Thermal Behavior of Polyethyloxazoline

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Synopsis

Polyethyloxazoline (PEOx) is a new water-soluble, thermoplastic polymer. It has a glass temperature of 56°C which increases to about 72°C on storage at room temperature. This increase is a manifestation of physical aging, and it occurs relatively fast with PEOx in comparison to other polymers. Also, the extent of this aging, as measured by the amount of enthalpy relaxation, is high for PEOx. It was shown that PEOx can be brought to 320°C without reduction of glass temperature, indicating an exceptional thermal stability.

INTRODUCTION

Polyethyloxazoline (PEOx) is a new water-soluble thermoplastic polymer which can be easily melt fabricated, and has excellent thermal stability.[1] It is also miscible with a number of other thermoplastic polymers.[2]

It is well known that amorphous polymers are not in thermodynamic equilibrium in their glassy state.[3,4] At storage temperatures below T_g, continuous reduction of free volume takes place due to molecular relaxation, and eventually an equilibrium state will be reached. The degree of such relaxation can be most conveniently followed by measuring the changes in the enthalpy by differential scanning calorimetry (DSC). This reduction of free volume or physical aging also manifests itself by changes in mechanical properties.[5] Accordingly, it was of interest to study the thermal properties and behavior of PEOx in some detail and to make comparisons with some polymers which have been previously studied. The results of this study are presented in this paper.

EXPERIMENTAL

PEOx is an experimental polymer from The Dow Chemical Co. It is a linear, amorphous polymer of the following structure:

$$\left[\; N - CH_2 - CH_2 \;\right]$$
$$\underset{\displaystyle CH_2 - CH_3}{\overset{\displaystyle C = O}{|}}$$
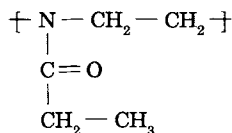
PEOx was characterized by size exclusion chromatography. It has $\overline{M}_w = 439{,}000$ and $\overline{M}_w/\overline{M}_n = 4.0$. Because of the hydrophilic nature of PEOx, it was dried under vacuum at about 70°C and then stored in a desiccator prior to any thermal measurements. Also, a commercially available Lexan, po-

lycarbonate sheet was also used for some comparative thermal measurements.

Glass transition temperatures and other thermal characteristics were determined using a Perkin-ELmer DSC-2 equipped with a Thermal Analysis Data Station (TADS). The computer–plotter combination permits storage and recall of data for manipulation such as subtraction and integration. The DSC was calibrated with Indium. The thermal behavior of PEOx was studied over a wide range of heating rates and storage times. However, in most cases a heating rate of 20°C min^{-1} was used, and quenching was done at the fastest setting on the instrument, 320°C min.$^{-1}$

The T_g was defined as the intersection of the heat capacity slopes from the glass to the transition region. Endothermic peak area (ΔH) was determined by integration of the area above the extension of the line representing the liquid state of the polymer. Specimens for the DSC experiments were prepared by placing the polymer (10–20 mg) in a tared DSC aluminum pan, transferring to a hotplate and then melting in the specimen pan at about 200–230°C for a short time (30 s). Sample weight was determined by difference.

BACKGROUND

The changes due to the physical aging process below the glass temperature are represented in Figure 1. The schematic 1(a) shows the enthalpy or volume reduction of the specimen from point A to point B upon storage at temperature T_a. Maximum enthalpy relaxation on extended storage corresponds to point C. This maximum enthalpy is given by the following expression :

$$\Delta H_{max} = [(C_P)_l - (C_P)_g] \times [T - T_a] \tag{1}$$

where $(C_P)_l$ and $(C_P)_g$ are the specific heats of the liquid and the glass, respectively, and T_a and T_g are annealing and glass temperatures, respectively.

Figure 1(b) shows the corresponding heat capacity curves. On storage at temperature T_a, the change in enthalpy is represented by an endothermic
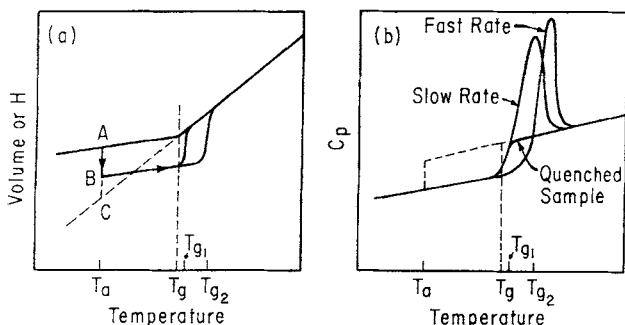

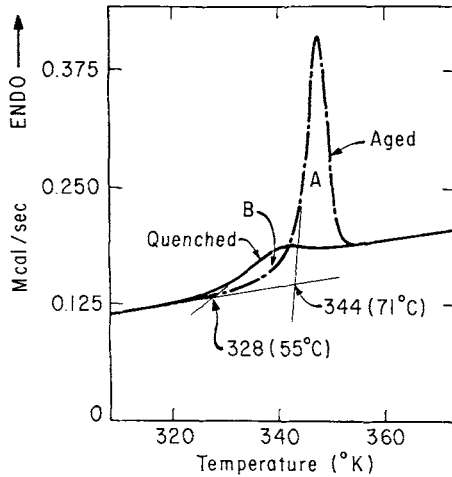Fig. 1.   Effect of heat history of polymers on their glass transition.

Fig. 2.   DSC traces of quenched and aged PEOx samples. Aging for 16 days at room temperature. The difference of areas "A" and "B" represents the excess enthalpy of the aged sample.

peak, or heat capacity overshot, which shifts to a higher temperature with increased rate of heating in the DSC. The area of the peak is normally less than the area indicated as ΔH_{max}, and its size depends on the proximity to the final equilibrium relaxed state.[3,4]

RESULTS AND DISCUSSION

The thermal properties of PEOx were found to depend strongly on the previous history of the specimen as well as on the heating rate in the DSC. Figure 2 shows the thermal scan for PEOx after storage at room temperature for 5 days. The glass transition temperature defined by the onset
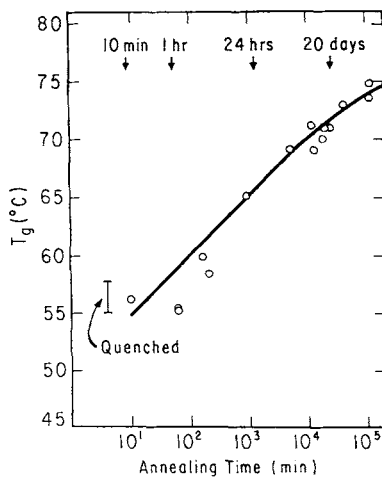

Fig. 3. T_g of PEOx vs. storage time at room temperature. Heating rate 20° min.[-1]
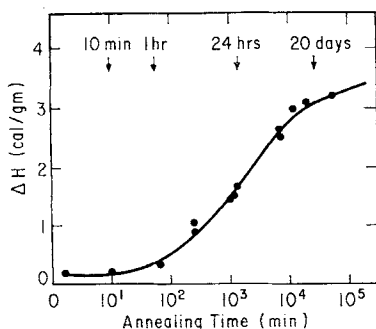
Fig. 4. Endothermic peak area of PEOx after storing in dry air at room temperature.

criterion mentioned above is seen to be 71°C, while the change in enthalpy on aging is 2.8 cal/g. When this sample was quenched from 460° K and the experiment repeated, the T_g was found to be 55°C and ΔH was only 0.21 cal/g. The definition of the excess enthalpy is illustrated by the difference of areas A and B.

Figure 3 shows the effect of storage time after quenching from the melt on the apparent PEOx glass transition temperature, while Figure 4 shows the change in enthalpy as a function of storage or annealing time on a logarithmic scale. It is apparent that after about 1 month's storage near equilibrium values of about 72°C and 3 cal/g, respectively, are reached. Also it is apparent from Figure 4 that the relaxation time spectrum for PEOx at room temperature peaks at about 24 h.

Figure 5 shows the effect of heating rate on T_g for PEOx samples stored at room temperature for more than 9 days (upper curve) and after quenching from the melt (lower curve). The data show that, at the rates of heating above 10° min.$^{-1}$, samples stored at room temperature have a T_g about 15°C higher than that of the quenched samples. At slower heating rates the difference in T_g is much smaller.

The size of the endothermic peak (without subtraction of B—Fig. 2), as a function of heating rate on samples stored at room temperature in excess
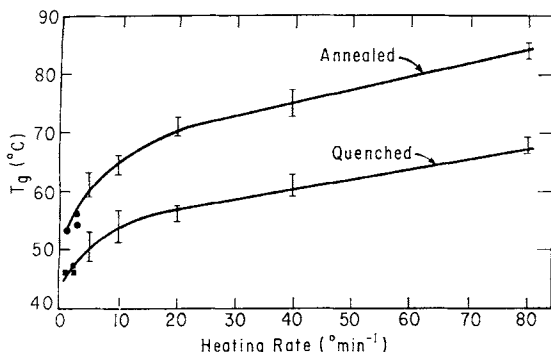

Fig. 5. T_g of PEOx vs. heating rate. Samples stored at room temperature for >9 days to anneal, and quenched from 460° K in DSC (320° min^{-1}).
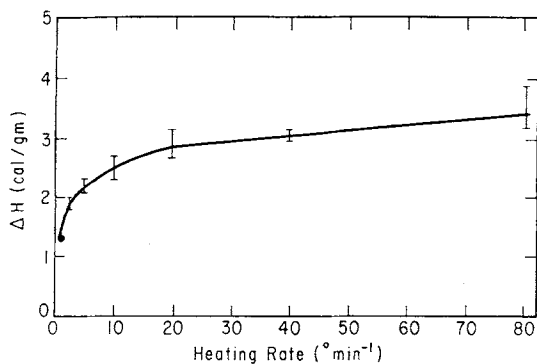
Fig. 6.   Endothermic peak area vs. heating rate. Samples stored at room temperature for
>9 days.

of 9 days is shown in Figure 6. For the purpose of comparison, the onset
temperature of Indium melting is shown as a function of heating rate in
Figure 7. It is noted that changing the heating rate from 10 to 80°C min^{-1}
increases the onset temperature by less than 5°C. It is clear that the sub-
stantially larger difference of about 30°C seen in Figure 5 is due to the
kinetic nature of the behavior of PEOx in the region of its glass transition
temperature. As a result of heating near T_g, Figure 8 illustrates the rapid
disordering of PEOx, which is manifested by the disappearance of the en-
dothermic peak. In this experiment PEOx samples which had been aged at
room temperature for more than 9 days were heated in the DSC to 80, 70,
and 60°C at two rates of 2.5 and 20°C min^{-1} and immediately quenched to
−10°C. After this process another thermal scan was obtained and the en-
dothermic peak area measured. From the results seen in Figure 8 it is
apparent that during the first heating significant loss of order takes place.
The slower the heating rate, the larger the portion of the endothermic peak
that disappears. Even heating the aged PEOx to 60°C at a slow rate produces
a loss of close to one-half of the peak area. Further, heating the aged sample
at the standard rate of 20°C min^{-1} to 70°C, where only a small rise of the
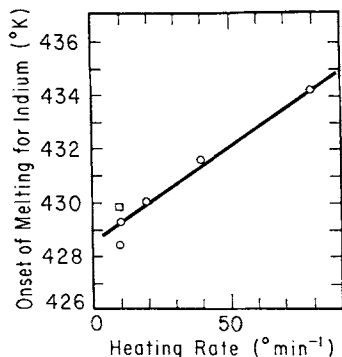

Fig. 7.   Onset temperature of Indium melting vs. heating rate. Standard calibration value
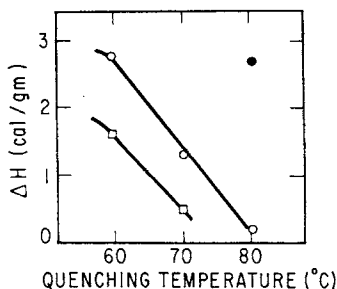of 429.78° K (□) is obtained at 10° min.$^{-1}$

Fig. 8.   Endothermic peak area after quenching in DSC (320° min^{-1}) from temperatures near T_g (○) 20° min^{-1} and (□)2.5° min^{-1} heating rate to quenching temperature. (△) ΔH after storage for >9 days and before quenching.

thermal scan has taken place, more than half of the equilibrium endothermic peak area of PEOx is lost in the subsequent run.

Finally, Figure 9 illustrates the general kinetic aspects of PEOx molecular relaxation at temperatures below T_g. The plot shows the enthalpic peak areas of PEOx, determined 1 h after annealing at various temperatures. It appears that the maximum rate of molecular relaxation occurs at about 40°C. The increase in this curve is, of course, due to the increased mobility of the molecules at increasing temperatures and the subsequent decrease due to the smaller amounts of free volume reduction which are possible at temperatures nearing T_g (Fig. 1). The reference line for maximum relaxation after long time annealing was obtained from thermal data using the relationship (1) in the Background section.

PEOx has a relatively short relaxation times in comparison to such polymers as poly(vinyl chloride) and polystyrene, since nearly complete relaxation takes place in a few days at room temperature. With most polymers relaxation occurs at very slow rates for comparable temperatures below T_g. In Figure 10, a comparison of rate dependence and the extent of enthalpy relaxation for PEOx and PVC is given. The measured endothermic peak area of PEOx is given as well as the excess enthalpy, calculated by obtaining the difference in the endothermic peak of the aged (16 days at room temperature) sample and the correction from the thermal scan of the quenched
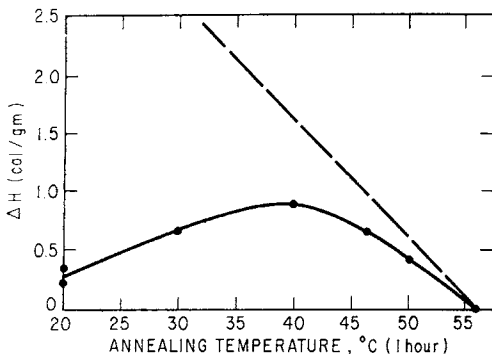

Fig. 9.   Effect of 1 h annealing of PEOx at various temperatures on endothermic peak area.
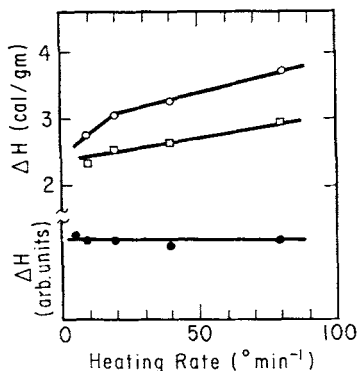
Fig. 10. (□) Excess enthalpy (defined in Fig. 2); (○) endothermic peak area of PEOx; (●) excess enthalpy of PVC vs. heating rate.

sample (area A – area B; Fig. 2). It is noted that while the excess enthalpy of PEOx shows some positive rate dependency, a PVC sample annealed at 65°C for 24 h gives a constant value of 0.35 cal/g. Straff and Uhlman[6] report the ΔH_{max} to be 1.32 cal/g at 65°C, or about one-half of the value for PEOx. The excess enthalpy of polystyrene after 1200 h at 92°C is 1 cal/g[7].

Another comparison (Fig. 11) shows that the peak temperature of the endothermic peaks of PVC and PEOx respond similarly to the change in the heating rates to 80°C min^{-1}.

Lexan polycarbonate sheet was used for further comparison of enthalpy relaxation between polycarbonate and PEOx. Figure 12 shows a thermogram for annealed and quenched specimens of polycarbonate. In addition to the relatively small endothermic peak of the annealed sample, it is also noted that the apparent T_g's for the two conditions are much closer than those for comparable PEOx experiments (Fig. 2). Lorenz[8] established a linear semilogarithmic relatioship between the endotherm area and the annealing time. His experiments extended to about 160 h, and the peak area measurements were in arbitrary units. It is estimated from our work that the excess enthalpy for polycarbonate is
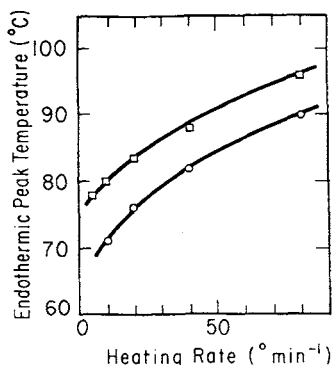

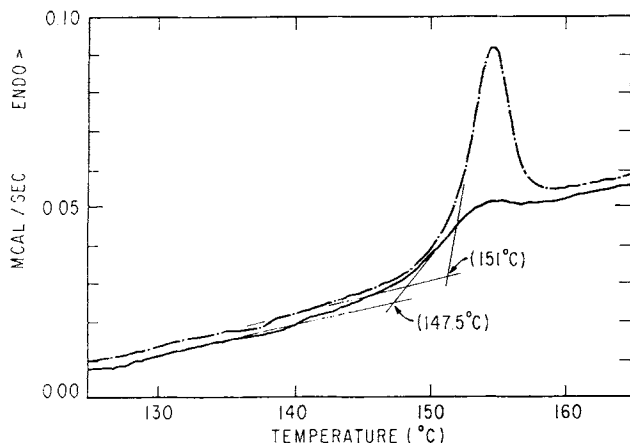Fig. 11. Endothermic peak temperature of PEOx and PVC vs. heating rate: (□) PVC, Ref. 5; (○) PEOx.

Fig. 12. DSC thermograms of polycarbonate (—·—·) annealed 1 h at 135°C and (—) quenched from 440° K (320° min^{-1}).

no more than 0.7 cal/g after a period of one month at 135°C. The slope of the line was established by the four annealing conditions shown in Figure 13. Finally, Figure 14 shows that the maximum in enthalpy relaxation for polycarbonate after 1 h of annealing is roughly 15°C below its T_g's. PEOx gave a similar result (Fig. 9). In comparison with the data on PEOx aging at room temperature (Fig. 4), it may be estimated that the endothermic peak area of polycarbonate is about one-half of that of PEOx when aged about 25–30°C below T_g for 24 h.

Thermal Stability of PEOx

Thermogravimetric analysis (TGA) techniques are usually employed to determine thermal stability of polymers, but this information has only a limited usefulness. TGA data give incipient depolymerization temperatures,
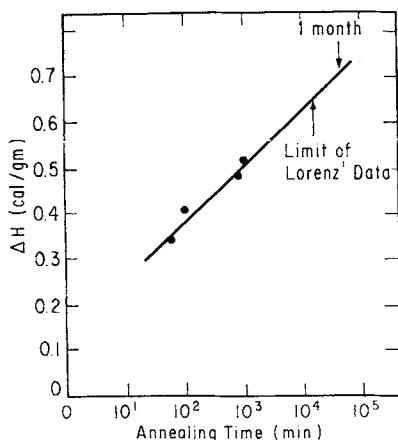

Fig. 13. Endothermic peak area of polycarbonate as a result of annealing at 135°C for various times: (●) this work.
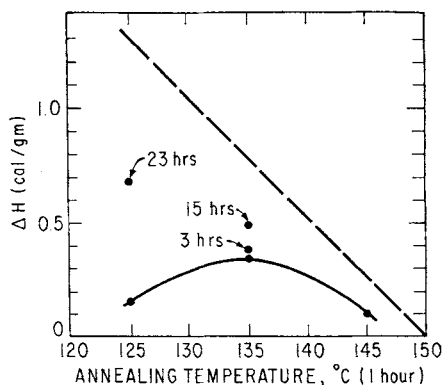
Fig. 14. Effect of 1 h annealing of polycarbonate at various temperatures on endothermic peak area.

i.e., the temperature where a precipitous weight loss starts. At this temperature, the polymer ceases to be of use, and these data serve for comparison with other polymers. TGA data for PEOx has been reported,[1] indicating that its stability is comparable to that of polystyrene.

Toh and Funt[9] reported the use of DSC for the study of thermal stability of polystyrene. They studied the change of T_g as a function of storage time at 317°C. Based on some of their discussion, a simplified procedure was devised to study the thermal stability of PEOx. T_g was determined after 5 min storage of PEOx sample in the DSC (N_2 atmosphere) at successively increasing temperatures. the results are shown in Figure 15. It is apparent that the glass temperature of PEOx remains constant at 56°C up to 320°C and then proceeds to drop to 47°C at 340°C for this particular accumulative heat history. Storage at 350°C, however, leads to a sticky oligomer with a T_g of 33°C.

This procedure indicates that there is no change in the T_g of PEOx after storage up to 320°C for short periods of time. The results imply that there has been no reduction in the number average molecular weight, according to the relationship proposed by Fox and Flory,[7] where
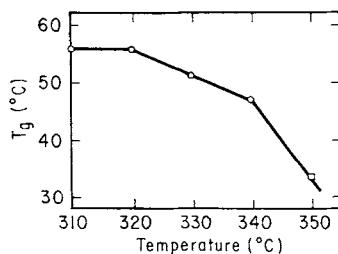
$$T_g = T_{g\infty} - \frac{K_1}{M_n}$$

Fig. 15. Effect of heating PEOx at high temperatures on T_g. Sample held at each temperature 5 min, then heated to next higher temperature: (□) sticky oligomer.

The results further imply that there are no plasticizing species formed during this heat treatment regime to 320°C, which would have a reducing influence on T_g. After the drop in T_g has taken place on a result of heat treatment for 5 min at 330°C, both reduced molecular weight and a low molecular weight component in the polymer would have the same effect of reducing T_g. Distinguishing these two contributions for the lowering of T_g would require a more extensive study.

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