

EFFECT OF EXCESS ENTHALPY RELAXATION ON PERMEATION OF CO₂ AND TOLUENE THROUGH PET FILM*

KE Yucai (柯毓才)

(Institute of Chemistry, Academia Sinica, Beijing)

Bischoff Manfred

(Institute of Plastic Testing, University Stuttgart, West Germany)

ABSTRACT

Structural change in an unoriented, amorphous PET film annealed at temperatures below T_g and the effect of excess enthalpy relaxation on permeation rates of CO₂ gas and toluene liquid in treated samples have been studied. The results suggest that the amount of excess enthalpy relaxation as determined from the endothermic peak in T_g interval, the T_g and density all increase with annealing time, but the trans-conformation component of samples decreases. No change of structure in the amorphous phase was found other than the normal densification of the molecular chain packing or a reduction in free volume had occurred during the annealing regimes. Therefore, the permeation rate of CO₂ gas in treated samples reduced. While the apparent permeation rate of toluene liquid increased with annealing time because of a creation of extensive cracks at film surface arising from both the increase in embrittlement of polymer and the swelling action of toluene liquid on treated samples.

INTRODUCTION

The transport of small molecules in crystalline polymer annealed at temperatures above T_g has been studied^[1,2]. It was found that the transport rates were higher for annealing samples than for unannealing ones. It was interpreted by assuming that the heat treatment caused a loosening structure of polymer chains in noncrystalline region, because the shorter interlamellar tie molecules would be either pulled out of the lattice or broken during annealing process.

It has long been recognized that glassy materials obtained under quenching conditions from above T_g are thermodynamically unstable^[3-5]. When these materials are stored or annealed below T_g (sub- T_g annealing), they would gradually approach to the equilibrium glassy state resulting from the slowly relaxation of molecular chains. The nonequilibrium state of these materials is characterized by excess thermodynamic properties, such as excess enthalpy or excess volume, relative to those of equilibrium glassy state. The process of a slow approach to equilibrium causes a reduction in excess free volume trapped in the glassy state during annealing and increase in densification of the molecular packing which, in turn, change dramatically the physical and mechanical properties of the materials. With shift toward an equilibrium state, the tensile strength, T_g and density of annealed samples increase, while the

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materials become stiffer and more brittle.

Little is known about the effect of excess thermodynamic properties on transport process of small molecules in glassy polymers. This study was undertaken, therefore, to investigate the structural changes in an unoriented, amorphous PET film annealed at 58.5°C (below T_g) and the effect of excess enthalpy relaxation on permeation rates of CO₂ gas and toluene liquid in treated samples.

EXPERIMENTAL

The PET film used in this study were provided by Kaile AG Co. They were essentially unoriented, amorphous samples verified by density and birefringence measurements. The thickness was $140 \pm 10 \mu$. They were not heated at a temperature slightly above T_g prior to the annealing experiment. Toluene liquid used as a penetrant was reagent grade and not further purified but dried before use.

The permeation rate in the system was detected by gas-chromatographic method^[7]. The schematic diagram of measuring cell was shown in Figure 1. A hydrogenation apparatus

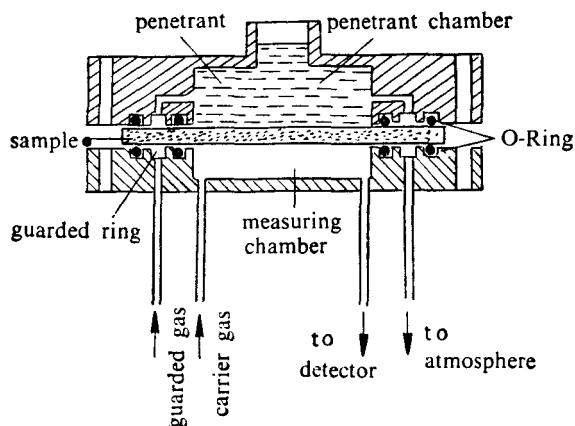


Fig. 1 Schematic diagram of measuring cell

must be connected between permeation measuring cell and FID for monitoring CO₂ gas. The CO₂ gas is reduced in the hydrogenation apparatus with hydrogen: $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$. The film sample was clamped between in the measuring cell, which was consisted of upstream penetrant chamber and downstream measuring chamber. Pour the penetrant into the upstream chamber and pass a carrier gas helium through the downstream chamber to FID of a detector. As the penetrant permeates through out the film, it is carried by the gas flowing to the detector. The resulting signal $S(t)$, which is monitored by a chart recorder and is proportional to the flux of the penetrant, gradually increases to a steady-state value S_p . The flux of carrier gas is maintained about 30 ml/min in this experiment.

The permeation rate, P , can be calculated by^[7]

$$P = J_s \quad l = \frac{1}{e} \frac{1}{A_m} K_p S_p$$

where J is the flow rate of penetrant through unit area of the film. J_s is the value at which a steady state is arrived, e is the calibrated factor of the detector to the concentration of penetrant, the attenuation of gas-chromatographic instrument is K_p , the thickness of the film is l in cm. A_m is the area of film in cm^2 . For calculation of permeability coefficient of gas-polymer system, the pressure difference of gas between upstream and downstream should be taken into account in above formula.

The permeation measurement temperatures were 45°C, 50°C and 55°C for permeation experiment of toluene in the film, 30°C for CO_2 . The precision of temperature measurement was $\pm 0.1^\circ\text{C}$.

Calorimetric measurements were made with a DSC Mettler T_A 2000 at a scan speed of $10^\circ\text{C}/\text{min}$. The enthalpies including the excess enthalpy at T_g were determined from the peak area and converted into units of heat energy by reference to a peak obtained from the heat of fusion of indium. The T_g of samples was determined as the point of intersection of the base line with a line tangent to the maximum slope of the endothermic peak.

Using IR spectrometer the trans-conformation component of the annealed samples were measured by the relative intensity of 973 cm^{-1} to 1053 cm^{-1} absorption band.

The densities of the samples were determined by a density-gradient column containing a mixture of calcium nitrate and water at $25 \pm 0.1^\circ\text{C}$. The density of the received sample was 1.3360.

RESULTS AND DISCUSSION

Figure 2 shows the DSC curves of the samples annealed at 58.5°C (The T_g of sample is

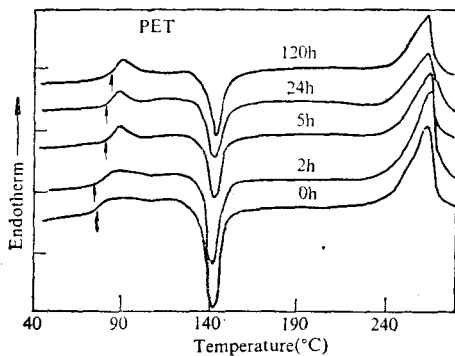


Fig. 2 DSC curves for PET film sample annealed at 58.5°C for varying lengths of annealing time

about 72°C determined by DSC) for varying annealing time. It can be shown that there are no changes in the cold crystallization temperature, T_c , melting point, T_m , as well as their enthalpies as shown in Figure 3. In the thermal studies^[8], using ΔH_m and ΔH_c , there is no evidence of a change in crystallinity with annealing time. The T_g , density and the amount of excess enthalpy relaxation as determined from the endothermic peak in T_g interval all increase rapidly at short annealing time except at the beginning two hours, but begin to level off at about 24 h or still more longer time as shown in Figure 4 and 5. The excess enthalpy value at which the

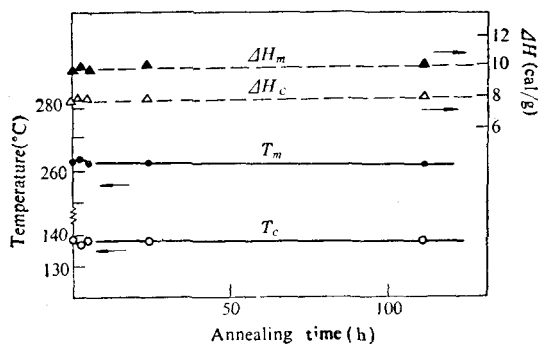


Fig. 3 Changes of T_c , T_m , ΔH_c , ΔH_m with time of heat treatment at 58.5°C

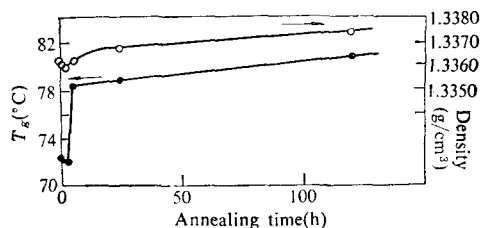


Fig. 4 Changes of T_g , density with time of heat treatment at 58.5°C

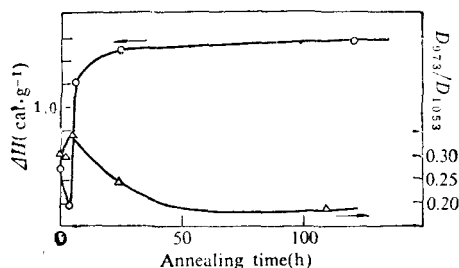


Fig. 5 Changes of enthalpy in T_g interval and of trans-conformation component with time of heat treatment at 58.5°C

equilibrium glassy state was arrived is about 1.60 cal/g. While the trans-conformation component of the samples decreases as shown in Figure 5. Thus that no structure formation associated with the development of crystalline nuclei or local ordered region, as indicated by Ito et al.^[9] earlier, other than the normal densification of the liquidlike packing or a reduction in free volume had occurred during the annealing regimes.

It must be pointed out here that the films used were not heated at a temperature slightly above T_g prior to the annealing experiment to ensure that the samples had initial glassy states. Therefore, they have also undergone sub- T_g annealing during storage at room temperature before annealing at 58.5°C. In other words, they have undergone to a certain extent volumetric recovery. When the annealing temperature raises from room temperature to 58.5°C, the enthalpy value will decrease first as a result of the expansion of whole sample, then increase and approach a limiting asymptotical value that corresponding the excess enthalpy value at

58.5°C.

From the results mentioned above, it can be expected that the permeation rate of small molecules in treated samples will be reduced as a result of densification or a reduction in free volume. Indeed, as illustrated in Figure 6, the permeation rate of CO₂ gas in treated samples

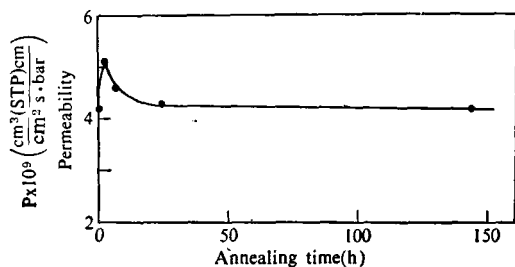


Fig. 6 Permeability of CO₂ in annealed PET film at 30°C with annealing time

reduced with annealing time and approached limiting value in a manner that essentially in parallel with the change in excess enthalpy. Whereas, the apparent permeation rate of toluene liquid increased as shown in Figure 7. Further, the permeation activation energy decreased with annealing time, as shown in Figure 8. It seems to be contrary to those results of excess enthalpy relaxation. Actually, it is not true the case, because of a creation of extensive cracks at film surface after permeation of toluene liquid in treated samples observed, especially for

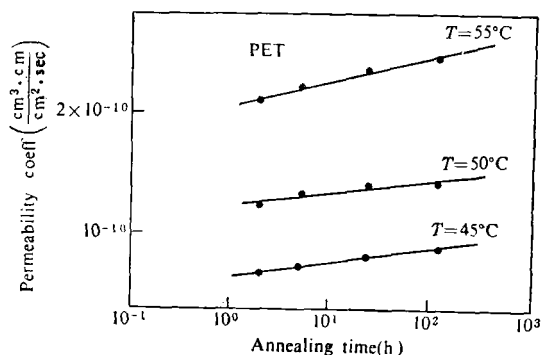


Fig. 7 Permeability of toluene in annealed PET film at 45°C, 50°C and 55°C with annealing time

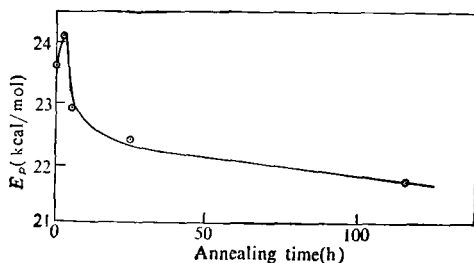


Fig. 8 Permeation activation energy of toluene through PET film samples with time of heat treatment at 58.5°C

the films where the annealing time was extended to 24 h or still more as illustrated in Figure 9.

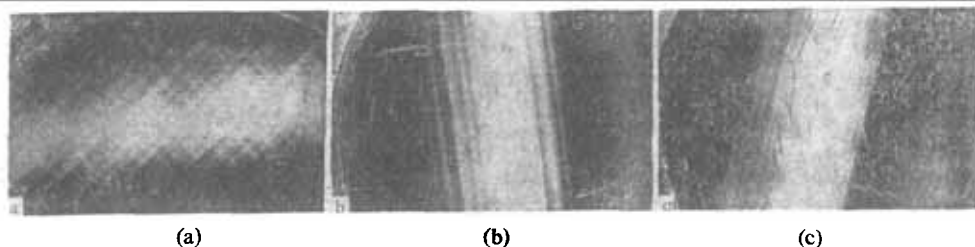


Fig. 9 Photograph of annealed PET films after permeation in toluene at 45°C
(a) annealing time, 0 h; (b) annealing time, 2 h; (c) annealing time, 24 h.

Mininni et al.^[10] have noticed that this polymer changes from a normally tough material to a highly embrittled species upon annealing at 51 °C for 90 min as a result of densification. They also determined the Arrhenius relationship between annealing temperature and the time required to bring about a ductile-to-brittle transition. According to this relationship, the annealing time required to become a highly embrittled species upon annealing at 58.5 °C is about 60 min. On the other hand, when the toluene liquid penetrated into the annealed samples, the film would be swollen and bent toward the toluene liquid. Therefore, at the diffusion advancing front, the swelling tensile stress exerted on inner glassy core and the compression stress on the outer swollen layer during swelling process. With increasing swelling degree of the sample, the swelling tensile stress increases. Consequently, a localized or completed fracture will be created on the film, when the tensile stress (or elongation) exceeds the ultimate strength (or elongation to break) of the glassy core as observations made earlier by Alfrey^[11] on styrene-divinylbenzene-several solvents systems during swelling process. Thus, with longer annealing times, the material becomes stiffer and more brittle, extensive cracks at the film surface will be clearly created during swelling process. In contrast, no cracks were revealed at film where CO₂ gas had penetrated because of the size of CO₂ gas (cross section area 8.19 Å²) and swelling effect much smaller than that of toluene (19.6 Å²).

CONCLUSIONS

From the results mentioned above, no structure formation associated with the development of crystallinity or local ordered region in the amorphous phase was revealed other than the normal densification of the liquidlike packing or a reduction in free volume had occurred upon sub-*T_g* annealing. Since the densification of the liquidlike packing enhanced, the permeation rate of CO₂ gas in treated samples reduced. While the permeation rate of toluene liquid increased with annealing time because of extensive cracks at film surface arising from both the increase in embrittlement of material and the swelling stress action of toluene liquid on treated samples.

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