

The Effect of Sorbed Penetrants on the Aging of Previously Dilated Glassy Polymer Powders.

Part III: The Effect of Exposure to Lower Alcohols on Enthalpy Relaxations in Poly(methylmethacrylate)

M. E. STEWART, D. L. SORRELLS, N. R. McCOY, W. J. KOROS*
and H. B. HOPFENBERG[†] *Department of Chemical Engineering,
North Carolina State University, Raleigh, North Carolina 27695-7905*

Synopsis

Enthalpy relaxations in glassy poly(methyl-methacrylate) have been studied through the endothermic, sub- T_g , aging peak observed in differential scanning calorimetry (DSC) thermograms. Powder samples were swollen by exposure to high activity methanol vapor and then aged in vacuum and in the presence of low activities of methanol, ethanol, and *n*-propanol at 308 K. The position and size of the DSC aging peak, which developed during aging, were monitored as a function of aging time. The aging peaks which developed for the alcohol-aged samples were smaller than those observed for similar samples aged in vacuum. These results suggest that the presence of dissolved penetrant in the samples retarded or arrested the relaxations which were observed in otherwise identical experiments performed in vacuo. Contacting the powder samples with 0.05 activity *n*-propanol or 0.10 activity ethanol during aging also appeared to arrest the shift in the temperature of the peak with aging time, whereas aging in the presence of 0.10 activity methanol or 0.05 activity ethanol appeared to have no effect on the temperature of the aging peak. These results are qualitatively consistent with a complementary study of the effect of the presence of lower alcohols on the time dependence of sorption capacity.

INTRODUCTION

An endothermic, sub- T_g peak is often observed in the differential scanning calorimetry (DSC) thermograms of annealed, or aged, polymeric glasses.¹⁻²⁵ The temperature at which the endotherm achieves its maximum value (T_{max}) typically increases with increasing aging time (t_e) and aging temperature (T_e) and T_{max} eventually merges with the T_g to produce a T_g overshoot at sufficiently long aging times and high aging temperatures. The endothermic peak is an example of physical aging²⁶ which typically occurs after quenching and subsequent annealing below T_g .^{1,6,25} Several other pre-aging perturbations, including increased hydrostatic pressure,^{6,12-20} mechanical deformation,^{1,21-24} and vapor swelling,¹⁻⁶ can contribute to the initiation of the observed endotherm.

*Present Address: Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712.

[†]Guest of the Department of Chemistry, Appalachian State University, Boone, NC 28608.

Berens and Hodge^{1,6} investigated the effects on the subsequent enthalpy recovery caused by maintaining previously dilated poly(vinyl chloride) (PVC) samples under various conditions during aging. The samples were dilated by exposing the PVC samples to high activity vinyl chloride monomer (VCM) and then rapidly desorbing the penetrant. Following the preswelling, the polymer relaxes slowly (toward equilibrium) during the aging period. Preswelling and aging are thus entirely analogous to the more familiar thermal quenching and annealing treatments often employed in DSC aging studies.^{1,6,25} The aging conditions studied by Berens and Hodge included applied hydrostatic pressure, tensile stress, compressive stress, the presence of sorbed carbon dioxide, and the presence of sorbed methyl chloride. Maintaining mechanical stresses or sorbed penetrant within the glass during aging suppressed the development of the aging peak, and the degree of peak suppression increased with increasing stress and increasing concentration of penetrant. Berens and Hodge reasoned that the decreased enthalpy recovery results from stresses within the polymer and that the stresses are, in fact, induced by swelling in the case of samples aged in the presence of penetrant. These swelling-induced stresses presumably oppose the relaxations which would normally occur during aging.^{1,6} A similar effect was reported by Ensore et al.,^{27,28} who studied the physical aging determined by the time dependence of *n*-hexane sorption in polystyrene. Polystyrene microspheres were swollen by exposure to high activity *n*-hexane and then aged in vacuum, low activity *n*-hexane, or alternating vacuum and low activity *n*-hexane. The sorption capacity of the samples decreased with increasing aging time for the vacuum-aged samples. The presence of low levels of *n*-hexane within the samples during aging, however, arrested the relaxations in sorption capacity. Similar results were recently reported by Stewart et al.²⁹ in Part 2 of this series for the sorption capacity of preswollen polystyrene aged in the presence of low levels of propane.

In the first paper of this series, Connelly et al.³⁰ reported the results of a study in which preswollen poly(methyl methacrylate) (PMMA) samples were aged in vacuum or in the presence of lower alcohols. The samples were subsequently probed with sorption studies using low concentrations of the respective lower alcohols. Consistent with other observations, the presence of low levels of *n*-propanol during aging completely arrested the relaxations in the *n*-propanol sorption capacity. Similar levels of ethanol in the samples retarded the relaxations in ethanol sorption capacity, but did not arrest them, and the presence of methanol in the samples during aging appeared to have no effect on the relaxations in methanol sorption capacity. The reason for this seemingly anomalous behavior, which has only been observed in PMMA, appears to be related to systematic effects which relate to the size and polarity of the penetrant and, ultimately, to coordination of the hydrogen bonding penetrant with the carbonyl group pendant to the PMMA chain.

In this study, the DSC thermograms of PMMA aged in vacuum and in the presence of the lower alcohols are compared to determine the effect of aging environment on the enthalpic relaxations suggested by the position of the endothermic, sub- T_g aging peak. The objective of this work is to complement the earlier studies on the relaxations in sorption capacity for the same systems reported in Part I of this series.

EXPERIMENTAL

Polymer Samples

The experiments were performed with samples of PMMA microspheres which were suspension-polymerized at North Carolina State University using a recipe provided by the B. F. Goodrich Company. Monomer and water were charged to a nitrogen-blanketed, stirred-reactor vessel maintained at 333 K, and polymerization was initiated by a small quantity of potassium persulfate and continued for 24 hours. Following polymerization, the particles were separated from the suspension by vacuum filtration, washed with water and chilled methanol, and then dried under vacuum. The polymer microspheres were nearly monodisperse with an average primary particle diameter determined from scanning electron microscopy of 0.550 microns. Gel permeation chromatography yielded a value of 386,000 for the number average molecular weight, and the T_g was determined to be 398 K from DSC measurements.

Penetrants

The methanol, ethanol, and *n*-propanol used in this work were obtained from commercial chemical suppliers. Certified ACS-grade methanol, used as both a preswelling and probing penetrant, was subjected to two freeze-thaw cycles under vacuum before use to remove dissolved gases. Reagent-grade ethanol and *n*-propanol were used without further treatment. Ultrapure nitrogen was used as a purge gas for the DSC.

Preswelling

Two different preswelling treatments were used. One set of samples was preswollen by exposing the polymer to 0.98 activity methanol vapor at 286 K for 14 days followed by rapid desorption of the penetrant. The other samples were preswollen by exposure to 0.80 activity methanol at 286 K for 14 days followed by rapid removal of the methanol. Preswelling conditions ensured a large degree of swelling (the approximate uptake of methanol during the two swelling treatments was 27 and 11 g per 100 g of PMMA, respectively) without particle coalescence. The preswollen samples were stored in sealed containers in a freezer maintained at 263 K after preswelling.

Aging

The nitrogen aging of polymer samples was performed in the DSC sample chamber with the chamber held at the indicated temperature. All other samples were aged in a water-jacketed vessel connected to vacuum service, a penetrant reservoir, and a pressure transducer. Samples were maintained at constant temperature by controlling the temperature of the water circulating through the vessel jacket.

DSC Measurements

DSC measurements were carried out on a Perkin-Elmer Model DSC-2 fitted with a Perkin-Elmer Model 3600 Data Station and a Perkin-Elmer strip chart

recorder. All scans were made at a heating rate of 40 K per minute using samples weighing between 3.2 and 3.8 mg. The polymer was heated from 290 to 440 K. When using the data station, Perkin-Elmer subroutines were used to determine the peak position, T_{\max} .

DSC measurements on preswollen samples aged in vacuum were conducted to obtain a basis against which the effects of aging in the presence of the lower alcohols could be compared. Samples of the PMMA which were previously diluted by exposure to 0.98 activity methanol vapor were aged in vacuum at temperatures of 303, 308, 328, and 348 K; and samples of the PMMA which were preswollen by exposure to 0.80 activity methanol were aged in vacuum at 308, 328, and 348 K. In addition, untreated (i.e., samples which were not preswollen prior to aging) PMMA samples were aged at 308, 318, 328, and 348 K. For experimental convenience, the samples aged at 318, 328, and 348 K were aged under a nitrogen purge in the DSC, since preliminary experiments demonstrated that the presence of nitrogen at one atmosphere during aging does not affect the position of the aging peak compared to vacuum aging. DSC thermograms of the samples were obtained at various aging times for each set of samples.

RESULTS AND DISCUSSION

The thermograms of many of the samples exhibited a broad endothermic peak upon which the relatively small aging peak was superimposed. The broad peak was observed even in untreated, unaged samples, and disappeared when the polymer was annealed at temperatures equal to or greater than 318 K. Quite possibly, the broad peak resulted from aging which occurred during the room temperature drying following polymerization or during the time the polymer was stored in the freezer following preswelling. Alternatively, the broad endotherm could result from the release of mechanical energy imparted to the sample during encapsulation in the DSC sample pans.

The difference in peak areas of the computer-normalized thermograms of the aged and unaged samples was interpreted as the peak resulting from the aging treatment per se. The Perkin-Elmer DSC II data station was used to compare the normalized thermogram of the aged samples with the normalized thermograms of unaged samples with otherwise similar treatments. Three Perkin-Elmer subroutines from the Thermal Analysis Data Station Standard programs were used to facilitate analysis. The first subroutine was used to normalize the thermogram of the aged sample and the thermogram of the reference sample by the respective sample weights. The normalized reference thermogram was then subtracted from the normalized thermogram of interest using a second Perkin-Elmer subroutine which subtracts the digitized forms of the thermograms point by point, interpolating where necessary. This procedure created a new calculated thermogram with increased definition of the aging peak. Peak limit temperatures (the bounds of the peak) were then determined from the subtracted thermogram by graphically extrapolating the postendothermic high temperature behavior to lower temperature. The two intersections of this extrapolation with the thermogram were used in a third Perkin-Elmer subroutine which calculated the peak area and T_{\max} between the limits. The subroutine used Simpson's rule to calculate the area of the

thermogram under the curve and interpolation near the apex to determine T_{\max} .

In general, the values of peak area and T_{\max} were relatively insensitive to the values of the peak limits used. For relatively flat endotherms, however, small variations in the peak limit temperatures occasionally produced rather large changes in the calculated values of T_{\max} and peak areas. In these instances, T_{\max} 's and peak areas were determined using several different sets of peak limit temperatures, and the values of T_{\max} and peak area which appeared closest to those that would have been selected by inspection of the subtracted thermogram is reported. At no time, however, were the calculated peak limit temperatures outside the range of uncertainty of the extrapolation involved in their determination.

Representative thermograms for the samples preswollen with 0.98 activity methanol and aged in vacuum at 303 K are presented in Figure 1. The thermograms clearly show the T_g of the samples and the broad endotherm. These thermograms also demonstrate the necessity of the data station sub-routines. The shaded areas in Figure 1 represent the peak areas of the aging peaks as determined using the procedure outlined above. The calculation procedure described previously provided a systematic means for separating the relatively small aging peaks from the broader endotherm characteristic of the unaged samples.

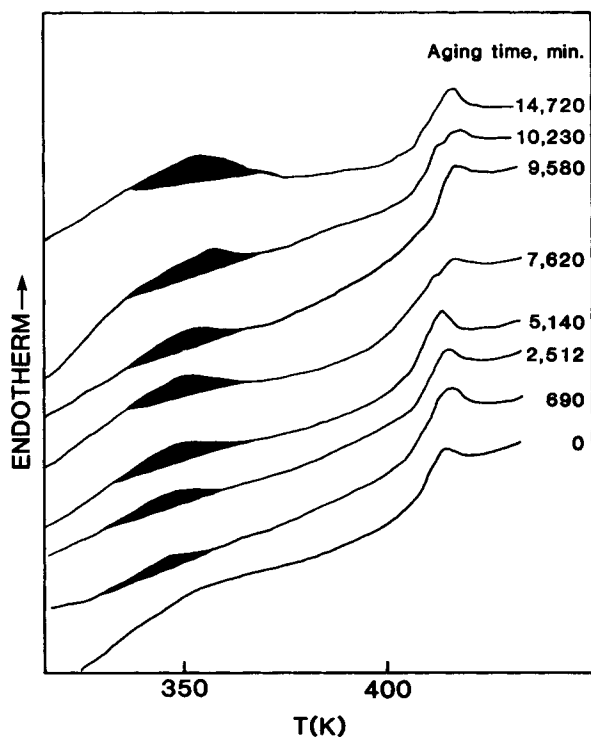


Fig. 1. DSC thermograms of preswollen PMMA aged at 303 K in vacuum for the indicated times.

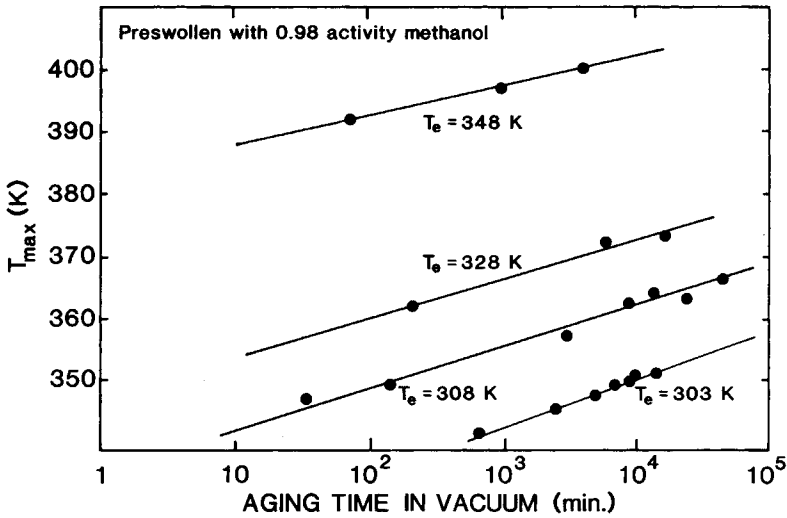


Fig. 2. T_{max} as a function of aging time for PMMA preswollen with 0.98 activity methanol aged in vacuum at the indicated temperatures.

The temperature at which the peak occurs has been shown to correlate well with the logarithm of the aging time.^{1,9} A plot of T_{max} versus $\log t_e$ for the PMMA samples, preswollen by 0.98 activity methanol and aged in vacuum at various temperatures, is shown in Figure 2. A similar plot for the samples preswollen with 0.80 activity methanol and aged in vacuum is presented in Figure 3, and a plot of T_{max} versus $\log t_e$ for untreated PMMA is shown in Figure 4. Figures 2–4 establish the generality of the shift in peak position with aging time and aging temperature for the PMMA samples used in this study. The positions and slopes of the plots for the two preswollen samples are comparable, and except for the results for samples aged at 348 K, the data for

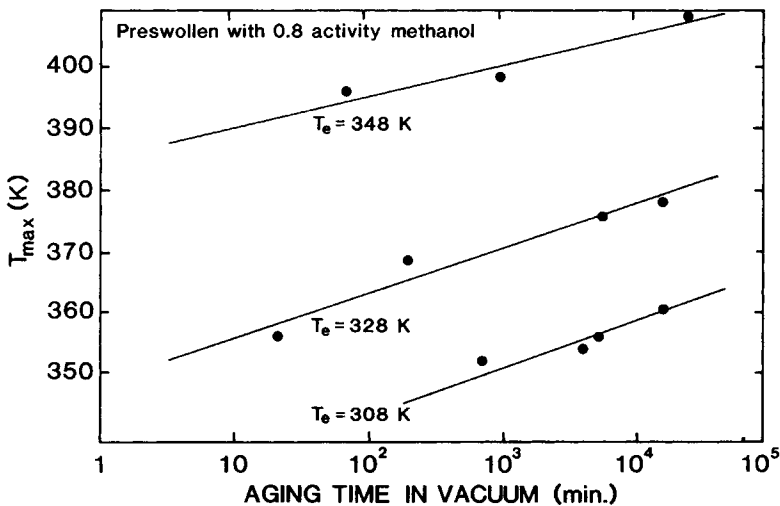


Fig. 3. T_{max} as a function of aging time for PMMA preswollen with 0.80 activity methanol aged in a vacuum at the indicated temperatures.

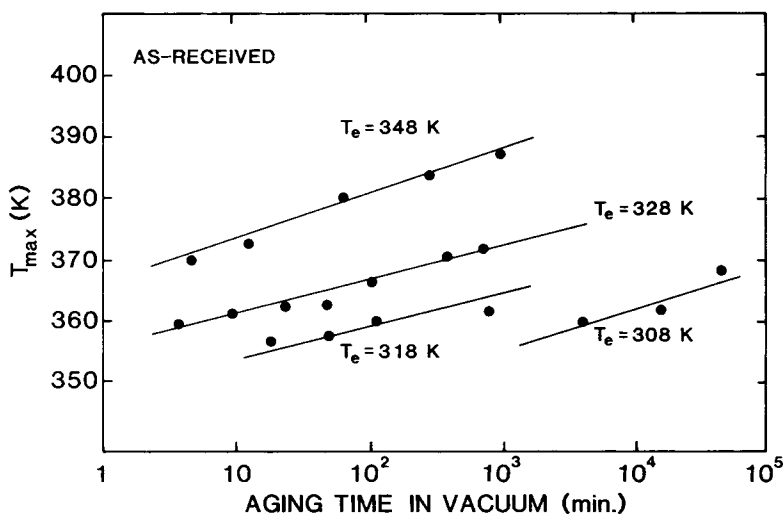


Fig. 4. T_{max} as a function of aging time for as-made PMMA aged in vacuum or in the DSC under a nitrogen purge at the indicated temperatures.

the untreated samples also appear very similar. The agreement between the results for the samples with three different pre-aging treatments is consistent with the observations of Berens and Hodge,¹ who found that the shift in peak position was dependent only on the aging time and temperature and not on the sample pretreatment.

A comparison of the magnitude of the aging peaks for the two preswelling treatments is presented in Figure 5 where the height of the aging peak, $C_{p \max}$, is plotted in arbitrary units against the log of the aging time for the preswollen samples aged at 308, 328, and 348 K. As shown in the figure, there is little difference in the peak heights of comparably aged preswollen samples. Berens and Hodge¹ have found that $C_{p \max}$ varies significantly for polymers with different initial states. The lack of obvious differences in the values of $C_{p \max}$ for the samples prepared by the two different preswelling treatments suggests, therefore, that the effect of the two treatments on the polymer are equivalent.

Effect of Aging in the Presence of Lower Alcohols on the Peak Position

To investigate the effects of the presence of the alcohols in the polymer during aging, samples of preswollen PMMA were aged either in the presence of low activities of methanol, ethanol, or *n*-propanol. Inferences about relaxations of the polymer were made from the results of periodic DSC measurements.

PMMA preswollen with 0.98 activity methanol was aged in 0.05 activity *n*-propanol ($p = 1.9$ mmHg) at 308 K for 30,000 minutes. The apparent equilibrium sorption level for *n*-propanol at this activity and temperature was 0.75 g per 100 g of PMMA. Periodically, the *n*-propanol was removed and samples were analyzed in the DSC. No sub- T_g aging peaks, other than the broad endotherm observed in all samples which were never aged above 318 K,

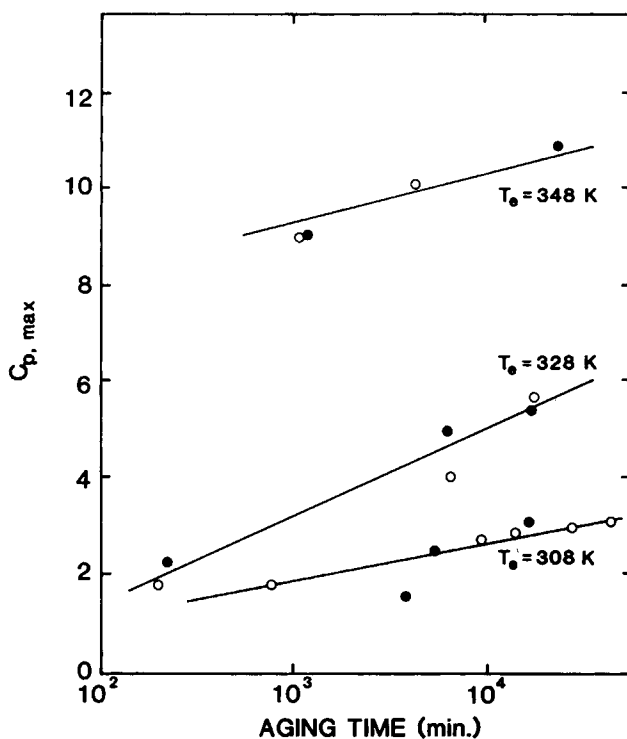


Fig. 5. $C_{p, \max}$ as a function of aging time for preswollen PMMA aged in vacuum at the indicated temperatures: (●) Preswollen with 0.98 activity MeOH; (○) Preswollen with 0.80 activity MeOH.

were observed in the thermograms of samples immediately following removal of the *n*-propanol. Additional samples were aged for 29,500 minutes in *n*-propanol and then aged for up to 52,250 minutes in vacuum. After vacuum aging, the thermograms of these samples developed sub- T_g aging peaks.

The variation of T_{\max} with vacuum aging time for these samples is compared in Figure 6 with the data for preswollen samples aged at 308 K in vacuum only. In the figure, the data for the samples aged in vacuum and *n*-propanol are plotted against their vacuum aging time only, not their total aging time. The agreement between the two sets of data is quite good and indicates that the samples aged in vacuum following *n*-propanol aging have undergone aging corresponding only to the period during which the samples were maintained under vacuum. Moreover, the peak heights for the propanol-aged samples were smaller than those for the vacuum-aged samples.

These results suggest that the presence of a low level of *n*-propanol in the polymer during aging arrests the relaxations in enthalpy which would otherwise lead to the enthalpy recovery aging peak in the preswollen samples aged in vacuum. These results are consistent with those of Berens and Hodge^{1,6} for enthalpy relaxations in PVC aged in the presence of carbon dioxide and methyl chloride. The results are also consistent with the sorption aging results of Connelly et al.³⁰ They found that the presence of low levels of *n*-propanol in PMMA during aging arrested the consolidation, as determined by cyclically

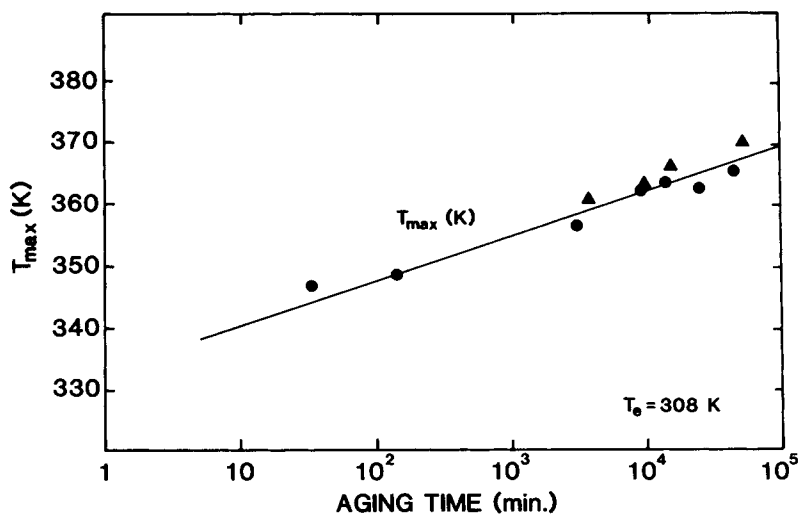


Fig. 6. T_{max} as a function of cumulative vacuum time for preswollen PMMA aged: (●) in vacuum only; (▲) 29,500 minutes in 0.05 activity *n*-propanol, then subsequently aged in vacuum. $T_e = 308$ K.

measured *n*-propanol sorption capacity, observed for preswollen samples aged in vacuum.

Berens and Hodge attributed the decreased enthalpy recovery of the samples aged in penetrant to swelling-induced stresses which oppose the relaxations normally occurring during aging.^{1,6} From a molecular point of view, these observations might alternatively be explained by the presence of penetrant, sorbed in the hole-filling mode of the glassy polymer, restricting the chain motions which would otherwise lead to relaxation in the absence of penetrant.

As Connelly et al.³⁰ reasoned from their data describing the effect of aging environment on the monotonic consolidation of sorption capacity, "Presumably, the Langmuir or hole-filling molecules are essentially space-filling and, therefore, retard consolidation whereas the Flory-Huggins or dissolved species are dilating and facilitate consolidation." The amount of penetrant sorbed in the hole-filling mode of sorption would, therefore, be important in retarding relaxations, rather than the total concentration of sorbed species.

Samples of PMMA preswollen with 0.98 activity methanol and samples of PMMA preswollen with 0.80 activity methanol were aged at 308 K in ethanol at an activity of 0.10 ($p = 10.2$ mmHg) for 29,500 minutes. The apparent equilibrium sorption level of ethanol for these conditions was approximately 1.4 g per 100 g of PMMA. Immediately after the ethanol was desorbed, DSC measurements were performed. Additional samples were then aged in vacuum following the ethanol aging and DSC measurements were made at various aging times.

As with the *n*-propanol-aged samples, no aging peaks were observed immediately following the ethanol aging. The samples aged in vacuum following the ethanol aging developed aging peaks, and again, the peak height was lower for the alcohol-aged samples than for the samples aged only in vacuum. The results for the variation of T_{max} with vacuum aging time for these samples are

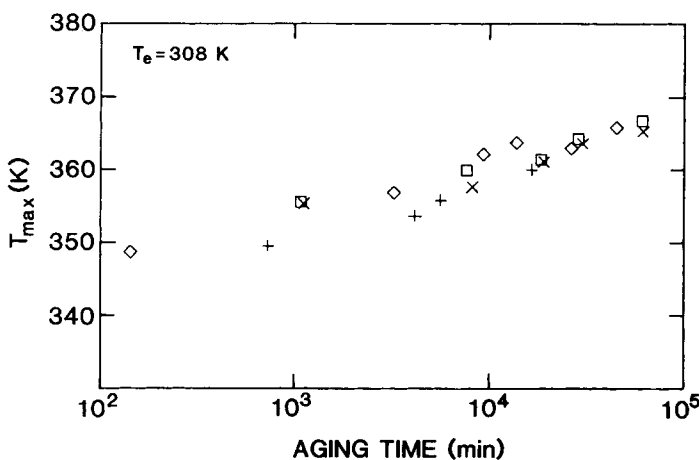


Fig. 7. T_{\max} as a function of cumulative vacuum time for preswollen PMMA: (x, □) aged 29,500 minutes in 0.10 activity ethanol, then subsequently aged in vacuum; (◇, +) aged in vacuum; (x, +) preswollen with 0.80 activity methanol; (◇, □) preswollen with 0.98 activity methanol.

compared with the results for preswollen samples aged in vacuum in Figure 7. The data for the samples aged in both ethanol and vacuum are plotted against aging time in vacuum only. The agreement between the two sets of data is quite good and indicates that the presence of a low level of ethanol in the polymer during aging also arrests the relaxations which lead to the development of aging peaks. Connelly et al.,³⁰ however, have shown that the presence of 0.10 and 0.05 activity ethanol during consolidative aging retarded, but did not arrest, the relaxations in sorption capacity at 308 K. In this instance, monitoring the aging process using DSC and sorption measurements give slightly different results, since the relaxations in sorption capacity were retarded during aging in 0.10 activity ethanol, while the relaxations which lead to the sub- T_g aging peak were arrested by the same penetrant at the same concentration. These differences are also apparent in the data of Figure 8, which were obtained using similar samples of PMMA. These samples were polymerized and preswollen separately and then aged in 0.05 activity ethanol and vacuum at 308 K.

In contrast to the 0.10 activity results, where the DSC aging behavior appears to be completely arrested while the sorption aging behavior is only retarded, the relaxations leading to the shift in position of the sub- T_g peak were unaffected by aging in the presence of 0.05 activity ethanol, even though the relaxations in sorption capacity were retarded under the same conditions.

The various preswollen samples were aged in the presence of 0.10 ($p = 20.8$ mmHg) methanol vapor at 308 K for 9,000 minutes. At these conditions, the apparent equilibrium concentration of methanol in the samples was approximately 1.1 g of methanol per 100 g of PMMA. Periodically, samples were removed for DSC measurements. Additional samples were aged in vacuum following the methanol aging. No sub- T_g peaks were found in the thermograms of samples studied immediately after the aging in the presence of the penetrant, while samples aged in vacuum and methanol developed small

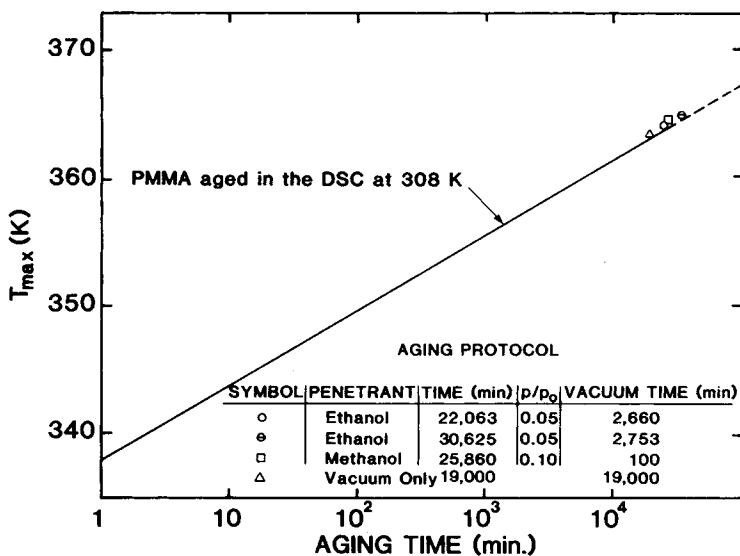


Fig. 8. T_{\max} as a function of total aging time for preswollen PMMA aged in various environments.

endothermic peaks. In this case, the T_{\max} for the alcohol-aged samples correlates best with the total aging time of the samples. The correlation is shown in Figure 9. Similar results for the peak position were obtained for a preswollen sample aged at 308 K for 25,860 minutes in 0.10 activity methanol followed by aging 100 minutes of vacuum as shown in Figure 8. The locations of the peaks indicate that aging has occurred in the presence of the methanol, however, the small size of the peaks indicates that the presence of methanol

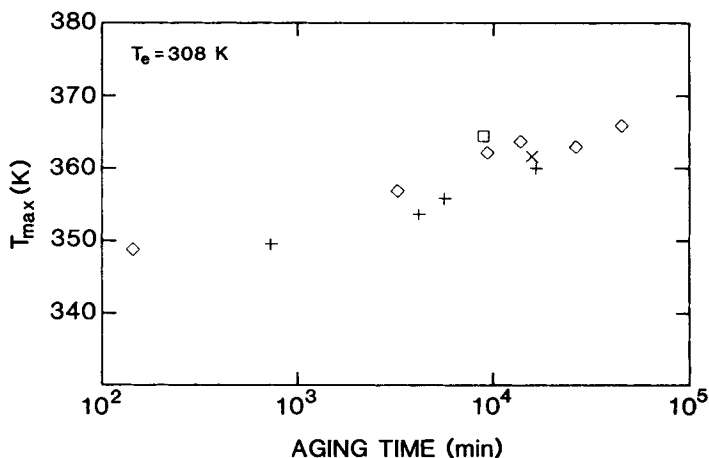


Fig. 9. T_{\max} for preswollen PMMA: (\times , \square) aged 8,800 minutes in 0.10 activity methanol, then subsequently aged in vacuum. (The abscissa value represents the total aging time in methanol and vacuum.); (\diamond , $+$) aged in vacuum; (\times , $+$) preswollen with 0.80 activity methanol; (\diamond , \square) preswollen with 0.98 activity methanol.

during aging does have an effect on the detailed nature of the aging behavior. The results for the shift in peak position are similar to the sorption aging results of Connelly et al.,³⁰ who found that the relaxations in sorption capacity which occurred in the presence of methanol were essentially identical to those occurring in vacuum.

SUMMARY

As with the previously reported sorption aging experiments, the DSC thermograms of preswollen PMMA samples aged in the presence of the lower alcohols exhibit a wide range of behavior. One common feature observed in all of the DSC aging experiments with the alcohol/PMMA systems, however, is the absence of an aging peak immediately following penetrant desorption. Presumably, this effect is due to the excess volume and enthalpy left in the polymer by the rapid desorption of the penetrant. The endothermic peak develops only with vacuum aging (annealing) following the alcohol aging. These observations are qualitatively consistent with the wealth of information on glassy samples dilated by rapid quenching.

Another common qualitative feature is the observation that the samples aged in the lower alcohols exhibited smaller peaks than the samples aged in vacuum. This was observed even for the methanol aging treatment which appeared to have no effect on the peak position. Apparently, the relaxations are retarded by penetrant molecules sorbed in the hole-filling mode of sorption which restrict the chain motions which would otherwise lead to relaxation of the excess enthalpy in the absence of penetrant, thereby producing smaller enthalpy recovery peak.

The data for aging in the presence of methanol and 0.05 activity ethanol indicate that it is possible for the presence of penetrant during aging to affect the amount of enthalpy recovery observed, without affecting the temperature at which the recovery occurs. In general, however, the presence of penetrant during aging can affect both the magnitude and the position of the endothermic peak.

Monitoring aging of the polymer through the growth and position of the sub- T_g aging peak and through the relaxations in sorption capacity appears to give slightly different results. Samples aged in 0.10 activity ethanol exhibited no discernable aging as measured by the DSC during the presence of ethanol, while previous studies indicate that the relaxation in sorption level continue in the presence of ethanol, but at a greatly reduced rate compared with vacuum-aged samples. Aging in 0.05 activity ethanol was also reported to retard the relaxation in sorption capacity, but in contrast to the 0.10 activity ethanol aging data, the enthalpic relaxations leading to the shift in the DSC aging peak were unaffected by aging under 0.05 activity ethanol. In addition, relaxations in sorption capacity were reported to be unaffected by aging in the presence of methanol, whereas the magnitude of the enthalpy recovery peak was affected by aging in the presence of methanol, even though the shift in peak position was not affected. The differences between the two techniques are to be expected since the two techniques measure different phenomena and, therefore, yield slightly different results and sensitivities.

The effect of aging in penetrant on the shift in peak position was varied. Under certain aging conditions the shift in peak position with aging time was

completely arrested by the alcohol aging, while under other conditions the peak position appeared to be completely unaffected. This wide range of behavior was also observed in previous sorption aging studies, however, and in general, the results of the present study agree qualitatively with those of the earlier sorption aging experiments.

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