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Original Research

Preparation and characterization of polypropylene/silica composite particle with interpenetrating network via hot emulsion sol–gel approach

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Abstract

A novel interpenetrating structural ultrafine polypropylene-silica nanocomposite particles were synthesized by a modified sol–gel approach in the presence of the melt polypropylene emulsion. A series of samples with different polypropylene content was prepared to investigate the unique characteristics of this original nanocomposite. The thermal gravimetric analysis and differential scanning calorimetry results showed that the nanocomposites had the interpenetrating structure and good thermal stability, and the crystallization behavior of polypropylene was confined by the silica matrix. The interpenetrating structure of nanocomposites was also suggested by the nitrogen adsorption–desorption measurement results. The scanning electronic microscope and transmission electron microscopy images indicated that the nanocomposites had irregular particle morphology. The nanoparticle tracking analysis results show that the mean size of the nanocomposites was around 160 nm. According to the results obtained from different measurements, a reasonable formation mechanism was proposed.

Keywords: Polypropylene; Silica; Nanocomposites; Sol–gel method; Interpenetrating structure

1. Introduction

In recent years, the organic-inorganic composite materials based on organic polymers and silica have been studied widely for their potential applications in optics [1–4], functional materials [5], and biosciences [6–9]. A series of organic-silica composite materials were designed for a variety of structures to meet different application requirements [10–12]. Among these different structural materials, the interpenetrating structural composite materials, the polymer–silica 3D networks are held together by permanent entanglement, have attracted much attentions for their excellent characterizes [13–15].

Recently, many researchers have synthesized various polymer–silica composites via different approaches. For example, Gabriela Bonilla etc. synthesized the ternary interpenetrating networks of polyurethane-poly(methyl methacrylate)-silica by the in-situ bulk polymerization [16]. Tomoki Ogoshi and Yoshiki Chujo prepared a highly transparent and homogeneous poly(vinylidene fluoride)-silica composite material by the in-situ interpenetration polymer network method [17]. Chang Hyun Lee etc. synthesized the sulfonated polyimide-silica containing interpenetrating polymer network through a complicated consecutive two-step synthetic method [18]. Isam M. Arafa etc. prepared the urea-formaldehyde-silica composites by the sol–gel method [19].

However, it is notable that, although many diverse organic polymers were chosen to form the interpenetration structural composite materials, but some widely used polymers which possess unique characterizes, such as polypropylene (PP) and polycarbonate have not been found yet.

Polypropylene is one of the commonly used polymers composed of linear $[-CH_2CH(CH_3)-]_n$ chains. Compared with the other polymers, the polypropylene has a great potential for various applications because of its many desirable properties, especially the low density, high melting temperature, good

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mechanical strength and thermal stability, superior solvent resistance and low cost. The incorporation of PP and silica may result in significant improvements in the properties of the composites compared with virgin polymer and silica. These improvements include increased mechanical strength and elastic modulus, improved heat and flame resistance, reduced gas permeability and increased biodegradability [20]. These properties have led to the application of polypropylene-silica composites in various industrial fields, e.g., the automotive, packaging, cell, medical and technical textile industries [21–23].

Commonly, the PP–SiO_2 composite materials could be prepared through simply mixing the silica and PP. However, this approach could not obtain a good dispersion of the silica or PP due to the significant difference of the interfacial adhesion characters between the PP and silica, and hence the expected exceptional characterizes of the composites may not be obtained. In order to improve the interfacial adhesion, there has been particular interest in composites of this type in which the PP is constrained within the pores of silica, sometimes down to the molecular level. Therefore, the PP–SiO_2 composites were usually synthesized to the nanocomposites with the core–shell or interpenetrating structures. In such nanocomposites, stable chemical crosslinking and/or ordered physical entanglement exist among PP and silica.

Compared with the other polymer–silica composites, the PP–silica nanocomposites with the interpenetrating structure have a chance to possess some special characterizes. Firstly, the interpenetrating structure may prevent the phase separation between PP and silica, which lead to a well stability during the preparation and application. With the merit of this characterize, the PP–SiO_2 nanocomposites could be used as the filler to improve the mechanical strength of the blend which is commonly prepared by simply mixing the silica and PP. Secondly, the PP–SiO_2 nanocomposites are natural amphipathic due to the interval distribution of the hydrophilic and hydrophobicity, and hence they may have a chance to be utilized as the hydrophobic interaction chromatography materials [24,25]. Moreover, the PP–SiO_2 nanocomposites have a good biocompatibility due to the nontoxicity of PP and silica. Thus, the PP–SiO_2 nanocomposites could be utilized as the medicine carrier in biological pharmacy field. Thirdly, the toughness of silica in PP–SiO_2 nanocomposites would be enhanced by PP and lead to a possibility of being used in lithium cells as the cathode material. Usually, the cathode materials which are made of silica in lithium cells are easy to be destroyed during the application due to the fragility of silica [26,27]. Therefore, the silica cathode materials are needed to be toughened for improving their performance. Although many polymers could be used as the candidate to fulfill this work, but PP may be regarded as the best one owing to the well toughness and a higher melting temperature compared with the other polymers.

Accordingly, from all the potential applications mentioned above, it is easy to find out the PP is an ideal candidate to form polymer–silica nanocomposites and the preparation and utilization of interpenetrating structural PP–SiO_2 nanocomposites possess a very high research value both in academic and industry.

However, the nature characterization of the PP brings it a lot of challenges to be composited with the silica. In fact, the PP–SiO_2 nanocomposites could not be synthesized by using the general methods, such as the emulsion polymerization, dispersion polymerization or the common sol–gel method due to the immense difficulty of finding a fine solvent and effective emulsify to make a stable PP emulsion in ambient temperature. Consequently, a special approach should be applied to synthesize the interpenetrating structural PP–SiO_2 nanocomposites. In the present investigation, the novel interpenetrating structural ultrafine PP–silica nanocomposite particles were synthesized through the modified sol–gel method in the presence of the PP emulsion. A series of samples with different PP content was synthesized to investigate the unique characteristics of the original nanocomposits. Based on the different test results, a reasonable formation mechanism was also proposed. The morphology and structure information of the nanocomposites were characterized by the scanning electronic microscope (SEM), transmission electron microscopy (TEM). The mean size and size distribution were measured by the nanoparticle tracking analysis (NTA). The thermal and crystallization behavior were determined by the thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) measurements and X-ray diffraction (XRD) analysis. The specific surface area, mean pore volume and mean pore size of the nanocomposites were measured by the nitrogen adsorption–desorption measurements.

2. Experimental procedure and characterization

2.1. Materials

Polypropylene (melting index of 12.3 g/10 min), tetraethyl orthosilicate (TEOS), xylene, and ammonium hydroxide were purchased from Beijing Chemical Reagents Company, China. Polyethylene-block-poly(ethylene glycol) (PE-b-PEG, Mw 1400, PE/PEG 1:1 by weight) was obtained from Sigma-Aldrich. All chemicals are analytical reagent and used as received without any further purification.

3. Experimental method

In a typical procedure, 4 mL boiling xylene was added to a melting mixture of 0.2 g PP and 1.3 g PE-b-PEG and stirred vigorously at 140 °C for 2 h. Then 10 ml TEOS was added and stirred until a clear solution (hydrophobic phase) was obtained. The hydrophobic solution was then poured into a boiling hydrophilic solution, 50 mL ethanol/30 mL ammonium hydroxide solution (25% by weight of NH_3), and stirred at 78 °C for 30 min to form a stable emulsion. Then the emulsion was cooled and stirred at 25 °C for 24 h. After the reaction, the resulting dispersion was centrifuged at 10,000 rpm for 20 min. The precipitate was washed with ethanol twice, and dried at 100 °C for 10 h.