

Study on Morphology of Compatibilized Poly (Vinyl Chloride)/Ultrafine Polyamide-6 Blends by Styrene–Maleic Anhydride

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ABSTRACT: Ultrafine polyamide-6 (UPA6) with a size of 4–8 μm was prepared via jet-milling. Blends of poly (vinyl chloride) (PVC) and UPA6 using a reactive copolymer styrene–maleic anhydride (SMA-18%) were prepared. The change in morphology and structure of the blends were studied using differential scanning calorimetry, scanning electron microscopy, and X-ray diffraction. The blend behavior was also determined experimentally using dynamic mechanical analysis. Contrasted to the original PA6, the crystallinity of the UPA6 decreased, the size of its crystallites were reduced, and its melting point decreased to 175°C. In all blends, PVC formed the continuous matrix phase. SMA is

miscible with PVC and tends to be dissolved in the PVC phase during the earlier stages of blending. The dissolved SMA has the opportunity to react with PA6 at the interface to form the desirable SMA-g-PA6 copolymer. This in situ formed SMA-g-PA6 graft copolymer tends to anchor along the interface to reduce the interfacial tension and results in finer phase domains. Cocrystallinity existed in PVC/(UPA6/SMA) at a ratio of 82/(18/5). © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 850–854, 2005

Key words: PVC; polyamide-6; compatibilization

INTRODUCTION

Poly (vinyl chloride) (PVC) has been widely used as an important general plastic because of its excellent corrosion resistance, electrical properties, self-extinguishing characteristics, low cost, and recoverability. But its sensitivity to notched impact, high temperatures, and poor processability limits its applications. PVC products are restricted to environments not exceeding 80°C and to nonstructural applications because of low strength.

Polyamide (PA) (nylon) is an important polymer class for engineering applications, with its excellent chemical resistance. However, poor dimensional stability and low impact strength are deficiencies of unmodified nylons. The inherent properties of PVC and nylon suggest that a combination of PA and PVC could produce materials with balanced properties, provided that the advantages of one component can compensate for the deficiencies of the other. Polymer blends of PVC and nylon have attracted great interest from both industry and academia. Hofmann^{1–5} and

Sherman⁶, respectively, reported the blends of PVC and polyamide compatibilized by two compatibilizers such as ethylene-acrylate-CO₂ copolymer (Elvaloy) and ethylene-acrylate-CO₂ grafted maleic anhydride (Fusabond) and two-step methods. Lian et al. compatibilized nylon terpolymer by EnBACO (ethylene-acrylate-CO copolymer) and EnBACO-MAH (maleic anhydride grafted EnBACO).⁷ The ternary copolymerized polyamide used by them has lower crystallization and melting point than regular nylon. Numerous papers have reported on structural, morphological, and other properties that could be developed via a solid-state mechanochemical method.^{8–13} Liu and Wang¹⁴ reported on the crystallinity and size of microcrystals of PA6 decreased during pulverization. Xiong et al.¹⁵ reported on nanocrystalline PVC with a low melting point of 128°C prepared via jet-milling.

In this study, blends of PVC and self-made ultrafine polyamide-6 (UPA6) with a low melting point were reactively compatibilized by a commercially available styrene–maleic anhydride (SMA) copolymer. The change in morphology and structure of PA6 and the compatibilization of components were investigated.

EXPERIMENTAL

Materials

PVC was provided by Sinopec Qilu, Ltd. (China), in the form of powder with a molecular weight (Mw) of

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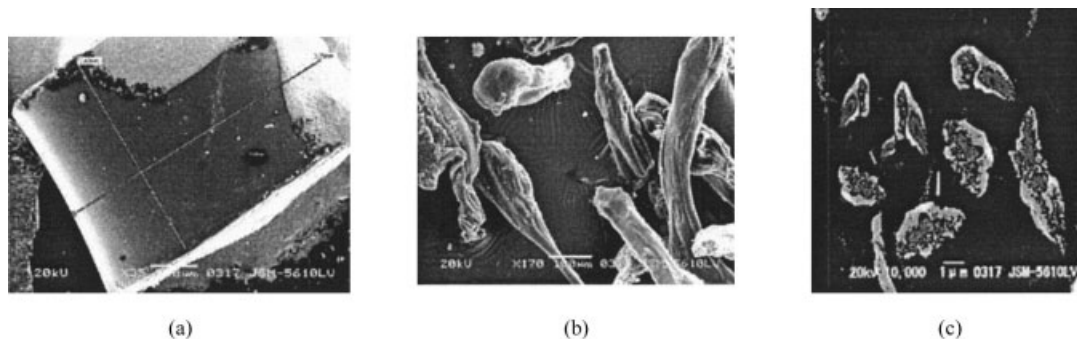


Figure 1 SEM micrographs of (a) unpulverized PA6; (b) PA6 during pulverization; (c) UPA6.

6.25×10^4 . The tacticity of the PVC was about 5%. Polyamide-6 is a commercial product (Novamid 1013B), produced by Sinopec YueYang Co., Ltd. (China). The SMA copolymer containing 18 wt% maleic anhydride was obtained from Shanghai Sinopec Research Institute (China).

Preparation of UPA6

Polyamide-6 was jet-milled in the Fluidized Bed Opposed Jet Mill, with the classifying gear at the speed of 9000 r/min and the temperature of 5°C.

Blend preparation

PVC and SMA were premixed in a high-speed mixer during 3 min to obtain a miscible blend. UPA6 was subsequently added to this premixed PVC/SMA blend. The mixing time was measured from the moment the UPA6 was added. Premixes were mixed in an XSS-30 Torque rheogoniometer and operated at 185°C/40 rpm for 10 min. After being mixed, the hot materials were immediately milled in an XK-160 two-roll mill at 20°C. The internal spacing of the two rolls was 1 mm. After being milled, the materials were cooled at high pressure.

TESTING AND CHARACTERIZATION

Phase-morphology study

The morphologies of UPA6 and blends were examined using a JSM-5610Lu scanning electron microscope (SEM). Cryogenically fractured surfaces of the specimens were coated with a thin film of gold prior to SEM examination.

Differential scanning calorimetry (DSC)

The thermal properties were studied using a DSC30 differential scanning calorimeter equipped with a low-temperature cell, using samples (5–10 mg) sealed in aluminum pans. The experiments were performed in

the temperature range from 0 to 250°C with a heating rate of 10°C/min. Each sample was scanned three times.

X-ray diffraction measurements

X-ray diffraction investigations were performed by means of a TBC-5200 X-ray diffractometer employing the symmetrical reflection method of registration. We used a copper target X-ray tube operated at 30 kV and 30 MA. Diffraction curves were taken in the range from 5 to 60°C with a step of 0.1°C. X-rays were monochromized and specimens were pressed in a sample holder.

DMA measurements

Dynamic mechanical analysis was performed using a Rheometric Scientific TMIV scanning DMA unit from –20 to 250°C. Prior to measurements the samples were dried in a vacuum for 24 h at 110°C.

RESULTS AND DISCUSSION

Morphologies of UPA6

Figure 1 shows SEM micrographs of both PA6 and UPA6. PA6 had a diameter of about 3–5 mm before being pulverized (Fig. 1a); during pulverization, its diameter was 200–400 μm (Fig. 1b); after being pulverized, its diameter was only 4–8 μm (Fig. 1c). It is suggested that the crystal structure was destroyed and chain segments of PA6 were rearranged, so that the melting point of UPA6 was lowered to 175°C compared with that of the uncrushed PA6 of 215°C (Fig. 2).

Curves in Figure 3a and b show the X-ray diffraction curves of both PA6 and UPA6, respectively. They reveal that the intensity of diffraction of UPA6 decreased and the width narrowed. It is evident that the size of microcrystals and the crystallinity of PA6 decreased during pulverization. This is consistent with earlier reported results.¹³

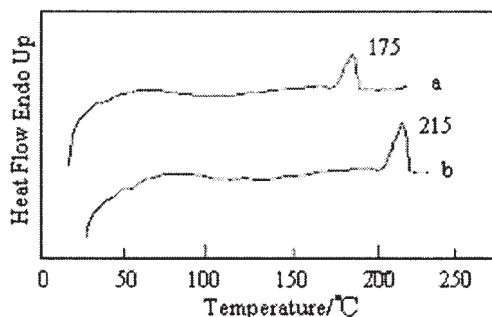


Figure 2 DSC spectra of (a) PA6 and (b) UPA6.

Chemical modification

A reactive compatibilizer is a copolymer with reactive functional groups able to react with one or both of a blend's components to reside at the interface and compatibilize the blends. The major chemical reactions involved in this reactive compatibilized blend system involve the anhydride groups of SMA copolymer and the terminal amine groups of PA6. The chemistry of the reactions is shown in Figure 4. The in situ-formed SMA-g-PA6 copolymer is located preferentially at the interface to act as an effective compatibilizer.

Morphologies

Melt-blended immiscible polymer blends possess complicated phase morphologies, which depend on interfacial tension, viscosity ratio of blends constitutions, volume fraction, and processing conditions. Pieces of one polymer may be drawn into filaments, which may remain as filaments, break up into smaller droplets, or connect with each other to give an interconnected network.

SEM photomicrography is the most convenient approach to differentiate the morphologies between the compatibilized and the uncompatibilized blends. The incompatible blends possess higher interfacial tension and usually result in coarser morphology than that of

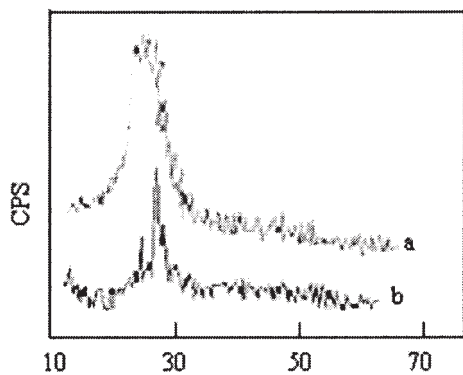


Figure 3 X-ray diagrams of (a) PA6 and (b) UPA6.

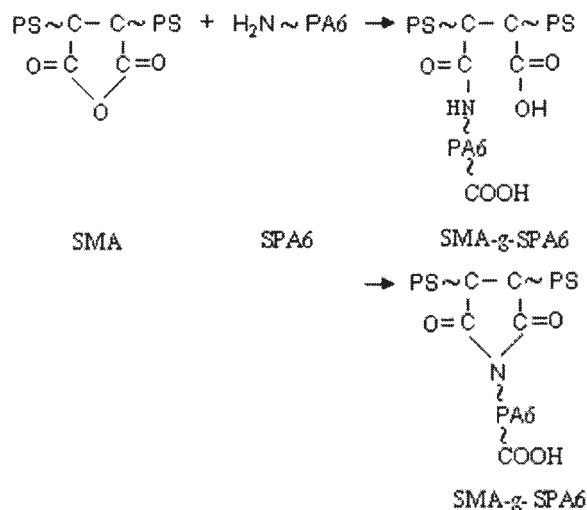


Figure 4 Reaction between a succinic anhydride group in SMA and a polyamide end group.

the corresponding compatibilized blends. Figure 5a–c shows the morphological structures of the tensile fracture surface. Figure 5a shows a typical brittle fracture. Figure 5b shows both brittle and tough fractures. Figure 5c shows a typical tough fracture. Figure 5d–f shows the SEM micrographs of the impact fractured surface. It is evident that the size of dispersed UPA6 domains in the uncompatibilized blends is much larger than that in the compatibilized blends. When the amount of SMA is increased, the size of the UPA6 is reduced and the interface change is more indistinct. The results suggest that the addition of SMA reduces the surface tension of UPA6 in PVC matrix, thereby decreasing the size of dispersed UPA6 domains.

Differential scanning calorimetry

Figure 6 shows DSC curves of uncompatibilized and compatibilized PVC/UPA6 blends. For the uncompatibilized blends (curve a), two crystal peak can be seen. One is around 210°C, which is identical to that of PVC, and the other is at 189°C, which is the crystal peak of UPA6. There is another crystal peak at about 165°C in the compatibilized blends (curves b and c). This may be the melting point of UPA6 or that of cocrystallization of PVC and UPA6.

Blends structure, as controlled by the type and amount of compatibilizer, was found to have no marked influence on the melting behavior (T_m and ΔH_m) of PVC and PA in the blends. The crystallization behavior of PVC and UPA6 was, however, found to depend on the blend structure. Thus, the crystallization temperature of PVC in the uncompatibilized blends and in blends containing low amounts of SMA was found to be higher than that of pure PVC, as determined using the same experimental conditions.

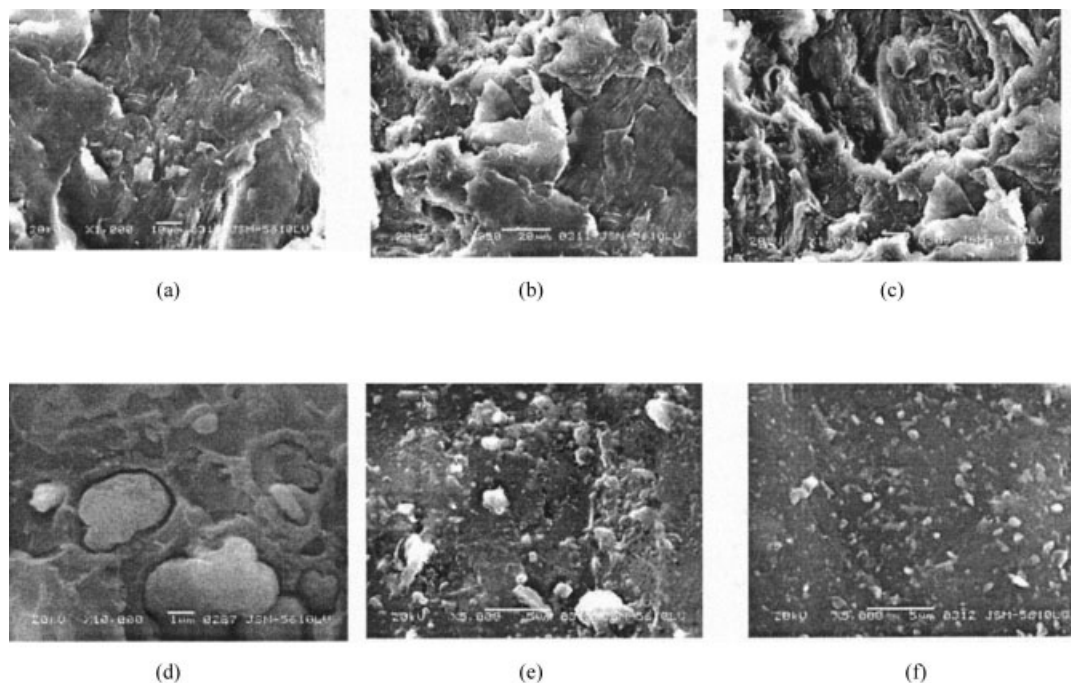


Figure 5 SEM micrographs of the tensile fracture surface of (a) PVC/PA6 = 82/18 blends; (b) PVC/PA6 = 82/18/3 blends; (c) PVC/PA6/SMA = 82/18/5, and the impact fractured surface of (d) PVC/PA6 = 82/18 blends; (e) PVC/PA6 = 82/18/3 blends; (f) PVC/PA6/SMA = 82/18/5.

This must be ascribed to the effect of nucleation of PA6, by contact with crystalline polyamide across the PVC-PA6 interface.

The crystallization behavior of polyamide also varied with the amount of SMA used in preparing the blends. For blends containing PA6, the crystallization temperature varied in the manner illustrated in Figure

6. In the concentration range from 0 to 5% SMA the crystallization temperature slowly decreased. This was accompanied by a broadening of the crystallization peak.

Dynamic mechanical analysis (DMA)

The dynamic mechanical behavior of the PVC/UPA6 = 83/17 series is shown in Figure 7. Both uncompati-

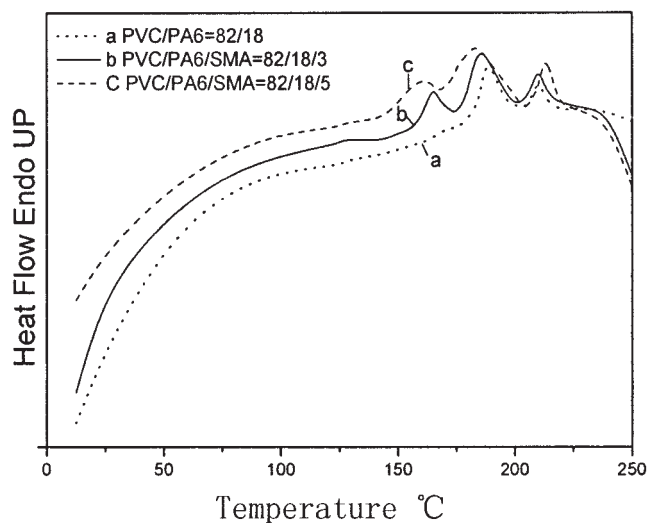


Figure 6 DSC spectra of uncompatibilized and compatibilized PVC/PA6 = 82/18 blends of (a) PVC/PA6 = 82/18; (b) PVC/PA6/SMA = 82/18/3; (c) PVC/PA6/SMA = 82/18/5.

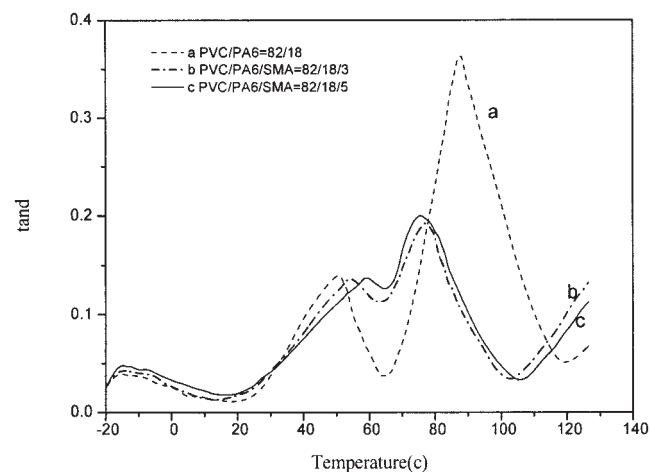


Figure 7 DMA spectra of uncompatibilized and compatibilized PVC/PA6 = 82/18 blends of (a) PVC/PA6 = 82/18; (b) PVC/PA6/SMA = 82/18/3; (c) PVC/PA6/SMA = 82/18/5.

bilized and compatibilized blends gave two glass transition temperatures, indicating phase separation of the blend components. The uncompatibilized PVC/UPA6 = 85/17 blends showed a very sharp T_g transition at 87°C for the PVC phase and a PA6 T_g transition at 51.5°C (curve a). The PVC T_g transition behavior of the compatibilized blends containing higher SMA was different; the peak broadened and shifted toward a lower temperature with increased quantity of SMA, as shown in curves b and c. The shape of the PA6 T_g transition peak remains the same as that of the uncompatibilized blend, whereas the PA6 T_g peak shifts slightly to a higher temperature with increased the quantity of SMA.

SMA has a T_g (120°C) above that of PVC and PA6, but the different quantities of dissolved SMA in the two phases have a different effect on their T_g . The dissolved free SMA copolymer in the PVC phase is responsible for the substantially lower PVC T_g observed because the dissolved SMA prevents the segments of PVC from moving freely. A small quantity of SMA-g-PA6 copolymer is expected to be distributed in the PA6 phase, causing only a slight increase. The distribution of the SMA-g-PA6 copolymer molecules along the interface is responsible for the PVC transition peak broadening.

X-ray diffraction

Figure 8 shows the micrographs of the X-ray diffraction. Curve a corresponds to UPA6, with a clear crystal peak. Curve c is the X-ray diffraction pattern of PVC, with almost no crystal peak. Curve b is the X-ray diffraction of PVC/UPA6 blends, with less of a crystal peak than UPA6 but more than PVC, which further indicates that PVC and PV6 were compatibilized.

CONCLUSIONS

Contrasted with the original PA6, the crystallinity of the UPA6 decreased, the size of its crystallite was reduced, and its melting point decreased to 175°C, so blends of PVC/UPA6 could be prepared. Polyblends of PVC and UPA6 were immiscible and incompatible, with poor interfacial adhesion and large phase domains. This commercially available SMA copolymer has been demonstrated to be a highly effective com-

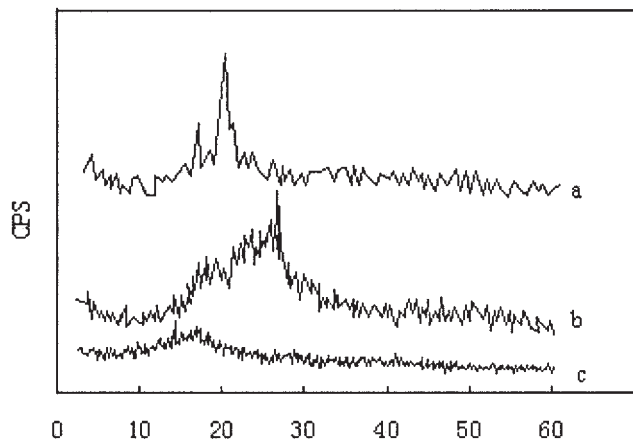


Figure 8 X-ray diagrams of (a) PA6; (b) UPA6/PVC; (c) PVC.

patibilizer by reducing the interfacial tension and enhancing the interfacial adhesion. The domain size of the compatibilized PVC/UPA6 was reduced with increasing content of SMA compatibilizer. A new crystal peak of the blends of PVC/UPA6 indicates that cocrystallization of PVC and UPA6 occurred.

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