Structural Changes during Uniaxial-Drawing and/or Heating of Poly(ethylene naphthalene-2, 6-dicarboxylate) Films

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The structural changes in the uniaxial-drawing process of an unoriented amorphous film of poly(ethylene naphthalene-2, 6-dicarboxylate) [PEN] and in the heating process of an oriented amorphous film of PEN were studied respectively using the heating/drawing device and the high-temperature furnace designed for the X-ray diffraction apparatus equipped with imaging plates.

Keywords: Poly(ethylene-2, 6-naphthalate)/ Oriented crytstallization/ X-ray diffraction/ Imaging plate/ Stress-strain curve/ Birefringence/ Density

Poly(ethylene naphthalene-2, 6-dicarboxylate) [PEN] possesses naphthalene rings in its main chain in place of all the benzene rings of poly(ethylene terephthalate) [PET]. Accordingly, PEN has a higher modulus and a higher melting temperature than PET, and thus has started to be utilized, e.g., for electric appliances such as videotapes. Except for a few structural studies, however, the solid-state structure of PEN has not been studied extensively. Here, some experimental results [1] will be shown, which were obtained in the studies on the structural formation/changes in an unoriented amorphous PEN film in the uniaxial-drawing process at various temperatures and on the oriented crystallization of the pre-deformed amorphous PEN film in the heating process using the X-ray diffraction system equipped with imaging plates [IP]: with this system, we can record a time-resolved series of two-dimensional X-ray diffraction/ scattering patterns and afterwards analyse their intensity profiles [2].

For time-resolved wide-angle X-ray diffraction [WAXD] measurements using the IP system in the uniaxial-drawing and/or heating process of polymer solids, a high-temperature furnace and a heating/drawing device were newly designed and constructed [3]. The working temperature range of the furnace is from room temperature to 500°C. The precision of temperature regulation is within ±0.5°C for a given temperature between room temperature and 200°C, and within ±1°C for 200°C through 500°C. For heat treatment, say at 180°C, it needs only 30 sec to reach 97% of the expected equilibrium temperature after introducing the specimen holder into the furnace which is thermostated beforehand at 180°C. The new heating/drawing device was also constructed. In this device, the specimen is to be stretched in the horizontal direction. The specimen temperature is controlled by blowing thermostated hot air vertically into the specimen chamber in order to attain uniform temperature distribution over the whole specimen and to raise the specimen temperature as quickly as possible up to a given temperature below

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Scope of research

Attempts have been made to elucidate the molecular arrangement and the mechanism of structural formation/change in crystalline polymer solides, polymer gels and elastomers, polymer liquid crystals and polymer composites, mainly by electron microscopy and X-ray diffraction/scattcering. The major subjects are: synthesis and structural analysis of polymer composite materials, preparation and characterization of elastomeric materials, structural analysis of crystalline polymer solids by direct observation at molecular level resolution and in situ studies on structural formation/change in crystalline polymer solids.

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160°C. The precision of temperature regulation is within ±1°C at a specimen temperature between room temperature and 160°C.

When an unoriented amorphous PEN film was stretched below T_g (=117°C), it could be elongated up to a draw raio [DR] of 4–5 via neck formation and this stretching resulted in an oriented amorphous film of PEN. The WAXD pattern of the film drawn using the heating/drawing device at 65°C up to DR=3.7 showed a broad, asymmetrical halo maximum on the equator: the higher-scattering-angle side of the maximum is steeper than its lower-angle side. This asymmetrical profile indicates that the polymer chains are not randomly oriented but ordered to some extent.

When the oriented amorphous film of PEN, which had been made by drawing an unoriented amorphous film of PEN up to DR=3.6 at 65°C, was heat-treated using the high-temperature furnace at a temperature below T_g, for example at 115°C, then practically no crystalline reflections were observed in the WAXD patterns. When it was heat-treated at 118°C, however, the crystalline reflections appeared gradually with time: all the crystalline reflections in this report were well attributed to the α modification [4]. Concludingly, highly oriented amorphous films of PEN are able to crystallize above T_g, which was also confirmed by the DSC measurement.

The oriented amorphous film (DR=3.6, 65°C) of PEN was heated using the furnace at a heating rate of 3°C/min. At 120°C, crystalline reflections of (010), (100) and (−110) were clearly observable. These equatorial reflections became sharper and increased in their intensities with increasing temperature up to around the melting temperature (270°C). This result suggests the increase in crystallite size with an increase in temperature. On the off-equatorial layer lines, however, streak-like scatterings were observed up to 160°C. These streaks demonstrate the existence of paracrystalline nature, which is caused by the axial shift of polymer chains with respect to one another in the direction of the chain axis. All the streaks became stronger in intensity with increasing temperature, and finally they turned to spot-like reflections above 180°C. The whole pattern of the final film (255°C) showed fairly high crystallinity and the so-called fiber orientation of crystallites.

When an unoriented amorphous film of PEN was drawn using the heating/drawing device at 150°C, the broad amorphous halo moved to and became concentrated on the equator in the WAXD pattern with increasing DR for DR<1.5. At DR=ca. 1.5, the crystalline reflections started to appear on the equator, and thereafter increased in their intensities with increasing DR. The reflections were accompanied by streaks on the off-equatorial layer lines, as mentioned above: the intensities of the streaks were greater than those observed in the heating process of the oriented amorphous film. The WAXD photographs were taken from the films, which had been drawn at various temperatures up to a given DR and then been quenched, in order to elucidate the relationship between structural information and some properties such as stress-strain curves, birefringence and density [5]. In the case of uniaxial drawing above 130°C, the crystalline reflections appeared to be superposed on the oriented amorphous halo in the WAXD photograph taken from the film quenched at a DR just before the onset of necking. Beyond this point, the necking took place. The birefringence and density increased via neck formation.

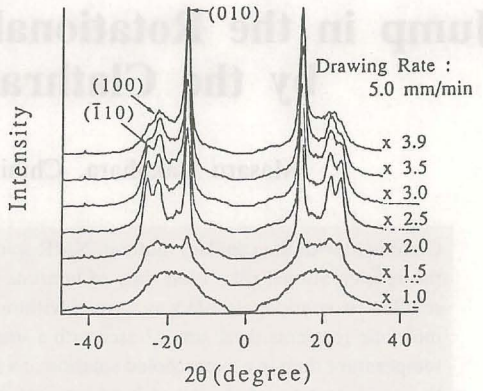

Figure 1. Equatorial intensity profiles of a time-resolved series of WAXD patterns obtained from an unoriented amorphous PEN film during uniaxial drawing at 150°C.

Figure 1 shows the equatorial intensity profiles of a time-resolved series of WAXD patterns which were obtained in the uniaxial-drawing process of an unoriented amorphous film of PEN at 150°C. At DR=ca. 2 (beyond the yield point), the (010), (100) and (−110) reflections became still stronger. These reflections are clearly separated from one another during neck formation, and then the (010) reflection became strong and sharp with increasing DR. The (−110) reflection, however, decreases in its intensity with increasing DR for DR>3.0, and finally the reflection has almost disappeared at DR=3.9. It is, therefore, concluded that in the drawing process of an unoriented amorphous film of PEN at a high temperature, the film has fiber structure accompanied by lattice distortion due to the axial shift of polymer chains relative to one another along the chain axis, and frequently the film finally shows uniplanar axial texture with the (−110) lattice planes parallel to the film surface: in the α modification, the unit cell contains one monomer unit of PEN and its naphthalene ring is set nearly parallel to the (−110) plane [4].

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