CrossMark

Highly ordered structured montmorillonite/brominated butyl rubber nanocomposites: Dramatic enhancement of the gas barrier properties by an external magnetic field

Hua Chen[a,b], Yingjun Li[a,b,c], Shanqiang Wang[d], Yintao Li[a,b], Yuanlin Zhou[a,b,*]

[a] State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, China
[b] School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, China
[c] Fundamental Science on Nuclear Wastes and Environmental Safety Laboratory, Southwest University of Science and Technology, Mianyang 621010, China
[d] People's Liberation Army Institute of Chemical Defense, Beijing 102205, China

ARTICLE INFO

ABSTRACT

This work is to develop a novel nanocomposites with high gas barrier properties. The permeability is reduced by aligning the magnetic nanoplatelets into a highly oriented manner in brominated butyl rubber (BIIR) latex via a low magnetic field. Iron oxide (Fe_3O_4) nanoparticles were deposited on the surface of montmorillonites (MMTs) modified with γ-aminopropyltriethoxysilane (APTES) and octadecyl trimethyl ammonium bromide (OTAB) to produce m-OMMTs nanocomposites. The morphology and microstructures of the prepared m-OMMTs and m-OMMTs/BIIR highly ordered nanocomposites were characterized by X-ray power diffraction (XRD), Fourier Transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), and transmission electron microscope (TEM). Systematic characterization demonstrated that APTES was chemically bonded onto MMTs and Fe_3O_4 nanoparticles and further confirmed the bond formation between Fe_3O_4 and MMTs platelets, which could ensure the adhesion between the Fe_3O_4 nanoparticles and MMT platelets. The modified magnetic MMT nanoplatelets (m-OMMTs) were added into BIIR latex and aligned in a low magnetic field $T_m = 80$ mT. Besides, a ellipsoidal shell model was presented to estimate the minimum magnetic field strength for aligning m-OMMTs in BIIR latex. Finally, the helium permeability measurements were performed by GDP-C gas permeation apparatus. It can be observed that the new method was proved very useful to align m-OMMTs embedded in polymer matrix leading to a highly ordered composite with excellent gas barrier properties.

1. Introduction

Polymers have replaced conventional materials in recent 20 years, because of their unique properties such as their functionality, lightweight, plasticity, and low cost. Polyethylene (PE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), poly(lactic acid) etc., were frequently used in packaging materials based on their higher barrier properties [1–6]. Composite tanks are wildly used in automobile and natural gas storage, which have also replaced the heavy mental tanks. However, their inherent permeability to gases and vapors limited their wide range of applications. An effective way to improve the gas barrier properties for polymers is incorporating some sheet-shaped filler into the matrix. The barrier properties of nanocomposites can obviously enhanced by loading impermeable lamellar fillers, such as layered double hydroxide, clay, graphite and graphene [7–9]. Those diffusing

gas molecules could bypass the lamellar powders of the nanocomposites, resulting in a more tortuous path through the polymer [10].

What's more, the gas barrier properties of nanocomposites depend not only on the size, dispersion, content of the particles, but also on their orientation in polymer. Several empirical models about permeability of nanocomposites to various gases have been proposed in various studies to predict their barriers properties, such as Cussler, Nielsen, Fredrickson, Bicerano, Gusev and Lusti [11–17]. According to Nielsen's model, the case that the orientation of the platelets is perpendicular to the diffusion direction corresponds to the maximisation of the tortuosity factor and, therefore, to the greatest reduction of the permeability [18]. According to current reports, electric, magnetic field, or mechanical stresses are used to achieve the orientation of nanoplatelets within engineering composites [19]. However, magnetic field is used widely among these methods due to its low cost, easily control and

simplicity. The particle-coated multiwalled carbon nanotubes are superparamagnetic and can be aligned on any substrate by deposition from an aqueous solution in an external field B = 0.2 T [20]. Jiao et al. prepared highly ordered graphite/epoxy resin nanocomposites via coating the graphite surface with Fe_3O_4 nanoparticles, and then aligned the magnetic graphite in polymer by using a low magnetic field (40 mT) [21]. Their study confirmed that helium barrier properties of ordered m-GNP/EP composites with 1.0 wt% magnetic graphite enhanced > 65%, compared with the randomly dispersed GNP/EP composites. Lv et al. prepared the orientation of CPC-Fe_3O_4-MMT in the surface-oriented films in which the aligning external magnetic field was 0.6 T and the water vapor permeability of the films is lower than that of the edge-oriented due to the prolonged tortuous paths for water vapor passing through [22]. However, the ordered magnetic montmorillonites (MMTs) used in brominated butyl rubber (BIIR) have been rarely reported recently.

In this study, we report highly ordered m-OMMTs/BIIR nanocomposites with good gas barrier properties. In order to improve the adhesion between Fe_3O_4 nanoparticles and MMT layers, we synthesized the immobilization of Fe_3O_4 nanoparticles on MMTs surface with the assistance of γ-aminopropyltriethoxysilane (APTES) [23–26]. And octadecyl trimethyl ammonium bromide (OTAB) was used to modify the above prepared magnetic MMTs to enhance the compatibility between fillers and polymer. A ellipsoidal shell was used to calculate the minimum magnetic field for aligning the magnetic fillers (introduced in the Supporting information). Besides, the morphology and microstructures of the fabricated m-OMMTs/BIIR highly ordered nanocomposites were characterized. Finally, the helium permeability measurements were performed by the gas permeation apparatus, and this simple treatment significantly enhances the gas-barrier film properties. Hence, the obtained ordered m-OMMTs/BIIR composites could be a promising candidate for gas barrier materials.

2. Experimental

2.1. Materials

MMTs (> 98%) with a cation exchange capacity (CEC) of 120 meq/100 g were purchased from Beijing Yi Wei specialized technology development Co., Ltd, China. Ferric chloride hexahydrate ($FeCl_3·6H_2O$), Ferrous chloride tetrahydrate ($FeCl_2·4H_2O$), APTES (≥ 99.7%), ammonia solution (NH_4OH), silver nitrate ($AgNO_3$), OTAB and ethanol (≥ 99.7%) were obtained from Sichuan Biotech Force Technology Co., Ltd., China. BIIR was procured from Langsheng, Germany (Bromine content 1.8%, 2030). All reagents except for OTAB (biochemical reagents) were of analytical grade and deionized water was purified by reverse osmosis.

2.2. Preparation of magnetically responsive MMT platelets (m-MMTs)

1 g of MMT was added into 100 mL of deionized water and dispersed using ultrasonic treatment for 1 h. Then 0.858 g of $FeCl_2·4H_2O$ and 2.334 g of $FeCl_3·6H_2O$ were respectively dissolved in 40 mL of deionized water and added to the MMTs suspension by stirring for 30 min at 60 °C. The pH of the system was adjusted to ~ 10 by 28 wt% ammonia solution with sustaining stirring for 30 min. After that 0.2 g of APTES was added drop by drop into the mixed solution and stirred for 1 h. The black precipitates were filtered from the suspension and were washed three times by deionized water and then dried at 80 °C for 48 h under vacuum condition.

2.3. Preparation of organic magnetically responsive MMT platelets (m-OMMTs)

To prepare m-OMMTs, 2 g of the as-prepared m-MMT was suspended in 200 mL of deionized water and ultrasonicated for 1 h to fully disperse the platelets. 0.565 g OTAB, which amount is equivalent to 1.2 CEC of MMT was added into 30 mL of deionized water and stirred at 60 °C to fully dissolve. And then the two suspensions were mixed quickly and stirred 2 h at 60 °C. The obtained m-OMMTs were separated by filtration, washed three times by water and dried at 80 °C. The platelets were stored in a dry environment until use.

2.4. Preparation of nanocomposites under a magnetic field

Nanocomposites were produced by emulsion compounding method and magnetic platelets described above. The samples of OMMTs, m-MMTs and m-OMMTs with various weight percents were dispersed in a amount of deionized water and sonicated for 1 h. Brominated butyl rubber latex was made in laboratory, whose solid content was ~ 45%. Magnetic platelets were carefully added into the latex and stirred at 60 °C for about 3 h to get the specific solid content. Then the obtained solution was placed in vacuum for 7 h to remove bubbles. Then the solution was immediately pour into a mold and placed under a low rotating magnetic field (80 mT) for 7 h at room temperature and another 2 h for rubber vulcanization at 120 °C after leaching in water for 24 h.

2.5. Characterization and measurements

Characterization Analysis Using XPS, TEM, SEM, FTIR, XRD, VSM and GDP-C. X-ray power diffraction (XRD) signals were recorded using Cu K_α (λ = 0.1542 nm) tube with scan range of 2theta = 3–80° and step size of 0.05°. Scanning electron microscopy (SEM, UItra55, Carl zeissNTS GmbH) and transmission electron microscope (TEM, Libra200, Carl zeiss irts) were used for identifying the micro- and nanosized structure of the magnetic MMTs and the prepared films. Fourier Transform Infrared Spectrometer (FTIR, FT-IR5700, US) was used for confirming the structure of samples. Magnetic properties of the samples were obtained by using a Vibrating Sample Magnetometer (VSM, Beijing Zetian Technology Co., Ltd, BKT-4500Z). X-ray photoelectron spectroscopy (XPS, Escalab 250Xi) signals were recorded with a monochromatic Al X-ray source (1486.6 eV). Helium permeation tests were conducted at 22.7 °C according to the ISO 15105-1:2007 differential-pressure method with GDP-C gas permeation apparatus.

3. Results and discussion

The structure of the samples and the preparation methods of the finished products are showed in Scheme 1. Si-O-H was obtained after APTES occurred hydrolysis. Si-O-H caused a reaction with the hydroxy on the surface of Fe_3O_4 to produce NH_2-Fe_3O_4. The surface silanol functional groups (Si-O-H) and aluminum functional groups (Al-O-H) of MMT layers reacted with Si-O-H of APTES hydrolysis to form NH_2-MMTs [27]. APTES is used to connect Fe_3O_4 nanoparticles with MMT layers and transform the sample's hydrophilicity. In order to improve the compatibility between magnetic MMTs and BIIR and increase the basal space of MMTs, OTAB was used to modify m-MMTs.

3.1. Structure and component of magnetic MMTs

The surface modification of MMTs with magnetic Fe_3O_4, APTES and OTAB was confirmed by the FTIR. Fig. 1 illustrates the comparison of raw material and experimental samples FTIR results. For pure MMTs, the peak at 3645 cm^{-1} can be assigned to the O-H stretching of inner hydroxyl groups between the interface Al-O octahedron and Si-O tetrahedron. The peaks at 3429 cm^{-1} and 1630 cm^{-1} can be attributed to O-H stretching and O-H deformation of adsorbed water respectively. The peak at 1046 cm^{-1} corresponds to the in-plane stretching vibration band of Si-O. Compared to the FTIR spectra of MMTs, NH_2-MMTs samples exhibit some new absorption peaks, such as the stretching CH_2 vibration band around 2923 cm^{-1}, and the deformation of C-H_2