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Full Length Article

Effects of content and surface hydrophobic modification of $BaTiO_3$ on the cooling properties of ASA (acrylonitrile-styrene-acrylate copolymer)

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ABSTRACT

For the field of cool material, barium titanate ($BaTiO_3$, BT) is still a new member that needs to be further studied. Herein, the effects of both content and surface hydrophobic modification of BT on the cooling properties of acrylonitrile-styrene-acrylate copolymer (ASA) were detailedly investigated, aiming to fabricate composited cool material. Butyl acrylate (BA) was employed to convert the surface of BT from hydrophilic to hydrophobic. The addition of unmodified BT could significantly improve the solar reflectance of ASA, especially when the addition amount is 3 vol%, the near infrared (NIR) reflectance increased from 22.02 to 72.60%. However, serious agglomeration occurred when the addition amount increased to 5 vol% and therefore led to a relatively smaller increase in solar reflectance and an obvious decline in impact strength. After surface hydrophobic modification, the modified BT (M-BT) presented better dispersibility in ASA matrix, which contributed to the improvement of both solar reflectance and impact strength. In addition, the temperature test provided a more sufficient and intuitive way to evaluate the cooling effect of the composited cool materials, and a significant decrease (over 10 °C) could be achieved in the temperature test when M-BT particles were introduced.

1. Introduction

Nowadays, undesirable heat directly generated from high-intensity solar irradiation troubles people a lot as it can easily raise the temperature inside buildings, cars and other outdoor applications [1,2]. Such undesirable heat leads to a huge amount of unnecessary energy consumption caused by the usage on electricity for cooling purpose [3]. In order to overcome this problem, solar-reflective cool materials have received great attention for their various advantages, such as environmentally friendly and cost-effective [4,5]. Solar-reflective cool materials, as its name implies, is able to reduce heat built-up and minimize the temperature by its high solar reflectance.

In recent years, polymer-inorganic hybrid composites have attracted extensive attention as they provide an effective way for the combination of the advantages of both polymer and inorganic particles, which offers a suitable method for the fabrication of cool material [6,7]. Since most cool materials are used outdoors, good weather resistance ability is of great necessity. Acrylonitrile-styrene-acrylate copolymer (ASA) applied as polymer engineering materials possesses unique core-shell structure, where poly(butyl acrylate) (PBA) serves as the rubbery core and poly(styrene-acrylonitrile) (SAN) is grafted onto the core to develop the shell layer [8]. This unique core-shell structure gives ASA many excellent properties, such as good toughness, chemical resistance, thermal stability and dimensional stability. What's more, the main chains of ASA contain no unsaturated structures, which provides ASA outstanding weather resistance ability [9]. All these excellent properties make ASA quite suitable for various outdoor applications. However, the relatively lower solar reflectance of ASA severely limits its application in the field of cool material.

For many researchers, inorganic particles with high solar reflectance are often employed in the manufacture of cool materials [7,10]. As reported in literature, inorganic particles with high refractive index are usually regarded as good reflectors [11–13]. Barium titanate ($BaTiO_3$, BT), which has attracted wide interests and been applied in various fields such as electronic material [14], catalysis [15] and bioengineering [16,17], possesses a high refractive of 2.40 [18]. This makes it possible to be a good candidate for

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cool materials. However, few literature reports the application of BT in the field of cool material. Therefore, using BT particles to improve the solar reflectance of ASA would be an interesting and meaningful work.

For polymer-inorganic hybrid composites, the inorganic particles tend to agglomerate in polymer matrix due to the qualitative difference between organic polymer and inorganic solid, which has negative effect on the properties of the hybrid composites [19]. As reported, surface hydrophobic modification of inorganic particles can effectively improve its dispersion stability in polymer matrix [20]. Besides, hydrophobic surface is also able to offer materials self-cleaning property [21,22]. Therefore, surface hydrophobic modification of BT particles is of great importance, aiming to improve the dispersibility of inorganic particles in polymer matrix and lower the water wettability of composited cool material.

In our present work, cool materials composed of ASA and unmodified/modified BT particles were fabricated. The effects of content of unmodified BT on the cooling properties of ASA were investigated. In addition, PBA chains were chemically grafted onto the surface of BT particles to improve the dispersibility of BT particles in ASA matrix and lower the water wettability of composited cool material.

2. Experimental

2.1. Materials

ASA (HX-960) was supplied by Zibo Huaxing Additives Co., Ltd., China. BT was commercially obtained from Foshan Songbao Electronic Functional Material Co., Ltd., China. 3-methacryloxypropyltrimethoxysilane (MPS, AR) and triethylamine (Et_3N, AR) were products from Sinopharm Chemical Reagent Co., Ltd., China. Xylene (AR), acetone (AR) and butyl acrylate (BA, CP) were all provided by Shanghai LingFeng Chemical Reagent Co., Ltd., China. 2,2′-azobis(2-methylpropionitrile) (AIBN, CP) was obtained from Shanghai No.4 Reagent & H.V. Chemical Co., Ltd., China. Zinc stearate was friendly provided by Nanjing Huage Electronics & Automobile Plastic Industry Co., Ltd., China. Dehydrated ethanol (EtOH, AR) was purchased from Wuxi Yasheng Chemical Co., Ltd., China. Prior to use, BA was distilled under reduced pressure to remove the inhibitor and AIBN was recrystallized from EtOH.

2.2. Surface hydrophobic modification of BT

2.2.1. The introduction of C═C groups onto BT particles by MPS

5 g pre-dried BT powder was firstly dispersed in 200 ml xylene with the aid of an ultrasonic disperser (NH-1000, Shanghai Hanuo Instrument Co., Ltd., China) for 30 min. Then, the dispersion liquid was swiftly poured into a three-neck round-bottomed flask and stirred for 1 h at room temperature. Afterwards, 0.25 g MPS and 0.6 ml Et_3N (as reaction catalyst) were added into the dispersion liquid under nitrogen atmosphere. The reaction was carried out under stirring at 80 °C for 3.5 h. After that, the BT particles grafted with MPS (BT-MPS) were separated from the solvent by centrifuge (7000 rpm, 10 min) followed by washing with EtOH for at least 3 times to remove physically adsorbed MPS. Finally, BT-MPS particles were dried in a vacuum oven at 60 °C for at least 12 h and then ground into powder.

2.2.2. Surface grafting of BA onto BT-MPS particles

Firstly, 5 g pre-dried BT-MPS powder was dispersed in 200 ml EtOH by ultrasonic for 30 min. Then, the mixtures of the dispersion liquid and 10 g BA monomer were rapidly transferred into a three-neck round-bottomed flask and stirred for 30 min at room temperature. Subsequently, the mixtures were heated to 70 °C and 0.1 g recrystallized AIBN was added. The reaction lasted for 4 h under stirring and nitrogen atmosphere. Then, BT-MPS particles grafted with BA (BT-MPS-BA, shortened to M-BT) were obtained after centrifuging at 7000 rpm for 10 min, washing with EtOH for 3 times, soxhlet extracting with acetone for 24 h and drying in a vacuum oven at 60 °C for 12 h.

2.3. Preparation of ASA/BT (or M-BT) hybrid composites

To fabricate ASA/BT (or M-BT) hybrid composites, ASA containing 1 vol% zinc stearate as processing aid was mixed with BT/M-BT particles in a two-roll mill at 180 °C and subsequently compression molded into sheets with thickness of 1 mm, 2 mm and 4 mm at 180 °C. The 1 mm sheets were prepared for temperature test. The dumbbell-shaped specimens cut from 2 mm sheets were used for tensile test. The 4 mm sheets were machined by a universal sample making machine for impact and flexural tests.

2.4. Characterization

2.4.1. Fourier transform infrared (FTIR) spectral analysis

FTIR spectra were obtained by using a FTIR spectrometer (Nexus 670, Nicolet, USA) to evaluate the effect of hydrophobic modification. The scanning range was from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.4.2. Thermogravimetric (TG) analysis

The samples were pre-dried in a vacuum oven. The measurement was performed by using a TG analyzer (Q50, TA instruments, America) under nitrogen atmosphere to determine the grafted amount of modified BT particles. The temperature increased from room temperature to 800 °C with a heating rate of 20 °C/min.

2.4.3. Dispersion test

The BT particles before and after the modification were dispersed in two-phase solvent composed of BA and distilled water. The dispersion state was recorded by a digital camera (PC1469, Canon, China).

2.4.4. Scanning electron microscopy (SEM) analysis

The dispersion of the inorganic particles in ASA matrix was detected by a SEM (JSM-5900, JEOL, Japan) with an accelerating voltage of 15 kV. The samples were fractured in liquid nitrogen and coated with gold before the observation.

2.4.5. Ultraviolet-visible-near infrared (UV–vis-NIR) spectral analysis

The UV–vis-NIR reflectance spectra ranging from 200 to 2600 nm were collected by using a spectrometer (UV-3600, Shimadzu, Japan) with an integrating sphere. Barium sulfate was used as a white reference. The solar reflectance R of the region (λ_0 to λ_1) could be determined via the following equation [23]:

$$R_{\lambda_0\to\lambda_1} = \left[\int_{\lambda_0}^{\lambda_1} r(\lambda)i(\lambda)d\lambda\right] \Big/ \left[\int_{\lambda_0}^{\lambda_1} i(\lambda)d\lambda\right] \quad (1)$$

where $r(\lambda)$ and $i(\lambda)$ are the solar spectral reflectance and irradiance at wavelength λ, respectively. The irradiance-weighted average reflectance comprises of the following three parts: UV reflectance (R_u) ranging from 280 to 400 nm, visible reflectance (R_v) ranging from 400 to 700 nm, and NIR reflectance (R_n) ranging from 700 to 2500 nm. And the total solar reflectance (R_{sol}) could be calculated