Isothermal Physical Aging of Poly(Methyl Methacrylate): Localization of Perturbations in Thermomechanical Properties

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SYNOPSIS

Effects of isothermal physical aging on poly(methyl methacrylate) (PMMA) were investigated for isothermal aging temperatures (T_a) from T_g −13 to T_g −128°C using a freely oscillating torsion pendulum (TBA). A single PMMA–glass fiber specimen, the effects of the thermal history of which could be erased by heating above T_g (=116°C, 0.7 Hz), was used for all experiments; this facilitated comparison of the unaged and aged specimen. The modulus was observed to increase linearly with the logarithm of isothermal aging time. Thermomechanical properties of the aged versus unaged specimen showed perturbations (e.g., increased modulus) principally in the vicinity of T_a. This suggests that different intermediate portions of the relaxation spectrum are specifically involved in the process of aging for different values of T_a.

INTRODUCTION

Physical aging is the process by which an amorphous glass spontaneously densifies in an attempt to achieve its equilibrium state.[1,2] During isothermal physical aging, at temperature T_a, the shear modulus increases and the mechanical loss (e.g., tan delta) decreases.[3,4] Several researchers have reported the effects of aging on the thermal properties of polymer glasses[5–14] after physical aging. There are contradictions in the literature about the effect of aging at T_a on the properties at temperatures above and below T_a.[6,8,10–14] Some reports contend that aging affects properties only between T_g and T_β[5,6,11] whereas others show changes in properties extending well below T_β to the lowest measuring temperature.[8,14] Recent work in this laboratory has shown for two high-T_g thermosetting systems (i.e., fully cured epoxy[7,10] and linear polyimide[13]) that the dynamic mechanical properties of isothermally aged specimens differ from unaged specimens principally in the vicinity of T_a. It was then of interest to investigate if localized perturbations in thermomechanical behavior due to isothermal physical aging develop in simpler polymers, for example, poly(methyl methacrylate).

Poly(methyl methacrylate) (PMMA) has been studied by dynamic mechanical analysis[15–17] and has been a subject of physical aging experiments.[5,11,14,18–23] In the present study, a freely oscillating torsional pendulum (≈1 Hz) has been used to investigate the aging behavior of PMMA in the glassy state. A single PMMA–glass fiber specimen, whose thermal history could be erased by heating above T_g (=116°C, 0.7 Hz), was used for all experiments; this facilitated comparison of the unaged and aged specimen. This report focuses on differences in the thermomechanical behavior of PMMA in the unaged and aged states for values of T_a from below the glassy state transition, T_β, to T_g. A more complete report will be published.[18]

EXPERIMENTAL

Materials

PMMA (M_n = 46400, M_w/M_n = 2.01) was purchased from Aldrich Chemical (cat. no. 18,225-7, 1990-91). The glass transition temperature, T_g = 116°C (0.7 Hz), is indicative of approximately 60% syndiotactic

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PMMA.[17] The PMMA was dissolved in tetrahydrofuran (THF, bp = 67°C) for impregnating a heat-cleaned glass braid [0.5 g PMMA/2.5 mL THF] for use in torsional braid analysis experiments.

Procedure

The torsional braid analysis (TBA) technique was used to measure the relative rigidity (proportional to the shear modulus) and logarithmic decrement (proportional to tan delta) of a PMMA–multifilamented glass braid composite specimen both during isothermal aging and temperature scans. All experiments were performed under a slow, steady helium purge. In the TBA technique the polymer–solvent–braid composite (the specimen) is mounted in a torsional pendulum that is free to oscillate at the lower end. The pendulum is intermittently set into motion and each of the resulting damped sine waves generated is analyzed to determine the frequency of oscillation and the decay constant, which are used to calculate the relative rigidity (defined as the square of the natural frequency of oscillation of the pendulum, f^2) and logarithmic decrement (equal to $\ln(A_i/A_{i+1})$, where A_i and A_{i+1} are the amplitudes of successive oscillations in a wave), respectively. Reviews of the TBA technique have been published.[24,25] The TBA apparatus is manufactured by Plastics Analysis Instruments, Inc.

The relative rigidity, f^2, in a TBA experiment is related to both the shear modulus, G', and the dimensions of the specimen,[24–26]

$$f^2 \cong (r^4/8\pi IL)G'$$

where r and L are the radius and length of the specimen, I is the moment of inertia of the oscillating system, and G' is the shear modulus of the specimen. During physical aging the modulus increases while the dimensions of the specimen decrease. The relative rigidity is always observed to increase presumably because the former outweighs the latter.[7]

Use of a glass braid composite permitted a single specimen to be used for all the experiments since aging effects could be eliminated by heating to above T_g and reintroduced below T_g after subsequent cooling. It is of interest to note that the composite nature of the TBA specimen does not significantly affect the aging process; the aging behavior was reported to be the same for a homogeneous film and a glass braid composite epoxy–diamine specimen.[10]

The time–temperature sequence of the experiment was as follows:

1. A glass braid was impregnated with the PMMA–THF solution and mounted in the TBA unit at 50°C.
2. The specimen was heated to 150°C at 1°C/m and held isothermally for 4 h to remove solvent.
3. The specimen was cooled from 150°C at 5°C/m to a predetermined temperature, T_a, and held for 14 h isothermally. TBA data were taken on a logarithmic time basis during isothermal aging.
4. The specimen was cooled to −100°C at 5°C/m and then heated at 1°C/m to 150°C. TBA data taken upon heating provided the thermomechanical spectra of the aged specimen.
5. The specimen was then cooled from 150 to −100°C at 5°C/m and then heated at 1°C/m to 150°C. TBA data taken upon heating provided the thermomechanical spectra of the unaged specimen, which were compared to the thermomechanical spectra of the aged specimen (of step 4).
6. Steps 3–5 were repeated for various values of T_a (the aging cycle).

The changes in properties after aging are sensitive to the cooling and heating rates. By using only one rate of cooling and one rate of heating for all aging experiments (the two rates not necessarily equal), differences in the results of aging experiments could then be attributed solely to differences in the value of T_a.[13]

RESULTS AND DISCUSSION

T_g and T_β Transitions of PMMA

Figure 1 shows the TBA thermomechanical spectra of the PMMA–braid specimen measured upon heating at 1°C/m after cooling from 150 to −100°C at 5°C/m. The glass transition temperature, T_g = 116°C at 0.7 Hz, and secondary glassy state transition temperature (or β-relaxation), T_β = 29°C at 1.5 Hz, are defined by the temperature and frequency of the respective maxima in the logarithmic decrement spectrum.

Isothermal Aging

Figure 2 displays the results during isothermal aging for several aging temperatures. The reduced shear modulus of the specimen, G'/G'_0, defined as the ratio of the shear modulus at aging time t to that at aging

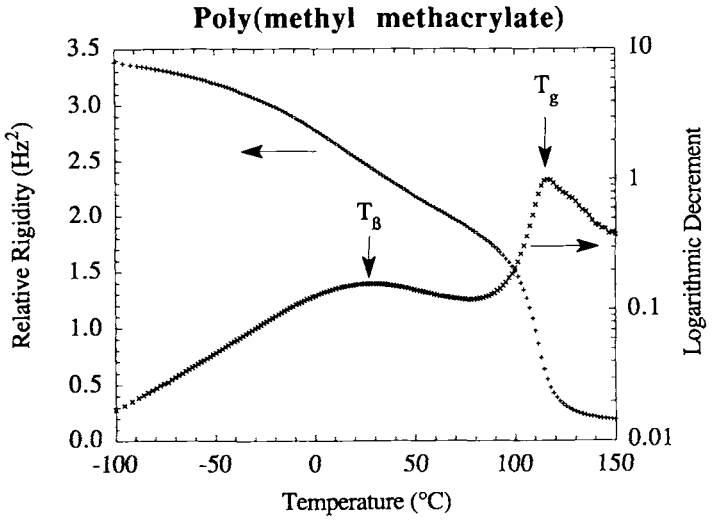

Figure 1 Poly(methyl methacrylate): TBA thermomechanical spectra. −100 to 150°C at 1°C/m after cooling from 150 to −100°C at 5°C/m.

time t = 15 m, is plotted versus log aging time for several values of T_a. Thermal equilibrium ($T_a = T_{\text{setpoint}} \pm 0.15$°C) was attained in less than 15 m after cooling for all values of T_a (data <15 m not presented). Changes in the reduced modulus of less than 0.1% due to physical aging can be measured (see Fig. 2). Linear regression analysis for each set of data resulted in all correlation coefficients greater than 0.95. G'/G'_0 is thus considered to increase linearly with log aging time.

Figure 3 is a plot of the aging rate of the specimen versus T_a. The aging rate, defined as the slope of G'/G'_0 versus log aging time, was obtained from a linear regression analysis of the data presented in Figure 2. T_g and T_β are marked as reference temperatures. The aging rate increases monotonically with increasing T_a. Note that no abrupt change in the aging rate occurs near the designated T_β. One isothermal aging experiment, data not shown, was performed at T = 138°C (i.e., $>T_g$) to determine if the specimen could be monitored so as to reach an equilibrium G'/G'_0 value. G'/G'_0 became constant immediately after thermal equilibrium had been attained.

The form of the temperature dependence of the calculated aging rate in this study is in agreement

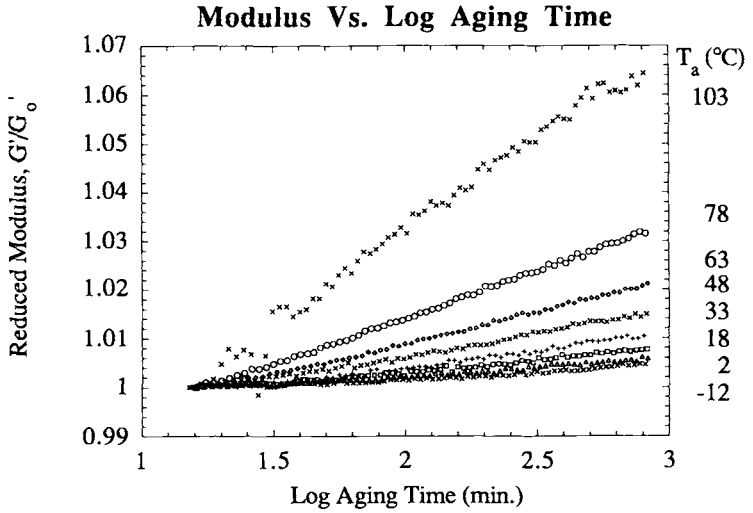

Figure 2 Reduced modulus versus log aging time for different aging temperatures. Note the linear relationship.

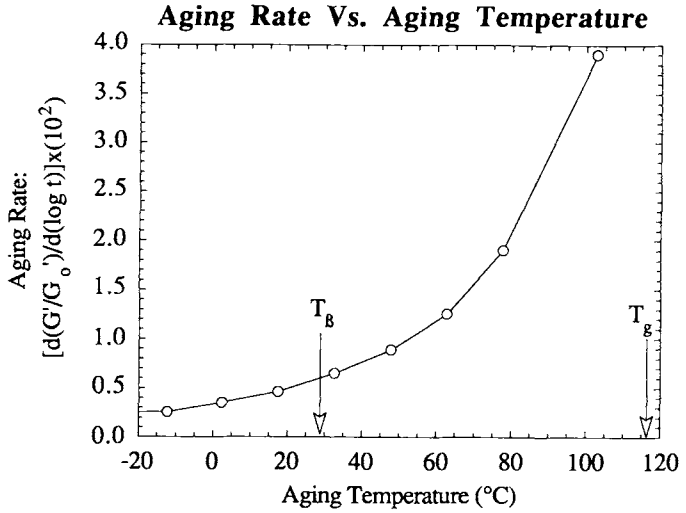

Figure 3 Aging rate of specimen versus aging temperature.

with an aging study of PMMA in which creep relaxation at low strain was monitored.[5] However, the same investigator reported the aging rate for a PMMA, measured by volume relaxation, to have local maxima versus T_a around 0 and −50°C (T_β = −31°C at 10^{-3} Hz).[23]

The separation of the contributions of temperature and departure from equilibrium structure on the aging behavior is a central theme in the study of the relaxation behavior of all glasses.[27,28] An Arrhenius plot of the aging rate did not result in a straight line; the plot was concave up.[18] Also, the isothermal aging rate does not correlate simply with the mechanical loss (i.e., logarithmic decrement).[18]

Perturbations in Thermomechanical Behavior Due to Isothermal Aging

Figure 4 shows the TBA behavior versus temperature of a specimen aged at 48°C and also of an unaged specimen. The principal differences are an increase in relative rigidity and a decrease in logarithmic decrement for the aged specimen in a narrow range about T_a = 48°C.

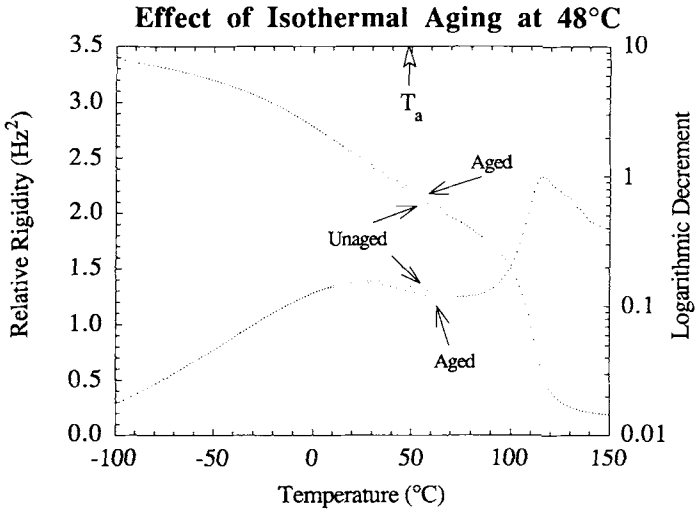

Figure 4 Effect of isothermal aging at 48°C. TBA thermomechanical spectra of unaged and aged specimen. The aged specimen was aged for 14 h.

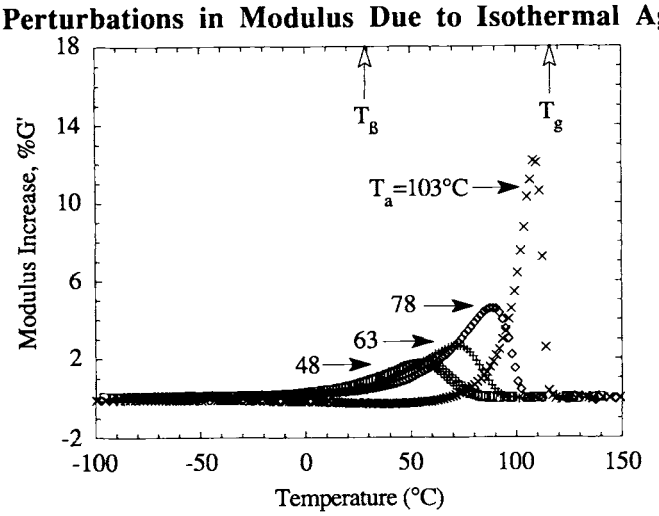

Figure 5 Perturbations in modulus versus temperature due to aging at different aging temperatures (T_a = 48, 63, 78, and 103°C).

Figures 5 and 6 are calculated from data such as those presented in Figure 4. In Figures 5 and 6 the percent change of the aged versus unaged specimen's shear modulus,

$$\%G' = \frac{100[G'(a) - G'(u)]}{G'(u)}$$

where a and u designate the aged and unaged states, respectively, is plotted versus temperature for different values of T_a. The data in Figure 6 ($T_a < 40$°C) has been magnified by a factor of 10 versus those in Figure 5 ($T_a > 40$°C). The effects of aging shown in Figures 5 and 6 are discussed below.

First, the perturbations due to aging are, to a large extent, localized about T_a. The localization indicates that aging at different values of T_a involves intermediate portions of the relaxation spectrum. This is in disagreement with the statement that physical aging influences all the relaxation times, τ_i, equally.[5,29] (Note: in the present work for $T_a < T_\beta$, small changes due to aging are measurable to −100°C.)

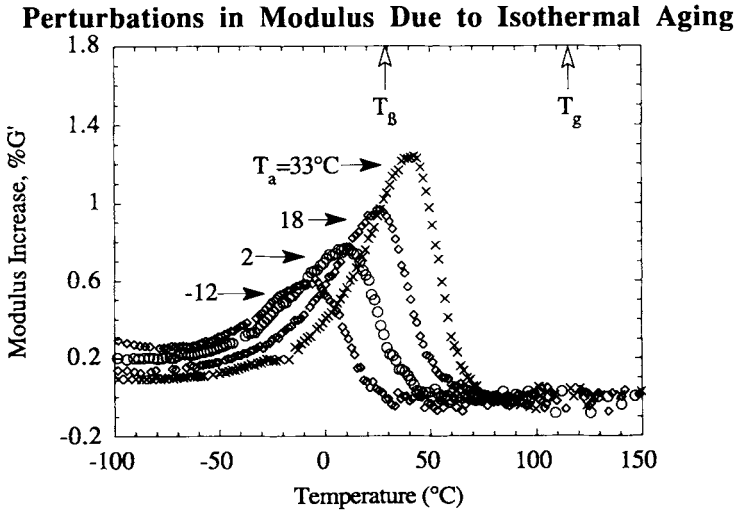

Figure 6 Perturbations in modulus versus temperature due to aging at different aging temperatures (T_a = −12, 2, 18, and 33°C). Note: the modulus scale has been magnified 10 times that in Figure 5.

Second, the peak in $\%G'$ is asymmetric. This reflects that during postaging heating the processes involved in determining $\%G'$ at $T < T_a$ are different from those at $T > T_a$. It has been shown that the path of $\%G'$ versus temperature below T_a is largely reversible.[13] However, the $\%G'$ versus temperature path is not reversible above T_a. For example, if the specimen is heated after isothermal aging at T_a to a temperature approximately 40°C above T_a (1°C/m), the effects of aging are essentially removed.[18] In this case the submolecular motions that had been "frozen" upon aging at T_a are essentially "released" on heating.

This has practical and theoretical significance. For example, to remove the effects of physical aging at $T_a \ll T_g$ it is not necessary to heat above T_g. This may have implications for glasses exposed to temperature cycling such as those used in encapsulating electronic devices that are at a higher temperature in the "on" than "off" state, T_{on} and T_{off}, respectively. Glasses under these conditions may only accumulate changes due to aging at T_{on}, the effects of aging at T_{off} being removed at T_{on}.

Third, the intensity of the peak in $\%G'$ decreases an order of magnitude with decreasing T_a over the range of temperatures studied. The changes due to aging at $T_a < T_\beta$ are small, yet well defined in Figure 6.

Fourth, the maxima of the peaks in $\%G'$ are at higher temperatures than their respective values of T_a.

CONCLUSIONS

Changes in the thermomechanical behavior of PMMA due to isothermal physical aging were found to be localized in a narrow temperature range about the aging temperature, T_a, for a wide range of T_a (values of T_a from just below T_g to below T_β). The localization suggests that isothermal aging involves an intermediate range of the relaxation spectrum that depends on T_a. This has practical and theoretical consequences when determining the temperature-dependent behavior of a glass after physical aging at T_a.

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