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The Effect of Volume Reorganization of Amorphous Poly(ethylene Terephthalate) on Thermal Properties

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ABSTRACT

When poly(ethylene terephthalate) was quenched from above T_g and then heated, it exhibited a step increase in thickness in the glass transition region at every rate tested. When the polymer was cooled more slowly than it was heated, a higher T_g and a slightly larger step increase in thickness were observed as the cooling rate was reduced. These experimental results appear to be adequately interpreted on the basis of the normal structural changes that occur in a glass as its thermal history is varied. Two observations, however, were not easily included in this view. First, the polymer, on cooling from above T_g, exhibited an abnormally high expansion coefficient over much of the range of temperature in which it exists as a fluid. Second, the polymer exhibited a step increase in thickness when it was heated at the same rate at which it had previously been cooled.

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INTRODUCTION

At any stage of its existence a polymer carries the imprint of its past. During fabrication into its various forms of fiber, film, etc., the segments of the polymer molecules are frequently "set" through the use of temperature, stress, and solvent in configurations and orientations, and confined to volume elements that are unable to adjust to equilibrium when the polymer is cooled more rapidly to the glassy state than the segments can relax. The polymer thus has a potential for change which may or may not occur at imperceptible rates depending upon the temperature. This capacity for change may be demonstrated by annealing the polymer at temperatures below the glass temperature (T_g). The polymer increases in density and, upon reheating, exhibits endothermal peaks near T_g by differential scanning calorimetry (DSC) and step increases in volume by dynamic volume dilatometry [1, 2]. These results have been interpreted as possibly indicating some first-order character in the glass transition [1-3].

Other authors [4-6] conclude that the absorption of thermal energy can be accounted for on the basis of the kinetics of the glass transformation, so that only the normal structural changes that accompany the approach to the equilibrium glassy state need be postulated. The excess enthalpy and volume trapped on cooling are held to be responsible for the subsequent behavior. Petrie [5] points out that the amount of energy absorbed is a function not only of the extent of enthalpy relaxation that occurs during the period of annealing and of the higher T_g which results from the relaxation, but also of the rate of testing. The energy absorbed thus depends on the temperature and time of annealing, and on the rate of heating during the thermal scan as well.

In the present study, most of the volume changes that may be made to occur with poly(ethylene terephthalate) in the vicinity of its glass transition by varying its thermal history appear to be satisfactorily interpretable on the basis of this latter hypothesis.

EXPERIMENTAL

Amorphous poly(ethylene terephthalate) (PET) was melt-extruded film, 50 mil (1.34 mm) in thickness, and was reported to have an intrinsic viscosity of 0.57 in phenol-tetrachloroethane at 30°C and a carboxyl end-group content of 35 meq/kg. Examination of the film between crossed polars revealed only slight orientation. The density of the as-received sample in a gradient column of sodium bromide solution was 1.3374 g/ml.

Thermal analysis was carried out by means of the Perkin-Elmer

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Model TMS-1 Thermomechanical Analyzer (TMA) and the Perkin Elmer Model 1-B Differential Scanning Calorimeter (DSC). When the TMA was used, the reading of the thermocouple indicating sample temperature was recorded directly. The glass transition temperatures were corrected for thermal lag. The change in film thickness with temperature was detected by TMA. Volume changes with temperature were followed by the volume dilatometer, the construction and operation of which have been described in detail by Bekkedahl [7].

RESULTS AND DISCUSSION

A representation of a typical thermogram obtained on the TMA with PET film is shown in Fig. 1. Region a represents the glassy state; Region b represents the step increase in thickness that is observed once T_g is exceeded; Region c represents the thermal expansion path followed by the fluid. T_g is taken as the intersection of the tangent lines to a and b. A measure of the jump in thickness may be obtained from the vertical distance between this intersection and the intersection obtained from tangent lines to b and c.

The as-received sample film expanded along the path indicated by Fig. 1. In the glassy Region a, the polymer had the normal linear expansion coefficient of $0.77 \times 10^{-4}/°C$. The step increase in thickness (Region b) varied somewhat from one sample to another, between 1 and 3% of the original thickness. Most of this increase is believed to be due to a slight orientation put into the film at the time of fabrication. Once the as-received sample has undergone this step increase, it is taken to be completely isotropic. In this case the relationship between linear and volume expansion coefficients is given by $3\alpha_l = \alpha_V$, where α_l is the linear expansion coefficient and α_V is the volume expansion coefficient. When the sample was again heated in the TMA, a step increase

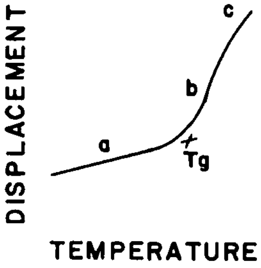

FIG. 1.

in thickness was again seen, but the increase amounted only to 0.2 to 0.4% of the sample thickness. This increase has its origin in the conditions of testing that obtain after the original orientation has been removed. In the work to be discussed below, the necessity for considering the prior history of the sample was eliminated by subjecting the sample to a heat treatment at 90°C. At higher temperatures the sample may undergo a significant degree of crystallization.

The linear expansion coefficient of the polymer in Region c (Fig. 1) was difficult to measure accurately because only a limited interval of temperature is available before the rate of crystallization becomes appreciable. A value of $4.9 \times 10^{-4}/°C$ for a heating rate of 20°C/min was estimated, which is much larger than the value of $1.7 \times 10^{-4}/°C$ that is characteristic of the isotropic fluid. It appears that under the conditions of the test, i.e., in this case a temperature rise of 20°C/min, the sample was unable to reach the equilibrium fluid state, and was therefore expanding at a much greater rate than it would if the expansion were between two states in thermal equilibrium.

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Thermal Behavior of the Quenched Sample

When the sample was quenched from 90°C to below T_g and reheated in the TMA at different programming rates, the step increase of Region b was again observed at each rate.

The step increase in thickness appeared to vary somewhat with programming rate, but the procedure for determining the increase was not sufficiently precise to allow the values at the various rates to

TABLE 1. Expansion Behavior of Quenched PET

Rate of heating (°C/min)	T_g (°C)	Expansion coefficient × 10^4	
		Below T_g $(°C)^{-1}$	Above T_g $(°C)^{-1}$
40	91	0.70	-
20	88	0.69	-
10	83	0.77	-
5	78	0.79	-
2.5	77	0.77	-
1.25	76	0.74	-
Volume dilatometer $(\alpha_l = \frac{1}{3}\alpha_v)$	67	0.77	1.7

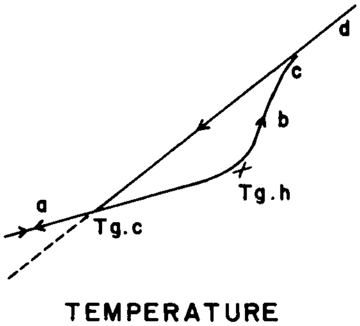

FIG. 2.

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be accurately differentiated. As indicated by Table 1, T_g increased with the rate of the test, as expected [5], and the expansion coefficient in the glassy region was approximately the same at all rates. The experimental results may be interpreted with the help of the hypothetical thermogram of Fig. 2. On cooling, the fluid is transformed to the glass at $T_{g.c}$. Subsequently, when the glass is heated at a particular rate, it is converted to the fluid at $T_{g.h}$. The higher the rate of temperature rise, the greater $T_{g.h}$. T_g may be defined as the temperature at which the response time of the molecular segments equals the time interval of the test. An increase in rate of temperature rise reduces the interval of the test. It therefore becomes necessary to reach a higher temperature, i.e., $T_{g.h}$, with each increase in rate of temperature rise in order to reduce the response time of the segments sufficiently to achieve equality with the time interval of the test.

Thus in Region b the polymer, now existing as a fluid, expands, as rapidly as segmental relaxation times permit, to equilibrium thickness. The rate of expansion drops off somewhat in Region c and approaches asymtotically the equilibrium rate of the fluid.

One would expect that if the sample were heated at an extremely slow rate, so that the polymer could approach the equilibrium free volume at each temperature more closely than was permitted by any of the rates for which a step increase in thickness was observed, the sample would not exhibit the step increase and would have a much lower T_g than was observed at the higher rates. This procedure was followed by volume dilatometry on the as-received sample. In the TMA the sample exhibited the behavior pictured by Fig. 1. In the volume dilatometer, with the temperature being adjusted for each point in the transition region at a rate not exceeding 0.1°C/min, the volume exhibited no discontinuity, T_g had the low value of 67°C, and the volume expansion coefficients in the glassy and fluid regions had the normal values of $2.3 \times 10^{-4}/°C$ and $5.3 \times 10^{-4}/°C$, respectively.

It should be pointed out that the step change in thickness of the as-received sample near T_g, which was earlier attributed to a slight orientation, was not observed as a volume change in the volume dilatometer because, as has been shown previously [8], a dimensional increase in the direction perpendicular to the plane of orientation is compensated by decreases parallel to the plane.

Expansion Behavior for Equal Cooling and Heating Rates

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It may be expected [4] that if the polymer fluid were first cooled at a particular rate, the polymer would lie at the same distance from equilibrium at each temperature during the descending and ascending parts of the cycle. In this case the polymer should exhibit neither endotherms nor step increases in thickness when first cooled and then heated at the same rates. This expectation, however, does not appear to be borne out experimentally. Thus for temperature regimes ranging from 40 to 1.25°C/min (cooling rate = heating rate), the PET sample exhibited during the heating part of the cycle not only step increases in thickness on the TMA (Fig. 1) but also endotherms on the DSC (Fig. 3). This result suggests that the polymer undergoes hysteresis between cooling and heating although the cooling and heating rates are equal, i.e., T_g on cooling ($T_{g.c}$) is less than T_g on heating ($T_{g.h}$) for each rate tested. Such an effect, if it were real, would mean that the mobility of the molecular segments at equal temperatures within the range from $T_{g.c}$ to $T_{g.h}$ is different during the descending and ascending legs of the cycle. Although the authors are unaware of any theoretical basis for such an effect, the possibility was tested by subjecting the polymer fluid to consecutive stages of cooling and heating. A representation of the type of thermogram obtained is presented in Fig. 4, which is interpreted in the following way. The polymer exists as the fluid above T_g. During the initial cooling, Region e is observed, in which the linear expansion coefficient appears to be much greater than the accepted value of $1.7 \times 10^{-4}/°C$. The explanation for this apparent step change, which is qualitatively similar to that observed on heating, is not known. Region d represents the interval of temperature over which the expansion coefficient corresponds approximately to the accepted value of the fluid. This interval was rather small when the test rate was 5°C/min or higher, but became larger as the test rate was lowered.

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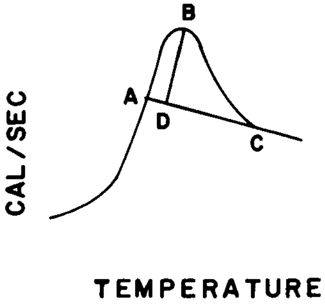

FIG. 3.

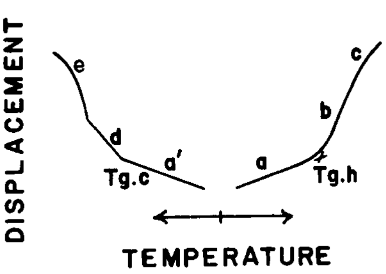

FIG. 4.

The experimental results are given in Table 2. The difference between $T_{g.c}$ and $T_{g.h}$ is appreciable at each of the rates cited. However, both $T_{g.c}$ and $T_{g.h}$ are expected to vary with rate: $T_{g.h}$ changes with rate whereas $T_{g.c}$ does not. It is conceivable, given the original premise, that the mobility of the polymer during cooling is sufficient at each of the rates employed to allow a close approach to equilibrium so that $T_{g.c}$ does not change significantly with rate in this range. However, the rate of change of $T_{g.h}$ with decreasing heating rate is so small as to make it uncertain that $T_{g.h}$ would extrapolate to the $T_{g.c}$ value of 69° C at a very low heating rate. Some doubt must exist, therefore, as to whether $T_{g.c}$ and $T_{g.h}$ may be compared when they are determined by the procedures that have been outlined.

TABLE 2. Expansion Behavior of PET Subjected to Equal Cooling and Heating Rates

Rate	$\alpha_1 \times 10^4$ (°C)$^{-1}$				
(°C/min)	Region d	Region a'	Region a	$T_{g.c}$ (°C)	$T_{g.h}$ (°C)
5	1.9	0.80	0.75	69	78
2.5	1.6	0.74	0.74	69	77
1.25	1.8	0.73	0.73	69	76

Expansion Behavior for Cooling Rate Less Than Heating Rate

The amount of free volume entrapped in a polymer decreases as the cooling rate decreases (4, 5). Therefore, the T_g observed at a given heating rate should increase for a polymer that is first subjected to successively lower cooling rates from above T_g. According to Fig. 2, the glassy Region a would intersect the equilibrium fluid line d at successively lower temperatures ($T_{g.c}$) as the cooling rate is reduced. The glass temperature observed during heating at the given rate ($T_{g.h}$) would then be raised by an amount sufficient to correspond with the reduction in free volume produced by the particular, prior cooling rate. Thus slow cooling produces glass with a higher density, which, for the given heating rate, would exhibit a higher T_g. One sees from Fig. 2 that this combination of higher density and higher T_g would, for the given heating rate, tend to make the step change in thickness somewhat greater.

A study was carried out in which prior cooling rates of 1.25 and 20°C/min were used with a heating rate of 20°C/min to above T_g. $T_{g.h}$ was about 2°C higher for the case in which the prior cooling rate was 1.25°C/min. Also the step increase in Region b (Fig. 1) was somewhat greater with the lower cooling rate; 0.39% compared to 0.27% based on the original thickness.

This same experiment was repeated on the DSC, using a 15-mg sample of PET. The results are given in Table 3.

The thermogram of Fig. 3 indicates the procedure used for the measurements: BD represents peak height, and ABC represents the area used in calculating the energy of the transition. The densities were obtained by the gradient method using sodium bromide solution

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TABLE 3. Effect of Cooling Rate on Thermal Properties of PET; Heating Rate of 20° C/min

Prior cooling rate (°C/min)	Density at 30°C (g/ml)	T_g (°C)	Peak height (mm)	Energy (mcal)
1.25	1.3372	75.3	35	4.65
20	1.3364	73.3	8	0.75

on replicate samples immediately after they were cooled at the prescribed rate.

The greater loss of free volume by the slow-cooled sample is shown by its greater density. The size of its endotherm relative to that of the fast-cooled sample (4.65 mcal compared to 0.75 mcal) is more pronounced than the difference in step change in thickness obtained on the TMA.

It is also possible, by first annealing the polymer below T_g, to produce the same effect as by slow cooling [1, 4, 5]. The greater the time of annealing at a particular temperature (or for a given time of annealing the higher the temperature of annealing), the larger the endotherm. The time and temperature of annealing were observed to have this same effect on the step change in thickness that occurs in the glass transition region. These experimental results may be explained on the basis of the molecular relaxation that occurs as a result of the annealing [5].

SUMMARY

The polymer, when quenched from above T_g and heated, exhibited a step increase in thickness in the glass transition region at every rate tested, presumably because the relaxation rate of the segments did not allow the expansion path of the equilibrium fluid to be followed. At the slow rate of temperature adjustment that was used in the volume dilatometer, no step increase in volume was observed. When the polymer fluid was cooled and then heated at the same rate, an endotherm on the DSC and a step increase in thickness on the TMA were observed. The explanation for this behavior is not known, but it is suggested that the polymer in a dynamic test may undergo hysteresis between cooling and heating. When the polymer was cooled more slowly than it was heated, a higher T_g and a slightly larger step increase in thickness were observed as cooling rate was reduced. This result was attributed to

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smaller amounts of free volume being entrapped in the polymer at the lower cooling rates.

Most of the experimental results appear to be adequately interpreted on the basis of the normal structural changes that occur in a glass as its thermal history is varied. Two observations, however, were not easily included in this view. First, the polymer, on cooling from above T_g, exhibited an abnormally high expansion coefficient over much of the range of temperature in which it exists as a fluid. Second, the polymer exhibited a step increase in thickness when it was heated at the same rate at which it had previously been cooled.

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