Low permeability styrene butadiene rubber/boehmite nanocomposites modified with tannic acid

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ABSTRACT

Layered inorganics are promising in the fabrication of elastomeric nanocomposites with enhanced barrier property. Recently, boehmite (BM) nanoplatelets have emerged as alternative layered inorganics to clays and double hydroxylates as the functional reinforcement for rubbers. In the present paper, natural tannic acid (TA) is introduced as a novel interfacial modifier in BM-filled styrene–butadiene rubber (SBR) nanocomposites. The modification mechanism and interfacial interactions in the nanocomposites are fully characterized. Due to the strengthened interface and the comparatively finer dispersion state of BM in the nanocomposites, significantly enhanced mechanical properties are found in the modified system. At higher BM loadings (higher than 40 phr), the modified system possesses a much lower gas permeability compared with the unmodified counterpart. Very interestingly, the TA-modified SBR/BM nanocomposites exhibit high tensile strength yet impressively low moduli compared with previously reported rubber nanocomposites filled with other nanofillers.

1. Introduction

Boehmite (BM), with an ideal formula of γ-AlO(OH), has gained significant attention for its special 2D geometry and alkaline surface chemistry [1–3]. Abundant aluminol (Al–OH) groups are located on the surface of BM sheets, which endows BM with special Lewis basicity instead of the acidity generally found in layered silicates [4]. BM has been widely used in diverse applications, such as absorbents [5], optical materials [6] and coatings [2]. In particular, similar to other 2D inorganics, such as graphene and clays, BM has been demonstrated to be a promising nanofiller for various polymers to impart low gas permeability and flame retardancy [7–9].

Generally, BM layers tend to severely agglomerate with each other due to strong inter-particle interactions caused by the surface Al–OH groups. In addition, inferior interfacial interactions are mostly found in the BM-filled polymer nanocomposites. The poor dispersion and insufficient interfacial interaction lead to unsatisfied ultimate performance of polymer/BM composites. To maximally transfer the potentials of BM into polymer matrices, great efforts have been developed to modify BM based on its surface chemistry. To date, silane coupling agents and various acids have been demonstrated to be efficient in modifying BM. For instance, bis-[3-(triethoxysilyl)-propyl]-tetrasulfide was utilized to modify BM through a silanization reaction between the aluminols of BM and ethoxy groups of silane. Upon modification, the resulting nitrile rubber/BM nanocomposites exhibited a largely improved mechanical

performance due to the combination of a strengthened interface and better dispersion of BM [10]. Based on the superficial basicity of BM, many acidic compounds, such as methacrylic acid [4], phosphoric acid diester or acrylic acid [11], and sulfonic acid [12], have been used to modify BM. Chen et al. used methacrylic acid as a modifier in styrene–butadiene rubber (SBR)/BM composites [4]. Methacrylic acid was believed to coordinate with BM, which greatly improved the compatibility between SBR and BM. Florjańczyk et al. reported that BM modified by phosphoric acid diester or acrylic acid exhibited a much higher reinforcing efficiency for carboxylated SBR [11]. Despite these achievements, the practical implementation of BM modification remains a great challenge because the abovementioned modification methods possess obvious drawbacks. For instance, silanes are sensitive to humidity, and silanization is highly dependent on reaction temperature, which leads to unmanageable side reactions and unsatisfied repeatability. Sulfonic acid and methacrylic acid will corrode processing machinery and are harmful to human beings [12], and phosphorus-containing substances are environmentally hazardous [13]. Thus, significant efforts are still being made to seek a facile yet effective and environmentally-friendly method to modify BM for achieving the mass preparation of rubber/BM composites.

Tannic acid (TA), i.e., a low cost and abundant hydrolysable tannins, may exert a tremendous effect on the modification of BM. Tannins are polyphenolic secondary metabolites of higher plants, widely distributed in nature. Due to multiple adjacent phenolic hydroxyl groups, tannins are capable of complexing with metal ions and macromolecules, such as proteins and polysaccharides, and show antioxidant activity by radical scavenging [14,15]. Due to their versatilities, tannins have been extensively used in industrial production, including tanning, pharmacy,

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water purification, food additive, and so on [16,17]. In light of the above considerations, we convinced that TA might be used as a versatile "green modifier" for various nanofillers based on metal oxides, such as BM.

In this contribution, TA was utilized to modify BM by using the specific coordination interaction between them. TA-modified BM is expected to be better dispersed in SBR matrix and have enhanced interfacial interactions with the rubber. The effects of TA on the mechanical properties and gas permeability of SBR composites were fully studied.

2. Experimental

2.1. Raw material

SBR, trademarked as SBR1502 (with 23.5 wt.% content of styrene), was manufactured by Lanzhou Petrochemical Co. Ltd., Lanzhou, China. Mooney value of the SBR was 52 (ML 1 + 4 100 °C). BM nanoplatelets, with Brunauer–Emmett–Teller (BET) surface area of 142.8 m^2/g, were produced by Shandong Aluminum Co. Ltd., Zibo, China. The average aggregated particle size of the BM was in the range of 1–20 μm. A single nanoplatelet of BM possessed a thickness of about 3 nm and an in-plane size in the range of 200–400 nm. TA purchased from Tianjin Fuchen Chemical Reagents, Tianjin, China was of analytical grade. Other rubber additives were industrial grade and used as received.

2.2. Preparation of SBR composites

The preparation of SBR/BM/TA composites was conducted in the following manner. First, BM and TA were successively incorporated into SBR in a HAAKE Polylab OS mixer at a pre-set temperature of 80 °C to prepare the SBR masterbatch. In the masterbatch, the weight ratio of SBR, BM and TA was 10:10:1. The resulting masterbatch was then diluted with certain amount of SBR on a two miller mixer, and the rubber additives were added. The BM loading in the composite was variable (10, 20, 40, 60 and 80 phr (parts per hundred parts of rubber)). The basic formulation for the rubber composites was as follows: 100 g of SBR, 5 g of zinc oxide, 2 g of stearic acid, 1 g of 2,2′-dithio-dibenzo thiazole, 1.5 g of N-cyclohexyl-2-benzothiazole sulfonamide, 1.5 g of sulfur, and variable amounts of BM and TA. Lastly, the resulted compounds were compression molded into 1 mm thick sheets at 160 °C for curing time determined by a vulcameter. For comparison, SBR/BM composites were prepared following similar protocols for the preparation of SBR/BM/TA composites without adding TA. In this work, the nomenclature BxTy represents a SBR/BM/TA composite with x phr BM and y phr TA, and the nomenclature BxT0 represents a SBR/BM composite with x phr BM and 0 phr TA.

2.3. Preparation of TA-modified BM

To envisage the modification of BM with TA and to eliminate any confounding influence from the SBR matrix, the model compound of TA-modified BM (TA-BM) was prepared as follows. BM was dispersed in water at a concentration of 5 mg/mL. TA was then added at a BM/TA weight ratio of 10/1 (the same weight ratio as that in SBR/BM/TA composites). The mixture was stirred for 2 h at 80 °C, followed by repeatedly washing with deionized water until the pH was close to 7. The resulting sample was dried at 80 °C overnight for further characterizations.

2.4. Characterizations

To disclose the reaction between BM and TA, BM and TA-BM were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). FTIR spectra were recorded on a Bruker Vector 70 FTIR spectrometer (Germany) with a resolution of 4 cm^{-1} from 3800 to 400 cm^{-1}.

XPS survey was carried out on a Kratos Axis Ultra DLD X-ray photoelectron spectrometer (Kratos Analytical, Eppstein, Germany) with an aluminium Kα source (1486.6 eV). TGA was conducted on a TA Q5000 thermogravimetric analyzer (TA instruments, USA) at a heating rate of 10 °C/min under nitrogen atmosphere.

The morphological structure and properties of the SBR composites were investigated by rubber processing analysis (RPA), transmission electron microscopy (TEM), gas permeability test, tensile test and vulcanization test. RPA was performed on a RPA 2000 analyzer (Alpha Technologies, USA) with frequency of 1.6 Hz at 60 °C. TEM observations for the ultramicrotommed samples were conducted on Philips Tecnai 12 TEM machine (Eindhoven, Netherlands). Mechanical properties were measured using a U-CAN UT-2060 instrument (Taiwan) following ISO standard 37-2005. Permanent set was the value of the incremental gauge length divided by the initial gauge length. The incremental gauge length was measured when the sample was settled for 3 min after tensile test. Nitrogen permeation test was carried out at 40 °C according to the ISO 2782 differential-pressure method with a home-made apparatus. The pressure on one face of the sample sheet (approximately 1 mm in thickness) was kept at 0.57 MPa with pure nitrogen gas, while the pressure was initially zero on the other face. The nitrogen permeability was calculated from the transmission rate of nitrogen determined by gas chromatography. The curing characteristics of rubber compounds were measured at 160 °C using an UR-2030 vulcameter (U-CAN Dynatex Inc., Taiwan).

3. Results and discussion

3.1. Interaction between BM and TA

The reaction between BM and TA was characterized by FTIR, XPS, TGA and solubility test. The FTIR spectra of BM and TA-BM are compared in Fig. 1. In the spectrum of BM, the absorption bands approximately 739 cm^{-1} (γ_{as}), 1070 cm^{-1} (σ_s), 3072 cm^{-1} (ν_s) and 3305 cm^{-1} (σ_{as}) can be assigned to aluminol groups of BM [11,18]. In addition, the peaks around 478 and 617 cm^{-1} are associated with the stretching vibrations in the distorted AlO$_6$ octahedron [19]. In the case of TA-BM, besides the aforementioned characteristic absorption bands for aluminols and AlO$_6$ octahedron, a new absorption peak at 1204 cm^{-1} and a shoulder at 1700 cm^{-1} are observed, which are due to the stretching vibrations of C—O and CO introduced by TA. This observation suggests that TA is adsorbed on BM even after vigorous washing, revealing the strong interaction between TA and BM. Such interaction between TA and BM may have originated from the complexation between catechol groups and metal oxide [20–22]. Here, the absorption band around 1502 cm^{-1} in TA-BM could be attributed to the C—C ring
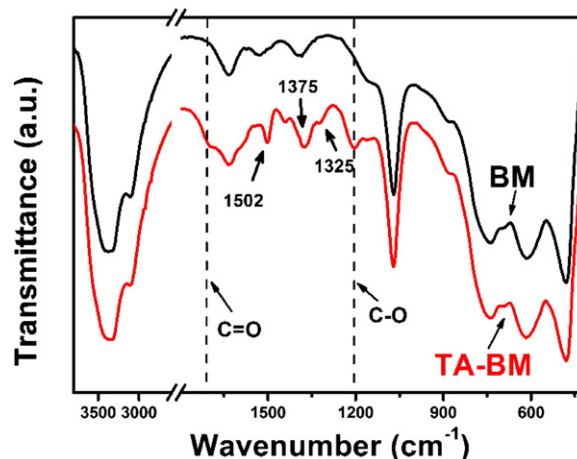

Fig. 1. Comparison between FTIR spectra for BM and TA-BM.