

Miscibility, crystallization and annealing studies of poly(vinylidene fluoride)/hyperbranched polyester blends



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ABSTRACT

In this study, miscibility and crystallization behavior of polyvinylidene fluoride (PVDF) and its blends with hyperbranched polyester (HBPE, 0 to 50 wt.-% of HBPE in PVDF) are investigated by means of DSC and FTIR techniques. Among the varying blend compositions, PVDF/HBPE (100/0 and 90/10) blend ultrathin film samples were subjected to thermal annealing at different temperatures (30–200 °C) in order to examine and compare their crystallization behavior. From FTIR data, the *all-trans* band (A_1) at $ca.$ 1280 cm^{-1} corresponding to the changes in ferroelectric β -crystalline phase for both the samples exhibits higher absorption intensity upon annealing at 90 °C, well below their melting temperature range ($T_m \sim 160$ °C), whereas, the sample melt-annealed at 210 °C exhibit reduced A_1 absorption intensity, which is attributed to the crystalline transformation from ordered ferroelectric phase into the disordered amorphous phase. Quantitative data from Factor analysis revealed the existence of higher ferroelectric β -crystalline phase content in PVDF/HBPE (90/10) blend ultrathin film sample than in commercially available PVDF and PVDF/TrFE (72/28) ultrathin film samples, which exemplifies the importance of this study. The enhanced ferroelectric characteristics exhibited by the PVDF/HBPE (90/10) blend ultrathin film samples can be well-suited for electronic applications such as non-volatile memory devices, sensors, etc.

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1. Introduction

Blending of polymers is a simple, cost-effective and less time consuming method to obtain new materials, whose properties are superior to those of the individual components. By changing the blend composition and combining different components, the properties of the final product can be tailor-made. Depending on the miscibility at molecular level, polymer blends can be classified as miscible, immiscible (or incompatible) and partially miscible blends.

Polyvinylidene fluoride (PVDF) is a commercially important electroactive polymer and quite a few reports have focused on the miscibility of PVDF with acrylic (amorphous) polymers such as poly(methyl acrylate) [1], poly(ethyl acrylate) [1], poly(methyl methacrylate), PMMA [2–7] and poly(ethyl methacrylate) [1,8]. In addition to that, PVDF is also reported to form miscible blends with polyvinyl fluoride [9], polyvinyl acetate, PVAc [10], polyvinyl pyrrolidone, PVP [11], poly-3-hydroxybutyrate, PHB [12], poly-1,4-butylene adipate [13], etc. The miscibility of these blends is assigned to the interaction between $-\text{CF}_2$ groups in PVDF and the carbonyl groups of the blend component.

Hyperbranched polymer (HBP) blends have received wide attention from researchers since last two decades [14–22]. Among them, Massa et al. studied the phase behavior of hydroxyl-terminated (OH-HBPE) and acetoxy-terminated hyperbranched polyesters (AcO-HBPE) blended with a variety of linear polymers such as polycarbonates, polyesters and polyamides [14]. The miscibility of OH-HBPE with linear polymer is due to the interactions arising out of H-bonding, while AcO-HBPE displayed lesser miscibility than OH-HBPE, which is consistent with the absence of strong bonding interactions in AcO-HBPE. In another study, the crystallization behaviors of polyethylene terephthalate (PET) in HB aliphatic polyesters were investigated using *in-situ* FTIR spectroscopy and DSC techniques [16]. From FTIR spectra, the shifting of C=O band to lower wave number due to increased dipole–dipole interaction between the blend components was observed. The significant increase in the crystallization rate of PET is credited to the influence rendered by the HBP composition and its terminal groups (hydroxyl, acetate and benzoate) on the crystallization behavior of PET, whereas a comparative study done for linear polyester/PET blend showed the decrease in crystallinity. Among different compositions of HBP/PET blends of different functional groups (hydroxyl, acetate and benzoate), maximum crystallization rate appeared at 12 wt.-% of HBP containing benzoate end groups and its influence on the crystallization behavior of

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PET was confirmed from both FTIR and DSC studies. Solution and melt blends prepared by mixing polyamide 6 and HB aromatic polyamides were found to have good miscibility as confirmed from viscosity and DSC data [19].

Though many reports are available for semi-crystalline PVDF/amorphous linear polymer blends, we investigated for the first time, the miscibility; thermal annealing and crystallization behavior of PVDF and its blends with HBPE in the present study. At first, the miscibility of HBPE with PVDF is studied using FTIR and DSC measurements. In the second step, the suitability of using the developed material for electronic applications is confirmed by studying the effect of annealing (from 30 to 200 °C) upon PVDF and PVDF/HBPE (90/10 w/w) blend ultrathin films using FTIR-grazing incident reflection absorption spectroscopy (FTIR-GIRAS). In the final step, Factor analysis (FA) was applied to extract the pure-component spectra as well as the ferroelectric β -crystalline content as a function of varying annealing temperatures for both PVDF and its blend ultrathin film samples.

2. Experimental section

2.1. Materials and sample preparation

PVDF powder ($M_w = 60,000$, Polysciences Inc., U.S.A), Acetone and DMF solvents (Sigma–Aldrich, U.S.A) were used as received. ITO-coated glass substrates used for FTIR-GIRAS measurement were purchased from SD Tech., Korea, and immersed in soap-deionized water mixture, deionized water, acetone, and isopropyl alcohol-deionized water mixture in a series for 2 h each. The substrates were cleaned with a nitrogen gun and kept under vacuum at 130 °C overnight. 2 wt.-% PVDF and its blends (5, 10, 15, 20, 30 and 50 wt.-% of HBPE) were dissolved separately in acetone: DMF (80:20 v/v) mixture and stirred overnight at 50 °C in a water bath to get a homogenous solution. Synthesis and characterization details of third generation HBPE (based on pentaerythritol as a core and dimethylol propionic acid as AB_2 monomer) were reported in our previous study [23]. The prepared stock solutions of PVDF and its blend samples were filtered out and used for further measurements.

2.2. Miscibility and crystallization studies

The stock solutions were cast on KBr pellets and dried initially at room temperature for 24 h and then under reduced pressure at 50 °C for 120 h to remove the solvent traces, if any. To determine the extent of miscibility in PVDF-HBPE blends, FTIR-transmission spectra (FTIR-TS) were recorded for the samples previously subjected to three different thermal treatment conditions (a) as-cast (AC), (b) melted at 210 °C for 20 min in a vacuum oven and then quenched to -5 °C (MQ) in a mixture of ice and NaCl salt and (c) melted at 210 °C. For DSC and XRD measurements, the stock solutions were poured into a glass beaker and maintained at room temperature for seven days to remove the maximum amount of the solvent. Later, they were kept in a vacuum oven at 50 °C for 5 days for complete removal of the solvent traces. The thick films (~ 1 mm) were peeled off from the beaker and used for analysis.

2.3. Annealing studies

PVDF/HBPE (100/0 and 90/10) blend samples were spin coated at 40 °C on ITO substrate at 1500 rpm for 0.5 min using a heat-controlled spin-coating setup as shown in Fig. 1 of Ref. 24. The spin-coated ultrathin film samples (120 ± 5 nm) were subjected to various annealing temperatures (30–200 °C) in a vacuum oven for 3 h and then slowly cooled to room temperature.

2.4. Characterization techniques

Unpolarized FTIR-TS and FTIR-GIRAS (at an incident angle of *ca.* 85° from normal to the surface) spectra were recorded using Bruker 66V FTIR spectrophotometer at a resolution of 2 cm^{-1} with 5 min scans at room temperature for the solution-cast as well as spin-coated samples. To determine the miscibility of the blends, the FTIR-TS absorption spectra of solution-cast samples were recorded at preset defined temperatures (210 °C) by mounting KBr pellets on a custom-made heating cell. Using Mettler-Toledo DSC-1, each sample (PVDF, HBPE and PVDF/HBPE blends) was heated ($10 \text{ }^\circ\text{C}/\text{min.}$) from 30 °C to its melting at 210 °C, and then quenched to $-80 \text{ }^\circ\text{C}$ ($100 \text{ }^\circ\text{C}/\text{min.}$). The same sample was again re-heated to 210 °C ($10 \text{ }^\circ\text{C}/\text{min.}$) to get the melting endotherms. X-ray diffraction (XRD) patterns were obtained using D8 Advance, Bruker with CuK_α radiation in the 2θ range, 3–80° at room temperature using Lynx Eye detector (silicon strip detector technology) for thick PVDF and its blend films as well as for powdered HBPE.

3. Results and discussion

Fig. 1 shows the FTIR spectra of PVDF and HBPE solution-casted on KBr pellet in the region of $1800\text{--}600 \text{ cm}^{-1}$ measured at R.T. The band at 1733 cm^{-1} represents the carbonyl band of HBPE. The FTIR spectrum of PVDF shows a number of absorption bands which are sensitive towards changes in the ferroelectric β -crystalline phase, particularly, the stronger absorption bands at 1274 and 840 cm^{-1} ($A_1, \vec{\mu} \parallel \vec{b}$) associated with $\nu_s\text{CF}_2$ for the *trans* sequence longer than TTTT and $\nu_s\text{CF}_2 + \nu_s\text{CC}$ for the *trans* sequence longer than TTT, respectively. The 1176 and 881 cm^{-1} absorption bands ($B_2, \vec{\mu} \parallel \vec{a}$) are associated with $\nu_{as}\text{CF}_2$ and $r\text{CH}_2$ modes, respectively. The 1411 and 1074 cm^{-1} ($B_1, \vec{\mu} \parallel \vec{c}$) absorption bands are assigned to $\omega\text{CH}_2 + \nu_{as}\text{CC}$ whose transition moment is along the chain orientation direction [25,26].

3.1. Miscibility studies between PVDF and HBPE

FTIR is a good analytical technique to study the miscibility of polymer blends by observing the changes in the carbonyl peaks [27,28]. One of the major contributors to the miscibility of blend component with PVDF is the specific interaction of either H-bonding between $\text{C}=\text{O}$ and $-\text{CF}$ (or $-\text{CH}_2$) and/or dipole–dipole interaction [10,13,29–33]. This type of H-bonding interactions in polymer blends can be identified by IR spectroscopy by verifying

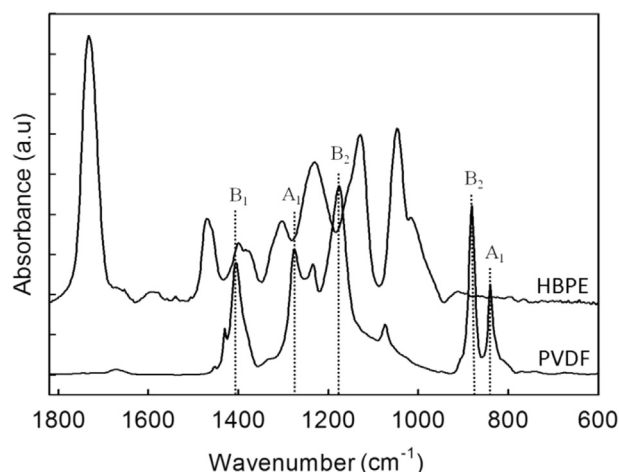


Fig. 1. FTIR-TS spectra of solution-cast PVDF and HBPE.

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