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Effect of PMMA on crystallization behavior and hydrophilicity of poly(vinylidene fluoride)/poly(methyl methacrylate) blend prepared in semi-dilute solutions

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Abstract

Films of poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA) blend were derived from a special procedure of casting semi-dilute solutions. Hydrophilic character and crystallization of PVDF were optimized by variation of PMMA concentration in PVDF/PMMA blends. It was found that a PVDF/PMMA blend containing 70 wt% PMMA has a good performance for the potential application of hydrophilic membranes via thermally induced phase separation. The films presented β crystalline phase regardless of PMMA content existed in the blends. Thermal analysis of the blends showed a promotion of crystallization of PVDF with small addition of PMMA which induced larger lamellar thickness of PVDF, leading to the largest spherulitic crystal of PVDF (10 wt% PMMA) is about 8 μm. SEM micrographs illustrated no phase separation occurred in blends, due to the high compatibility between PVDF and PMMA.

Keywords: Poly(vinylidene fluoride) (PVDF); Hydrophilicity; Crystallinity; Blends

1. Introduction

Poly(vinylidene) fluoride (PVDF) as a semi-crystalline polymer, has wide applications due to its excellent physical and chemical properties, such as good mechanical strength and toughness, high abrasion resistance, great resistance to outdoor exposure and sunlight as well as good thermal stability [1] and recently the medical grade PVDF has been found very useful in biomedicine because of its biocompatibility [2]. Especially, PVDF is quite suitable for manufacture of membrane due to its chemical resistance. However, the high crystallinity and low surface tension properties give it very low permeation values. During the ultrafiltration process, high hydrophobic property and low fouling resistance PVDF membranes lead to the sensitivity in protein adsorption, and thus pores of the membrane are blocked [3,4]. This produces a higher rate of membrane fouling. In order to overcome the disadvantage, a number of studies have been dedicated to make them more hydrophilic. One procedure is chemical treatment of surface with a strongly alkaline solution either in the presence of an oxidizing agent or with a polymerization initiator and monomers such as acrylic acid, to graft or coat polyacrylamid, poly(acrylic acid), poly(vinyl alcohol) and cellulose derivatives [5]. This kind of modification occurs only near the materials surface. Another efficient possibility for improving the hydrophilicity of PVDF is polymer blending with hydrophilic polymers. As PVDF is highly miscible with oxygen-containing polymers which is related to the interaction between the fluorine atoms and carbonyl groups of the partner polymer [6], several pairs of blends have been investigated, such as PVDF/poly(vinylpyrrolidone) (PVP), PVDF/poly(ethylene glycol) (PEG), PVDF/sulfonated polystyrene, PVDF/poly(vinyl acetate), and PVDF/poly(methyl methacrylate) (PMMA) [4]. Compared to the former method, polymer blending, especially solution mixing is more effective and widely used presently, because of its facile preparation of the blends.

A series of blends of PVDF showed that PVDF and PMMA have high compatibility [7–11]. Hydrophilic PVDF membrane

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via phase-inversion process has been prepared through addition of PMMA which is a hydrophilic material enhancing hydrophilicity and flux rate of PVDF membrane [12,13]. Furthermore, the existence of crystallized phase at the surface would affect the surface hydrophilicity. Addition of PVP above 50 wt% content in PVDF/PVP blends has a promotive effect on hydrophilicity, as no crystalline PVDF domains on the film surface [14].

With respect to PVDF crystal phases, it is well known that four of PVDF crystalline phases exist, so called α, β, γ, and δ [15–17], and especially β phase of PVDF results in pyro- and piezo-electric properties, which is very useful in electrochemistry [18,19]. It has been reported that different crystalline phases of PVDF could be obtained by solution casting in different conditions. And the crystal forms of PVDF mainly depend on the crystallization temperature rather on the kind of solvent. It has been illustrated that the solution crystallization temperature at $T < 70\,^{\circ}\mathrm{C}$ always results in the β phase of PVDF crystals [20,21]. In addition, the incorporation of other polymer into PVDF also influences crystallization of PVDF. For instance, the addition of PMMA at 10 and 15 wt% reduces the crystallization rate of α phase, and favors the β phase formation [22,23]. Lee and Ha [24] found that both α and γ phases of PVDF were obtained upon blending with poly(methyl acrylate) (PMA). However, the α phase predominated in the blends contained polyvinyl acetate (PVAc).

In our previous work in Ref. [25], it is studied that PVDF has crystallinity leading to the formation of the spherulitic structure with large hole between them in PVDF membranes via thermally induced phase separation. In order to retard crystallization of PVDF and simultaneously obtain hydrophilic PVDF membrane, PMMA was chosen to blend with PVDF. Most researcher's work blends of PVDF prepared in concentrated region [26] (total polymer concentration >5 wt%) [20–23] in which each segment of the polymer chain does not have a sufficient space available. In this condition, it is difficult for the motion of polymer chains. In order to make more space for chains' motion, semi-dilute solution [26] was used to obtain homogeneous solution in which polymer chains are overlapped and entangled and the overall chain motion is slow. This can study the interaction between polymer chains of components in the blend well. The present work dealt with solution casting with 2 wt% polymer concentration which located in semi-dilute region, with components of PVDF and PMMA in different proportions. The hydrophylilcity of PVDF blending with PMMA under different polymer ratios is investigated. Simultaneously, the crystallization behavior of PVDF with different composition of PMMA addition is discussed.

2. Experimental

2.1. Materials

PVDF powder (Kynar K-761, $\bar{M}_{\mathrm{w}} = 441,000$) was obtained from Elf Atochem of North America Inc. (USA). PMMA resin (HR1000L) was obtained from Kuraray Co., Ltd. (Japan). *N*,*N*-dimethylformamide (DMF) was used as solvent and methanol as the extractant. Both of them were obtained from Sinopharm Chemical Reagent Co., Ltd. (China).

2.2. Preparation of samples

Films of polymeric blends with different concentration of PMMA were prepared by casting polymer solutions containing 98 wt% DMF, after continuous stirring at 50 °C for 24 h, onto polytetrafluoroethylene (PTFE) substrate which was kept at 50 °C in a vacuum oven. Then, DMF was allowed to evaporate for about 24 h with the solidification of the mixtures. Eventually, the films were cooled at 25 °C, and then peeled from the substrate. Average thickness of the films was about 30 μm. Final methanol was used as the extractant, which is non-solvent of the two polymers and can exchange the involatile solvent DMF in the film. In order to guarantee removal of residual solvent DMF in the films, this was done by immersing the films in methanol at 25 °C for 24 h, and then further dried in vacuum oven at 25 °C for another 24 h, repeating these two steps nine times. After that, the samples without the residual DMF were obtained.

To prepare smooth surface samples for the contact angle test, samples after extraction with methanol were put between two thermally resistant polyester thin films refreshed with ethanol and then compression-molded at 180 °C between two steel boards by the platen vulcanizing press with the first pressure of 5 MPa for 10 min and second pressure of 10 MPa for 5 min. Subsequently, the samples and the two steel boards were quickly cooled freely on another cold platen vulcanizing press with the pressure of 12.5 MPa at 25 °C.

2.3. Scanning electron microscopy (SEM) observation

The samples were fractured in liquid nitrogen, and both the cross section of the samples and the surfaces of the samples were sputtered with Au in vacuum. Then, the scanning electron microscope (JSM-5900, JEOL, Japan) with an accelerating voltage of 15 kV was used to examine the samples cross sections and the surfaces of the samples.

2.4. Wide angle X-ray diffraction (WAXD) measurement

WAXD (XRD-6000, Shimadzu, Japan) was used to analyze the PVDF crystal structure of samples. The radiation source (Cu Kα X-ray) was operated at 40 kV and 30 mA, with the scanning angle ranging from 5° to 60° and the scanning velocity of 4°/min.

The Bragg equation was used to calculate the interplanar distance (*d*-value) and the equation is given as [27]:

$$d_{hkl} = \frac{\lambda}{2\sin\theta}$$

where $\lambda = 1.542$ Å, θ is the Bragg angle. And lamellar thickness L was calculated using the Scherrer equation [27]:

$$L = \frac{k\lambda}{(B \cdot \cos\theta)}$$