β-Phase of poly(vinylidene fluoride) formation in poly(vinylidene fluoride)/poly(methyl methacrylate) blend from solutions

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ABSTRACT

The effect of single and mixed solvent on the crystallization behavior of the PVDF/PMMA blend from solutions was investigated. The films cast from the good solvent N,N-dimethylformamide (DMF) dominantly yielded the β-phase crystal with the highest crystallinity of PVDF. Those deposited from the methyl ethyl ketone (MEK) and tetrahydrofuran (THF) exhibited a mixture of α- and some extra β-phase crystals and presented the low crystallinity of PVDF. The crystallization behavior and morphology of the films cast from the mixed solvent (THF/DMF) revealed an enormous dependence on the DMF content. The increased DMF content in the mixed solvent enhanced the interactions between polymers and solvents, and favored the β-crystal of PVDF formation but hindered the α-phase of PVDF formation. Thus, the total crystallinity of PVDF in the blend film was decreased with the DMF content increasing, because of the decreased α-phase of PVDF. In addition, the morphological feature revealed that the voids between the PVDF spherulites were eliminated remarkably by blending with PMMA. The average size of the connected spherulite on top surface of the film can grow into larger as DMF content increased.

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1. Introduction

Poly(vinylidene fluoride) (PVDF) has been paid more attentions in the past few decades because of its excellent physical and chemical properties [1]. This provides a wide range of scientific and industrial applications, such as food and beverage applications, semiconductor manufacturing, mining industry, etc. Recently, the medical grade PVDF has been found very useful in biomedicine because of its biocompatibility [2], and quite suitable for manufacture of membrane due to its chemical resistance. On the other hand, PVDF is a semicrystalline polymer with at least four crystalline phases, α, β, γ and δ [3]. A better understanding of the processing effect on the crystalline-phase formation during the product preparing is necessary. It has been illustrated that the solution crystallization temperature at $T < 70\,°C$ predominantly results in the β-phase of PVDF; temperature between 70 and 110 °C leads to a mixture of α- and β-phase; above 110 °C, α predominates [4]. Tazaki et al. reported the crystallization and gelation of PVDF solution. They revealed that the PVDF chains packed together into the γ-phase in γ-butyrolactone solution and

α-phase in other ketones as crystallization occurred [5]. In Cheng's work [6], it has reported that at lower temperature (25 °C), PVDF solution precipitated into a uniform morphology composed of the β spherulits from 1-octanol/DMF. By contrast, when PVDF was precipitated at higher temperature (65 °C), the formed crystal structure became largely in the α-phase. In addition, the incorporation of other polymer into PVDF would also influence the crystallization of PVDF [7–9]. As reported, the crystallization behavior of the crystalline polymer is obviously affected by the cast solvents and the blending polymers [10–12]. However, less work focused on mixed solvent contribution to the crystal formation of PVDF/PMMA blends from solutions. Usually, the cast films of pure PVDF exclusively in the β-phase possess a high degree of porosity [13,14], which makes them opaque and fragile with a decrease of the mechanical and electrical properties. Those pores formed in the films, which can cause a degradation of the electrical properties (lower dielectric constant) and do not allow the poling of the films. This limits the application for the piezo-, pyro- and ferroelectric effects [15]. Sencadas et al. [15] applied a pressure perpendicular to the surface of the film at elevated temperature to obtain nonporous films of PVDF, resulting in the much thinner films.

Based on our previous work [16,17], PVDF crystallization behaviors dramatically affect the final product's properties. Especially, during the thermally induced phase separation (TIPS) process [18,19], from which considerable interest has been

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generated, the large macrovoids were formed which dispersing in the PVDF spherulites. In order to avoid these macrovoids between the PVDF spherulites, poly(methyl methacrylate) (PMMA) was blended with PVDF, which performing excellent miscibility [20]. As 30 wt% PMMA incorporated with PVDF, not only the crystallization of PVDF is reduced, but also the hydrophilic character is improved. It has been demonstrated that this composition (PVDF/PMMA = 70/30) provides the best balance of optical properties, solvent resistance, hardness, mechanical strength and weatherability as well [21]. In this study, PVDF/PMMA (70/30) blend sample prepared from solutions was investigated. The effect of the single solvents and mixed solvents on the crystallization behavior and morphology of the resulting samples is discussed.

2. Experimental

2.1. Materials

PVDF (Kynar K-761) powder was supplied by Elf Atochem of North America Inc. (USA). PMMA resin (HR1000L) was obtained from Kuraray Co. Ltd. (Japan). N,N-Dimethylformamide (DMF) was obtained from Sinopharm Chemical Reagent Co. Ltd. (China). Methyl ethyl ketone (MEK) and tetrahydrofuran (THF) were purchased from Ling Feng Chemical Reagent Co. Ltd. (China).

2.2. Films prepared by solution casting

Both MEK and THF were good swelling agents [22] at 60 °C for PVDF and good solvents for PMMA at room temperature [23]. The DMF was a strongly polar solvent which is good solvent for PVDF [23] and also can dissolve PMMA at room temperature in this work. Thus, suspension of PVDF/PMMA (70/30) blend was prepared by dissolving in MEK and THF at 60 °C, with stirring for 24 h; i.e. PMMA was dissolved completely in this condition and the undissolved particles in the suspension is PVDF powder. Then, the MEK and THF suspension were deposited on the substrate and maintained in the vacuum oven at 50 °C. After that, the cracked samples were obtained.

Homogeneous solution was obtained by dissolving in DMF at 50 °C, with stirring for 24 h. After cast the solution onto the glass substrates for complete evaporation of the solvent for 24 h at 50 °C, the films (thickness: ~30 μm) were peeled from the substrates.

In addition, the mixed solvents of THF/DMF (with different mass ratios: 9/1, 8/2, and 5/5), which can dissolve the polymers as in DMF, were used to investigate the crystalline-phase formation of PVDF in the blend. The sample preparation method is the same as those by DMF and smooth films were obtained. The all of the blend samples gained in this work were denominated as $MF_{0.7}$ films (PVDF/PMMA = 70/30) and the initial polymer concentration was always 10 wt%.

2.3. Fourier transform infrared spectroscopy (FTIR) measurement

FTIR spectra of films were obtained on a FTIR spectrometer (Vector-22, Bruker, Germany) in the 400–1000 cm^{-1} wave number range with resolution of 4 cm^{-1}.

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

WAXD (XRD-6000, Shimadzu, Japan) analyses of the films were performed to reveal the crystal structures in the films. The wavelength of the X-ray was 1.542 Å (Cu Kα radiation, 40 kV and 30 mA) and the scanning velocity was 4°/min. The Bragg equation and Scherrer equation [24] are applied to calculate the d-value and the lamellar thickness $L_{h\,k\,l}$ in the direction perpendicular to the (h k l) crystal plane, as reported in previous work [20,25].

2.5. Differential scanning calorimetery (DSC)

Thermal behaviors of the $MF_{0.7}$ films from various solvents were examined using a thermal analysis apparatus (DSC-7C, PerkinElmer, USA). An appropriate amount of the sample (typically 10 mg) was sealed in an aluminum pan. The temperature was raised from 50 to 180 °C at a heating rate of 10 °C/min. The melting temperatures T_m^{on}, T_m^p and T_m^f observed in the melting curves are taken as onset melting temperature, peak melting temperature and final melting temperature, respectively. Crystallinity of the films was calculated by dividing the measured heat of fusion (ΔH_m) (determined from the melting curves) by the value for perfect PVDF crystal, as reported in our previous work [17,20].

2.6. Scanning electron microscopy (SEM) observation

Surface morphologies of the two sides of the films were observed using a scanning electronic microscope (JSM-5900, JEOL, Japan). The top and bottom surfaces of the films were referred to those formed at the air/solution interface and at the solution/substrate interface, respectively. The sample was sputtered with a thin layer of Pt in vacuum and observed under 15 kV acceleration voltages.

3. Results and discussion

3.1. Effect of different solvents on the crystalline-phase formation of PVDF in the blend films

3.1.1. FTIR spectroscopy

FTIR spectra of samples prepared from MEK, THF, and DMF are shown in Fig. 1a–c. The vibrational spectra of the three principal
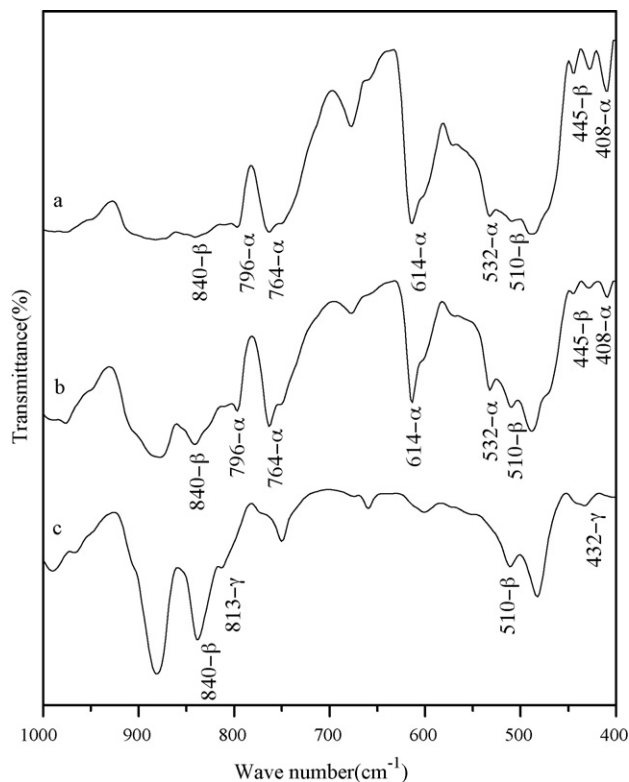

Fig. 1. FTIR spectra for $MF_{0.7}$ samples prepared from different solvents: (a) MEK; (b) THF; (c) DMF.