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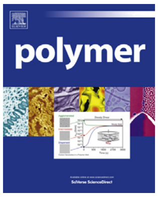

Morphologies of miscible PCL/PVC blends confined in ultrathin films

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ABSTRACT

Morphologies of ultrathin films (10–60 nm) of miscible poly(ε-caprolactone)/poly(vinyl chloride) (PCL/PVC) blends have been investigated under isothermal crystallization conditions by real time atomic force microscopy, and electron diffraction techniques. It was found that the morphology and growth rate of PCL/PVC blends strongly depend on the blend composition, crystallization temperature and film thickness. At a film thickness of 30 nm, the truncated lozenge-shape morphology of pure PCL crystals, found when the growth rate is slow, bent with increasing PVC content to form S-shaped or inverted S-shaped crystals, the curvature increasing by lowering the crystallization temperature. Electron diffraction patterns reveal that these crystals are flat-on single crystals with the PCL molecular chains (*c* axis) in the blends slightly tilted with respect to the lamella normal, while the *b* direction of the crystal lattice, corresponding to the fast growing direction of the growth front, follows a S line. Upon decreasing the film thickness (<30 nm), the S-shaped or inverted S-shaped crystals transform into four-branch dendritic lamellae.

1. Introduction

Poly(ε-caprolactone) (PCL) and poly(vinyl chloride) (PVC) form one of the few miscible polymer blends. Its miscibility in the amorphous phase has been well established [1–4], whereas the crystalline phase is made of pure PCL. The melting point of PCL decreases and the amorphous interlamellar spacing increases with the PVC concentration, but the crystalline unit cell remains the same [5,6]. In bulk samples, spherulites are formed but the spherulitic growth rate of PCL is depressed upon adding a non-crystallizable component [7–12].

Detailed morphological analyses of this blend in thick films have been made [8,12,13] but rarely in ultrathin films where it is expected to be different [14–18]. In a previous study, it was found that, below 30 nm, the growth rate of pure PCL decreases with the film thickness, and the morphology changes from a truncated lozenge shape to a parallelogram-like shape [19]. The crystallization kinetics of PCL/PVC blends, containing between 0 and 40 weight % PVC, was also reported for films ranging from 100 to 2000 nm in thickness [12]. In that range, growth rates were found thickness dependent for the blends but not for pure PCL. As X-ray photoelectron spectroscopy indicates a PCL enrichment at the blend surface, it was concluded that the growth rate of the spherulites is controlled by the PCL concentration in the enriched layer.

In this paper, the influence of the blend composition, crystallization temperature and film thickness on the morphology of PCL/PVC blends confined in ultrathin films is explored. Isothermal crystallization was followed between 30 and 54 °C for film thicknesses ranging from 10 to 60 nm. Morphological variations are discussed in terms of diffusion of the polymer chains from the melt to the growing crystal. The origin and occurrence of bent lamellae in blends is particularly discussed.

2. Experimental

2.1. Materials

Poly(ε-caprolactone) with molecular weight of $M_n = 10{,}000$, (PDI = 1.4), and poly(vinyl chloride) with $M_n = 82{,}000$ (PDI = 1.6) were purchased from Aldrich Chemicals and used without further purification. In order to prepare ultrathin films, polymers were dissolved in tetrahydrofuran (THF), with stirring for 24 h at room temperature and in the absence of light. Blend compositions indicated in this paper are always weight compositions.

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2.2. Sample preparation

Ultrathin films were prepared from solutions of concentrations between 1.75 and 10.0 mg/ml (the corresponding film thicknesses vary between 10 and 60 nm, respectively) onto cleaned Si substrates using a spin-coater (Headway Research Inc, EC101), at 3000 rpm for 60 s. Si substrates (p-type single-side polished (100) silicon wafers) were cleaned by immersion in a sulfochromic acid solution, as described previously [19]. The substrates were then rinsed with nanopore water, dried in an oven and allowed to cool to room temperature before coating by solution. To keep the solution in a saturated atmosphere around the sample and to allow a uniform evaporation, a glass dome was placed to cover the whole spin coater stage. Since high humidity leads to dewetting during spin coating, dry nitrogen gas was purged through the glass dome. Blends with eight different PCL and PVC composition ratios, including pure PCL, were prepared.

2.3. Atomic force microscopy

A Nanoscope III Multimode instrument (Digital Instruments (DI), Santa Barbara, CA), operated in tapping mode and equipped with a temperature controller, was used to examine the in-situ morphology of the films and to determine their thickness. The films were melted at 70 °C for 5 min in order to remove any crystallization before the AFM observations, and then brought to the required crystallization temperature for appropriate crystallization times. AFM measurements were done at the crystallization temperature. Film thicknesses were measured on melted films by profilometry using the AFM [19].

2.4. Transmission electron microscopy

A JEOL JEM-1230 instrument, operating at 120 kV, was used to observe the transmission electron microscopy (TEM) bright field images and selected area electron diffraction (ED) patterns of crystallized samples. Calibration of the camera length was carried out using Au as the standard material. Ultrathin films for TEM observation were first prepared by spin coating solutions on carbon-coated mica and thermally treated like AFM samples. Subsequently, the carbon film (covered by the polymer film) was stripped, floated onto the surface of water, and collected on copper grids.

3. Results

3.1. Composition and T_c dependent morphology

Fig. 1 shows the morphologies of 30 nm thick PCL/PVC blends of various compositions, crystallized at 54 °C, with, in several cases, the corresponding ED patterns. Systematic changes in morphology are seen as a function of composition. Pure PCL shows a lamellar morphology with a truncated lozenge shape (Fig. 1a) which exhibits two (100) and four (110) growth faces, as already shown in Ref. [19]. With the addition of PVC, this morphology is modified keeping, however, the general truncated lozenge shape. At first, the four (110) growth faces become poorly defined and their tips are not sharp anymore (Fig. 1b); then, at 5 or 10% PVC, the tips become unrecognizable (Fig. 1c and d); at 15% and above, one of the two (110) growth face (at each end) starts to grow faster than the other (Fig. 1e), showing a bent at the tip and a general inverted S-shaped crystal as shown in Fig. 1f, g and 1h. In these last examples, one (110) sector is broader than the other near the growth tips. In Fig. 1, only inverted S-shaped lamellae are shown but, at any composition, regular S-shaped and inverted S-shaped lamellae are observed simultaneously in equal number (with this system, no C-shaped crystals were observed but, as will be shown in a forthcoming paper, both S-shaped and C-shaped crystals are observed with other PCL/polymer blends in which the PCL-polymer interaction parameter is lower). Some of the pictures also show overgrowths but this will be discussed in a later section.

The crystallization temperature strongly influences the morphology of PCL/PVC blends. This is true at every composition but, for illustration purposes, the 60/40 PCL/PVC composition will be used in most of the following sections since it shows the greatest effect. Fig. 2 shows AFM images of 60/40 PCL/PVC blends, crystallized at 54, 50 and 45 °C, at a film thickness of 30 nm. It is found that, at high T_c, the S-shaped curvature is less pronounced (Fig. 2a), and the fast growing faces are broader in comparison with those obtained at lower T_c (Fig. 2c). Almost no overgrowth can be observed on top of the basal lamellae for the higher temperatures, for which the S-shaped crystals are more “plump” or “fleshy” (Fig. 2a), whereas a large number of very small overgrowths are observed above a dendritic lamella for the lower T_c (Fig. 2d).

ED patterns (not shown) reveal that these crystals have a high crystallographic order and can be considered as single crystals. All the sharp diffraction spots correspond to (*hk*0) projections of the PCL reciprocal lattice and suggest that the lamella is oriented flat-on,with PCL chains perpendicular to the lamella plane, i.e., oriented normal to the substrate surface. A more detailed analysis of ED patterns will be made when discussing Fig. 5.

3.2. Thickness dependent morphology

The film thickness has a profound effect on the morphology of PCL/PVC blends. Fig. 3 shows a series of AFM images of films of different thicknesses crystallized at 45 and 50 °C. In the case of relatively thick films of 60 and 30 nm, crystallized at 45 °C, S-shaped morphologies, regular in one case and inverted in the other, with irregular growth fronts are shown in Fig. 3a and b, respectively; thinner films of 15 and 10 nm show a dendritic shape in Fig. 3c and d, respectively, with four main branches that orient almost perpendicular to each other and form a cross. One arm of the cross is longer than the other, and both arms are slightly bent. These bents seem to be S-shaped with two opposite bending directions, i.e., one is counterclockwise (Fig. 3c) and the other is clockwise (Fig. 3d), corresponding to inverted S-shaped and regular S-shaped, respectively. The crystal grown in the 10 nm films (Fig. 3d) is more “swiss-cheesy” than it is in the 15 nm film (Fig. 3c) because the lamellar crystal (10–15 nm) is thicker than the melted layer and the polymer chains need to diffuse from a larger distance to reach the lamellar growth front as compared to thicker films. At 50 °C, the thicker films of 60 and 30 nm have almost the same shape as those obtained at 45 °C but the “ S ” is less prominent (Fig. 3e–f). However, in thinner films of 15 and 10 nm, a parallelogram with concave faces is observed (Fig. 3g–h). These parallelograms still retain some concavity and, interestingly, can be generated by filling the empty space between the dendrites observed in Fig. 3c and d.

In the bended lamellae of Figs. 1–3, a prominent S-curved line appears in the center of the crystal. Relative to this central “spinal cord”, there is a difference on opposite sides of the lamellae, especially near the growth tips, i.e., one side is obviously broader than the other, indicating a significant asymmetry of structure at corresponding fold surfaces, as shown in Fig. 1c–e. In Fig. 3c, the same asymmetric trend is found on the two longer arms, i.e., the width on one side of the spinal cord is longer than on the other side. In Fig. 3d, the asymmetry extends to the point where one of the two sides of the crystal parallelogram appears to have vanished, which corresponds to the disappearance of two of the