

NOTES

Structural Studies of Nylon 1010 Treated at Atmospheric and High Pressures

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Nylon 1010 is a polyamide produced in China as an important engineering plastic and is widely used. In common with other polyamides, it is characterized by high strength, high toughness and abrasion resistance. Nylon 1010 features lower moisture absorption and thus higher dimensional stability. The good mechanical properties of nylon 1010 make it attractive in industry and fundamental investigation.

The condensed structure of nylon 1010 crystallized from melt or glass solid at atmospheric pressure has been studied extensively.^{1–5} The structure of nylon 1010 is strongly dependent on thermal history. However, few studies have been carried out on the structure of nylon 1010 annealed at high pressures. Similar works on annealing of some other polyamides were performed about twenty years ago.^{6–8} This article deals with the structure of nylon 1010 annealed at atmospheric and high pressures by means of X-Ray diffraction and DSC.

EXPERIMENTAL

Nylon 1010 in the form of pellets was supplied from Jilin Shjijingou Union Chemical Co., China. The melting flow rate (MFR) is 10g/10min according to the manufacturer. Viscosity-average molecular weight is 1.34×10^4 . The pellets were dried in a vacuum oven at 80°C for 24 h prior to use. Subsequently, they were injection-moulded into $\phi 6 \times 8$ mm cylindrical samples at 200°C. The cylinders were used for high-pressure experiments.

High-pressure experiments were performed on a 4.9×10^6 N belt-type high-pressure apparatus. A cross-section of high-pressure cell assemblage is shown in

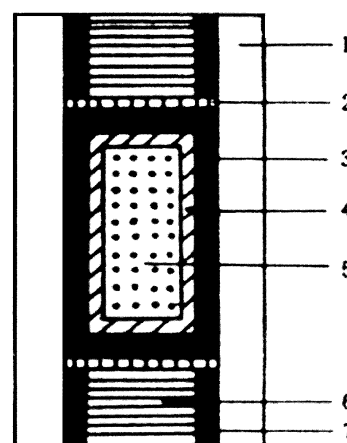


Figure 1. Cross-section of high pressure cell assemblage; 1: pyrophyllite cylinder; 2: molybdenum foil; 3: graphite heater; 4: h-BN capsule; 5: starting material; 6: pyrophyllite; 7: steel current.

Figure 1. The dimensions of the capsule made of hexagonal boron nitride (h-BN) for sample holding are $\phi 6 \times 8$ mm.

The magnitude of pressure generated inside the cell was determined by a calibration curve. This curve was established by determining the applied loads corresponding to phase transformation pressures of bismuth, thallium, and barium. The temperature of the sample was controlled by electric power supplied through the carbon heater and calibrated by inserting a Pt30% Rh-Pt16% Rh thermocouple in the cell.

High-pressure samples of nylon 1010 were prepared by placing cylindrical samples into cells as shown in Figure 1. After closing the cell, the pressure was increased as required, and the sample was heated to the annealing temperature of 250°C in about 3 min. After maintaining the sample at the desired pressure and

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temperature for 30 min, the sample was quenched to room temperature prior to the release of applied pressure. Nylon 1010 samples at atmospheric pressure were prepared by putting the melt of 250°C into different mediums.

X-Ray diffraction measurements were carried out on a PW1700 Philips diffractometer with Cu- K_{α} , Ni-filtered radiation over the range of diffraction angles (2θ) from 5° to 50°. The conditions were as follows: voltage was 40 kV, a current of 20 mA was used, and scan speed was 4° min⁻¹.

DSC measurements were performed on a Perkin-Elmer DSC-7 calibrated with indium and zinc standards under a nitrogen atmosphere. The scanning speed was 10°C min⁻¹.

RESULTS AND DISCUSSION

Nylon 1010 crystal displays typically three peaks at $2\theta = 8.5^{\circ}$, 20.0° , and 23.9° on X-Ray diffraction patterns, corresponding to (002), (100), and (110/010) planes, respectively.^{3–5} This crystal belongs to the triclinic system with lattice dimensions: $a = 4.9\text{Å}$, $b = 5.4\text{Å}$, $c = 27.8\text{Å}$, $\alpha = 49^{\circ}$, $\beta = 77^{\circ}$, and $\gamma = 64^{\circ}$. The triclinic crystalline structure of nylon 1010 is referred to as α -form nylon 1010, which is stable at low temperatures. With increasing temperature, the distance between (110/010) planes increases slowly and finally becomes the same as that between (100) planes. The two peaks at $2\theta = 20.0^{\circ}$ and 23.9° combined together to form single strong peak, as pseudo-hexagonal crystal structure or γ -form nylon 1010, obtained at high temperatures.

The transition of α -form to γ -form was found by Brill in studying the structure of nylon 66.⁹ The transition phenomenon is general and unique in polyamides and named Brill transition. The temperature at which transition occurs is the Brill transition temperature. For nylon 1010, the transition temperature is dependent on the size of original α -form crystals. This is the size effect of Brill transition in nylon 1010. The smaller the original crystal, the lower is the transition temperature. When crystal size is small enough, the γ -form nylon 1010 is stable even at room temperature.¹⁰

Figure 2 gives the X-Ray diffraction patterns of nylon 1010 samples obtained at atmospheric pressure. Nylon 1010 crystallizes easily. Even quenching the melt immediately, one cannot obtain the completely amorphous sample at room temperature.² Nylon 1010 melt and its quenched sample exhibit a structureless broad peak in X-Ray diffraction. The halo peak of the melt is centered at $2\theta = 19.0^{\circ}$ whereas that of the glass solid is centered at $2\theta = 21.5^{\circ}$. The difference of the

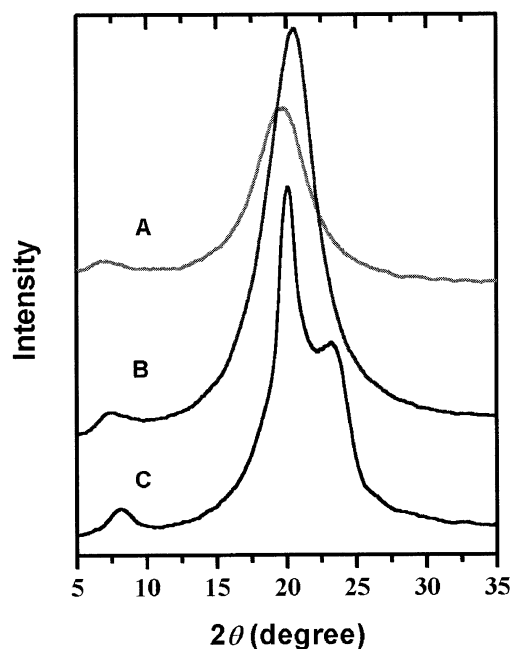


Figure 2. X-Ray diffraction patterns of nylon 1010 samples measured at room temperature. The samples were prepared by quenching the melts of 250°C to liquid nitrogen (A), to water of 25°C (B), and by cooling the melt in air (C).

angles is due to the dense packing of molecular chains in nylon 1010 solid.

After annealing the quenched nylon 1010 at room temperature, a pronounced peak at $2\theta = 20.0^{\circ}$ and a small peak at $2\theta = 7^{\circ}$ were observed as shown in Figure 2A. The sample prepared by dipping the nylon 1010 melts into water displays similar X-Ray diffraction as shown in Figure 2B. However, the two peaks show a little red shift and the diffraction intensity is enhanced. This is the diffraction of γ -form nylon 1010. During quenching, plenty of crystallites were formed. When annealing at room temperature, the Brill transition occurs. Hence, stable γ -form nylon 1010 was detected. For the sample prepared by cooling the melt slowly at room temperature, the typical diffraction pattern of α -form is observed as shown in Figure 2C. This is due to the molecular chains sufficiently adjusted to form larger α -form crystals. The triclinic crystal structure thus remains at room temperature.

Figure 3 shows the DSC curves of nylon 1010 samples obtained at atmospheric pressure. Although the samples display different X-Ray diffraction patterns, melting curves have similar profiles. Brill transition is a continuous and thermodynamically reversible process of phase transition. It involves great change in lattice dimensions as well as volume. However, no obvious endothermic or exothermic phenomenon was observed.¹¹ Brill *et al.*⁹ thought that the two diffraction peaks due to destruction of 2-dimensional hydrogen bonds and the newly formed network of hydrogen

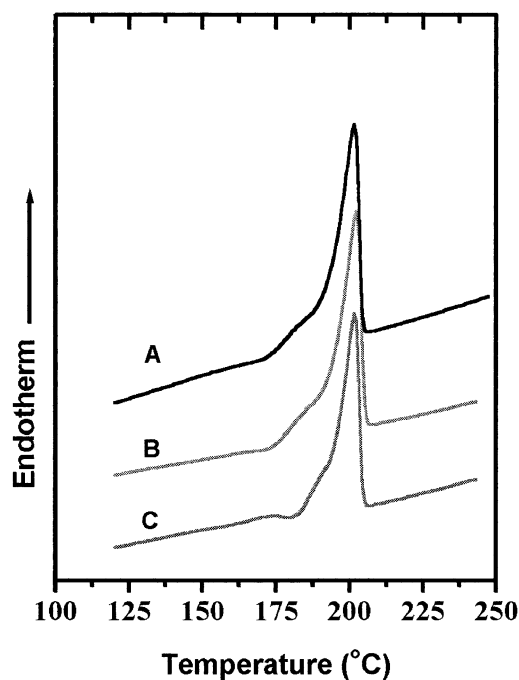


Figure 3. DSC curves of nylon 1010 samples prepared under atmospheric conditions at a heating speed of $10^{\circ}\text{C min}^{-1}$. Symbols are the same as in Figure 2.

bonds. But some researchers^{12,13} argue that the hydrogen bonding planes are not destroyed. Hirschinger *et al.*^{14,15} deduced from high-temperature NMR and computer simulation that Brill transition represents large-scale motion of aliphatic segments instead of destruction of original hydrogen bonds. DSC was in agreement with that for quenched nylon 1010 samples and rapidly cooled ones.²

Figure 4 gives X-Ray diffraction patterns of nylon 1010 annealed at high pressures. Characteristic diffraction peaks of the α -form nylon 1010 can be observed for the high-pressure annealed samples except those pressurized at 1.0 GPa and 1.2 GPa. With increasing pressure, the intensity of the peak at *ca.* 23.5° was enhanced, while that of the peak at *ca.* 20.5° decreased. Similar results were reported for other polyamides.⁷ For the sample annealed at 2.5 GPa, the diffraction of (100) planes is depressed thoroughly. At the same time shifting of the three peaks in the direction of higher angles was noticed, indicating the smaller spacing between crystal planes and dense packing of nylon 1010 chains in the crystal lattice. Annealing of nylon 1010 under high-pressure thus improves the crystal structure but the crystal form of triclinic system was unchanged.

For nylon 1010 samples treated at 1.0 GPa and 1.2 GPa, only the broad peak centered at *ca.* 20.0° is observed in Figure 4, indicating crystals of atmospheric pressure were not detected. The two samples were insoluble in solvents such as formic acid, a good solvent for nylon 1010. Thus cross-linking seems to oc-

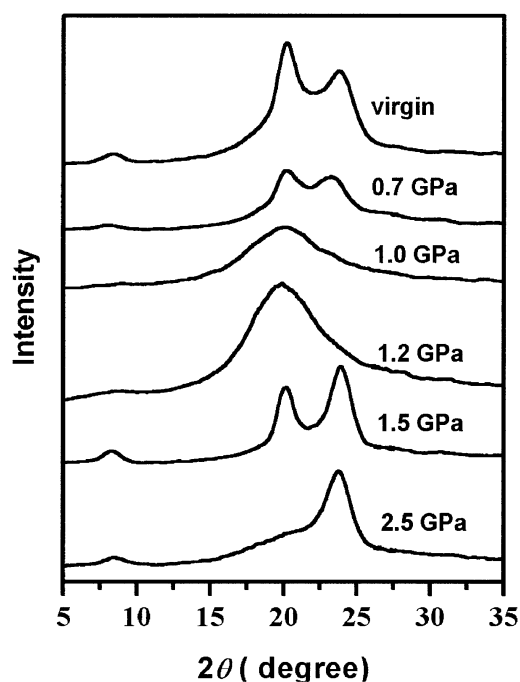


Figure 4. X-Ray diffraction patterns of nylon 1010 samples pressed at the marked pressures.

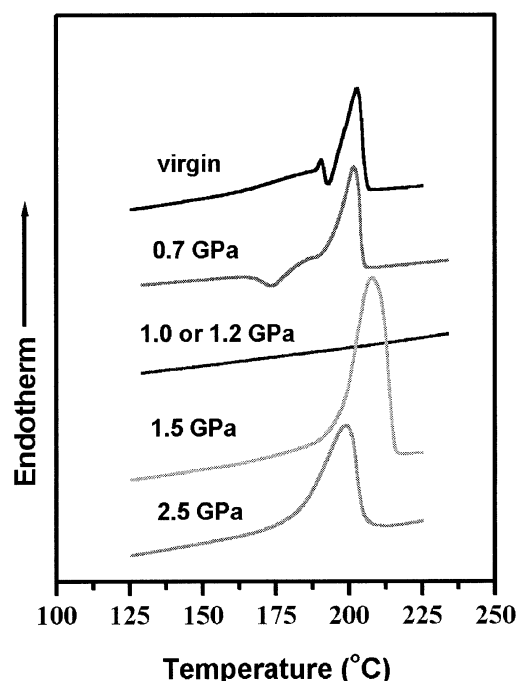


Figure 5. DSC curves of nylon 1010 samples pressed at the marked pressures at a heating speed of $10^{\circ}\text{C min}^{-1}$.

cur when nylon 1010 is annealed at 250 at 1.0–1.2 GPa for 30 min. Cross-linking was reported to occur in nylon -11 and -12 when samples were treated at 320 and 1.0 GPa. It seems that cross-linking occurs at the highest pressure.^{6–8} Cross-linking occurs in a certain pressure range in this study.

Figure 5 gives the DSC curves of the nylon 1010 samples obtained at high pressure. The samples underwent continuous melting and re-crystallization dur-

ing DSC scanning. Nylon 1010 contained a distribution of crystallites of different degrees of perfection, which was strongly dependent on its previous thermal history.¹ As shown in Figure 5, the virgin nylon 1010 exhibits double melting peaks. The peak located at 190°C is the melting of unstable crystals and that at 203°C is the melting of more stable crystals. Between the two melting peaks a re-crystallization peak can be observed. The melting temperature of the sample annealed at 0.7 GPa was lowered to 201°C and a cold crystallization peak was observed at 173°. For samples annealed at 1.0 GPa and 1.2 GPa, no melting peaks were found. The cooling curves were scanned from 250°C to room temperature at 10°C min⁻¹, but no crystallization peaks were detected.

When pressure increased to 1.5 GPa, the melting temperature increased to 208°C. This is the highest melting temperature obtained in this work. But one cannot infer from the 5°C increase of melting temperature that extended-chain crystals formed in nylon 1010. The folded chains of nylon 1010 may thus be extended and the thickness of the folded-chain lamellae may increase at this pressure and temperature. Only one broad melting peak is shown for the samples annealed at 1.5 GPa and 2.5 GPa. This means that high-pressure annealing of nylon 1010 leads to dense packing of polymer chains, which depressed the re-crystallization during the DSC scanning.

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