



High-performance rubber/boehmite nanoplatelets composites by judicious *in situ* interfacial design



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ABSTRACT

Interfacial interaction plays a vital role in the final properties of polymer composites as it affects the filler dispersion and stress transfer in the composites. In this study, we utilized two types of phosphate ester, hydroxyethyl methacrylate phosphate (PH) and butyl phosphate (PB), as modifiers in boehmite (BM)-filled styrene-butadiene rubber (SBR) to tailor the interfacial structures in the composites. The modification mechanism of phosphate ester on BM and the interfacial structure in the composites are characterized. In PH-modified BM/SBR composites, a covalently bonding interface is obtained because PH can act as molecular bridge that can form covalent linkage with both BM and SBR chains. Consequently, the resulting composites show significantly improvements in the physical and mechanical properties of the composites. While in PB-modified BM/SBR composites, the properties of the composites are slightly improved due to the lack of covalent linkage in the interface.

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1. Introduction

Recently, rubber composites filled with layered nanofillers, such as montmorillonite [1], graphene [2,3], and boron nitride [4] have drawn extensive interests in both academic and industrial communities. Incorporating layered nanofillers into rubbers can improve their mechanical properties and impart the composites functional properties [3–6]. However, due to the high specific surface area of layered structure, layered nanofillers tend to severely aggregate in rubber matrices. Thus, it is of great importance to modify the nanofillers to improve the filler dispersion and enhance interfacial interaction between nanofillers and rubber matrices.

Boehmite nanoplatelet (BM), an oxo-hydroxide of aluminum, is composed of Al–O double layers and surface hydroxyl groups [7]. Recently, BM has been widely incorporated into some kinds of polymers such as polyethylene [8], polyurethane [9] and epoxy resins [10]. Generally, it has been observed that BM tended to aggregate into agglomerates in polymer matrices due to the high surface energy. In addition, weak interface interaction is commonly resulted in BM-filled polymer composites. To take full advantage of

the reinforcement of BM, great efforts have been developed to modify BM in rubber composites based on the active sites of aluminol (Al–OH) groups on the platelet. For instance, based on the silanization reaction between the aluminols of BM and ethoxy groups of silane, BM was successfully functionalized with aminopropyl triethoxysilane [11] and bis(γ -triethoxysilylpropyl) tetrasulfide [12], respectively. Methacrylic acid was employed to modify styrene-butadiene rubber (SBR)/BM composites through the coordination between BM and carboxylic acid [13]. Upon modification, the mechanical properties of the modified BM-filled polymer composites were enhanced due to the improved dispersion of BM and the strengthened interfacial interaction. However, the state-of-the-art modifications are far from satisfactory for practical applications of BM/polymer composites for the below reasons. Silanization is sensitive to moisture and temperature, readily resulting in side reaction, while methacrylic acid will corrode processing machinery and cause health issues such as respiratory injury. Therefore, more efforts are still required to seek an effective and reliable method to modify BM for the practical implementation of BM in polymer composites.

It was reported previously that BM could adsorb phosphate through anion exchange reaction [14], and form covalent linkage via Al–O–P bridging [15]. Based on the reaction between BM and phosphate ester, Florjańczyk et al. used triethyl phosphate as a modifier in carboxylated SBR/BM composites. The results showed that the dispersion of BM in rubber matrix was improved

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remarkably with the addition of triethyl phosphate [16]. However, in their case, the mechanical properties of carboxylated SBR/BM composites modified by triethyl phosphate exhibited limited enhancements in spite of the remarkably improved dispersion of BM. The limited improvements on mechanical performance may be attributed to the fact that triethyl phosphate cannot react with rubber chains, and thus the interfacial adhesion is not efficiently strengthened upon modification. With this in mind, in the present work, hydroxyethyl methacrylate phosphate (PH, Fig. 1), a phosphate ester with reactive unsaturated alkyl groups, was utilized to modify BM-filled rubber composites. To highlight the effects of strengthened interface bonding on the ultimate performance, butyl phosphate (PB, Fig. 1), an unreactive phosphate ester counterpart, is also used to modify BM in SBR for comparison. The BM/SBR composites modified by both phosphate esters were fully characterized and compared. The effects of the interfacial strengths on the ultimate performance of rubber composites were revealed.

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. BM, with surface area of 142.8 m²/g (Brunauer-Emmett-Teller method), was produced by Shandong Aluminum Co. Ltd., Zibo, China. The content of Al₂O₃ was no less than 80%, the bulk density was 0.4–0.6 g/mL. The average aggregated particle size of the BM was about 1–20 μm. The single nanoplatelet of BM possesses thickness of about 3 nm and in-plane size in the range of 200–400 nm. Hydroxyethyl methacrylate (HEMA, purity ≥96%) purchased from Aladdin. Butyl phosphate (purity ≥96%) was purchased from Alfa Aesar. Phosphorus pentoxide (P₂O₅) purchased from Fuchen Chemical Reagents, Tianjin, China, was analytical grade. PH was synthesized according to the method represented in supporting information. Other rubber additives, including zinc oxide (ZnO), stearic acid (Sta), 2-mercaptobenzimidazole (MB), sulfur (S), dicumyl peroxide (DCP) were industrial grade and used as received.

2.2. Preparation of PH/BM/SBR and PB/BM/SBR composites

The preparation of PH/BM/SBR composites was described as follows. First, BM and PH were successively incorporated into SBR in HAAKE PolyLab OS mixer at a pre-set temperature of 80 °C to prepare SBR masterbatch. In the masterbatch, the weight ratio of SBR, BM and PH was variable (10:10:x, where x = 1.25, 2, 3, 4, 5). The resulting masterbatch was diluted with SBR on a two-millier mixer, and then rubber additives were added. In the diluted

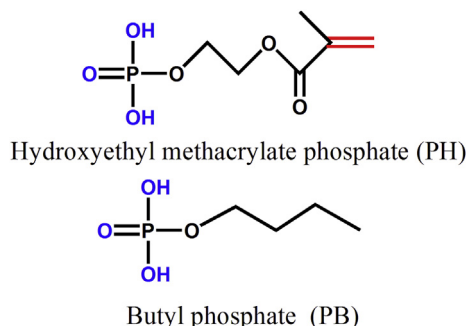


Fig. 1. Molecular structures of PH and PB.

compounds, BM loading was fixed at 40 phr (parts per hundred parts of rubber), and the PH content was variable (5–20 phr). The basic formulation for the rubber composites is as follows: SBR, 100 g; BM, 40 g; ZnO, 5 g; Sta, 2 g; MB, 1 g; S, 1.5 g; DCP, 1 g. Lastly, the compounds were compression molded at 160 °C for curing time determined by the vulcameter. For comparison, PB/BM/SBR composites were also prepared following the similar protocol except replacing PH with PB. In the work, the code SH-y represents the PH/BM/SBR composites with y phr of PH, and the code SB-y represents the PB/BM/SBR composites with y phr of PB.

2.3. Preparation of PH-modified BM (PH-BM) and PB-modified BM (PB-BM) model compounds

The model compound of PH-BM was prepared as follows. BM was dispersed in ethanol at a concentration of 5 mg/mL, into which PH was added with a BM/phosphate weight ratio of 1/1. The mixture was then stirred for 2 h at 80 °C, followed by repeatedly washing with ethanol. Finally, the resultant was dried at 80 °C overnight for further characterizations. PB-BM was prepared according to the similar protocol.

2.4. Characterizations

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Bruker Vector 70 FTIR spectrometer with a resolution of 4 cm⁻¹ and a range from 3800 to 400 cm⁻¹. X-ray photoelectron spectroscopy (XPS) survey was carried out on a Kratos Axis Ultra DLD X-ray photoelectron spectrometer (Kratos Analytical, Germany) with an aluminum K α source (1486.6 eV). Solid-state ²⁷Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) measurements were performed on a Bruker AVANCE III HD 400 spectrometer. Chemical shifts are reported with respect to external Al₂O₃ (²⁷Al) standards. Thermogravimetric analysis (TGA) was conducted on a TA Q5000 thermogravimetric analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere. Rubber processing analysis (RPA) was performed on a RPA 2000 analyzer, with a frequency of 1.6 Hz at 60 °C. Dynamic mechanical analysis (DMA) investigation was carried out on a TA DMA Q800 in tensile mode at a frequency of 5 Hz and a heating rate of 3 °C/min from –80 to 80 °C. Differential scanning calorimetry (DSC) measurement was performed on a NETZSCH Instruments DSC 204 F1 to determine the heat capacity increment (ΔC_p) of the composite at the glass transition temperature. Prior to the measurement, the instrument was calibrated by a sapphire sample. The sample was isothermal at –70 °C for 5 min, followed by heating to 30 °C at 10 °C/min under a nitrogen atmosphere. Transmission electron microscopy (TEM) observation for the ultramicrotomed samples was done by Philips Tecnai 12 TEM machine at an accelerating voltage of 30 kV. Tensile test was conducted on a U-CAN UT-2060 instrument following ISO standard 37-2005. Nitrogen permeation test was carried out on an i-Gastra 7100 gas permeability tester (Labthink, China) following GB/T7755-2003. Crosslink density was determined by the equilibrium swelling method in toluene and calculated according to the classic Flory-Rehner equation [17]. The curing characteristics of rubber compounds were measured at 160 °C by using UR-2030 vulcameter.

3. Results and discussion

3.1. Interaction between phosphate ester and BM

FTIR spectra of pristine BM, PH, PB, PH-BM and PB-BM are shown in Fig. 2(a). In the spectrum of pristine BM, the intensive signals for stretching vibrations in the distorted AlO₆ octahedron

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