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A Study of the Physical Aging in Semicrystalline Poly(ethylene terephthalate) via Differential Scanning Calorimetry

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Investigations found that physical aging in semicrystalline polymers occurred only in the amorphous phase, and it was affected by both degree of crystallinity (f_c^w) and crystalline morphology.[1] In the present paper, we report that when the f_c^w of semicrystalline poly(ethylene terephthalate) (PET) was within a definite range which depends on crystallization temperature, dual endothermic peaks appear in the glass transition temperature (T_g) region in differential scanning calorimetric (DSC) curve of samples subjected to physical aging.

Amorphous PET films had a thickness of ca. 0.15 mm, a viscosity-average molecular weight of ca. 1.63×10^4, a density of ca. 1.335 g cm^{-3} which means that samples were amorphous, and an optical birefringence of ca. 6×10^{-4} which means that they were isotropic. Measurements by both DSC and wide-angle X-ray diffraction also showed that samples were amorphous.

As-received PET films were cut into equal circles with a diameter of ca. 5.7 mm. They were held in an oven in nitrogen atmosphere at 300 ± 0.5 °C (ca. 45 °C above their melting point of ca. 255 °C) for 5 min to completely eliminate their thermal history. Then they were quenched in air to room temperature. It has proved that there was no crystallization induced by this process. Subsequently, these quenched samples crystallized isothermally in an oven at different temperatures for different time to obtain different f_c^w. Then the obtained semicrystalline samples were physically aged in an oven at 68 ± 0.5 °C for different time. At last they were stored in a desiccator before DSC measurement.

The f_c^w of semicrystalline PET was calculated by measuring their density. The density of samples (ρ) was measured at 25 ± 0.1 °C by using a density gradient tube filled with carbon tetrachloride and n-heptane. The f_c^w was calculated by taking the density of perfect PET crystalline lamellae (ρ_c) to be 1.455 g cm^{-3} and that of amorphous samples (ρ_a) to be 1.335 g cm^{-3}. Then

$$f_c^w = (\rho_c(\rho - \rho_a))/(\rho(\rho_c - \rho_a)) \tag{1}$$

Physically aged samples of ca. 5.0 mg were sealed in aluminum pans, and their thermal properties were measured by using a TA2910 DSC. Indium and tin were employed for the temperature calibration, the heat capacity was evaluated with respect to sapphire as a standard, and a nitrogen gas purge with a flux of ca. 30 mL min^{-1} was used to prevent oxidative degradation of samples during the heating run. The rate of heating run in DSC was 10 °C min^{-1}.

Figures 1 and 2 present DSC curves of amorphous PET and semicrystalline PET with a fairly high f_c^w of ca. 0.39 (obtained by isothermal crystallization at 130 °C for 7.5 min) subjected to physical aging, respectively. It can be seen that in both cases there was single endothermic peak appearing in the T_g region, and the peak shifted to higher temperature with increasing physical aging time (t_{pa}). Besides, magnitude of the peak also increased with increasing t_{pa} in both cases.

These experimental results are consistent with many others.[2-4] Some interesting differences between these two extreme cases can be found. First of all, in the former case, when t_{pa} increased from 0.75 to 384 h, the peak temperature (T_p) increased from ca. 80.1 to ca. 85.9 °C, while in the latter case, T_p increased from ca. 85.0 to ca. 98.0 °C for the same increase in t_{pa}. It can be seen that, for the same t_{pa}, T_p in the latter case was higher than that in the former case. Second, for the same t_{pa}, the magnitude of the peak in the latter case was lower

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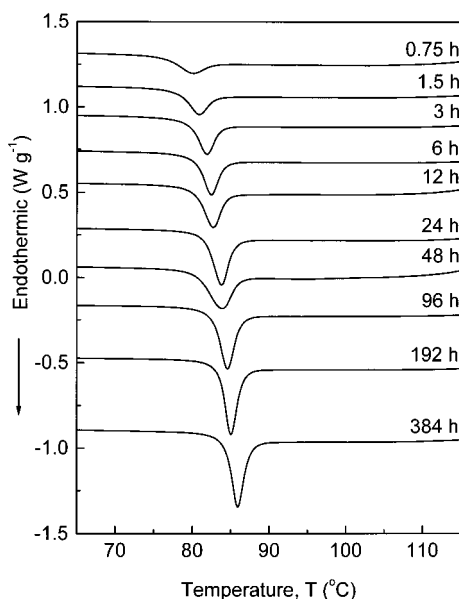
Figure 1. DSC curves of amorphous PET subjected to physical aging for different t_{pa} indicated beside each curve.
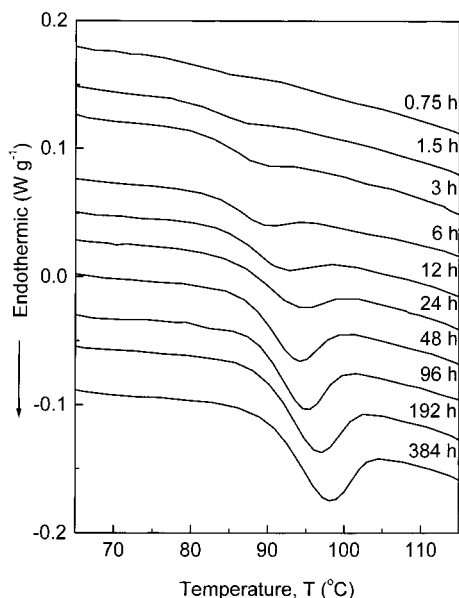

Figure 2. DSC curves of semicrystalline PET with a fairly high f_c^w of ca. 0.39 (obtained by isothermal crystallization at 130 °C for 7.5 min) subjected to physical aging for different t_{pa} indicated beside each curve.

than that in the former case. Third, in the former case the endothermic peak was visible after a t_{pa} of only ca. 10 min, while in the latter case the t_{pa} needed for the appearance of endothermic peak was over 30 min.

Those mentioned above are two extreme cases where the f_c^w of samples was either very low (even as low as zero, for amorphous samples) or fairly high. However, in our experiments a novel phenomenon was found when the f_c^w was between those two cases: there were dual endothermic peaks appearing in the T_g region in DSC curve.

Our experiments showed that when dual endothermic peaks appeared, there were still an exothermic cold crystallization peak appearing at ca. 137 °C and an endothermic melting peak appearing at ca. 255 °C. It was also found that both dual endothermic peaks and exothermic cold crystallization peak shifted to higher temperature, and the magnitude of each peak increased
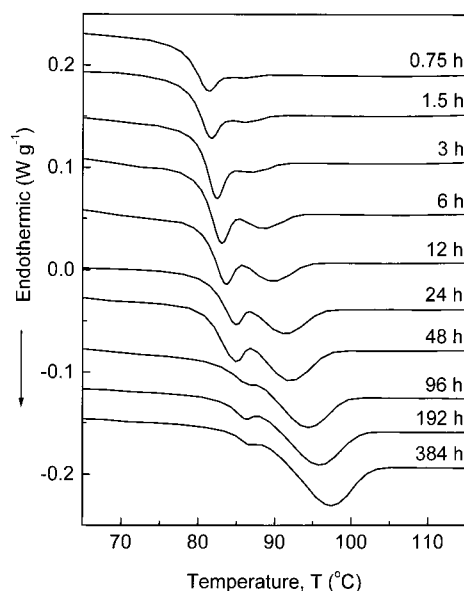

Figure 3. DSC curves of semicrystalline PET with a f_c^w of ca. 0.17 (obtained by isothermal crystallization at 120 °C for 7.0 min) subjected to physical aging for different t_{pa} indicated beside each curve.

with increasing rate of heating run in DSC. The most important is that the shape of DSC curves at different rates kept unchanged. Besides, measurement of the density also showed that there was no obvious increase of f_c^w occurring in the temperature range of the dual endothermic peaks when samples were heated in DSC. Therefore, it can be concluded that there was really no cold crystallization occurring between the dual endothermic peaks. Similar experimental results were also found by other researchers.[5,6] In fact, because the samples were isotropic and unoriented, their cold crystallization temperature (T_{cc}) was ca. 137 °C for amorphous samples. T_{cc} of semicrystalline PET with a fairly high f_c^w was still far from the temperature range of the dual endothermic peaks. Very low T_{cc}, even as low as ca. 90 °C, was found only in highly oriented PET fibers.[7]

Figure 3 shows an example for the course of evolution of the dual endothermic peaks, where the samples had a f_c^w of ca. 0.17 (obtained by isothermal crystallization at 120 °C for 7.0 min). The behavior in other cases, where the dual peaks also appear, was the same as that shown in this example. It can be seen that both endothermic peaks shifted to higher temperature with increasing t_{pa}. When t_{pa} increased from 0.75 to 384 h, T_p^L (lower peak temperature) increased from ca. 81.0 to ca. 86.5 °C, while T_p^U (upper peak temperature) increased from ca. 85.9 to ca. 97.4 °C. However, the evolution of magnitude of the dual peaks was very different from each other. The magnitude of upper temperature endothermic peak increased with increasing t_{pa} in the whole process of physical aging, while that of lower peak first increased but then (after a t_{pa} of ca. 6 h) decreased with increasing t_{pa}.

By comparing Figure 3 with Figures 1 and 2, it can be seen that the lower endothermic peak had the same temperature range as that in amorphous samples and the upper peak had the same range as that in semicrystalline samples with the fairly high f_c^w.

Figure 4 exhibits the different ranges of f_c^w to obtain the dual endothermic peaks. It can be seen that both lower and upper limits of f_c^w increased with the increase in crystallization temperature. When the samples crys-
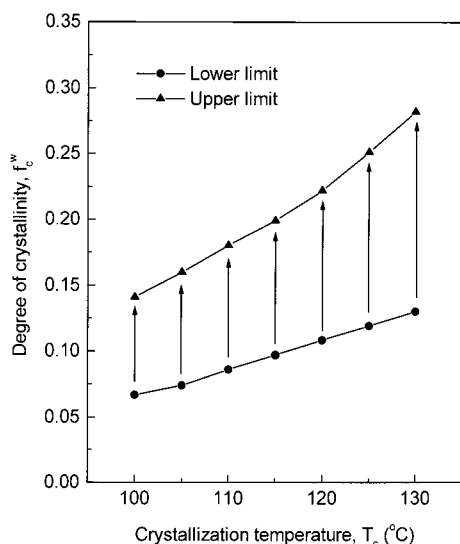
Figure 4. Range of the f_c^w of semicrystalline PET, whose DSC curve shows dual endothermic peaks, corresponding to different T_c.

tallized at 100 °C, the range of f_c^w was from ca. 0.067 to ca. 0.141, whereas the range was from ca. 0.130 to ca. 0.282 when crystallized at 130 °C.

Crystallization of PET is a complex process since it is influenced by numerous factors. Crystallization temperature, pressure, moisture, molecular weight, remnant catalyst, solvents, and nucleating agents all have profound effects on f_c^w, crystallization rate, and crystalline morphology.[8] Therefore, although here only f_c^w of the samples is considered, crystalline morphology really also plays an important role.

References and Notes

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