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The effect of water absorption on the physical ageing of amorphous poly(ethylene terephthalate) film

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Abstract

Amorphous poly(ethylene terephthalate) (PET) films with different thermal histories were annealed at 30°C in a desiccator, in a humid atmosphere and in liquid water respectively, for investigation of enthalpy relaxation by differential scanning calorimetry (DSC). For the quenched sample annealed in a humid atmosphere, the evolution of the endothermic peak near the glass transition temperature (T_g) with annealing time is remarkable. For the aged samples further annealed in the humid atmosphere and water, the shape of the endothermic peak changed from a single peak into broad double peaks with annealing time. However no such change of the endothermic peak can be observed for both the quenched and the aged samples further annealed in the desiccator. The experimental results showed that the change of the DSC curve was reversible, involved only with the physical process. The results may indicate that some ordered structure formed during the physical ageing process. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate); Physical ageing; Water absorption

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1. Introduction

The amorphous state of polymers quenched from the melt or rubbery state is known to be a non-equilibrium state. Annealing below the glass transition temperature (T_g), known as sub-T_g annealing or physical ageing of the quenched amorphous sample will bring it to a state closer to equilibrium with the relaxation of volume and enthalpy. Differential scanning calorimetry (DSC) has been widely used to study physical ageing phenomena in glassy polymers [1–9]. The sub-T_g annealed sample shows an endothermic peak close to T_g in the DSC heating curve. The magnitude and temperature of the peak increase with annealing time and temperature.

Physical ageing of amorphous poly (ethylene terephthalate) (PET) has been studied extensively in the past years [6,10–16], but only few papers were about the effect of water absorption on the ageing behavior, although Jabarin et al. [17] noted that the absorption of water will affect T_g, cold crystallization temperature and orientation of PET significantly.

In this paper, amorphous PET samples with different thermal histories further annealed at 30°C in a desiccator; in humid atmosphere and in liquid water were studied by DSC measurement in order to elucidate the influence of water on the aged and quenched amorphous PET sample as reflected in the change of position, magnitude and shape of the endothermic peak near T_g.

2. Experimental

2.1. Materials

A ~200 mm wide sheet of amorphous PET was produced by melt extrusion at 290°C through a slit die followed by quenching onto a chilled roll at 20°C. It had a density of 1.3363 g/cm^3 and a birefringence of less than 2×10^{-4} indicating no measurable amount of crystallinity and orientation. Its T_g was 76°C as determined in the DSC curve (middle point of transition step) at a heating rate of 10°C/min. The sheet had a thickness of 0.10 mm and was stored in a vacuum oven at room temperature for the following annealing process.

2.2. Annealing process

The dry amorphous PET sheet was first heated to 92°C for 15 min to erase the thermal history, then air quenched to room temperature to obtain the quenched sample (sample Q). Sample Q was immediately annealed at 63°C in a

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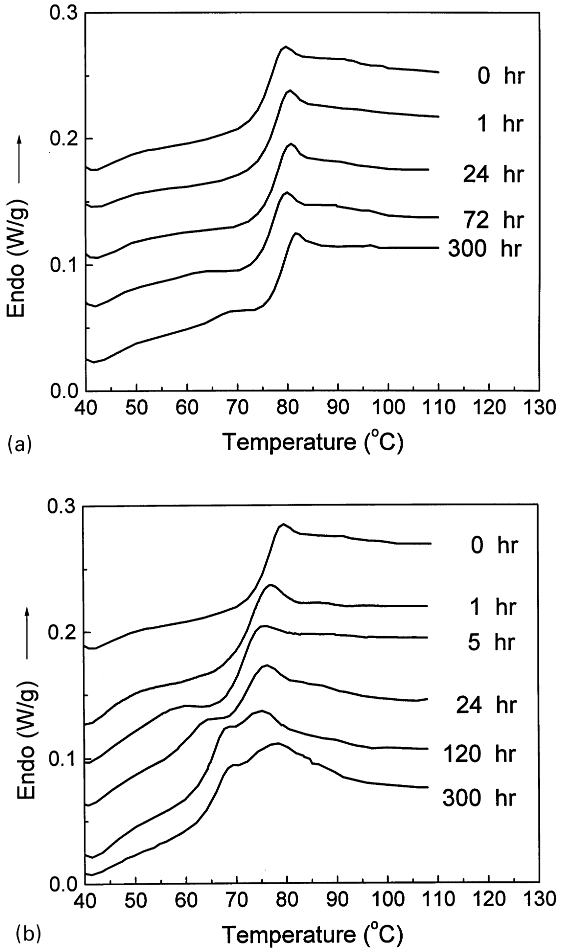

Fig. 1. The DSC curve of sample Q annealed: (a) in a desiccator; (b) in a humid atmosphere for different times at 30°C.

desiccator with silica gel as the desiccant for 10 days to get the long time aged sample (sample A).

Sample Q and sample A were further annealed at 30°C in different environments: (a) in a desiccator; (b) in a humid atmosphere of relative humidity ~70%; (c) in liquid water.

2.3. DSC measurements

After the annealing process, the sample was used for the DSC measurement immediately. The surface of the sample dipped in liquid water was blotted by filter paper before DSC measurement. A TA2910 differential scanning calorimeter was used at a heating rate of 10°C/min under nitrogen atmosphere. Samples for DSC measurement were carefully prepared to have approximately the similar weight (6.0 ± 0.5 mg).

3. Results and discussion

The DSC curves of sample Q annealed at 30°C in the desiccator, in a humid atmosphere are shown in Fig. 1(a) and (b), respectively. A small endothermic peak before T_g in the DSC curve develops during annealing in both cases, and both the position and magnitude of the peak increase with increasing annealing time. However, a difference should be noted. The development of the endothermic peak of the sample annealed in the humid atmosphere proceeds faster than that annealed in the desiccator, but this does not necessarily mean that water absorption accelerates the enthalpy relaxation of the sample. Sample Q annealed in a humid atmosphere for a very long time (e.g. 300 h), which showed a relatively larger endothermic peak at a higher temperature, was placed in the desiccator for 24 h, and the peak became smaller, analogous to the sample annealed in the desiccator for 300 h.

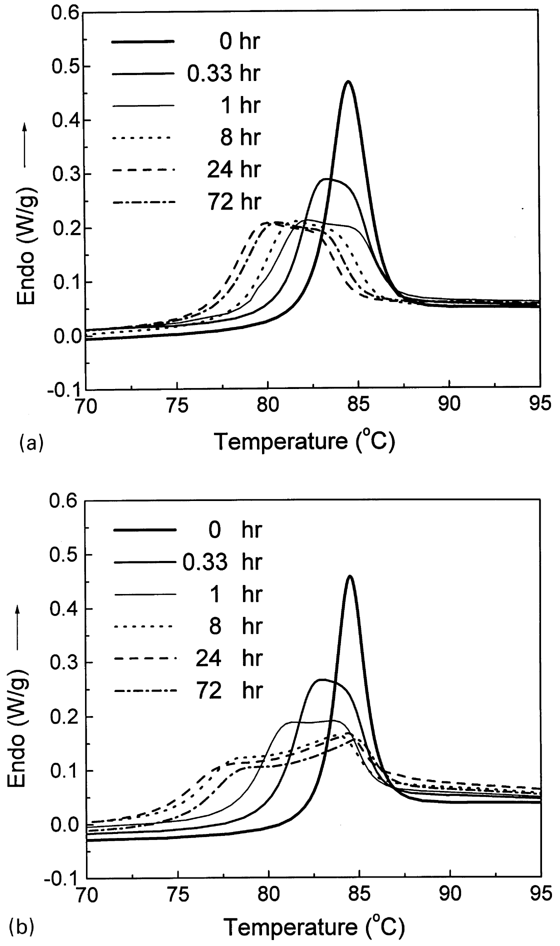

Fig. 2. The DSC curve of sample A further annealed: (a) in a humid atmosphere; (b) in liquid water for different times at 30°C.

Fig. 2(a) and (b) are the DSC curves of the long time aged sample A further annealed at 30°C in a humid atmosphere and liquid water for different time periods respectively. The endothermic peak near T_g shows dramatic changes with annealing time. The peak changes from a single peak into a broad one with a shoulder. The endothermic peak of sample A annealed in liquid water becomes broader than that in the humid atmosphere.

The double peaks in Fig. 2(a) and (b), taken as T_U and T_L with some arbitrariness corresponding to the upper and

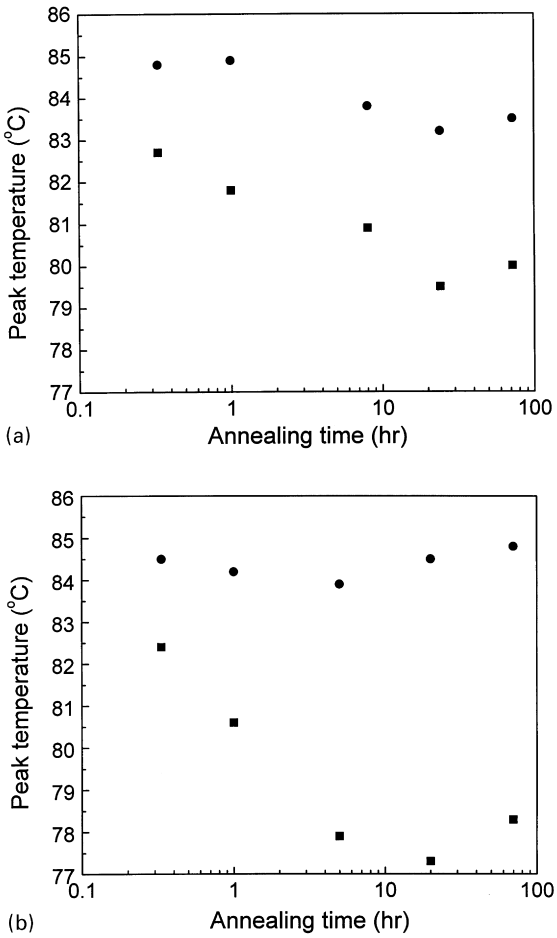

Fig. 3. Change of T_U and T_L during further annealing of sample A: (a) in a humid atmosphere; (b) in water. ●, T_U-the upper one of the double peaks, ■, T_L-the lower one of the double peaks.

lower temperature peaks respectively, as a function of annealing time, are shown in Fig. 3(a) and (b). T_L decreases with annealing time. However, T_U decreases a little with the annealing time.

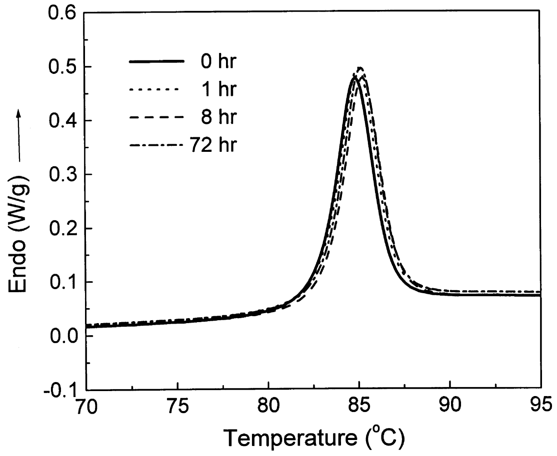

Fig. 4. The DSC. curve of sample A further annealed in a desiccator for different times at 30°C.

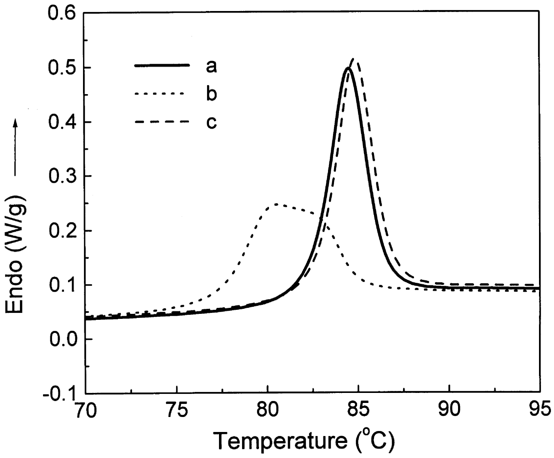

Fig. 5. The DSC curve of sample A with different annealing histories: (a) original sample A; (b) sample A annealed in a humid atmosphere for 72 h at 30°C; (c) sample A annealed in a humid atmosphere for 72 h, then further annealed in a desiccator for 24 h at 30°C.

Fig. 4 is the DSC curve of sample A further annealed at 30°C in the desiccator for different annealing times. No significant changes in the shape of the endothermic peak near T_g are observed with increasing annealing time.

After annealing in the humid atmosphere for 72 h, sample A was taken out and placed in the desiccator for 24 h and then brought out immediately for DSC measurement. The broad endothermic peak owing to water absorption changes back into the original shape and position as shown in Fig. 5. This result indicated that the effect of water absorption on the structure of amorphous PET was a reversible process. Therefore, hydrolytic degradation or other possible chemical changes were not involved in the process of annealing the sample in the humid atmosphere, only physical process in the amorphous region was related to the change of the endothermic peak in the DSC curve.

It is very interesting to note that several authors also found two endothermic peaks near PET's T_g during the physical ageing process in recent years. Itoyama [12] proposed a model of three different modes of structural rearrangement during physical ageing of amorphous PET to explain the two endothermic peaks near T_g in the DSC curve. Montserrat and Cortes [13] found similar double peaks while investigating physical ageing of semi-crystalline PET. Boyer [18,19] proposed a double T_g model resulting from the certain crystallinity of the polymer. All the above researchers attribute the double peaks to the two different structures in the amorphous region of PET.

The existence of double peaks in the DSC curve was probably corresponded to the two different intermolecular interactions respectively, i.e. the upper peak resulted from the interaction between the chains of amorphous PET, the lower one was due to the interaction between H_2O and the chain of amorphous PET. It has been suggested [14–16] that some ordered structure formed due to the interaction between the chain during physical ageing, thus H_2O was more prone to enter the rest region within the sample when the annealed sample was further annealed in a humid atmosphere. The T_U did not change much is in accordance with this interpretation.

The enthalpy relaxation of amorphous PET stored at room temperature is very slow. Short time storage does not have an appreciable effect on the enthalpy relaxation of the sample, but this does not mean that effect of storage could be neglected. In the author's opinion, the amorphous PET sample should be isolated from humidity in the annealing experiments and storing process while investigating the various properties of amorphous PET.

Acknowledgements

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