by repeated washing with deionized water and centrifugation. The product was dried at 50 °C for 8 h. Next, a certain amount of Fe(III)-ion-treated HNTs was dispersed in hexane. Rd was then added, and the oxidative polymerization of Rd lasted for 12 h at room temperature under vigorously stirring. After the polymerization, PRd wrapped HNTs were obtained by repeated washing with hexane and centrifugation.

2.3. Preparation of SBR/HNTs composites

Pristine HNTs and PRd-HNTs were compounded with SBR via two-roll milling. The basic recipe for the compound was as follows: sulfur, 1.5 phr; ZnO, 5 phr; stearic acid, 1 phr; 2,2-dibenzothiazole disulfide (DM), 0.5 phr; N-cyclohexyl-2-benzothiazole (CZ), 1.5 phr; and the filler contents were variable. The rubber composites containing x phr of pristine HNTs is designated as H-x. The rubber/PRd-HNTs composite with x phr of PRd-HNTs is named as HR-x. During the preparation of PRd-HNTs for HR-x samples, the HNTs/Rd ratio was 15:1. The rubber compounds were subjected to compression molding at 150 °C for optimized curing time (Tc90), which was measured using a curing rheometer.

To examine the effects of the wrapping amount of PRd on the interfacial property of the resulting rubber composites, PRd-HNTs with different wrapping amounts were prepared. The production of these samples was accomplished by changing the initial HNTs/Rd ratio for the polymerization. The initial HNTs/Rd ratio was set as 15/1, 15/0.75, 15/0.5, 15/0.25 and 15/0. The actual wrapping amount of PRd on HNTs was determined by thermogravimetric analysis (TGA), as summarized in Table 1. All preparation processes for the rubber composites were performed according to the aforementioned protocols.

2.4. Measurements and characterization

Fourier transform infrared spectra (FTIR) were recorded on a Bruker Vector 33 FT-IR spectrometer. The dried HNTs and PRd-HNTs samples were ground to fine particles, and then, the FTIR spectra were recorded in transmission mode against a KBr single-beam background spectrum. Thermal gravimetric analysis (TGA) was conducted on a TGA Q500 instrument (USA) under nitrogen purging at a heating rate of 10 °C/min from 35 °C to 700 °C. The hydrophobicity of PRd-HNTs was verified by the extraction experiment. Approximately 0.1 g of HNTs and 0.1 g of PRd-HNTs were separately added to two glass tubes. The tubes were filled with 10 mL toluene, followed by bath sonication for 20 min. After further filling of 10 mL deionized water, the tubes were subjected to further bath sonication for 20 min. After standing, the observation on the retention of PRd-HNTs in solvent was made. X-ray photoelectron spectroscopy (XPS) was performed with a Kratos Axis Ultra DLD X-ray photoelectron spectroscope (UK) with Al Kα radiation of 1486.6 eV. The high-resolution surveys (pass energy of 40 eV) were performed at spectral regions related to silicon and aluminum.

Curing behavior was determined using a U-CAN UR-2030 vulcameter (Taiwan) at 150 °C. Swelling experiments were performed by immersing the vulcanized rubber sample in toluene at room temperature for 72 h, and then, the volume fraction of the rubber in the swollen rubber (Vr) was determined. The detailed calculation procedures are described elsewhere [28]. Dynamic mechanical analysis (DMA) was performed on a TA DMA Q800 instrument in tension mode with a dynamic strain of 0.5%. The samples were scanned from −60 to 60 °C. The frequency and heating rate were set as 1 Hz and 3 °C/min, respectively. The scanning electron microscope (SEM) images were collected on a Hitachi S-4800 field emission scanning electron microscope (Japan). The samples frozen in liquid nitrogen and then brittle fracture, the cryogenically fractured surface of the samples through a conductive adhesive sticked on the sample stage, it can be tested after spraying gold. Transmission electron microscopy (TEM) for the ultramicrotomed samples was conducted on a Tecnai G2 F30 S-Twin electron microscope operated at an accelerating voltage of 30 kV, Sample used the ultrathin sectioning preparation method before testing. The tensile

Table 1
Compositions of SBR/PRd-HNTs composites with variable PRd wrapping (SBR/HNTs = 100/30).

Sample code	PRd (phr)	HNTs/rhodanine ratio
Pristine HNTs	0	15/0
PRd-HNTs-1	0.14	15/0.25
PRd-HNTs-2	0.41	15/0.5
PRd-HNTs-3	0.89	15/0.75
PRd-HNTs-4	1.58	15/1