Reactive and Functional Polymers 109 (2016) 64–69

Contents lists available at ScienceDirect

Reactive and Functional Polymers

journal homepage: www.elsevier.com/locate/react

The preparation and study of poly(vinylidene fluoride)/ultrahigh-molecular-weight polyethylene/SiO_2 hollow fiber membrane with network enhanced structure

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ARTICLE INFO

Article history:
Received 8 April 2016
Received in revised form 13 October 2016
Accepted 21 October 2016
Available online 24 October 2016

Keywords:
Poly(vinylidene fluoride)
Ultrahigh-molecular-weight polyethylene
Hollow fiber membrane
Blends
Pore

ABSTRACT

The compatibility of poly(vinylidene fluoride) (PVDF)/ultrahigh-molecular-weight polyethylene (UHMWPE) blends is studied by methods of solubility parameter and melting temperature decreasing. And the melting behavior and crystallization properties are researched by rheological properties testing and differential scanning calorimetry. Based on these, PVDF/UHMWPE/SiO_2 blends hollow fiber hydrophobic membranes with network enhanced structure and porous structure are prepared by thermally induced phase separation (TIPS) and screw extrusion spinning method, with mineral oil as diluent. Then the membrane morphology is observed by scanning electron microscopy (SEM). Finally, properties of membrane are studied by porosity and pore diameter analysis, stretching experiment and contact angle measurement. The results show that the porous structure is improved by interface pores formed due to the poor compatibility between PVDF and UHMWPE. Moreover, the network enhanced structure with rough surface is built by PVDF spherical micro-particles and SiO_2 inorganic particles connected with UHMWPE micro-fibrils. The structure can strengthen mechanical properties of membrane.

1. Introduction

Membrane distillation technology has been widely applied to water desalination, waste water reuse, food and beverage industries, heavy metal removal, and other industrial areas because of its desirable properties, such as low operating temperature, low operating pressure, less energy loss, and ease to industrial expansion [1]. Materials used in membrane distillation should have characteristics of low surface energy, high porosity, excellent mechanical property, thermal and chemical stability, and so on.

Materials used in membrane distillation mainly include the followings, polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF), and polypropylene (PP) [2]. The surface energy of PTFE, PVDF and PP is 18–20 dynes·cm^{-1}, 25 dynes·cm^{-1}, and 29–31 dynes·cm^{-1}, respectively. The most commonly used material among these is PTFE, due to its hydrophobicity, weather resistance and chemical stability. But its cost is higher, and the only method for PTFE to form pores is stretching, which is difficult to control pore size. There are many methods to prepare PVDF membrane, but non-solvent induced phase separation method and thermally induced phase separation (TIPS) method were used more in the preparation of PVDF membrane. The forming condition of PVDF membrane is easier to control in TIPS process. Moreover/in addition, the performances of PVDF basically satisfy the requirements of membrane distillation.

In TIPS process, a polymer is dissolved in a diluent at elevated temperature to form a homogenous solution. With the loss of heat, liquid-liquid phase separation possibly occurs. At the same time the diluent droplet begins to aggregate, grow and form cell shape pores. Above processes are called coarsening [3]. When cooling temperature is lower than crystallization temperature, solid-liquid phase separation will occur. Then membrane is characterized as spherocrystal structure (polycrystalline aggregates that lamellae grow by symmetry or its variant structure, such as rod crystal and leafy shape crystal) [4].

Moreover, the surface roughness has strong effect on hydrophobic property. It is more difficult for hydrophobic surface to be wetted when the value of roughness is greater [5]. The rough surfaces with PVDF spherical micro-particles can be built when the PVDF spherulites have enough time and space to aggregate and grow. The method for increasing time and space include low concentration of PVDF [6], high dissolution temperature [7], slow solidification rate [8,9]. But through these, the membrane has loose structure and poor strength. Ultrahigh molecular polyethylene (UHMWPE) is a kind of polyethylene with molecular weight of more than 1.0×10^6. It has advantages of excellent strength, high modulus, anti-ultraviolet, ocean corrosion resistance, self-lubricating, and hydrophobic property [10]. The UHMWPE deform at about 85 °C [11]. However, the temperature of membrane distillation is about 60–85 °C. Thereby, the UHMWPE membrane cannot apply in

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http://dx.doi.org/10.1016/j.reactfunctpolym.2016.10.005
1381-5148/

distil under high temperature. Through blend modification, which is an effective way to overcome the weakness of a single material, UHMWPE is expected to be applied in the field of membrane distillation. Currently, TIPS is the most common method to prepared UHMWPE porous membrane. Both Hu [12] and Zhou [13] used TIPS method to fabricate UHMWPE microporous membrane with high strength. And Wang [14] prepared UHMWPE fibers and discovered the network structure like loofah heart in UHMWPE.

In this study, PVDF, UHMWPE and SiO_2 were blended to prepare ternary hybrid hollow fiber membranes. In order to enhance the hydrophobic property and mechanical strength, we attempted to build a network to enhance structure with rough surface, which was composed of PVDF spherical micro-particles and SiO_2 inorganic particles connected with UHMWPE micro-fibrils. This research would have significance on enriching membrane material of distillation membrane.

2. Experimental

2.1. Materials

The UHMWPE (MIII) was purchased from Beijing No.2 Reagent Plant (Beijing, China) with a weight-average molecular weight of 3.65×10^6. The PVDF (W#1300) provided by Kureha Chemical Industry Co., Ltd. was dried for 24 h in a vacuum oven prior to use. The mineral oil (7#) and gasoline were produced by Oil Refinery Plant of Daqing Petrochemical Company. The antioxidant (*n*-Otadecyl-β-(4-hydroxy-3, 5-di-*tert*-butyl-phenyl)) propionate, 1076# was a commercial product of Tianjin Lisheng chemical Plant. The micro-size SiO_2 (2–6 μm diameter) was produced by Tianjin Chemical Research Institute. Alcohol and glycerol were analytically pure.

2.2. Preparation of PVDF/UHMWPE/SiO_2 hybrid hollow fiber membranes

The steps for preparing PVDF/UHMWPE/SiO_2 ternary hybrid hollow fiber membranes were showed as follows. First, mineral oil and SiO_2 were mixed well at 20 °C for 1 h when the rotating speed was 45 rad/-min (mass ratio of SiO_2 to polymers was 4:5). Then, 15 wt% polymers (mass ratio of UHMWPE to UHMWPE/PVDF was 0–100 wt%, the default value was 80 wt%) and 0.3 wt% antioxidant (it could avoid the degradation of UHMWPE) were dissolved in the mixture of mineral oil/SiO_2 and were stirred at 40 °C for 3 h. After mixing uniformly, the solution was poured into twin-screw.

In spinning, the spinneret with outer diameter of 10.5 mm and inner tube diameter of 7.8 mm was used. The hollow fibers were spun by gel-spinning process (air-gap = 15 cm) [15]. The spinning temperature was 190 °C. The temperature of environment was 20 °C and the relative humidity was 65%. The take up velocity was 11–12 m/min. The extrusion rate of casting solution was in the range of 35–36 ml/min and the flow rate of internal cooling bath was in the range of 3–3.5 ml/min. The gel hollow fibers were formed by the extrudate immersed in cooling medium (20 °C air), with mineral oil acted as internal cooling bath. The gel-hollow-fibers were put into gasoline for 48 h to extract mineral oil. After that, the gasoline was extracted with alcohol. Before SEM test, the resulting membranes were putted into glycerol-water solution (volume ratio of parts glycerol to water was 3:2) for 24 h and then were dried in air, which could retain the porous structure.

2.3. Study on the compatibility of PVDF and UHMWPE

2.3.1. Rheological properties testing

Rotary rheometer (AR1000, TA Co., America), equipped with parallel plates of 25 mm diameter and 1 mm plate spacing, was used to measure the viscoelastic properties at a temperature of 170 °C. Samples were compression-molded disks. All samples were pretreated at a constant temperature of 170 °C for 3 min. The shear rate ranged from 0.01 s^{-1} to 100.00 s^{-1}.

2.3.2. Differential scanning calorimetric experiment

Melting point, melting distribution and crystallinity degree were determined using the differential scanning calorimeter (DSC, 200F3, NETZSCH Co., Germany). The samples were heated from 0 °C to 200 °C at a heating rate of 20 °C·min^{-1} under nitrogen atmosphere. After waiting at least 5 min to ensure complete melting and equilibrium, the samples were cooled at the rate of 20 °C·min^{-1}. The sample weight was approximately 5 mg. The onset of the endothermic peak during the heating was taken as the melting point temperature. The crystallinity was calculated from heats of fusion taken from the thermograms and the calculation was showed as Eq. (1) [16]:

$$X_c = \frac{\Delta H}{\Delta H_m} \times 100\% \tag{1}$$

where ΔH is the melting enthalpy, ΔH_m the standardized enthalpy of pure crystal. The ΔHm of UHMWPE is 273 J·g^{-1} [17] and that of PVDF is 104.7 J·g^{-1} [18].

2.4. Morphological examination

The structure and morphology of membrane were observed by scanning electron microscopy (SEM, Quanta200, FEI Co., Netherlands). The cross section of the membrane was freeze-fractured under liquid nitrogen. The membrane samples were gold sputtered and analyzed by SEM.

2.5. Porosity measurement

The porosity of the blend membrane was determined by measuring the true density and the bulk density [19]. The sample was put into a density bottle (10 ml) filled with alcohol and the equation of cubage was expressed as

$$10 = \frac{M_a}{\rho_a} + \frac{M_m}{\rho_t} \tag{2}$$

where M_a and M_m are the weight of residual alcohol in density bottle and dry membrane, respectively, ρ_a the density of alcohol, and ρ_t the true density of membrane. Therefore, the true density (ρ_t) was calculated according to Eq. (3):

$$\rho_t = \frac{M_m \tilde{n} \rho_a}{10\rho_a - M_a} \tag{3}$$

To measure the bulk density, blend membrane was swollen at 20 °C for 12 h and the wet weight (M_{wm}) was measured. The free liquid on the surface of the swollen membrane was padded dry with filter papers before weighing. The dry weight (M_{dm}) was measured after the sample was dried under vacuum. The bulk volume (V_b) was calculated by Eq. (4):

$$V_b = \frac{M_{wm} - M_{dm}}{\rho_a} + \frac{M_{dm}}{\rho_t} \tag{4}$$

The bulk density (ρ_b) was calculated by Eq. (5):

$$\rho_b = \frac{M_{dm}}{V_b} \tag{5}$$

The porosity (ε) of the sample was calculated by Eq. (6):

$$\varepsilon(\%) = \left(1 - \frac{\rho_b}{\rho_t}\right) \times 100 \tag{6}$$