

Surface Crystalline Characteristics of Polyurethane Investigated by Atomic Force Microscopy

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SYNOPSIS

A polyester-urethane was synthesized by the reaction of 2,4-toluylene diisocyanate (TDI) with poly(butylene glycol adipate) (PBGAD) using 1,4-butanediol (BDO) as a chain extender. Atomic force microscopy was employed to examine the surface morphologies of polyurethane (PU) films formed by heat treatment as well as at room temperature. At both conditions the surface of the PU film appeared as a spherulitic structure with a varied diameter and vertical height. Furthermore, the crystalline structure of heat-treated film was denser than that of the film formed at ambient. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethane (PU) is a segmented polymer comprising alternating sequences of soft segments and hard segments which constitute a unique microphase separation structure. In the case of a high degree of phase separation, hard segments tend to produce crystalline regions, and randomly arranged soft segments form amorphous regions.¹ For PU, the characteristic of crystalline and noncrystalline coexistence exerts a profound effect upon the mechanical properties.² Up to now, a wide variety of techniques have been used to study crystalline behavior; small-angle light scattering and a polarizing microscope have revealed that the hard segments of PU with a high degree of microphase separation can form spherulites.³

Recently, with the development of atomic force microscopy (AFM), the characterization of the polymer surface has been essentially improved. The surface morphology down to the nanoscale, in particular, the three-dimensional image, can be obtained with AFM.^{4,5} Some researchers have investigated the crystalline of polypropylene and the morphology of liquid crystalline polymers by AFM.^{6,7}

However, to our knowledge, no AFM study of the crystalline characteristic of the PU surface has yet been reported. This work is concerned with an AFM examination of crystalline on the surface of PU film at different conditions.

EXPERIMENTAL

Materials

2,4-Toluylene diisocyanate (TDI), chemical grade, was purchased from the Tianjin Polyurethane Product Co. Poly(butylene glycol adipate) (PBGAD) with a hydroxy value of 108 was supplied by the Jinling Petroleum Chemical Co. 1,4-Butanediol (BDO), ethyl acetate, and acetone, analytical grade, were used as received.

PU Synthesis

A prepolymer composed of TDI and PBGAD with molar ratio of 2.4 : 1 was prepared at 70°C for 6–7 h. After determining the isocyanate concentration, an equivalent amount of dried and degassed BDO was added into the prepolymer obtained. The chain-extension reaction was carried out at 80°C for 9 h in ethyl acetate.

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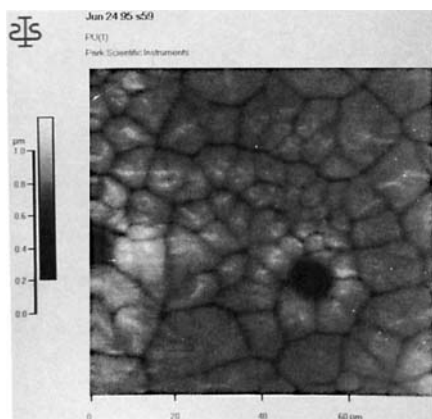


Figure 1

Preparation of PU Films for AFM

PU was further diluted with ethyl acetate to form a 0.5 wt % diluted solution, of which 2 μL was deposited on a freshly cleaved silicone wafer washed by acetone. To check the discrepancy in the crystalline structure of PU films formed at different conditions, the deposited solution was heated to 80°C in oven for 30 min and cooled naturally or left at room temperature to yield dried films.

AFM Imaging

Surface topographs were taken using Park Scientific autoprobe scanning force microscope with a 100 μm scanner head. A Si_3N_4 probe on a triangular cantilever was used to obtain images in a contact mode at a scan frequency of 4 Hz. All the measurements were operated in a repulsive mode using a force of 40 nN.

Wide-angle X-ray Diffraction (WAXD)

X-ray diffraction diagrams of PU films formed at different conditions were recorded using a D/Max X-ray diffractometer, $\text{CuK}\alpha$ target, and graphite monochromator. The angle of diffraction (2θ) was varied from 5 to 40°.

RESULTS AND DISCUSSION

The AFM topographic image (80 \times 80 μm) for heat-treated PU film is presented in Figure 1. At first glance, it seems that there appear many irregularly shaped stones tiling together at random on the surface. However, a careful observation indicates that

at some regions several groups of "stones" radiate symmetrically from different central nuclei. From the intensive X-ray diffraction peak displayed in Figure 2, it can be recognized that the "stones" have developed crystalline regions, which resemble "spherulites" ranging in size and shape with diameters of the order of 5–20 μm . In some regions, some clumps array symmetrically along a central axis; a feature of leaves is generated. In other areas, it can be observed that some spherulites show multipetal flower features. A possible explanation of this observation is that hard segments of PU have a comparatively large area to orient or arrange due to the freedom of the chain segments on the surface.⁸ An individual spherulite's surface is not smooth, but appears, to some extent, rough. To acquire a more accurate estimation, a spherulite was selected to be magnified (Fig. 3). At higher magnification, a clear picture of a spherulite with an eight-petal flower feature comes into view; its diameter is about 20 μm and the thickness of each petal ranges from 450 to 500 nm. Furthermore, the thickness changes with the variation of distance from the central nucleus; the difference between the outer edge and central point is about 300 nm. It is conceivable that the roughness of the surface arises from the arrangement and folding of the hard segments of PU.

Figure 4 displays the topographic image (60 \times 60 μm) for PU film formed at an ambient condition. From the picture, the crystalline structure looks very similar to that in Figure 1. The spherulites with varying diameters ranging from 5 to 17 μm appear at different regions; nevertheless, the spherulites are not as perfect as those in Figure 1 due to that the crystalline regions arrange in a looser manner. A

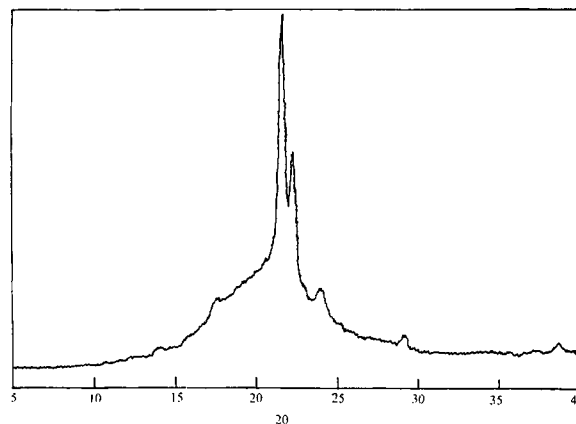


Figure 2 WAXD pattern of PU-1 film formed by heat treatment.

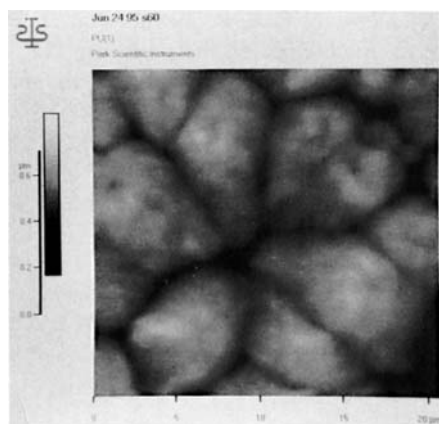


Figure 3

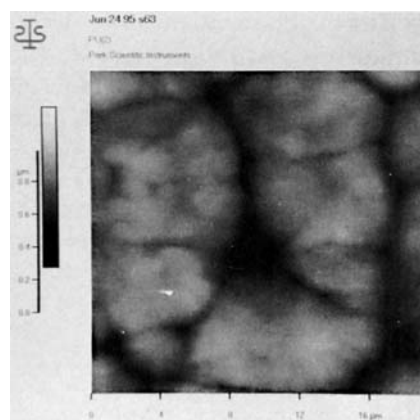


Figure 5

smaller scale scan (Fig. 5) shows that the spherulitic structure is not distinct compared with that in Figure 3; its diameter is approximately $17 \mu\text{m}$ and the vertical height varies from 760 to 800 nm and is greater than that of spherulite shown in Figure 3. This may be attributed to the loose arrangement of chain segments on the surface in this case. Although crystalline regions yield a flower-petal pattern, the contour of each "petal" is less clear. A more plausible explanation of the difference in crystalline structure between heat-treated film and a non-heat-treated one is that in the case of heat treatment the chain segments of PU have access to reorient or rearrange fully during the cooling of elevated temperature. This allows more hard segments to aggregate to form dense hard-segment domains in which a relatively perfect crystalline region develops. Whereas a less perfect spherulitic structure of non-heat-treated film may be owing to that at lower temperature hard seg-

ments and soft segments do not separate fully; consequently, part of the soft segments are dragged into the hard-segment domains, which weakens the crystallization of hard segments. Thus, in Figure 4, the morphology of the crystalline structure appears less dense. Figure 6 demonstrates the X-ray diffraction curve of PU film formed at an ambient condition. As shown in Figure 6, its intensity decreases compared with that in Figure 2. This implies that the crystallization of the film obtained by a nonheat treatment becomes weak.

CONCLUSION

AFM images were recorded of PU films formed at different conditions. The topographic images of

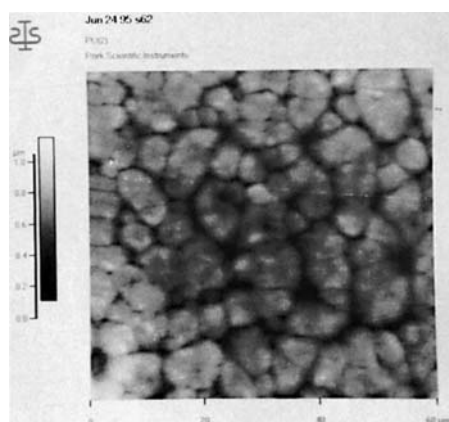


Figure 4

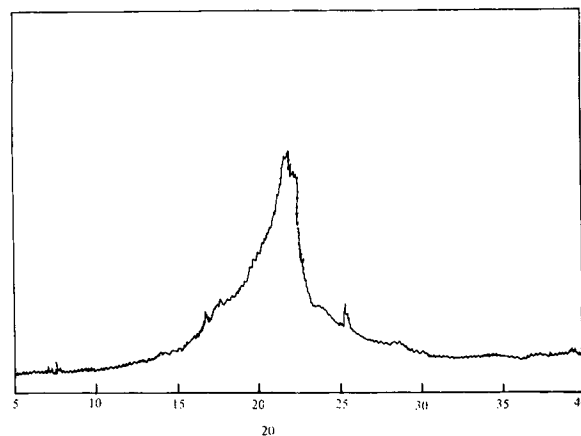


Figure 6 WAXD pattern of PU-1 film formed at ambient condition.

AFM allowed us to obtain quantitative descriptions and a three-dimensional fine structure of spherulites of the PU surface. The imaging of PU films indicates that the spherulitic structure of PU is dependent upon the conditions of sample preparation.

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