Factors Affecting the Strength of a Polyhydroxy Ether

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Synopsis

The effects of moisture content, aging, annealing, irradiation, temperature, and rate of testing on the tensile yield strength of the polyhydroxy ether derived from bisphenol A and epichlorohydrin are described and discussed. In particular, annealing at temperatures below T_g is shown to cause significant increases in strength which are associated with an endothermal process in the glass transition region having an activation energy of 32.8 kcal./mole. The nature of this process and its occurrence in other polymers is discussed. Annealed and unannealed specimens are shown to obey the previously proposed empirical relationship, $1/\sigma = a + m \log t$, where σ is the tensile yield strength, t is the time to yield. The values of the constants a and m have been derived.

INTRODUCTION

We have recently[1] shown that irradiation of the polyhydroxy ether derived from bisphenol A and epichlorohydrin reduces the molecular weight leading to a decrease in tensile yield strength. As other factors also affect tensile yield strength, it was of interest to compare their effects on both irradiated and unirradiated polymer. The present paper describes a study of the influence of moisture content, aging, heat treatment, and temperature and rate of testing on the strength of polyhydroxy ether. Most significantly, annealing in the temperature range 40–80°C. is shown to increase the strength by up to 35%. This effect, which is similar to that previously observed for polycarbonate[2] has been related to concurrent changes in the thermogram of the polymer.

EXPERIMENTAL

Specimens

Dumbbells, of a type previously described,[3] were injection-molded from phenoxy resin (Bakelite FRDA 8060, bisphenol A polyhydroxy ether) at a mold temperature of 60°C. and dwell time of 25 sec.

Post-Treatment

Drying. Specimens were dried in an evacuated desiccator over phosphorus pentoxide (P_2O_5) at room temperature.

Aging and Moisture Absorption. Specimens were kept at $20 \mp 1°C$. and $70 \mp 2\%$ R.H.

Annealing. Specimens were heated at a fixed temperature ($\mp 0.5°C$.), either in vacuum or in air, for specified periods and then cooled rapidly to room temperature.

Irradiation. Specimens were irradiated in an evacuated chamber (10^{-3} mm.) at a dose rate of 1 Mrad/min. to doses up to 100 Mrads.

Test Methods

Tensile Measurements. The term strength as used in this paper refers to tensile yield strength or breaking strength in the absence of yield. This was measured at $20 \pm 1°C$., except where otherwise stated, immediately after the specified treatment at crosshead speeds within the range 10^{-1}–10^4 in./min. by using equipment previously described.[4,5] Results quoted are the average of not less than three replicates.

Differential Scanning Calorimetry. A Perkin-Elmer differential scanning calorimeter, DSC-1, was used. Specimens, approximately 20 mg., were cut from tensile dumbbells, weighed accurately and heated at $16°C./$ min. in an atmosphere of dry nitrogen. No difference in thermogram was observed between specimens with and without the equilibrium moisture content. Under the conditions outlined T_g was determined as 89–$90°C$.; Reinking et al.[6] quote $100°C$. from resiliency measurements. Annealed specimens exhibited an endotherm in the region of T_g. For each annealed specimen the energy change involved in the endotherm was calculated[7] from the difference in area between the thermogram of the specimen and that of the same specimen rerun after cooling at $16°C./$min. from $120°C$. The activation energy associated with the endotherm (E_1) was determined by calculating[8] the activation energy ($E_1 + E_2$) of the peak in the thermogram of the annealed specimen and that (E_2) of the glass transition in the thermogram of the same specimen rerun after quenching.

RESULTS AND DISCUSSION

It was found that all the factors examined, water content, aging, annealing, temperature, and rate of testing, and radiation dose affected the strength of polyhydroxyether specimens. For convenience their effects will be considered separately.

Water Content

The changes in weight of specimens during 18 months after molding are shown in Figure 1. Drying over phosphorus pentoxide in vacuum removed traces of water remaining after molding whereas exposure to 70% R.H. resulted in absorption of about 1% of water before equilibrium was attained. Figure 2 shows the strength at various rates of testing of specimens tested after 18 months under the above conditions. Assuming that aging for 18 months did not affect "dry" and "wet" specimens differently, it is apparent
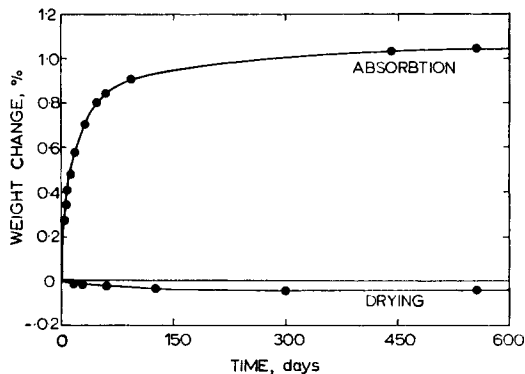
Fig. 1. Changes in weight of specimens after molding: (upper curve) specimens kept at 20°C., 70% R.H.; (lower curve) specimens kept at 20°C. in vacuum over P_2O_5.
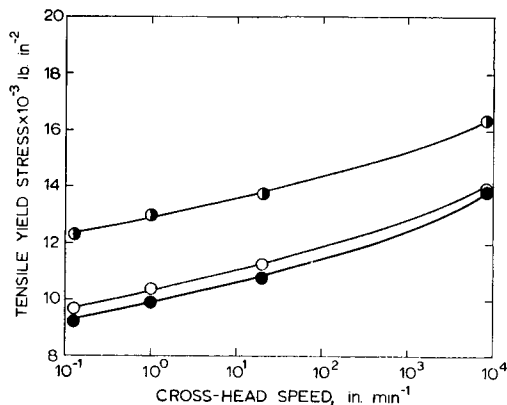

Fig. 2. Tensile yield stress vs. crosshead speed of specimens: (●) after 18 months at 20°C., 70% R.H.; (O) after 18 months in vacuum over P_2O_5; (◐) after 18 months at 20°C.; 70% R.H., followed by 68 hr. at 76°C.

that the presence of water reduced the strength by about 400 lb./in.² This suggests that the absorbed water reduces the intermolecular attraction of the polymer chains and thus acts as a plasticizer.

Aging

The strengths of unirradiated and irradiated specimens aged for 2 or 30 months before testing are shown in Figure 3.

Unirradiated specimens exhibit an increase of nearly 800 lb./in.² consequent upon the further aging while the effect on irradiated specimens increases with dose to 1550 lb./in.² at a dose of 100 Mrad. Although the specimens examined after 2 months had a different moisture content from those examined after 30 months (Fig. 1), it is apparent from Figure 2 that if they had had identical moisture contents the difference in strength due to aging would in fact be greater. It is probable that the observed ag-
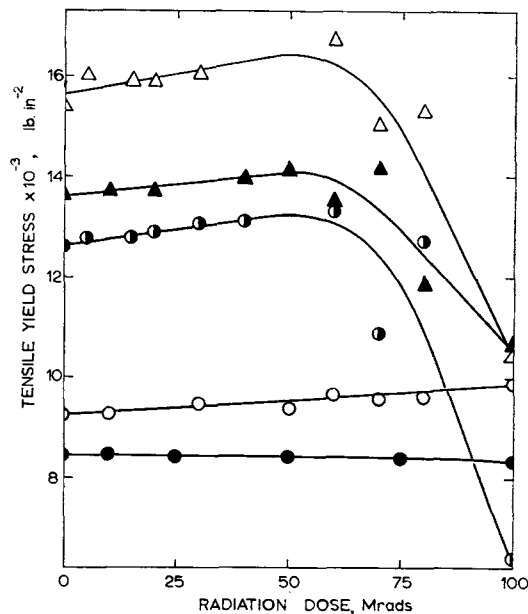
Fig. 3. Tensile yield stress of irradiated specimens tested: (●) at 0.1 in./min. after 2 months at 20°C., 70% R.H.; (O) at 0.1 in./min. after 30 months at 20°C., 70% R.H.; (◑) at 0.1 in./min. after 30 months at 20°C., 70% R.H., followed by 144 hr. at 76°C. in vacuum; (▲) at 8500 in./min. after 30 months at 20°C., 70% R.H.; (△) at 8500 in./min. after 30 months at 20°C., 70% R.H., followed by 144 hr. at 76°C. in vacuum.

ing effect is a manifestation of the annealing process, discussed below, which occurs more rapidly at elevated temperatures.

Annealing

The strength of specimens annealed at 76°C. initially increased rapidly but approached a limiting value after about 150 hr. (Fig. 4). The curve in Figure 4 is a plot of the empirical relationship

$$\sigma - \sigma_0 = [t/(2.87t + 22.4)] \times 10^4 \text{ lb./in.}^2$$

where σ_0 is the strength before annealing and σ is the strength after t hours at 76°C. From this equation annealing at 76°C. can lead to a maximum increase in strength of about 35%.

To determine the effect of temperature a series of specimens were annealed either in vacuum or in air at temperatures within the range 45–95°C. for 24 hr. From the isochronal plot (Fig. 5) it can be seen that the increase in strength after 24 hr. reached a maximum at 75–80°C. and thereafter fell. No difference in strength was observed between specimens annealed in air or in vacuum.

The pattern of strength changes caused by annealing is similar to that observed for polycarbonate.[2] Thus in both cases the strength increased
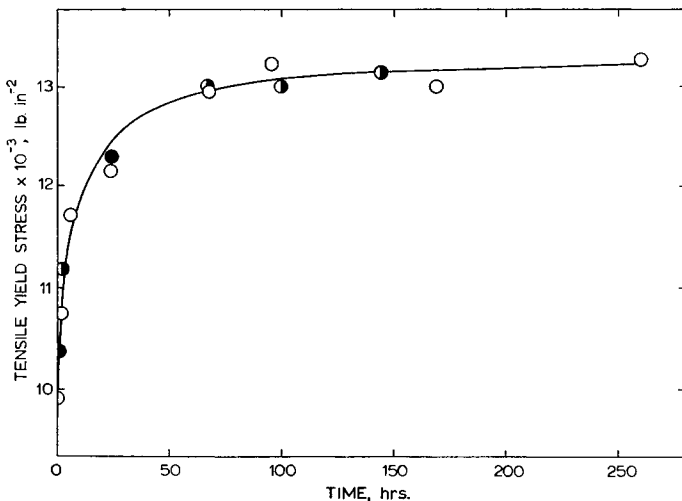
Fig. 4. Tensile yield stress of specimens vs. time of annealing at 76°C.: (◑) in air; (◐) in vacuum. Tested at 1 in./min.
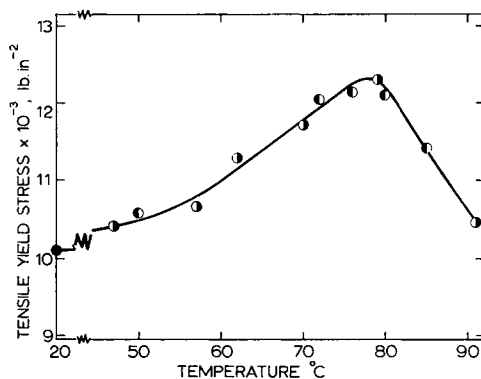

Fig. 5. Tensile yield stress vs. temperature for specimens annealed at a fixed temperature for 24 hr.; tested at 1 in./min.

with time to a limiting value; the latter increased with temperature to a maximum (polyhydroxy ether, 75–80°C.; polycarbonate, 130–135°C.) and thereafter fell. The subsequent decrease is due to the influence of the glass transition (polyhydroxy ether, 89–90°C.; polycarbonate, 142°C.) and in polyhydroxyether was accompanied by a reduction in length and increase in cross-sectional area of the specimen as molding stresses were relieved. The increased strength of both polymers was accompanied by small decreases in extension and energy to yield. The similarity in behavior suggests that, as for polycarbonate,[2] the relatively rapid cooling, which occurs during molding, freezes the polymer chains into position. When heated, some local motion of the polymer chains becomes possible, and they move into preferred, and presumably more ordered, positions
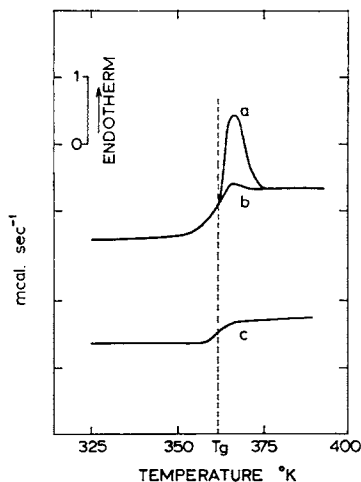
Fig. 6. Thermograms of polyhydroxyether: (*a*) after annealing at 76°C. for 56 hr.; (*b*) specimen from (*a*) re-run after rapid cooling; (*c*) before annealing.
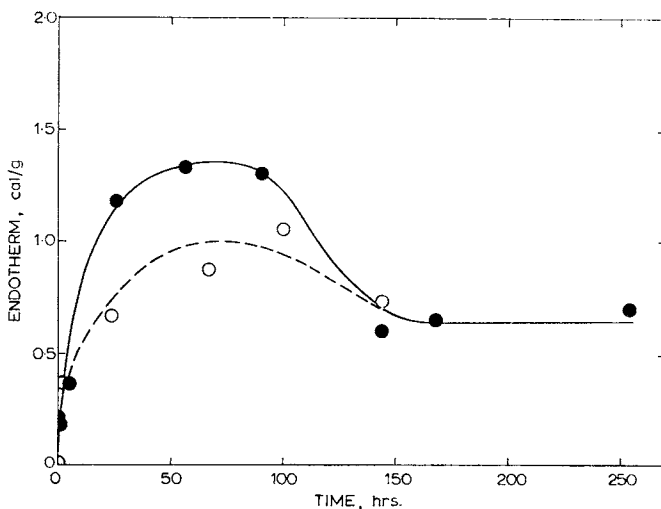

Fig. 7. Endotherm at 93–94°C. vs. time of annealing at 76°C. for specimens: (●) unirradiated; (○) irradiated (40 Mrads).

producing an increase in strength of the specimen.   At temperatures above 80°C. this ordering enters into competition with the disordering effect caused by free rotation of the polymer chains at the glass transition and consequently the strength of the specimens decreases.

Examination of annealed and unannealed specimens by differential scanning calorimetry revealed no differences in the thermogram at temperatures below T_g.   However, annealing produced an endotherm in the thermogram at 93–94°C. which disappeared when the specimen was heated at 16°C./min. to 120°C., cooled at 16°C./min., and re-examined at a

heating rate of 16°C./min. (Fig. 6); when cooled at 1°C. min. over the region 120–80°C. an endotherm was again observed when the specimen was re-examined, at a heating rate of 16°C./min. although it was reduced in magnitude. The endotherm increased to a maximum with time of annealing at 76°C. and then decreased to a steady value, approximately 0.65 cal./g., after 150 hr. (Fig. 7). Despite the change in magnitude of the endotherm its activation energy remained constant though some scatter of results was associated with short times of heating. A mean activation energy for the endothermal process of 32.8 kcal/mole was obtained (Table I).

TABLE I
Mean Activation Energies Obtained from Thermograms

	Activation energy, kcal./mole	
	Unirradiated specimens	Irradiated specimens
Endotherm + glass transition ($E_1 + E_2$)	90.4	84.9
Glass transition (E_2)	57.6	54.3
Endotherm (E_1)	32.8	30.6

An examination of irradiated (40 Mrads) specimens revealed identical behavior (Fig. 7) apart from a reduction in the maximum value attained by the endotherm. The measured value of the activation energy of the endotherm (Table I) was slightly less than that of the unirradiated specimens. The lower values of both E_1 and E_2 for irradiated specimens may be associated with the lower molecular weight of the irradiated specimens.

It is apparent that the appearance of the endotherm is associated with the increase in strength and that the magnitude of both changes is essentially constant after the same period of heating. The occurrence of a maximum in Figure 7 and the absence of a maximum in Figure 4 suggests, however, that the relationship between the two effects may be complex. However, the endotherm can reasonably be associated with the proposed reordering of the structure within the amorphous region.

An examination of polycarbonate by differential scanning calorimetry has revealed[9] that annealing produces a similar endotherm in the glass transition region. Similar behavior in poly(vinyl chloride) homopolymer and acetate copolymer has been attributed[10] to an alignment of stereoregular chain segments of adjacent polymer molecules. For the homopolymer this orientation process had an activation energy of 47.8 kcal./mole. Related phenomena in the glass transition regions of poly(methyl acrylate), poly(methyl methacrylate), and polystyrene have been interpreted[11] in terms of the excess free volume, frozen in when a polymer is quenched to below the glass transition temperature, which is then slowly released during prolonged annealing.

It is probable that the observed behavior is general for predominantly amorphous polymers with substituent groups. When such a polymer is cooled rapidly to well below its glass transition temperature, substituents can hinder attainment of the preferred equilibrium orientations. Annealing just below the glass transition temperature causes a decrease in free volume which will lead to some local rearrangement. The increased strength can then be associated with a more favorable orientation attained by this means.

Temperature and Rate of Testing

The temperature at which strength measurements are made has a pronounced effect on the strength of the polyhydroxyether. Figure 8 illustrates the variation with temperature of the strength of unannealed specimens tested at 1 in./min.

The effect on the strength of increasing the rate of testing is shown in Figures 2, 3, and 9. For unirradiated specimens an increase in cross-
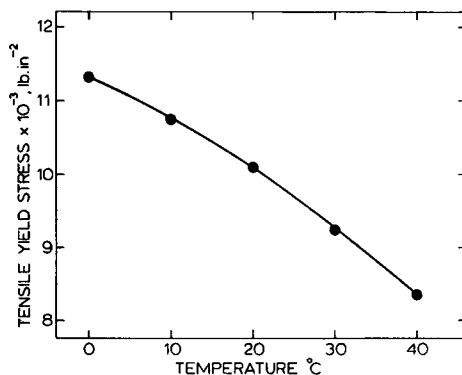

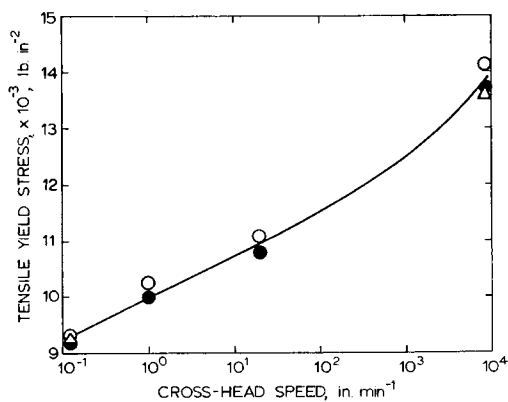Fig. 8. Tensile yield stress vs. temperature of test at 1 in./min.

Fig. 9. Tensile yield stress vs. crosshead speed of test for specimens stored at 20°C., 70% R.H. for 30 months: ($\triangle$) unirradiated; ($\bullet$) previously irradiated (10 Mrads); (O) previously irradiated (50 Mrads).

head speed from 1.25×10^{-1} to 8.5×10^3 in./min. increased the strength by approximately 4000 lb./in.,[11] and failures remained ductile.   In the case of irradiated specimens (Fig. 9) an increase in speed from 1.25×10^{-1} to 8.5×10^3 in./min. led initially to a comparable increase in strength but with radiation doses above 50 Mrads the increased speed led to brittle failures and decreased strength although the latter remained greater than the low speed strength.   This embrittlement of specimens was also observed at low rate of testing after heat treatment of irradiated specimens (Fig. 3).
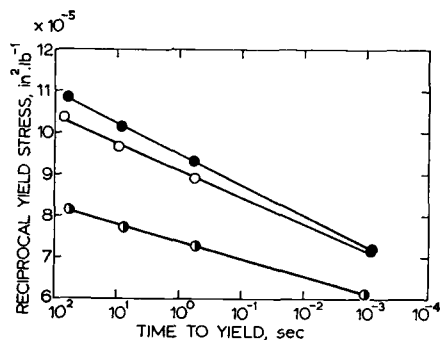

Fig. 10. Reciprocal tensile yield stress vs. time to yield for specimens: (●) after 18 months at 20°C., 70% R.H.; (O) after 18 months in vacuum over P_2O_5; (◑) after 18 months at 20°C., 70% R.H., followed by 68 hr. at 76°C.

For a number of thermoplastics one of us has previously shown[4] that a plot of reciprocal yield strength versus the corresponding time to yield is linear over six decades of strain rate in the region of ductile and transitional failures.   Furthermore it was suggested that this linearity is maintained until brittle failures are observed with increased rates of strain.   In Figure 10 the present results (corresponding to those shown in Fig. 2) are plotted in this manner to illustrate the applicability of the empirical relationship

$$1/\sigma = a + m \log t$$

where σ is the yield strength and t is the time to yield.   The numerical values of the constants a, the reciprocal of the 1-sec. yield strength, and m, the time dependence of the yield strength are given in Table II.

TABLE II
Values of the Constants a and m in the Equation, $1/\sigma = a + m \log t$[a]

Condition of specimens	a	m
After 18 months at 20°C., 70% R.H.	9.4×10^{-5}	0.74×10^{-5}
After 18 months in vacuum over P_2O_5	9.1×10^{-5}	0.65×10^{-5}
After 18 months at 20°C., 70% R.H. followed by 68 hr. at 76°C.	7.4×10^{-5}	0.43×10^{-5}

[a] σ in lb./in.², t in sec.

It can be seen that the time dependence of the yield strength varies according to the condition of the specimen; the annealed specimen is the least time-dependent and has the highest 1-sec. yield strength, 13,560 lb./in.^{2}.

Radiation

At a low rate of testing (0.125 in./min.), radiation does not appreciably affect the strength of specimens when these are tested soon after irradiation (Fig. 3). After storage, the strength of irradiated specimens increases relative to unirradiated specimens. This difference is maintained when the specimens are annealed and tested either at low or high rates. However, either high rates or heat treatment result in loss in ductility of the more highly irradiated (>50 Mrads) specimens, and fractures become transitional or brittle in character. High-speed embrittlement of specimens ductile at low rates of testing has similarly been observed with irradiated polycarbonate.[5]

CONCLUSIONS

The observed variations in tensile yield stress can be attributed to four factors, orientation, viscoelasticity, molecular weight changes, and plasticization. Reorientation of segments of the polymer chain occurs during annealing at temperatures below T_g and leads to an increase in strength and the appearance of an endotherm in the thermogram. The effect of aging is probably a manifestation of the same effect occurring slowly at room temperature. Increases in the time and temperature of testing cause changes in the viscoelastic responses of the polymer and lead predictably to reduction in strength. Reduction in molecular weight of the polymer causes subsequent loss of strength, increases the rate dependence of the polymer, and there are indications that it also facilitates the orientation process occurring during annealing below T_g. The effect of plasticization is illustrated by the decrease in strength caused by the presence of the equilibrium water content in the polymer.

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