

Rapid Communication

ATOMIC FORCE MICROSCOPY STUDIES OF POLYCAPROLACTONE RINGED SPHERULITES*

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Abstract The surface morphology of free-surface PCL ringed spherulites was investigated by using atomic force microscopy. The spherulites were obtained by crystallization of PCL/PVC blends of different compositions. It was found that the ringed spherulite exhibited regularly fluctuating rings on its surface. Compared with the bright-dark ring pattern of the spherulite under a polarizing microscope, it was proved that the optical characteristics of the ringed spherulite under polarizing microscope coincided with its surface characteristics. The bright rings in polarizing micrographs of the spherulite coincided with the convex rings on its surface, while the dark rings coincided with the concave rings.

Keywords AFM, Surface morphology, Ringed spherulites, PCL/PVC blends

INTRODUCTION

Of the instrumentation developed in the past 20 years the most important for polymer morphology investigation is the family of microscopic techniques. Atomic force microscopy^[1] (AFM) might be one of the most promising techniques attracting more and more polymer scientists. In addition to its excellent resolution AFM has the benefits of simplicity in terms of operation and sample preparation. Noteworthy is the fact that there is no need for procedures such as microtoming and gold coating usually used in electron microscopy. During the height imaging of the morphological features of the sample surface a feedback loop of the instrument may ensure that the distance between the probe and the sample keeps constant within atomic dimensions. Thus a three-dimensional image of the sample surface can be created during the probe scanning.

As a special kind of spherulite, ringed spherulites have been widely investigated, especially for polycaprolactone (PCL) crystallized in PCL/PVC blends^[2-6]. However there is no report on the AFM studies of ringed spherulites in the literature. In this work AFM was used to investigate the surface morphology of the PCL ringed spherulites in PCL/PVC blends. The relationships between the AFM results and the polarizing micrographs of the ringed spherulite are discussed.

EXPERIMENTAL

A PCL sample of $M_w = 40,000$ used in this work was supplied by Scientific Polymer Products Inc., and a PVC sample of $M_w = 55,000$ was offered by Qilu Petrochemical Company, China. The PVC sample was purified by a dissolution-precipitation procedure to remove the impurities before blending with PCL. The solvent and precipitant used were tetrahydrofuran and *n*-heptane, respectively. PCL and PVC were blended in tetrahydrofuran solutions.

The PCL/PVC solution of 2% g/mL concentration was dropped onto a piece of glass-cover, which was then kept at 40°C for slow evaporation of the solvent. The sample on the glass-cover was melted at 160°C for 2 min

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and then moved to a hot stage kept at 40°C for free-surface crystallization of the sample.

The morphology of the ringed spherulites was observed by using a polarizing microscope manufactured by the Olympus Limited Company, Japan. An AutoProbe-CP atomic force microscope of Park Scientific Instruments was also used in this work. Its scanning scope was 60 μm × 60 μm, and the scanning rate was 1 μm/s.

RESULTS AND DISCUSSION

The AFM results showed that the surface of the PCL ringed spherulites in PCL/PVC blends exhibited regularly fluctuating rings, which looked like water waves, as shown in Fig. 1(a). Figure 1(b) is a two-dimensional graph of the surface, giving a pattern with alternative bright-dark rings. In an AFM pattern the brightness reflects the height fluctuation of the sample surface. The bright rings in Fig 1(b) represented the convex regions, while the dark rings represented the concave ones. Figure 1(c) gives a sectional view of the spherulite surface cut along the radius direction, and the center of the spherulite is located at the origin of the coordinate. It shows that the largest fluctuation of the surface for the ringed spherulite is about 0.4 μm, and the separation of the rings is about 20 μm.

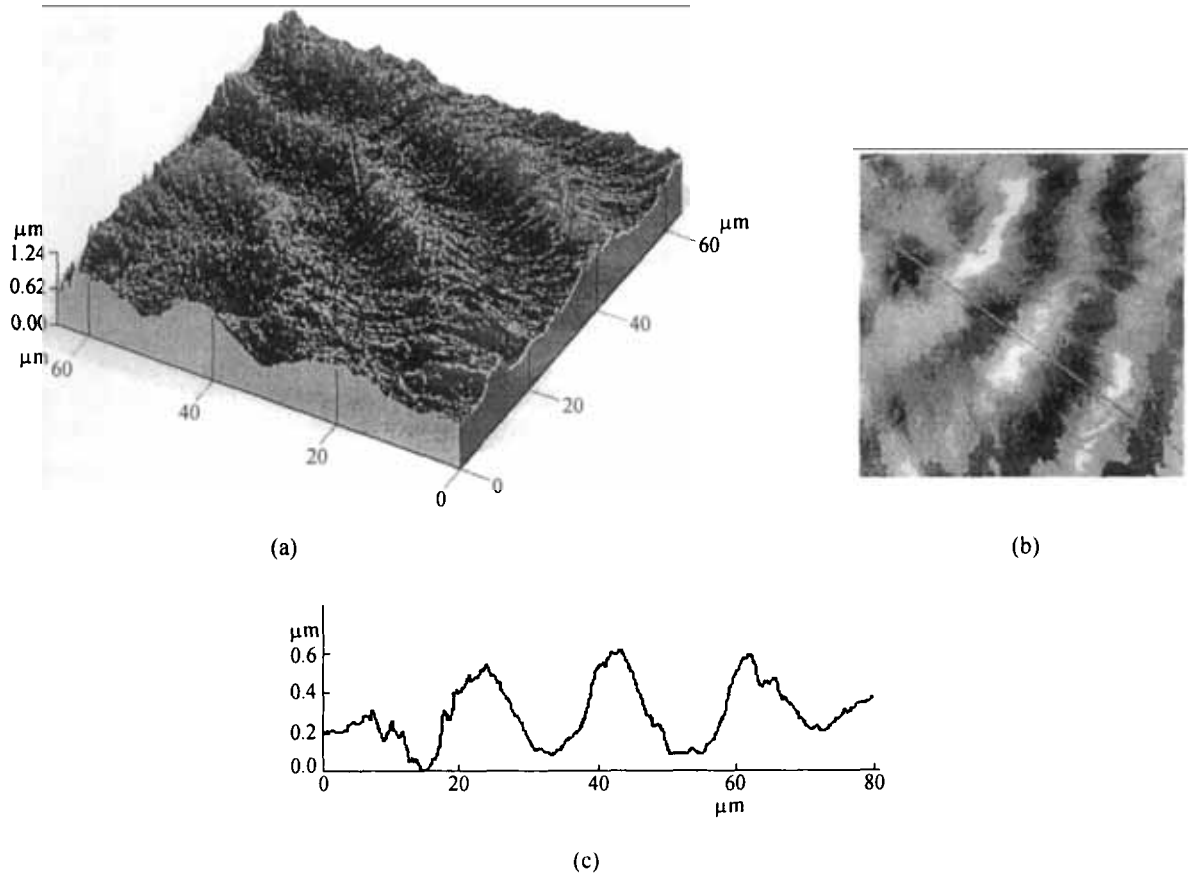


Fig. 1 AFM results: (a) three-dimensional figure of the ringed spherulite surface; (b) two-dimensional figure of the ringed spherulite surface; (c) the sectional view of the ringed spherulite surface

Usually the morphology of ringed spherulites was observed under a polarizing microscope. Figure 2 is a polarizing micrograph of a PCL ringed spherulite in PCL/PVC blend under crossed polaroids. A typical pattern with alternative bright-dark rings was obtained. The separation of the rings has the same order of magnitude as that observed in AFM studies. In order to confirm the relevance and coincidence of the results obtained in AFM and polarizing microscopy (PLM) studies the same ringed spherulites in samples of different blend compositions

were carefully observed by using both techniques. A central label technique on the free surface of the spherulite was used to ensure that the same ringed spherulite could be observed in the comparative studies of AFM and PLM. The ring widths of PCL spherulites in blends of different PVC contents determined by the two techniques were compared. The results are given in Fig. 3. The ring widths decrease with increasing PVC content of the blends. Figure 3 clearly indicates that the widths of the convex and concave rings (AFM data) agree very well with the widths of the bright and dark rings (PLM data), respectively. It implies that the results of the two methods in studies of ringed spherulites are comparable, and AFM will be a very useful technique in these studies.

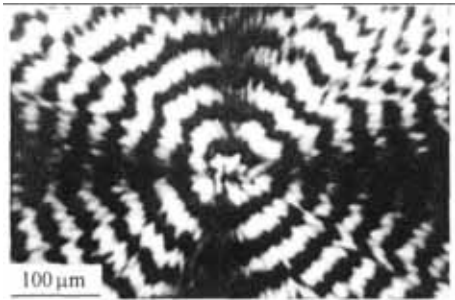


Fig. 2 Polarizing micrograph of a ringed spherulite under crossed polaroids

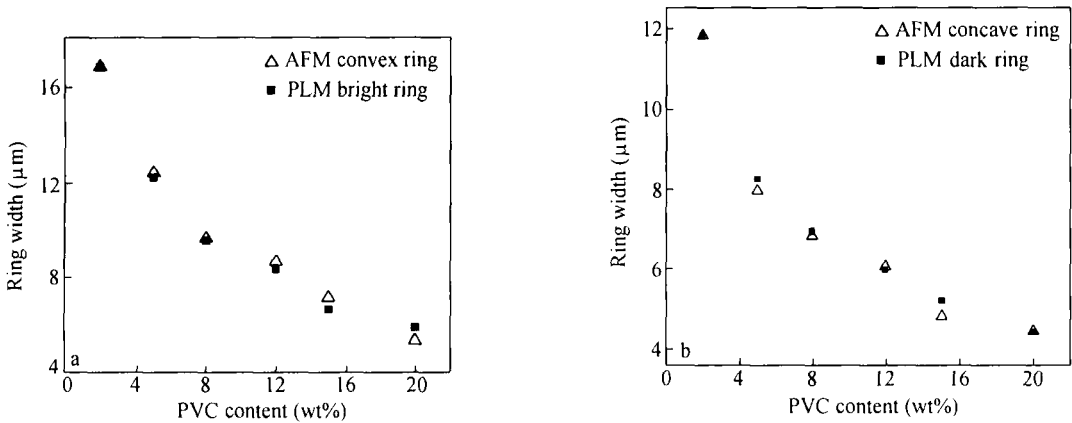


Fig. 3 Comparison of ring widths determined by AFM and polarizing microscopy for ringed spherulites in PCL/PVC blends of different PVC content: (a) widths of convex rings and bright rings, (b) widths of concave rings and dark rings

The alternative bright-dark ring pattern of spherulites under a polarizing microscope indicates the existence of a periodical variation of birefringence of the spherulites along their radius direction. In the literature this optical phenomenon was ascribed to the twist of the lamella structure within the spherulite^[7]. Now our results strongly suggest another possible origin of this special optical behavior of ringed spherulites. That is the periodical variation of the thickness within the spherulites. The mechanism and the driving force for the formation of ringed spherulites with periodically varied thickness during crystallization are of great interest for further studies.

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