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Oriented recrystallization of pre-oriented thin polymer films

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Abstract

The effects of a thin vacuum evaporated carbon film on the subsequent melting and recrystallization behavior of pre-oriented thin polymer films were studied by transmission electron microscopy and electron diffraction. It is found that a thin vacuum deposited carbon layer can keep the orientation of the pre-oriented thin polymer films after a complete melting and recrystallization. This process is repeatable. The recrystallization of the polymers can be performed even with the polymer films heated to a temperature more than 100°C above their melting temperatures and kept at that temperature for more than 10 h. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Oriented crystallization; Thin polymer films; Transmission electron microscopy and electron diffraction

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1. Introduction

Polymer materials with high orientation are of great interest for their special mechanical and optical properties. For preparing highly oriented ultra-thin polymer films, skillful experimental techniques, such as a special melt-drawn technique [1], friction transfer processes [2], and crystallizing thin polymer films epitaxially on oriented substrates [3,4], have been developed. Using these techniques, ultra-thin highly oriented polymer films can be easily prepared. When heating the oriented polymers above their melting points and recrystallizing them, they will lose their preferred orientation. During the work on polyethylene crystals, Bassett [5] has developed a detachment replication technique, which can preserve the orientation of a monolayer polymer crystal by subsequent dissolution at a temperature more than 10°C above the used dissolution point. This technique has been used in the morphological studies of complex crystals [6] and to follow changes on deformation into drawn films [7]. In both instances the evaporation of a thin carbon film on polyethylene confers on the layer receiving the ability to remain its crystallographic orientation well above the normal melting or dissolution temperature. The early work was more concerned with evaporation on lamellar fold surfaces and the retained orientation of the *hk*0 reflections. In the present work, we find that the orientation of oriented edge-on polymer lamellae can be retained by vacuum evaporating a thin carbon film on them.

The purpose of this paper is to present some experimental results regarding the maintenance of the high orientation of an oriented thin polymer film after complete melting and subsequent recrystallization, with exceeding its melting temperature by more than 100°C.

2. Experimental

The polymers used in this work are high-density polyethylene (PE), Lupolen 6021DX, from BASF AG Ludwigshafen, Germany, and Polybutylene 1 (PB-1), purchased from polymer laboratories. Uniaxially oriented thin films of PB-1 and PE were prepared according to the melt-drawn technique introduced by Petermann and Gohil [1]. The obtained highly oriented films, ca 50 nm thick, were transferred onto the TEM copper grids and subsequently vacuum evaporated with a thin carbon layer (about 5 nm thick). After vacuum evaporation, the oriented thin polymer films were heated far above the melting temperatures of the corresponding polymers for different times, and subsequently cooled at different rates to room temperature. For electron microscopy observations, a Philips CM200 TEM operated at 200 kV was used in this study. Bright-field (BF) electron micrographs were obtained by defocusing the objective lens [8–10].

3. Results and discussion

Fig. 1 shows the BF electron micrograph and the

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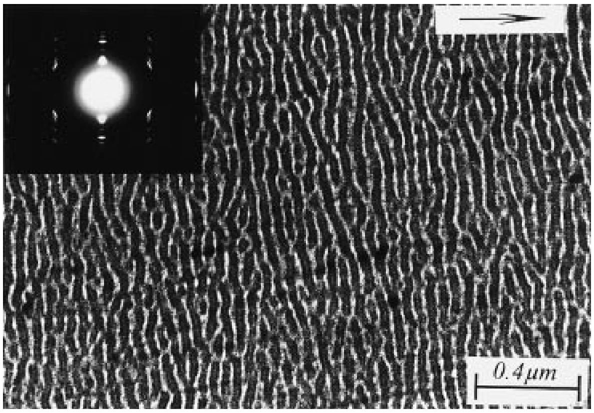

Fig. 1. BF electron micrograph and the corresponding electron diffraction pattern (inset) of the as prepared melt-drawn oriented PE thin films. The arrow shows the chain direction of the oriented PE crystals.

corresponding electron diffraction pattern (insert) of the melt-drawn PE highly oriented thin film in the as drawn state. The arrow indicates its molecular chain direction. It can clearly be seen that the HDPE oriented film consists of oriented lamellae aligned perpendicular to the drawing direction. On the corresponding electron diffraction pattern (inserted in Fig. 1), the sharp reflection spots confirm that the melt-drawn PE film exhibits a high degree of fiber texture, which is concluded by the appearance of the (110), (200), and (020) reflections on the equator.

Fig. 2 shows the BF electron micrograph and electron diffraction pattern (insert) of such a melt-drawn PE oriented film, which has been heat-treated at 150°C for 15 min and then isothermally crystallized at 120°C for 2 h. The arrow shows the drawing direction of the film during its preparation. Unambiguously, parallel aligned PE lamellae can be seen with their chain directions still in the drawing direction. This means that the vacuum deposited thin carbon film has kept the orientation of the PE melt-drawn film after a complete melting and recrystallization. The appearance of sharp reflection spots on the corresponding electron diffraction pattern indicates again a high orientation of the recrystallized PE thin film. But on the equator of the electron diffraction, the (200) reflections have completely disappeared, while the intensity of the (110) reflections has decreased tremendously. This implies that the recrystallized PE film exhibits a double texture orientation, i.e. besides the chains arranged still in the drawing direction, the *b*-axes of the PE crystals are now preferentially aligned in the film plane [11]. Moreover, very small crystallites between the lamellar crystals can also be observed. They may have been created during cooling the film from the crystallization temperature to room temperature.

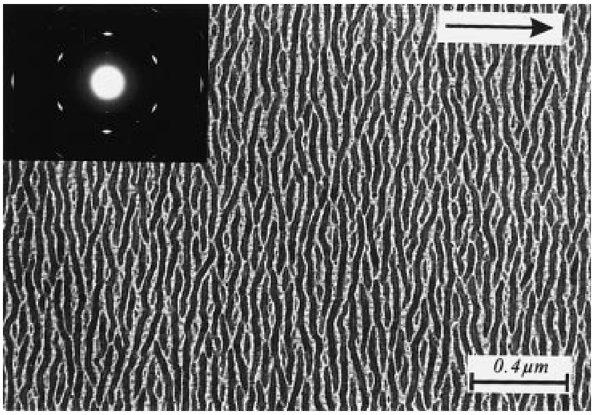

Fig. 2. BF electron micrograph and its corresponding electron diffraction pattern (inset) of the carbon deposited melt-drawn oriented PE films, which have been heated to 150°C for 15 min and crystallized isothermally at 120°C for 2 h. The chain direction of the oriented PE crystals is indicated by an arrow.

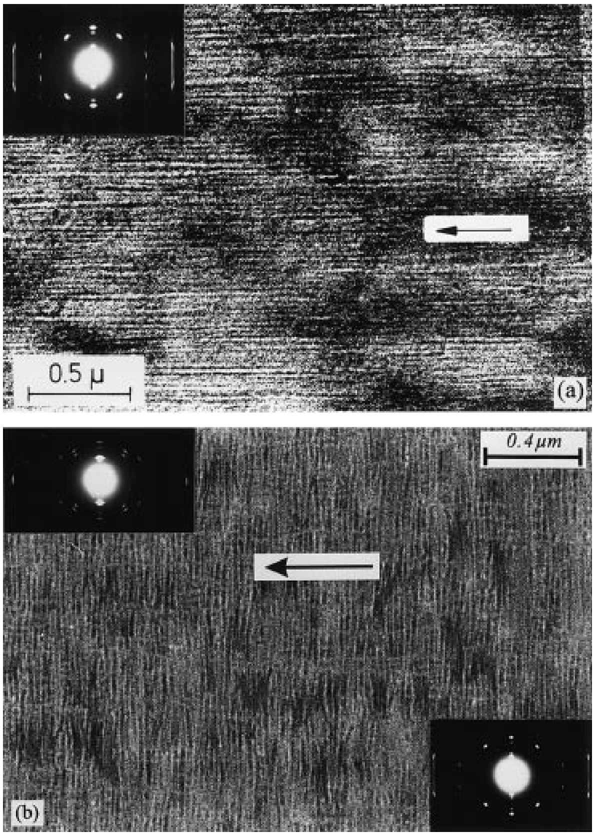

Fig. 3. BF electron micrographs and their corresponding electron diffraction patterns (inset) of the carbon deposited highly oriented PB-1 films (a) in the as prepared state, and (b) after heating to 200°C for 15 min and then cooled directly to room temperature on air. The arrows indicate the chain orientation directions of the PB-1 crystals. The electron diffraction pattern inserted in the upper left corner of (b) is taken direct after the recrystallization of the molten PB-1 thin films, while the electron diffraction pattern inserted in the lower right corner of (b) represents the diffractions of a PB-1 film a week after its recrystallization at room temperature.

From the above-mentioned BF and electron diffraction results, it is concluded that a thin deposited carbon layer can preserve the high orientation of the melt-drawn PE films during melting and recrystallization, but the structure on a nanoscopic scale is changed. It was found that a thin deposited carbon film can keep the orientation of PE melt-drawn film (i) by heating it to a temperature as high as 250°C, (ii) by any crystallization conditions, such as isothermal crystallization, slow cooling, and/or fast quenching, (iii) by repeating the melting and recrystallization processes for 10 times and (iv) even by keeping the film at 150°C for more than 10 h.

It has further been observed that this method is not only valid for PE but also for many other polymers. As a second demonstration of the effect, the BF electron micrographs and electron diffraction patterns (inserts) of carbon deposited PB-1 melt-drawn films before and after the melting and recrystallization processes are shown in Fig. 3. Unlike the PE, the melt-drawn PB-1 film consists of needle crystals with the axes of the long needle crystals aligned in the drawing direction, see Fig. 3a. The corresponding electron diffraction pattern (insert of Fig. 3a) reveals the high orientation of PB-1 with the hexagonal unit cell system [12,13]. After heating the carbon deposited PB-1 film to 200°C and cooling directly to room temperature on air, its molecular orientation remains, but the morphology of it changes from fibrillar to lamellar structure (compare Fig. 3a and b). The corresponding electron diffraction (insert in the upper left corner of Fig. 3b) shows that after recrystallization the oriented PB-1 lamellar crystals posses a tetragonal unit cell, which transforms to the stable hexagonal form (electron diffraction pattern insert in the low right corner of Fig. 3b) after a period of time [13–17].

When placing the melt-drawn thin polymer films simply on carbon-coated TEM copper grids and performing the same thermal treatment, no such effects have been observed. The morphologies of the molten and recrystallized polymer films are spherulitic. At this stage of our investigations, we can only speculate about the origin of this effect. The transformation of the fibrillar crystals with the hexagonal crystal structure ($3 * 1$ helix) in the used oriented PB-1 films into a lamellar morphology with the tetragonal crystal structure ($11 * 3$ helix) after the heat-treatment and recrystallization confirms that the original crystal structure is completely changed. These observations (chain conformation, crystal structure, and morphological changes) exclude a superheating of the original crystal structure [18]. A physical crosslinking between the surface macromolecules and the carbon film may be the origin of the maintenance of the chain orientations. The surface macromolecules may keep oriented (but not in a crystalline state) during the high annealing temperature and are the nuclei for the recrystallizing material. This hypothesis can explain, why in the case of the carbon detachment replicas of polymer single crystals their reappearance only occurs when heating them not more than 10°C above their melting points because only the fold surface part of the macromolecules is fixed by the carbon film. In our case, the extended macromolecular stems of the crystals are attached to the carbon film. Consequently, a much longer part of the chain and a much stronger fixation to the carbon film can be expected, leading to higher temperatures in order to destroy their orientation. Further experiments are under way to investigate the resulting morphologies and crystal structures.

4. Conclusions

With a vacuum deposited thin carbon layer, the orientation of pre-oriented polymer thin films can be preserved by a subsequent melting and recrystallization processes. Orientationally fixed macromolecules onto the deposited carbon layer may act as oriented nuclei for the recrystallization.

Acknowledgements

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