



Study on the miscibility, crystallization and crystalline morphology of polyamide-6/polyvinylidene fluoride blends



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ABSTRACT

The miscibility, crystalline structure and morphology, as well as, properties of Polyamide 6 (PA6)/polyvinylidene fluoride (PVDF) blends (with up to 50 wt% of PVDF) were studied. Small Angle X-ray Scattering study above the melting point of PVDF shows that the blends have very limited miscibility with approximately 5 wt% of PVDF inclusion in PA6 amorphous lamellar region. SAXS results also indicate a certain degree of PA6 inclusion into PVDF region though quantitative evaluation is unavailable with the limited blends studied in this work. The fine PVDF dispersion in the PA6 blends with up to 50 wt% of PVDF with an average size about 150 nm is supposed to be the result of the partial miscibility. The partial miscibility has great effects on the morphology and properties of the blends. Crystallization of both components are suppressed in the blends, especially on the PVDF component, which shows a significantly lowered crystallization temperature (up to 30 °C) during a cooling and a dramatic drop in crystallinity. Morphological studies together with Small Angle Light Scattering (SALS) show that spherulites, consisting of PA6 skeleton with dispersed PVDF domains (~150 nm) engulfed among PA6 fibrils, are formed in the blends. The PA6 based spherulites become more defective with the increase in PVDF content, resulting in short/broken fibrils and undetectable PA6 spherulites for the blends with 30–50 wt % of PVDF at the temperature over the melting point of PVDF, say 185 °C. The blends show a significantly improved toughness compared with neat PA6, due to the partial miscibility which leads to the fine dispersion of PVDF domains in PA6 spherulites.

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1. Introduction

Polyamide-6 (PA6) is a semi-crystalline engineering thermoplastic with good mechanical properties, but suffers from high moisture uptake, poor resistance to thermal oxidation and UV radiation, and low impact strength under low-temperature or dry condition. It is a common strategy to blend a fraction of other polymers with PA6 to overcome these disadvantages; these polymers include polypropylene (PP) [1,2], polyethylene (PE) [3,4], polyolefin-based elastomers (poly(ethylene-1-octene) [5,6], poly(propylene-co-ethylene) [7]) et al. However, the overall improvement is limited due to the poor miscibility between PA6 and these polymers. Recently, poly(vinylidene fluoride) (PVDF) has emerged as a promising material to modify PA6 due to its low moisture-uptake and good resistance to thermal oxidation and UV

radiation, as well as its relatively strong intermolecular interactions with PA6 [8–10]. Besides PA6, other polyamides such as PA11 and PA12, are also considered to have hydrogen bonds or dipolar intermolecular interactions with PVDF [11,12]. However, sea-island morphologies were observed by Transmission Electron Microscopy (TEM) for PA6 blends with 20 to 80 wt% of PVDF [8] and the blends are classified as totally immiscible in overall composition range [8–10,13]. On the other hand, blending PVDF with PA6 can significantly improve the toughness of PA6 matrix [8–10]. Na et al. [9] hypothesized that the improved toughness of the PA6 blend with PVDF was due to α to β transition of PVDF crystal and fibrillation of β -crystal, based on their polarized IR spectra collected during stretching experiment of a 50/50 PA6/PVDF blend. However, this hypothesis may not be validated as neat PVDF itself can transit from α phase to β phase during mechanical stretching process [14–16]. That is, the toughening mechanism remains unclear.

In the present work, the miscibility, crystallization and morphology of PA6 blends with 10–50 wt% of PVDF were further

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studied with multiple techniques. The studies were carried out both at room temperature (crystalline PA6/crystalline PVDF blends) and at high temperature (crystalline PA6/amorphous PVDF blends). For crystalline/amorphous polymer blends, the amorphous component can stay within lamellar stacks [17–19], incorporated within the spherulites [20], or reject out of the spherulites [21]. The degree of inclusion of amorphous component in lamellar stacks can be studied with small angle X-ray scattering. The complicated morphology of PA6/PVDF blends at spherulitic and lamellar levels is discussed based on direct morphological studies and investigations with scattering techniques. The mechanism of improved toughness with addition of PVDF to PA6 is also addressed in this paper.

2. Experimental

2.1. Materials and sample preparation

Commercial PA6 (B33L) with a melt flow index (MFI) of 8.33 g/10 min (ASTM D1238, 235 °C/2.16 kg) was obtained from BASF Corporation. PVDF (VP830) with a melt flow index (MFI) of 3.98 g/10 min (ASTM D1238, 230 °C/5 kg) was obtained from Dakin Industries. Both materials were dried under vacuum at 80 °C for 24 h before using. The blends of PA6 and PVDF were obtained with a Haake-Rheomix twin-screw extruder at 240 °C with screw rotating speed of 110 rpm. Neat PA6 and PVDF are also extruded under the same processing conditions for comparison with the blends.

2.2. Mechanical test

Rectangle bars (80 mm × 10 mm × 4 mm, ISO 180 standard) for impact testing were injection-molded by a Haake-MiniJet micro-injector, with the barrel at 275 °C, the mold at 60 °C, and the injection pressure at 650 bar. Notched Izod impact measurements were carried out by a Noselab Ats IMPats-50 pendulum impact tester at room temperature with 10 parallel specimens.

2.3. Differential scanning calorimetry (DSC)

Melting and crystallization behavior of the blends were characterized by a TA Q100 DSC in nitrogen atmosphere. Indium and zinc strands were used for DSC calibration. For the non-isothermal crystallization experiments, samples were first heated to 260 °C and maintained for 5 min to eliminate thermal history, and then cooled down to 25 °C. Subsequent heating was also carried out to study the melting behavior for the non-isothermal crystallization. The heating and cooling rates were both 10 °C/min. The normalized crystallinity (χ_c) of PA6 or PVDF component was determined by $\chi_c = (\Delta H_m / \Delta H_m^0) / \phi$, where ϕ is the weight fraction of PA6 or PVDF. The theoretical heat of fusion ΔH_m^0 for 100% crystallized PA6 and PVDF, used for evaluation of crystallinity, is 230 J/g and 104 J/g, respectively [22]. For isothermal crystallization experiments, the samples were quenched from the molten state to a crystallization temperature and maintained at this temperature until the crystallization process was complete. The samples were then heated back to 260 °C at a rate of 10 °C/min for the study of melting behavior.

2.4. Scanning electron microscopy (SEM)

The compression-molded samples were first cryofractured in liquid nitrogen. The PVDF phase was etched by dimethyl sulfoxide (DMSO) at 80 °C for 12 h. The samples were then treated for vacuum drying and gold sputtering before studying with SEM (FEI co. XL-30, ESEM-FEG). The SEM images were analyzed with Nano Measurer software. PVDF domain size distribution and its average

size were quantitatively evaluated with randomly selected over 100 PVDF domains from the SEM images of selected PA6 blend with 30 wt% of PVDF.

2.5. Wide angle X-ray diffraction (WAXD)

WAXD patterns of the blends were collected with a Bruker D8 DISCOVER 2D X-Ray diffractometer. The X-ray was generated by ImS micro Focus X-Ray source, incorporating a 50 W sealed-tube X-ray generator with Cu target and operating at 45 kV, 0.9 mA. The X-ray wavelength is 0.154 nm and the intensities were recorded on a VANTEC-500 2D detector system with a pixel size of 68 × 68 μm^2 . The distance from the sample to detector was 199 mm and the data collection time was 5 min.

2.6. Small angle X-ray scattering (SAXS)

SAXS samples with thickness about 600 μm were prepared by compression molding at 260 °C and then cooled to room temperature with a rate of 40 °C/min. SAXS data were collected by Bruker NANOSTAR SAXS instrument equipped with heating unit with temperature range from room temperature to 300 °C. The X-ray source is $\text{I}\mu\text{S}$ -type generator, operating at 40 kV and 650 μA and the wavelength (λ) is 0.154 nm (Cu K α). The scattering intensity was detected by Hi Star area detector with 1024 × 1024 pixels and 100 μm pixel size. The sample-detector distance is 1057 mm. For study at high temperature, the sample was wrapped into a thin aluminum foil to improve thermal conductivity. SAXS data was first collected at room temperature. Then the sample was heated to 185 °C with a rate of 5 °C/min and SAXS data at 185 °C was collected. The data collection time was 1800s. The SAXS data were calibrated for background scattering.

2.7. Polarized optical microscopy (POM)

Samples were sandwiched between two glass slides and placed on an Olympus BX51 microscopy stage equipped with a Linkam heating stage. The samples were melt at 260 °C for 5 min, and then cooled to room temperature at a rate of 40 °C/min. The prepared sample thickness is about 40 μm . For high temperature experiments, the sample was heated to 185 °C at a rate of 5 °C/min to melt the PVDF component in the blends. The morphological pictures were taken by a CoolSNAP CCD camera connected to the microscope. A 1/4 wavelength compensator was used to improve the image contrast.

2.8. Small angle light scattering (SALS)

The POM samples were directly used for SALS experiments. A Compass 315M-50 laser (Coherent, USA) with a wavelength of 532.0 nm was used as the source of polarized monochromatic light. Linearly polarized laser light was scattered by the sample and then filtered with an analyzer polarized perpendicular to the polarization direction of the incident light (also referred as cross polarized mode, H_V). The patterns were captured using a PIX-1024BRXL camera (Princeton Instruments, USA) equipped with a G6 × 16–1.9 Macro-L camera lens (Spacecom, Japan).

2.9. Atomic force microscopy (AFM)

Sample for AFM observation was prepared by sandwich a sample between a polyimide (PI) film and a glass slide. The crystallization procedure was the same as the POM sample preparation. After completion of crystallization, the PI film was removed and the sample surface was then used for AFM observation at room

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