Synthesis of polypropylene/ZnS composite using the template prepared by supercritical CO₂

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Abstract

A new template membrane, acrylic acid grafted microporous polypropylene (PP) membrane, was prepared using the supercritical (SC) CO₂ as a solvent. Then zinc ions were anchored in the membrane by forming a monodentate complex with the carboxyl groups in the template membrane. Subsequent treatment with Na₂S aqueous solution led to the formation of ZnS nanoparticles within the PP matrix, resulting in ZnS/PP nanocomposite. UV–Vis and Fourier Transform Infrared (FTIR) spectra, and energy-dispersive X-ray analysis (EDS) confirmed the existence of ZnS in the grafted membrane. Field emission scanning electronic microscopy (FE-SEM) and transmission electron microscopy (TEM) images showed that the ZnS nanoparticles distributed uniformly in the composite.

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1. Introduction

Nanomaterials have been the subject of intense current research because of their special physical and chemical properties that can change between the molecular and bulk limits. Consequently, there is a considerable interest in the fundamental understanding of nanomaterial properties and in their applications in electronic, optical, and mechanical devices [1], drug delivery and bioencapsulation [2] and many other fields.

Among the numerous techniques reported, template synthesis is an elegant approach [3] through which inorganic and organic constituents can be introduced into the void spaces of nano-/microporous host materials. The generated structure can be homogeneous or heterogeneous short, squat fibrils, long needle-like fibrils, tubules, tapered conical elements, depending on the pore size and geometries and the nature of the material and pore wall [4]. Nano-/microporous polymeric hosts are commonly used, and the most popular porous polymer templates include crosslinked polymer networks and porous polymeric membrane. The former can lead to the production of nanoparticles including metals [5], oxides [6], sulfides [7], etc. However, porous membrane can mould nanowires and nanotubules in addition to nanoparticles according to different pore geometries and material
nature. Most studies were performed using track etch membrane because they cast different kinds of nanotubules and nanowires with monodisperse diameters and lengths. It has been extensively employed to prepare metals [8], semiconductors [9] and polymers [10,11], and even metal/semiconductor/polymer heterostructures [12].

Other than track etch membrane, some other types of porous membrane have also been used as templates to produce nanomaterials. Since 1980s, perfluorinated ion-exchange membranes (Nafion®) have been used as matrix to prepare semiconductor [13] and magnetic particles [14]. In Nafion, sulfonic acid groups (–SO3H) can bind ions such as Cd2+, Fe3+, and small particles (e.g., of CdS, Fe2O3) can precipitate inside the membrane pores after further treatment. Recently, Neves et al. succeeded in preparation of micro and nanocomposites containing conducting polymer (polyaniline) using the porosity of poly (vinylidene fluoride) and sol–gel silica membranes as templates [15].

In the present Letter, we report a novel porous polymer membrane template, AA (acrylic acid) grafted PP microporous membrane, for the preparation of ZnS/PP nanocomposites. We first grafted a commercially available microporous PP membrane with AA using SC CO2 as a solvent, of which the principle was similar to that preparing polymer composites [16–18]. It is known that the density of SC CO2, and thus its solvent strength, is continuously tunable from gas-like to liquid-like by changing pressure and/or temperature. Moreover, SC CO2 has low viscosity, high diffusivity, and near zero surface tension. Therefore, the monomers and initiator can diffuse into the substrates in shorter time and distribute more uniformly. All these advantages of SC CO2 are favorable to modifying porous membranes effectively and, therefore, preparing a well-controlled template. The grafted membrane was subsequently immerged in a ZnSO4 aqueous solution and the carboxylic groups on the graft chain of the membrane reacted with Zn2+, resulting in a polymer-metal complex. Finally, the complex reacted with Na2S, leading to the formation of ZnS nanoparticles within the membrane pores, and ZnS/PP composite was obtained in which the ZnS was uniformly distributed.

2. Experimental

2.1. Materials

Porous PP membrane (Celgard® 2400) was obtained from Daicel Chemical Industries, Ltd., Japan (thickness: 25 μm, pore size: 125 nm × 50 nm, porosity ratio: 38%) and it was washed with acetone and dried in a vacuum oven at 50 °C for 6 h before use. A.R. grade acrylic acid (AA) (Beijing Yili Fine Chemicals Company) was purified by vacuum distillation. Benzoyl peroxide (BPO, Beijing Jinlong Chemical Reagent Company) was used after recrystallization in chloroform. Carbon dioxide (Beijing Analytical Instrument Factory) with purity of 99.95% was used as received. ZnSO4 and Na2S (A.R. Grade) were purchased from Beijing Chemical Factory and used without further purification.

2.2. Preparation of grafted PP membrane

In a typical experiment, the substrate PP membrane and AA + BPO mixture were loaded in a stainless steel autoclave of 32 ml. Then the autoclave was placed into a constant temperature water bath of 35 °C. After the system had reached thermal equilibrium, CO2 was charged into the autoclave by a syringe pump (Model SB-80, Beijing Aircrafts) up to 12.0 MPa. During this process, the membrane was swollen and was impregnated with AA + BPO. After a certain soaking time, the fluid in the system was released. The impregnated membrane was transferred into another stainless steel vessel and the air in the vessel was replaced by N2. The grafting reaction was carried out at 75 °C for 6 h. After the reaction, the vessel was cooled to room temperature. The samples were then Soxhlet-extracted using methanol for 24 h to remove the unreacted monomer and homopolymer.

2.3. Synthesis of ZnS nanoparticles in the grafted membrane

A piece of grafted membrane (10 mm × 10 mm) obtained by above procedures was first immerged into 50 ml 0.2 mol L−1 ZnSO4 aqueous solution under stirring. After 30 min, the grafted membrane
complexed with Zn$^{2+}$ was taken out and washed by distilled water. The membrane was then dipped into 50 ml 0.2 mol L$^{-1}$ Na$_2$S aqueous solution under stirring for 30 min and washed again with distilled water thoroughly and then dried in a vacuum oven at 80 °C for 8 h and weighed. Weight increase of the sample was calculated from the weight change before and after treatment by the ZnSO$_4$ and Na$_2$S aqueous solutions.

2.4. Characterization

FTIR (Tensor 27, Bruker) spectroscopy was used to characterize the grafted membranes before and after the treatment by the ZnSO$_4$ and Na$_2$S aqueous solutions. The UV–Vis absorption spectrum of the ZnS-containing membrane (dissolved in o-dichlorobenzene) was measured with a TU-1201 spectrophotometer (Beijing General Instrument Factory). The morphology of various samples was observed with FE-SEM and TEM. The samples were sputtered with a thin layer of gold before SEM observation with Philips SPEC XL30 FE-SEM. In the preparation of samples for TEM observation, ZnS-containing membrane was embedded in epoxy resin. Upon completion of resin cure, the embedded sample was microtomed at ambient temperature, and the resulting thin sections were imaged with a Jeol-2010 TEM operated at 200 kV equipped with an energy-dispersive X-ray analysis system (EDS).

3. Results and discussion

3.1. Preparation of the grafted PP membrane

In this work, the monomer (AA) was first impregnated into the membrane with the aid of SC CO$_2$ at 35 °C, and was then grafted on the matrix at 75 °C for 6 h. In order to control the grafting level, the concentration of the monomer was varied in the range from 0.05 to 0.5 mol L$^{-1}$, and the concentration of BPO in AA was 1 wt%. Fig. 1 illustrates the dependence of the degree of grafting (Dg) on the monomer (AA) concentration. Dg almost increases linearly with monomer concentration in the concentration range studied. This is easy to understand because the monomer distributes between the SC CO$_2$ phase and PP solid phase during the soaking process. The monomer concentration studied in this work is relatively low (<0.5 mol L$^{-1}$), and saturation adsorption of AA cannot be reached. Increasing monomer concentration favors the adsorption of the monomer on the PP substrate, resulting in larger degree of grafting. Therefore, the grafting level can be controlled by the concentration of the monomer in the fluid phase.

The success of grafting AA onto PP membrane was also confirmed by the appearance of a strong
band at 1725 cm\(^{-1}\) on the FTIR spectrum of the grafted membrane, as shown in Fig. 2a.

3.2. Complexation of carboxylic groups in grafted membrane with Zn\(^{2+}\)

A polymer-metal complex is a coordination complex resulting from the reaction of a ligand anchored on a macromolecular matrix with a metal ion [19]. In the present work, the grafted AA provides the PP membrane numerous carboxylic groups which serve as ligands when the grafted membrane encounters Zn\(^{2+}\). For example, treating the membrane with 17.4 wt\% grafted AA by 0.2 mol L\(^{-1}\) ZnSO\(_4\) solution for 30 min at 70 °C, 8.82 wt\% increase was achieved after thorough washing and drying, which was due to the formation of carboxyl–Zn complex.

The complexation is also confirmed by a FTIR spectra comparison of the grafted and complexed membrane, as shown in Figs. 2a and b. The main differences in the two spectra are their intensity of the bands at 1725, 1542 and 1252 cm\(^{-1}\). The band at 1725 cm\(^{-1}\) is attributed to the stretching vibration of free C=O groups without forming carboxylates. The large intensity drop of this band in Fig. 2b indicates the reaction of carboxyl group with Zn\(^{2+}\). The bands at 1542 and 1454 cm\(^{-1}\) are due to the COO\(^-\) asymmetric stretching (V\(_{as}\)) mode and symmetric stretching mode, respectively. The V\(_{as}\) mode of the COO\(^-\) group originates from the carboxylate coordinated to cations [20]. Therefore, it does not appear obviously on the spectrum of the grafted membrane before ZnSO\(_4\) treatment. Since the IR band due to V\(_{as}\) mode of the COO\(^-\) cannot be observed for the bidentate configuration [21], the coordination of COO\(^-\) groups is monodentate for Zn\(^{2+}\). On the other hand, the IR band due to free C=O group is very weak for the ZnSO\(_4\) treated membrane, which indicates that the oxygen atoms in C=O group predominated the formation of coordination bond other than the negatively charged oxygen ions of –COO\(^-\) groups after dissociation of carboxyl groups. The presence of the band at 1252 cm\(^{-1}\) is due to C–O bond vibration of the carboxylic groups [22]. The decrease of this band may result from the hindrance of the complexed Zn ions.

3.3. Synthesis and characterization of ZnS/PP composite

ZnSO\(_4\) treated membrane possesses zinc carboxylate complexes, which can further convert to zinc sulfide precipitates when they react with S\(^2-\). The membrane treated with Na\(_2\)S aqueous solution took a slight brown color, while it was white before the treatment, which indicates the formation of ZnS particles. After the treatment the free C=O stretching mode vibration at 1725 cm\(^{-1}\) disappears, indicating that surplus Na\(^+\) has replaced the H\(^+\) in carboxyl groups unreacted with Zn\(^{2+}\), and the enhancement of COO\(^-\) V\(_{as}\) mode at 1454 cm\(^{-1}\) indicates the complexation continues and tends to completion during the Na\(_2\)S treated procedure. Except these, there is no obvious change in the spectrum of treated membrane though ZnS particles were formed in the membrane. This is due to that ZnS is an infrared transparent material in the frequency range of 400–5000 cm\(^{-1}\) and just for this reason ZnS can be used as infrared windows.

Fig. 3 shows the UV–Vis spectra of grafted PP and ZnS containing membrane (with 17.4% weight increase) in o-dichlorobenzene. There is an absorption band at ca. 335 nm in Fig. 3b, which indicates the existence of ZnS in the polymer matrix [23].

The outer surface morphologies of the PP membrane and the composites were studied with
Fig. 4. FE-SEM images of outer surfaces of the original microporous membrane (a), 30% AA grafted PP membrane (b), ZnSO₄, Na₂S treated membrane with a weight increase of 28% (c).

Fig. 5. FE-SEM images of the cross section of 30% AA grafted PP membrane (a), ZnSO₄ and Na₂S treated membrane with a weight increase of 28% (b), TEM image (c) and EDS spectrum (d) of the section of ZnS containing membrane (Dg = 36.6%, weight increase = 15.03%). The inset in (c) corresponds to a diffraction pattern taken from this image.
The FE-SEM images of the surfaces of the samples are shown in Fig. 4. The matrix has a highly porous structure consisting a series of fine fibrils linked together by nodules (Fig. 4a). As can be seen, the fine fibrils become plump and decrease in number after AA grafting. In other words, pores in the grafted membrane shrunk. This is easy to understand because some spaces in the pores are occupied by grafted poly (acrylic acid) after grafting. As to the ZnS containing membrane, it gets another layer of ZnS precipitates besides the PAA grafted layer, which leads to the further shrinkage of the pores. This can be observed from Fig. 4c. There are many long concavities on the outer surface of the final ZnS containing membrane. They result from the fibril arrays filled by PAA layer and ZnS subsequently.

In order to investigate the inner morphology of the composites, the FE-SEM images of the cross section surfaces of the AA-grafted and the ZnS containing membrane are compared in Fig. 5. There are much less pores in the composite, and ZnS particles disperse in the grafted polymer matrix, which appear as small white dots in the FE-SEM photograph (e.g., indicated by arrows). The figure shows that ZnS particles disperse uniformly in the composite. This results mainly from the fact that SC CO$_2$ has high diffusivity and low viscosity comparing with liquids, and near zero surface tension. Thus, the monomer and the initiator molecules can diffuse into any space in the PP matrix with a faster rate, provided that the size of the space is larger than that of the molecules [16–18]. Therefore, the monomers and the initiator are more uniformly grafted in the PP matrix.

The uniform distribution of ZnS particles in the polymer matrix was also revealed by the TEM image, as shown in Fig. 5c. And the corresponding selected area electron diffraction indicated that the resulted ZnS particles were amorphous, which agrees with the X-ray diffraction (data not shown). Fig. 5d gives the EDS spectrum of the ZnS containing membrane (Dg = 36.6%, weight increase = 15.03%), which clearly indicates the presence of ZnS.

In summary, the AA grafted PP porous membrane was first prepared using SC CO$_2$ as the solvent for AA and BPO. Then ZnS nanoparticles were synthesized by subsequent treatment with ZnSO$_4$ and Na$_2$S aqueous solutions, and the AA grafted PP/ZnS composites were obtained with uniform ZnS nanoparticles. And obviously, such a grafted membrane template may be employed to synthesis some other nanoparticles or composites through a similar route.

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References
