SHORT COMMUNICATION

Novel Primary Dispersion in Viscoelastic Behavior of Ferroelectric Nylon 6

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The ferroelectric property of even-numbered nylons was first reported on nylon 6 in 1995 by Itoh *et al.*¹ Possibility of ferroelectrics had been hardly taken into consideration for such even-numbered nylons due to their molecular structure, in contrast to odd-numbered nylons (nylon 7 and nylon 11).^{2,3} The authors reported that the amorphous nylon 6 thin film prepared by quenching from the melt showed the *D-E* hysteresis phenomena.¹ It was suggested by Yanagisawa *et al.*⁴ that packing of molecular chains in the as-quenched ferroelectric nylon 6 is looser (density is less than 1.00 g/cm³: amorphous A) than that in the paraelectric amorphous phase (density is 1.09 g/cm³:⁵ amorphous C) included in the slow-cooled nylon 6 (partly crystallized). However, the structural nature of the amorphous A and the precise mechanism of the *D-E* hysteresis appearance seem to be still unclear. In this paper, the experimental results obtained by dynamic mechanical analysis of the as-quenched nylon 6 film are briefly reported. Such information is considered to be helpful to understand the ferroelectric behavior observed in the as-quenched nylon 6.

EXPERIMENTAL

The original nylon 6 film (15 μ m thick, $M_n = 17,900$ and $M_w = 57,700$; measured by GPC method) was supplied by Toyobo Co. Ltd. As-quenched nylon 6 films were prepared by rapidly immersing the molten ones into liquid nitrogen. A rectangular sheet 30 mm long, 0.5 mm wide and 0.1 mm thick was used for the viscoelastic measurement, adequate to analyze relaxation phenomena in low frequency range. The measurement was performed by a dynamic mechanical measurement apparatus (Rheovibron DDV-2-EP visco-elastometer, Orientec Co.) with frequencies (*f*) of 3.5, 11, 35 and 110 Hz at a heating rate of 0.5 K/min and only 110 Hz at 2.0 K/min. The temperature was changed from 123 K or room temperature to 453 K, and the strain amplitude was 16 μ m. In some cases, water absorption into the sample was protected by covering both surfaces of the film with aluminum foil, although quality of the viscoelastic measurement data deteriorates for such samples and it was hard to perform the experiment below room temperature. The thermal property was measured by a differential scanning calorimetry (DSC) apparatus (DSC220C, Seiko Instrument Inc.) at a heating rate of 2.0 K/min (the DSC method) using the as-quenched sample, both surfaces of which were covered with aluminum foil.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of dynamic storage modulus E' , dynamic loss modulus E'' and $\tan \delta$ at 110 Hz for the slow-cooled nylon 6 film, which exhibits typical three types of relaxation processes. The γ relaxation appears around 150 K and the β relaxation appears around 230 K, both of which have been classified into local mode

Figure 1. Temperature dependence of E' , E'' and $\tan \delta$ for slow-cooled nylon 6 ($f = 110$ Hz). Heating rate is 2.0 K/min.

relaxation.⁶ The viscoelastic relaxation behavior around 350 K is usually designated to be the α relaxation which is considered to be caused by the onset of micro-Brownian motions of amorphous polymer chains. Aspects of β and γ relaxations for the quenched nylon 6 were similar to those of the slow-cooled sample as shown in Figure 2, while a new intense relaxation peak appears in the $\tan \delta$ curve and in the E'' one around 300 K, where the α relaxation also appears weakly around 350 K. Such a novel relaxation process is named as α' relaxation observed only in the as-quenched nylon 6 film.

The DSC exothermic peak appears around 330 K as shown in Figure 3a, which is higher than the $\tan \delta$ peak temperature of α' relaxation (*ca.* 300 K) in Figure 2. Figure 3b shows the $\tan \delta$ peak of the as-quenched nylon 6, both surfaces of which are covered with aluminum foil to protect water absorption into the sample during the measurement. Comparing Figure 3a with b, the apparent peak of the $\tan \delta$ well agrees with the rising point of the exothermic peak in the DSC curve around 330 K. It is noted again that the exothermic peak temperature in DSC is higher than that of the as-quenched nylon 6, both surfaces of which are not covered with aluminum foil. This fact suggests that the absorbed water during the measurement (only few hours) may reduce the temperature of the α' relaxation seriously. It was confirmed that the α' relaxation finally disappeared after the sample was exposed to air at room temperature for 12 h. It may be one of the reasons why we do not find any reports for the α' relaxation. Such α' relaxation never appears in the slow-cooled sample, which suggests that the water occlusion may not change the α relaxation to α' one in the amorphous C.

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Figure 2. Temperature dependence of E' , E'' and $\tan \delta$ for as-quenched nylon 6 ($f = 110$ Hz). Heating rate is 2.0 K/min.

It is considered that the amorphous A does exist independently from amorphous C (not a continuous pathway to stable phase). The authors have never noticed such reports about polymorphs in the amorphous state (polyamorphism) and/or the amorphous to amorphous phase transition in the field of polymer science.

The exothermic peak is caused by the structural transformation from amorphous A to more energetically stable phases (amorphous C and/or mesophase).⁴ Considering such situation, the sudden decrease of $\tan \delta$ in α' relaxation at 328 K (apparent peak temperature in Figure 3b) is explained by formation of such stable phases. It means that the real $\tan \delta$ peak temperature is higher than 328 K; peak of real $\tan \delta$ curve is concealed by occurrence of the stable phases. The sudden decrease (from 2.2×10^3 to 9.0×10^2 MPa) and subsequent recovering (from 9.0×10^2 to 1.5×10^3 MPa) in the E' curve (the apparent downward peak in Figure 2) are also explained by the same reason; the stable phases should possess higher modulus than the amorphous A.

The activation energies for α (ΔH_α) and α' ($\Delta H_{\alpha'}$) relaxation processes in the as-quenched sample were estimated on the basis of the following relation: $\ln a_T = (\Delta H/R)(1/T_s - 1/T_{s0})$, where R is gas constant and a_T is the so-called shift factor. T_{s0} was assumed to be the steepest point for the positive gradient region of the $\tan \delta$ curve (α' relaxation) or negative one of the $\tan \delta$ curve (α relaxation) measured at 110 Hz. The value of $\tan \delta$ at T_{s0} is expressed as $\tan \delta_0$. In other $\tan \delta$ graphs (3.5, 11 and 35 Hz), T_s was estimated from the intersection of each $\tan \delta$ curve and the horizontal line with height of $\tan \delta_0$. Each $\tan \delta$ graph for α and α' relaxations was supposed to be symmetric. The obtained graphs could be approximated as straight lines in the dispersion maps.

The value of $\Delta H_{\alpha'}$ was estimated to be about 150 ± 11 kcal/mol, and ΔH_α was about 46 ± 6 kcal/mol. Activation energy of α' relaxation process is almost three times that of α relaxation process. It is noted that the value of ΔH_α in the slow-cooled sample was also 50 ± 3 kcal/mol, which was estimated from the graph of $\ln f$ vs. $1/T_p$ (T_p is the $\tan \delta$ peak temperature).

Such results suggest that domain size of the coherent motion of chain segments in α' relaxation is larger than that in α relaxation. Since the NH absorbance in FT/IR spectra does not change so seriously but remains weak through the transformation from amorphous A to the stable phases with increasing temperature,⁴ the hydrogen bonding between amide groups

Figure 3. (a) DSC and (b) $\tan \delta$ ($f = 110$ Hz) curves of as-quenched nylon 6. Both surfaces of the samples are covered with aluminum foil during the measurement. Heating rate is 2.0 K/min in both cases.

seems to be kept imperfect even through such structural transformation. However, the D - E hysteresis phenomena or the α' relaxation is not observed in the stable phases. Looser packing in the amorphous A is considered to make the large-scale molecular motion easy in comparison with the stable phases with closer-packing of the molecules, when rotational motion of amide groups is also activated and D - E hysteresis loops can be observed in the amorphous A.

The quenched amorphous nylon 6 shows such interesting structural and physical properties. However, amorphous A is too unstable thermally to be applied as ferroelectrics. Recently we found that the γ -ray irradiation to the quenched nylon 6 stabilized the structure of the amorphous A by introducing crosslinks between the molecular chains, remaining the loose molecular packing of amorphous A. As future work, we will also examine the viscoelastic, ferroelectric and thermal properties of the crosslinked amorphous A precisely. Such study may clarify the aspect of the molecular motion as well as mechanism of the D - E hysteresis appearance in the amorphous A with extremely loose molecular packing.

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