

Effects of Mechanical Deformation on Endothermic Peaks in Aged Amorphous Poly(ethylene terephthalate)

Yong WANG and Deyan SHEN[†]

*Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080,
People's Republic of China*

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ABSTRACT: The effect of mechanical deformation on endothermic peaks of aged amorphous Poly(ethylene terephthalate) (PET) films were studied using differential scanning calorimetry (DSC). Three deformation methods, uniaxial tension, uniaxial compression and densified compression were used. The results showed that after deformation, irrespective of tensile or compression, endothermic peaks disappeared with increase of the density. For compressed films followed by annealing, two endothermic peaks appeared. These findings can be explained on the basis of cohesive entanglements, which seem to be an important feature of physical aging of glassy polymers.

KEY WORDS Physical Aging / Endothermic Peak / Deformation / Differential Scanning Calorimetry / Cohesional Entanglement /

Recently, there has been increasing interest in the effects of thermal treatment below T_g or physical aging of amorphous polymers. This is important because it affects a great number of mechanical, dielectric and thermal properties.¹ Physical aging phenomena in amorphous polymers have been observed by measuring methods such as dilatometry,^{2,3} calorimetry,^{4–6} mechanical and dielectric spectroscopy^{1,7,8} small-angle X-ray scattering techniques,^{9–11} infra-red spectroscopy,^{12–15} and positron annihilation lifetime spectroscopy.^{16,17} From these studies the mechanism of physical aging has been related to molecular conformation^{4,12} and free volume.^{4–7,17} Differential Scanning Calorimetry (DSC) studies demonstrate a correlation between thermal treatment below T_g and endothermic peaks in glassy polymers. Petrie⁴ suggests that the enthalpy, ΔH , as determined from the peak, can be used to characterize the “free volume” of an amorphous polymer, where free volume decreases with increasing enthalpy. However, morphological studies suggest that physical property changes induced by annealing below T_g cannot be interpreted solely in terms of these changes in free volume.^{18,19} Thermal treatment below T_g can change the size and arrangement of an apparent nodular texture in Poly(ethylene terephthalate) (PET)²⁰ and Poly(carbonate) (PC).²¹ This suggests that a re-appraisal of the usual concept of free volume and free volume distribution is appropriate. It appears in these cases that some structural order becomes dominant when an external stress is applied to material.^{11,22}

DSC traces of glassy polymers are significantly dependent on aging. A sub- T_g annealed sample shows an endothermic peak close to T_g in the DSC heating curve. In this communication the effects of uniaxial extension and compression of materials in the glassy state on peaks were investigated by DSC.

EXPERIMENTAL

Materials

Air-quenched melt-extruded PET films of 0.15 mm thickness were amorphous by WAXD, birefringence and FT-IR measurements.²³ T_g was 76°C as determined by DSC (20°C min⁻¹). The amorphous PET samples were heated to 92°C and annealed for 10 min. The samples were then immediately quenched in an ice water bath, removed, immediately dried, and annealed at 65°C for different times.

Uniaxial Extension

It was performed at 67°C on a Tension Tester. Dog bone-shaped samples were cut from films of amorphous PET. The dimensions of the samples were 20 mm (length) by 5.0 mm (width) by 0.15 mm (thickness).

Uniaxial Compression

Aged, 12.8 mm diameter × 0.15 mm discs of amorphous PET sheet were compressed under various pressures from 0.15 mm to different sizes at room temperature.

Densified Compression

The pressure cell consisted of a steel cylinder of 12.8 mm inner diameter and 30 mm usable length. The 12.8 mm diameter × 0.5 mm thick discs of amorphous PET were inserted in the pressure cell at room temperature and 500 MPa pressure was applied for 10 min. The dimensions of the discs nearly did not change.

DSC measurements were performed using a Perkin-Elmer Model 4 system. The heating rate was 20°C min⁻¹.

The densities of the PET films were measured in a density-gradient column of carbon tetrachloride and *n*-heptane at 25°C. A set of calibrated (± 0.0001 g cm⁻³) glass floats was used to ensure linearity and accuracy. Each density was the average of three samples.

RESULTS

Aging gives rise to an endothermic peaks for amorphous samples at about the glass transition tempera-

[†] Author to whom all correspondence should be addressed.

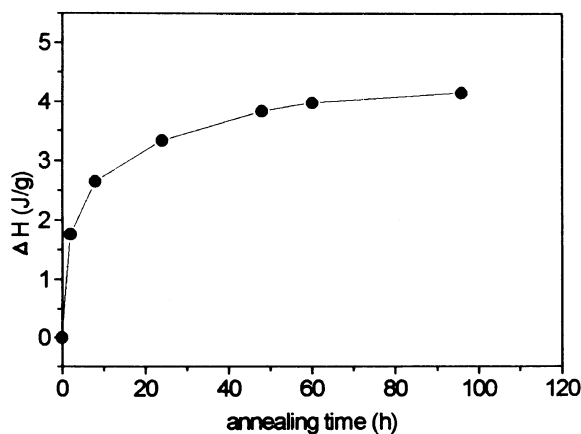


Figure 1. Magnitude of endothermic peak (ΔH) as a function of sub- T_g annealing time for amorphous PET films. $T_a = 65^\circ\text{C}$.

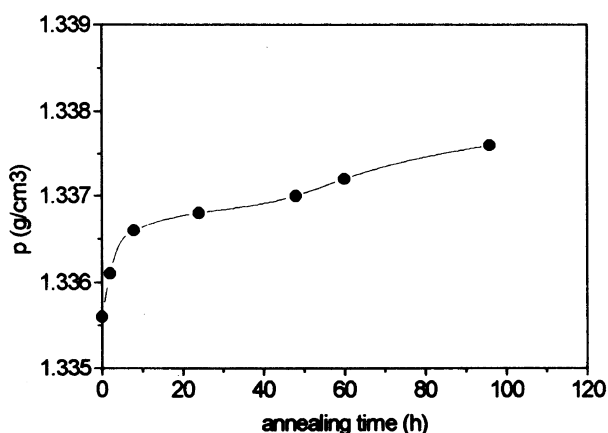


Figure 2. Dependence of the density of amorphous PET on sub- T_g annealing time. $T_a = 65^\circ\text{C}$.

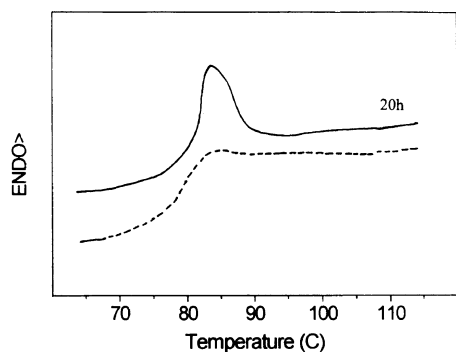


Figure 3. DSC curves of amorphous PET films. Solid curve is for the annealed sample before drawing. Dotted curve is for the annealed sample drawn beyond the yield point.

ture if the aged sample is heated in a calorimeter. The magnitude of the endothermic peak, ΔH for amorphous PET annealed at 65°C as a function of annealing time are shown in Figure 1. ΔH increased steeply and leveled off with increasing ageing time. The time dependence of the density is shown in Figure 2. The densities of amorphous PET also increase gradually with aging time.

However an opposite effect on endothermic peak was observed for samples under mechanical tensile deformation. DSC curves of the annealed films before and after drawing beyond the yield point are shown in Figure 3.

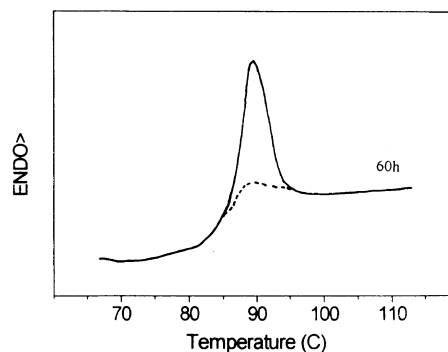


Figure 4. DSC curves of amorphous PET films. Solid curve is for the annealed sample before uniaxial compressing. Dotted curve is for the annealed sample compressed from 0.15 to 0.090 mm.

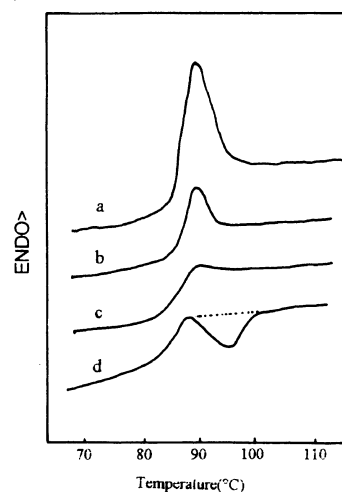


Figure 5. DSC curves of amorphous aged PET films uniaxial compressed with different compression ratios. (a) annealed sample before compressing; (b) compressed from 0.15 to 0.110 mm; (c) compressed from 0.15 to 0.085 mm; (d) compressed from 0.15 to 0.065 mm.

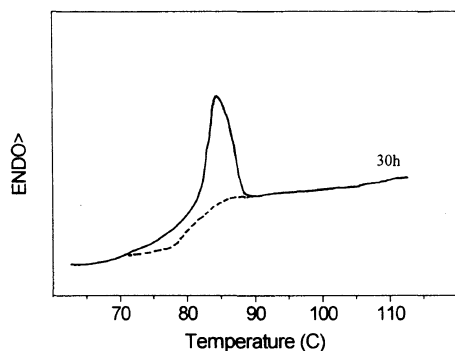
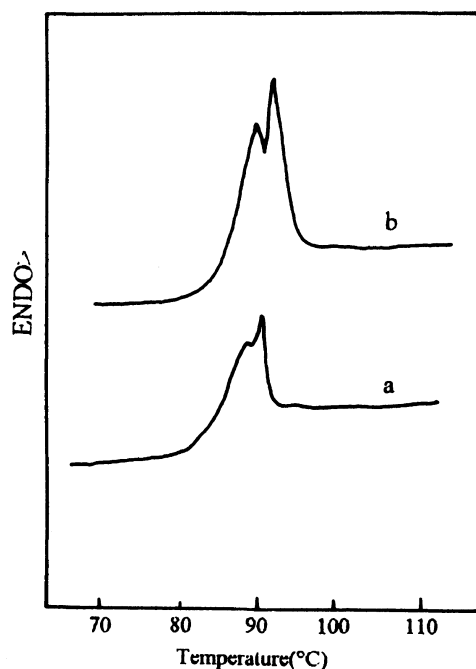
After drawing the DSC endothermic peak due to annealing was largely eliminated, and the density increased from 1.3368 to 1.3401 g cm^{-3} . The endothermic peaks of the annealed samples could be decreased by mechanical drawing to about the same level as that of the original quenched state.

In Figure 4 similar result is observed when the annealed samples is under uniaxial compression, where the peak first increased annealing at 65°C for 60 h, and then it decreased to the original level by mechanically compressing from 0.15 mm to 0.090 mm. The density increase from 1.3372 to 1.3405 g cm^{-3} , DSC curves of the annealed films with different compression ratios are shown in Figure 5. The top curve represents the sample annealed at 65°C for 72 h. The other three curves are for the annealed sample compressed to 0.110, 0.085, 0.065 mm, respectively. With increasing compression ratio, the endothermic peak decreased. With further compressing, the peak disappeared and followed by a exothermic peak, and the density also increased with the compression ratio (see Table I).

To get rid of the dilatation effects in deformation, another type of compression was used. The aged thick discs of amorphous PET were inserted in the pressure cell and compressed at 500 MPa. The results are shown in Figure 6. The object of this second study was to

Table I. Density of amorphous aged PET films with different compression ratios

Sample	Deformation history	Density (g cm^{-3})
a	Aged, 65°C, 72 h	1.3374
b	From 0.15 to 0.110 mm	1.3386
c	From 0.15 to 0.085 mm	1.3403
c	From 0.15 to 0.065 mm	1.3431

**Figure 6.** DSC curves of amorphous aged PET films identified compressed. Solid curve is for the annealed sample before compressing. Dotted curve is for the annealed sample after compressing.**Figure 7.** DSC curves of amorphous PET films with different thermal and mechanical histories. (a) after compressing, annealed at 65°C for 36 h; (b) after compressing, annealed at 65°C for 72 h.

demonstrate that deformation accompanied decrease in endothermic peak and the density increased after compressing. Since the deformation in compress-densification should not accompany dilatation, this was considered as a crucial evidence that the free-volume model is unsuitable.

In addition, an interesting phenomenon was found when the compressed PET films were sub- T_g annealing. The DSC curves are shown in Figure 7 for the compressed PET annealed at 65°C for the indicated times. Two endothermic peaks appeared and grew in magnitude and position with annealing time. As mentioned above, the

compressed PET film showed complicated thermo-mechanical histories before annealing as compared with the quenched PET. Therefore, it is evident that the endothermic peak depends strongly on the glass-forming histories or initial structural feature.

DISCUSSION

The results presented above cannot be explained only by increase or decrease in specific volume. This reaffirms the fact that the specific volume alone is not sufficient to characterize the state of a glassy material. An interesting question is whether the specific volume or the local structural order (or indeed, another parameter) is more important in determining the properties of glassy materials. Figure 3 shows that a sample aged physically, can be brought to the original state (*i.e.*, "rejuvenated"²⁴) by application of a moderate tensile stress. Based on the specific volume concept, this can be explained by strain-induced dilatation possibly resulting in increase in free volume in the glassy polymer. The peak is reduced with increase of free volume, despite the fact that drawing leads to increase of density. However the results in Figures 4–6 show that such rejuvenation can also be achieved by uniaxial compression or even compress-densification deformation, neither of which produces dilatational effect. We hypothesize that annealing at a temperature below T_g produces local ordered zones in the sample, or increases the dimensions of ordered zones possibly present in the amorphous sample.

Qian^{25–28} put forward the concept of cohesive entanglement of neighbouring chain segments in the condensed state. The attractive cohesive interaction energy of each site is very small, so that they are easily entangled and disentangled. These cohesive entanglements are important to the physical properties of polymers near T_g and their glassy state. Below and around T_g the average spacing along the chain between cohesive entanglements is much smaller than that of the topological entanglements. When these cohesive entanglements lock up the long-range cooperative conformational changes of the chain which are necessary for rubbery elasticity, the polymer exhibits glassy state properties. At temperatures higher than T_g , cohesive entanglement spacing is necessarily greater than the length of chain segment motion needed for rubbery elasticity. Rapid quenching of the samples from the melt or from the rubbery state to the temperatures below T_g does not allow sufficient time for the formation of new cohesive entanglements so that the sample on heating displays a simple step endothermic curve. Sub- T_g annealing should result in the formation of new cohesive entanglements along the chain. Variation in the cohesive entanglements spacing may possibly give rise thermal history effects. A sudden endothermic process to disengage the cohesive entanglements is necessary before the transition from glassy to rubbery state on heating, thus resulting in an endothermic peak on the DSC curve.

The DSC peak arises from some structural reorganization or cohesive entanglements during annealing. So the disappearance of the endothermic peak is interpreted

as the result of disruption of cohesive entanglements present in the aged sample. It is more likely that the effect of deformation, irrespective of tensile or compression, disrupts the local packing of segments or cohesive entanglements from their low-energy state achieved by the physical aging and elevates it to a more disordered state of high energy. The appearance of two endothermic peaks indicates the structure of amorphous glassy polymers to be complicated, rather than homogeneous, and strongly dependent on the histories of glass forming. The appearance of two peaks also suggests that different chain aggregates (cohesive entanglements) are formed in the amorphous matrix of the compressed PET glass.

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