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Role of a small amount of comonomer on the physical aging of poly(methyl methacrylate) copolymer investigated by dynamic viscoelasticity

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Abstract

The physical aging of a poly(methyl methacrylate) (PMMA) copolymer having a small amount of ethyl methacrylate was investigated below its glass transition temperature (T_g) using dynamic viscoelastic measurements. The results were compared with those from homo-PMMAs to investigate how the comonomer in the copolymer affects the physical aging of the glass. Annealing temperatures were classified into two categories by the glass transition temperature of a poly(ethyl methacrylate) (T_{gPEMA}; ca. 65°C). The relaxation rate of the copolymer was faster than those of the homo-PMMAs when the samples were aged below T_{gPEMA}, but the rates were equal when aged at above T_{gPEMA}. The experimental results are discussed in terms of the segmental motion. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Physical aging; Poly(methyl methacrylate) copolymer; Viscoelastic properties

1. Introduction

The mechanical properties of supercooled polymeric glasses evolve towards their equilibrium values with elapsing time when held below their glass transition temperature (T_g) [1–14]. This process is called physical aging, and is a relaxation phenomenon due to a change in the chain conformation caused by the molecular thermal motion.

Studies of physical aging by measuring the dynamic viscoelastic properties of glassy polymers have shown that the storage modulus (E') increases and the loss modulus (E'') and loss tangent ($\tan\delta = E''/E'$) decrease with the aging time [15–26]. The shapes of the temperature dispersion curves of the viscoelastic functions change during aging [1,20–27]. The change appears at successively higher temperatures with elapsing aging time or with elevating aging temperatures. These results indicate that the structure of the polymeric chain in the glassy state relaxes over larger segment scale lengths at longer aging times [23–26], and also that the scale of the movable segments is related to the aging temperature [20,21,23]. Our previous work has shown that the relaxation rate does not depend on either molecular weight [23] or molecular weight distribution [24].

In this work, we investigated how a small amount of comonomer in a polymeric material affects the physical aging in the glassy state and then compared these results with the results from homo-polymers [23].

2. Experimental

2.1. Materials

The material used in the study was a poly(methyl methacrylate), PMMA037B ($M_w = 84\,000$, $M_w/M_n = 1.9$, $T_g = 108°\mathrm{C}$) supplied from Scientific Polymer Products, Inc. This is a random copolymer composed of methyl methacrylate (96.1 mol%) and ethyl methacrylate (3.9 mol%). The sample will be referred to as PMMA84, the 84 denoting the M_w. The film samples were prepared by a solvent casting method and then the samples were finally dried in vacuum at 190°C for 3 days; the preparation method was described in detail in our previous publication [23]. The sample films were heated at 190°C for 10 min on a compression-molding machine to eliminate any previous thermal histories and were then cooled in one of two ways. One was slow cooling from 190°C toward room temperature (RT; 15–25°C). The average rate of the cooling was 0.7°C min^{-1} and the sample thus obtained was denoted SC. The other was rapid quenching

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Table 1
Sample codes and various thermal histories applied to PMMA84 samples (Thermal histories were applied to the samples in two steps: (1) slow cooling or quench from 190°C and (2) annealing and aging at 80°C or physically aging at RT. The sample codes include a summary of thermal histories: QU stands for quench, SC slow cooling, QA quench and annealing, and QP quench and physically aging)

Code	I, annealing hours at 80°C	II, physical aging days at RT
PMMA84-QU	–	–
PMMA84-SC	–	–
PMMA84-QA1	6	–
PMMA84-QA2	24	–
PMMA84-QA3	72	
PMMA84-QA4	150	–
PMMA84-QP1	–	3
PMMA84-QP2	–	33
PMMA84-QP3	–	144
PMMA84-QP4	–	266
PMMA84-QP5	–	552

in an ice-water bath, this sample was denoted QU. The film samples were less than 0.1 mm in thickness.

Various thermal histories were applied to the QU samples below T_g, and these are summarized in Table 1. A number of QU samples were annealed and then aged at 80°C for various lengths of time, as shown in Column I in Table 1, and subsequently cooled slowly to RT. These samples were denoted QA. In addition, several QU samples were kept at RT for varying lengths of time, as shown in Column II in Table 1; these physically aged samples are denoted QP.

2.2. Measurements

The specimens were rectangular and the dimensions were approximately $30 \times 4 \times 0.1$ mm^3. The temperature dispersion of the dynamic viscoelastic functions, E', E'', and tan δ of the samples was measured at an angular frequency of 1 s^{-1} and at an elongational strain of 0.05% using a Rheometrics RSA-II. All measurements were performed on heating at a heating rate of 2°C min^{-1}.

3. Results

The temperature dispersion curves of E', E'', and tan δ for three typical thermal histories, i.e. PMMA84-QU, -SC, and -QA4 samples are shown in Fig. 1. The figure clearly demonstrates a general effect of thermal history on the viscoelastic properties of the samples, most notably by comparing the QU and SC samples. The temperature at the onset of the steep decrement of the E' curve for the SC sample is higher than that for the QU sample (see inset in Fig. 1(a)); the curves for the QU and SC samples overlap above 120°C within the experimental errors. The E'' and tan δ curves show clearly the effect of thermal history on the dynamic viscoelastic properties. The values of E'' and tan δ for the QU sample are higher than those of the SC sample at low temperatures. This implies that the QU sample has a larger amount of un-relaxed segments than the SC sample. On the other hand, the curves for the QU sample also coincide well with those of the SC sample above 120°C. The E' curve for the QA4 sample falls at 98°C and starts to agree with the curve of the QU sample at 104°C (see inset in Fig. 1(a)) within the experimental errors. The E'' and tan δ curves for the QA4 sample are close to those of the SC sample below 94°C and agree with those of the QU sample above 100°C. The tan δ curve is particularly suitable for demonstrating the effect of thermal history because tan $\delta(= E''/E')$ is independent of any experimental error introduced by the geometry of the samples.

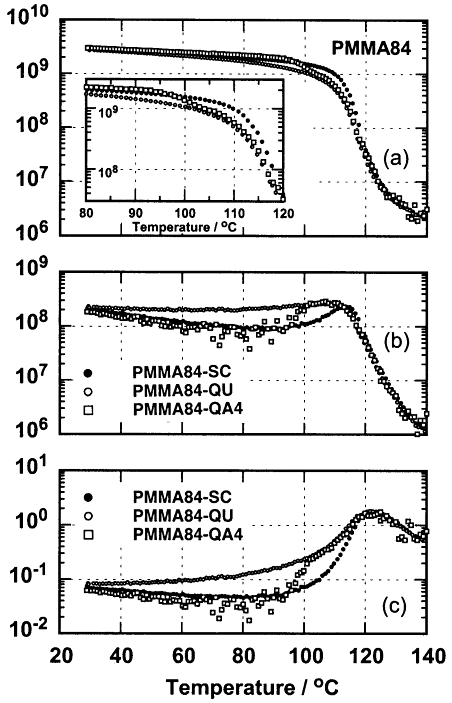

Fig. 1. The temperature dispersion curves of E', E'', and tan δ of PMMA84 samples with three typical thermal histories: PMMA84-QU, -SC, and -QA4. PMMA84-QA4 was annealed at 80°C for 150 h after being quenched from 190°C and then cooled slowly to RT.

The temperature dispersion curves of tan δ for the QA, QU and SC samples are shown in Fig. 2. The dispersion curve of the QU sample is an envelope of the curves of the QA samples above 100°C. For the QA samples, the temperature at which the curve starts to turn up and subsequently merges into the curve of the QU sample moves to higher values as the aging time increases.

Fig. 3 shows dispersion curves of tan δ for the QP samples along with those for the QU and SC samples. Fig. 3(a) covers a wide temperature range (20–140°C), while Fig. 3(b) is a magnification of Fig. 3(a) from 40 to 90°C. Physical aging is observed for the QA samples aged at

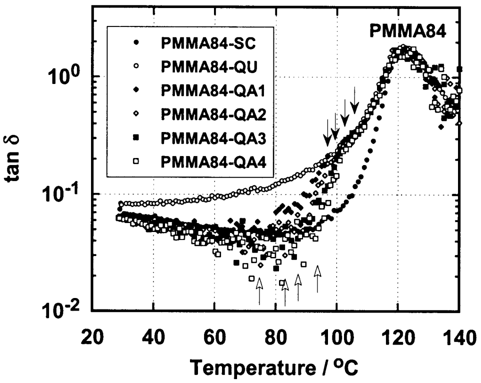

Fig. 2. The temperature dispersion curves of tan δ of PMMA84-QA samples along with PMMA84-QU and -SC samples. Black and white arrows indicate T_H and T_L at which point the curves of QA samples merge into the curve of QU sample and turn up steeply, respectively.

RT, where RT is far below T_g. The results show a similar tendency to that shown in Fig. 2. The tan δ curves for the QA samples merge into that for the QU sample at high temperatures. The temperature at which the curve for the QA sample starts to up turn also moves to higher temperatures with aging time, while the temperature range is lower than that of the QA samples. Physical aging as indicated by the change in the dynamic viscoelastic properties of PMMA84 is similar to that of other polymers [1,16,19–27].

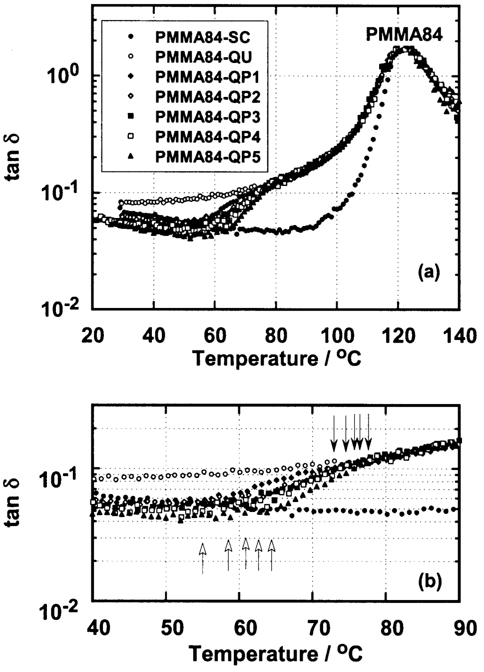

Fig. 3. The temperature dispersion curves of tan δ of PMMA84-QP samples along with PMMA84-QU and -SC samples. (a) A wide temperature range. (b) A magnification of (a). Black and white arrows point out T_H and T_L, respectively.

4. Discussion

We focus on two temperatures in Figs. 2 and 3. One is the temperature (T_H) at which the tan δ curves of the QA and QP samples merge into the curve of the QU sample; the other is the temperature (T_L) at which those curves turn up steeply. T_H and T_L are indicated by a white and black arrows, respectively, in Figs. 2 and 3; the temperatures are plotted in Fig. 4 for the QA and Fig. 5 for the QP samples. Also plotted in Figs. 4 and 5 are results for aged homo-PMMA samples (weight-average molecular weights of 575 000 (PMMA575) and 72 000 (PMMA72)) [23]. The agreement of the tan δ curves of the QA and QP samples with that of the QU sample above T_H suggests that the former samples keep a memory of their previous thermal history, i.e. of having been quenched from 190 to 0°C, and that the QA and QP samples have the same structure as the QU sample above T_H. The increase of T_H and T_L during aging suggests that the chain conformation of the QA and QP samples has been changing and relaxing continuously due to the thermal segmental motion at each annealing temperature. The length scale of segmental mobility depends on the temperature, and the movable segmental length increases with increasing aging temperature [20,21]. We can regard T_H and T_L as a measure of the segmental relaxation length scale and T_H can be characterized as the temperature corresponding to the maximum segmental relaxation scale length. The change in T_H and T_L to higher temperatures corresponds then to a development of the segmental relaxation from a smaller to a larger scale of segmental conformation. The larger scale segmental conformations relax after the smaller ones have relaxed.

As can be seen in Fig. 4, a plot of both T_H and T_L against aging time for the three PMMA samples annealed at 80°C results in two unique lines. This suggests that we cannot distinguish copolymer PMMA from homo-PMMA when aged at 80°C. We can see from the figure that there is no

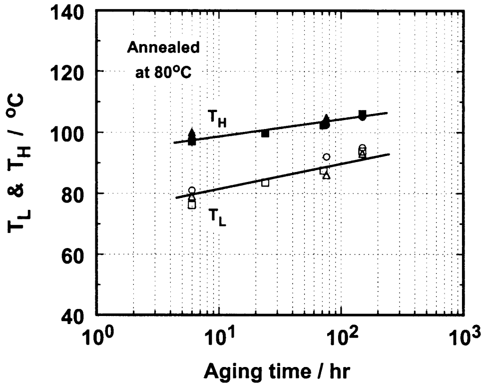

Fig. 4. Semi-logarithmic plots of T_H and T_L for PMMA84-QA samples (Fig. 2) against aging time at 80°C. Results from homo-PMMAs (PMMA575 and PMMA72) [23] are also plotted: the weight-average molecular weight is 575 000 for PMMA575 and 72 000 for PMMA72. (■, □) represents for PMMA84, (●, ○) for PMMA575 and (▲, △) for PMMA72: the closed symbols represent for T_H and the open symbols for T_L.

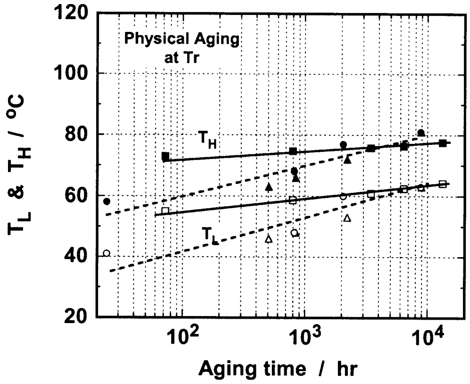

Fig. 5. Semi-logarithmic plots of T_H and T_L for PMMA84-QP samples (Fig. 3) against aging time at RT. Results from homo-PMMAs (PMMA575 and PMMA72) [23] are also plotted. Symbols as in Fig. 4. Solid lines represent for PMMA84; broken lines represent for homo-PMMAs.

molecular weight dependence for the relaxation [23]. The results suggest that the minor comonomer component in the copolymer (PMMA84) plays no role in the chain relaxation at that temperature. On the other hand, as seen in Fig. 5, data for T_H and T_L of PMMA84 aged at RT are quite different from those of the homo-polymers PMMA575 and PMMA72 at times before 2000 h. At times longer than 2000 h, the value for T_H for both the copolymer and homo-polymers converge, as do the values for T_L. These results suggest that the copolymer relaxes faster than the homo-polymers do at short times, while both the copolymer and the homo-polymers relax at a similar rate at longer times.

As stated above, aging temperatures for PMMA84 are classified into two categories; the minor comonomer component plays a role in the segmental relaxation at RT, but does not at 80°C. Note that the T_g of poly(ethyl methacrylate) is approximately 65°C [28–30] and the value is between RT and 80°C. Ethyl methacrylate (EMA) is the minor comonomer component of PMMA84. The EMA segments would be more flexible than the methyl methacrylate (MMA) segments in the main chain. When PMMA84 is at RT, MMA segments adjacent to EMA segments can move and relax faster than those MMA segments far removed from EMA segments, while the EMA segments also move and relax fast at the same time. Thus, PMMA84 relaxes faster than homo-PMMAs do during the short times of annealing at RT. At longer times, however, the effect of EMA segments on the relaxation of the main chain is no longer seen. Small-scale segmental conformations, including EMA segments and MMA segments adjacent to EMA segments, will have already relaxed, and only the larger scale segmental conformations will relax at this time. The larger scale segmental conformations of PMMA84 should be the same as those of homo-PMMAs. Therefore, PMMA84 relaxes with the similar rate to homo-PMMA at longer times.

When PMMA84 is at 80°C, the EMA segments should be so flexible that the EMA segments follow the MMA segmental motion, while the motion of the EMA will not affect the MMA segmental motion. Moreover, the characteristic segmental length of PMMA84 at 80°C would be larger than both the EMA segment length and the MMA segments adjacent to EMA segments. At a temperature where the characteristic segmental length is large, movement at such a scale would eliminate the loci of the smaller and faster segmental motions; which has been suggested experimentally using a sample which was quenched from the molten state, aged at a given temperature and then annealed above this aging temperature but below the T_g [3,20,23]. When we consider that the characteristic segmental length of PMMA84 is equal to that of PMMA575 and PMMA72 at 80°C, we would expect the three PMMAs to relax at the same rate at this temperature.

5. Conclusion

The physical aging of PMMA84, having a small amount of ethyl methacrylate (EMA) as a comonomer, was investigated below its T_g using dynamic viscoelastic measurements. The results were compared with those from homo-PMMAs. The sample was quenched from above its T_g and then aged at RT and 80°C. The shape of the temperature dispersion curves of the viscoelastic properties for the aged samples changed with aging. The results suggest that the chain conformation relaxes continuously over larger segmental scale lengths because the scale of the movable segments is related to temperature.

Aging temperatures for PMMA84 were classified into two categories; the minor comonomer component plays a role in physical aging at RT but does not at 80°C. We believe that the T_g of a poly(ethyl methacrylate), ca. 65°C, causes the division of the annealing temperatures into two classes, and we can consider that EMA segments are more flexible than MMA segments in the main chain.

When the samples were aged at RT, the rate of the change of the tan δ curves of the PMMA84 was different from those of homo-PMMAs at short times. The reason is that MMA segments adjacent to EMA segments can move faster than those far removed from EMA segments because the EMA segments are more flexible than MMA segments, while at the same time, the EMA segments are also moving and relaxing rapidly. At longer times, the relaxation rate of PMMA84 was close to that of the homo-PMMA. This reason is that small-scale segment conformations have already relaxed at shorter times and only the larger scale segmental conformations are relaxing at longer times, and we can consider the larger scale segmental conformations of PMMA84 the same as those of the homo-PMMAs. When the samples were annealed and aged at 80°C, the changing rate of the tan δ curves of PMMA84 was the same as those of the homo-PMMAs. The reason is that the characteristic segmental length of the PMMA84 at 80°C is the same as that of the homo-PMMAs at this temperature and the motion eliminates the loci of the smaller segmental motion. In future work, we will investigate the concentration dependence of the comonomer on physical aging.

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