Effect of the Thermal History of Polymers on Their Dynamic Mechanical Properties

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Synopsis

A torsion pendulum was used to compare quenched and annealed specimens of representative polymers with respect to their dynamic mechanical properties. Among amorphous polymers, the effects of thermal history appear to be both moderate and similar for different polymers. For some crystalline polymers, the effects of thermal history are again moderate. However, the effects are very great in one of the crystalline polymers selected, presumably because it is easily supercooled below its melting point.

INTRODUCTION

It is known that the mechanical properties of some polymers depend upon the thermal history of the specimen.[1] This dependence is perhaps best known as it affects properties such as tensile strength and ultimate elongation, where the strain is substantial. However, thermal history can have important effects on dynamic mechanical measurements also, where the strains are very small. The present investigation was undertaken to determine to what extent the dynamic mechanical properties of typical amorphous and crystalline polymers would be affected when the thermal history was varied.

EXPERIMENTAL

Apparatus

We examined our polymers as solid films which were used as the torsion element in a torsion pendulum. The specimens were 5 cm. long, 1 cm. wide, and of uniform thickness from 0.014 to 0.025 cm. The bob, which hung free, weighed 6.75 g. and had a rotational inertia of 140 g.-cm.[2]. The torsion element was enclosed in a thermostatted chamber which was continuously swept with nitrogen. Temperature stations below room temperature were approached from above, while those above room temperature were approached from below. In a normal run, the properties at lower than ambient temperatures would be measured during the first day. During the night the specimen would be warmed back to room temperature, and the properties at higher temperatures would be measured the next day.

The usual formulas[2] were used to calculate the dynamic rigidity modulus G' and the logarithmic decrement δ. The values of both G' and δ were corrected by the method of Inoue and Kobatake[3] in order to take into account the weight of the bob.

Preparation of Specimens

Poly(methyl methacrylate) and polystyrene were chosen to represent amorphous polymers. Film of a commercial grade of poly(methyl methacrylate) was cast from toluene/acetone 70/30 solution (Lucite 6011, Electrochemicals Department, E. I. du Pont de Nemours & Company). Mild preliminary baking of this film was followed by baking for 5 days at 150°C., a procedure which earlier work[4] at this laboratory had shown reduces the residue of solvent in the film to a spectroscopically undetectable level. Immediately after baking, a portion of the film was quenched in ice water, while another portion was annealed by leaving it in the oven, turning the oven off, and letting it cool to room temperature.

Film of a commercial grade of polystyrene (Styron, general molding grade, Dow Chemical Company) was compression-molded at 150°C., then quenched in ice water. Part of the film was subsequently annealed by baking for 20 min. at 115°C., then turning off the oven and leaving the film in the oven until it had cooled to room temperature.

Polypropylene, poly(vinylidene fluoride), and a copolymer of tetrafluoroethylene with isobutylene were chosen to represent crystalline polymers. One film was compression-molded at 183°C. from a commercial sample of polypropylene (Hercules, Inc.) and cooled by circulating water through the platens of the mold. Another film was molded from the same sample of polypropylene at 250°C., quenched in ice water, then annealed by baking for 1 hr. at 150°C., turning off the oven, and leaving the film in the oven until it had cooled to 70°C. During the annealing, the film was kept in an atmosphere of nitrogen.

The films of poly(vinylidene fluoride) were cast from a solution of a commerical sample (Kynar, supplied by Pennsalt Chemicals Corporation) in dimethylacetamide. After drying, they were baked for 7 min. at 210°C. Then one film was quenched in ice water; the other was annealed by turning off the oven and letting it cool to 48°C.

The copolymer of tetrafluoroethylene and isobutylene was an experimental material, substantially a regularly alternating copolymer. A film was compression-molded at 240°C. in the usual way. Part of the film was then annealed by baking for 3.5 hr. at 70°C., then turning the oven off and leaving the film in the oven until it had cooled to room temperature.

RESULTS AND INTERPRETATION

Curves showing the temperature dependence of G' and δ for each polymer studied are given in the accompanying figures.

Considering first the amorphous polymers (Figs. 1–4), we note that the quenched specimens exhibit a more rapid drop-off in the modulus curve and
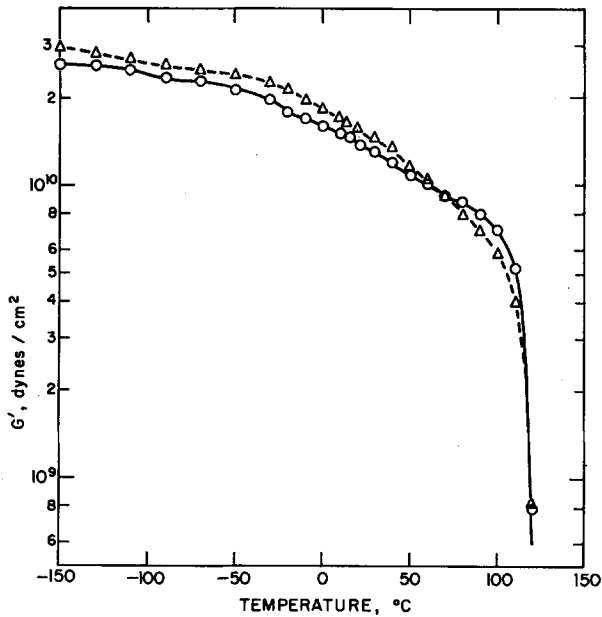
Fig. 1. Temperature dependence of the dynamic rigidity modulus for poly(methyl methacrylate): (O) annealed; (Δ) quenched.
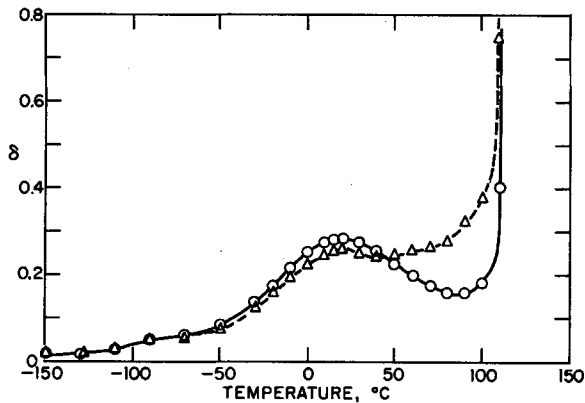

Fig. 2. Temperature dependence of the logarithmic decrement for poly(methyl methacrylate): (O) annealed; (Δ) quenched.

a correspondingly higher level in the decrement curve than do the annealed specimens. These differences begin to appear at temperatures as much as 60°C. below the glass temperature (T_g). They can be qualitatively explained as the effect of thermal history on the density of the structure. A quenched specimen can be expected to be less dense[1] than an annealed specimen of the same composition, even though both may be completely amorphous. Since its structure contains more free volume, the quenched
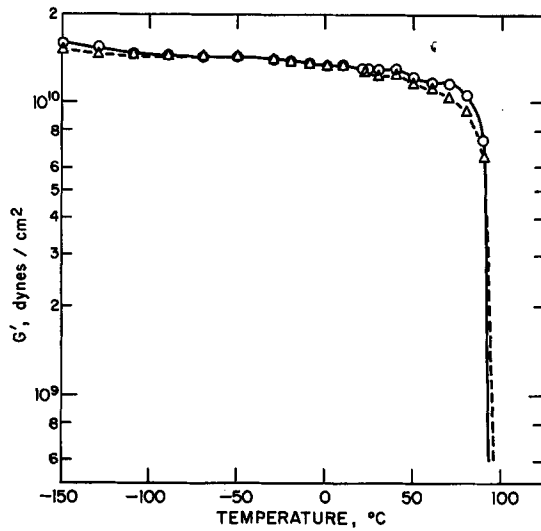
Fig. 3. Temperature dependence of the dynamic rigidity modulus for polystyrene: (O) annealed; (Δ) quenched.
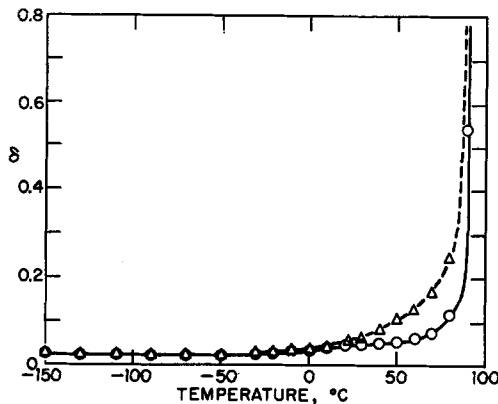

Fig. 4. Temperature dependence of the logarithmic decrement for polystyrene: (O) annealed; (Δ) quenched.

specimen, as it is warmed, will begin to "sense" the glass transition at temperatures farther below T_g than can the annealed specimen. Indeed, if the warming rate is sufficiently rapid, one could expect T_g for the quenched specimen to be somewhat lower than for the annealed specimen. Otherwise, annealing will take place in the quenched specimen as T_g is approached, and little if any difference in T_g between the two specimens can be expected.

Figure 1 indicates that at temperatures below 70°C. the quenched specimen of poly(methyl methacrylate) was more rigid than the annealed specimen. We have no explanation for this difference; it may be an artifact.
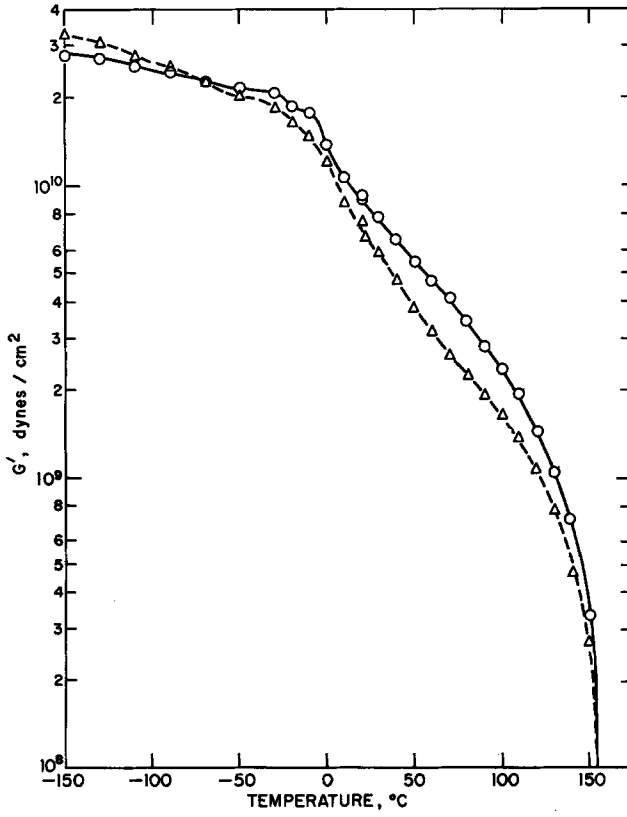
Fig. 5. Temperature dependence of the dynamic rigidity modulus for polypropylene: (O) annealed; (Δ) conventionally molded.
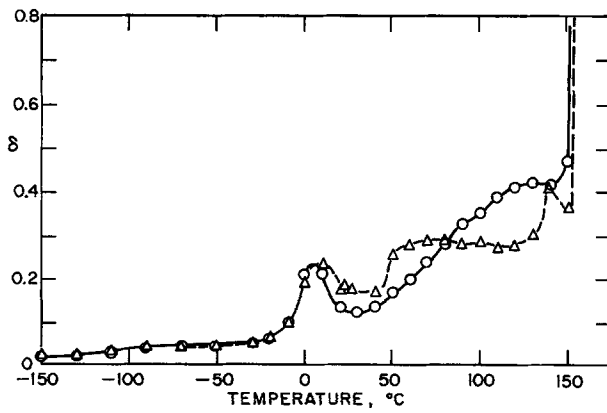

Fig. 6. Temperature dependence of the logarithmic decrement for polypropylene: (O) annealed; (Δ) conventionally molded.
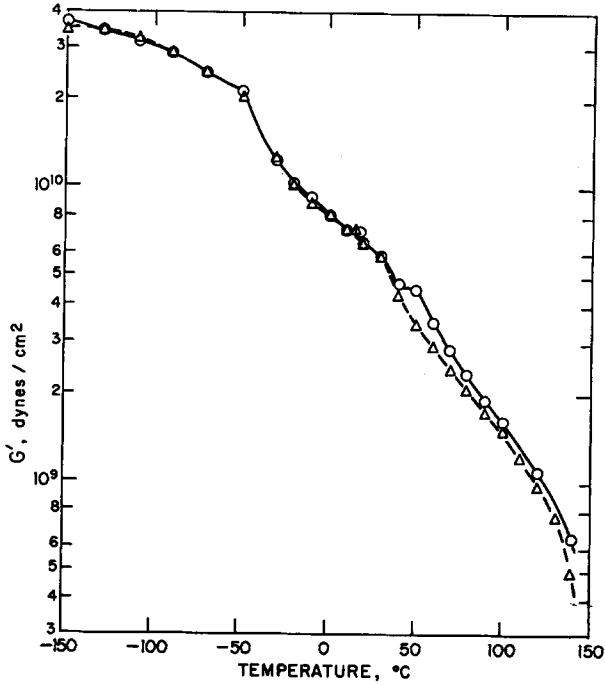
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Fig. 7. Temperature dependence of the dynamic rigidity modulus for poly(vinylidene fluoride): (O) annealed; (Δ) quenched.
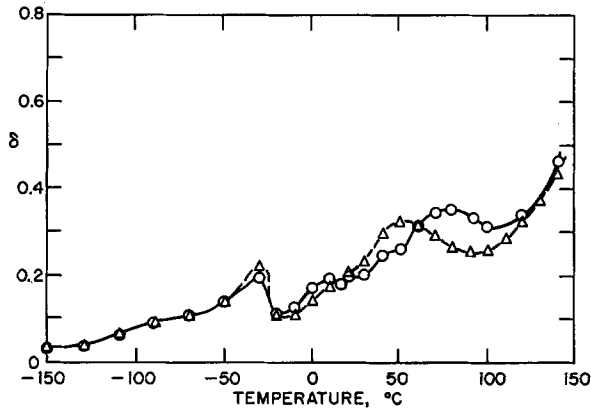

Fig. 8. Temperature dependence of the logarithmic decrement for poly(vinylidene fluoride): (O) annealed; (Δ) quenched.

Turning now to the crystalline polymers, we see in Figure 5 that the annealed specimen of polypropylene is generally more rigid than the conventionally molded specimen at the same temperature. Presumably the process of crystallization had proceeded further in the annealed specimen, yielding the stiffer structure. The effect of thermal history on the decre-
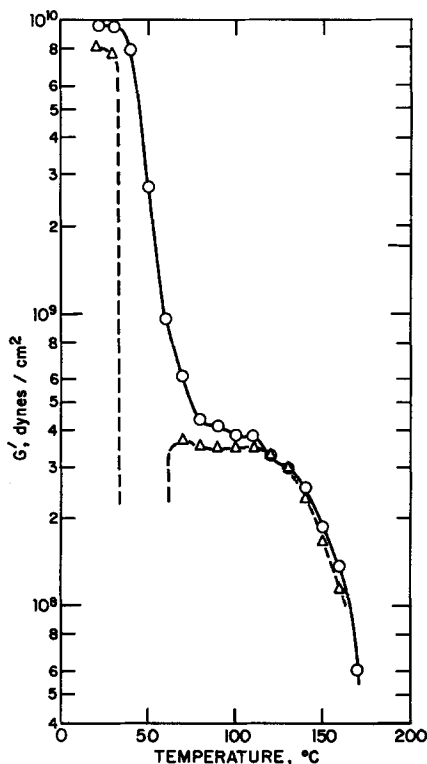
Fig. 9. Temperature dependence of the dynamic rigidity modulus for tetrafluoroethylene–isobutylene copolymer: (O) annealed; (Δ) conventionally molded.

ment curve is shown in Figure 6. The peaks at 5 and 10°C. evidently correspond to the glass temperatures of the two specimens. We do not know the exact source of the long sloping shoulder, between T_g and the melting point, in the curve for the annealed specimen. However, it is apparent that this shoulder is shifted downward in temperature by quenching, presumably because the structure is made less dense and intermolecular slippage is facilitated.

The curves for the specimens of poly(vinylidene fluoride) (Figs. 7 and 8) follow a pattern similar to that for polypropylene. The annealed specimen is a little more rigid than the quenched specimen in those regions where a difference can be detected. The decrement curves have peaks at 30°C., corresponding to the glass temperature. A peak between T_g and the melting point, and occurring at 75°C. in the annealed specimen, is shifted downward to about 50°C. in the quenched specimen. Again, this shift can probably be attributed to a less dense structure in the quenched specimen.

Thus far, we had found the effects of thermal history to be fairly regular and moderate, whether we had selected an amorphous polymer or a crystalline polymer for study. However, we obtained quite different results from
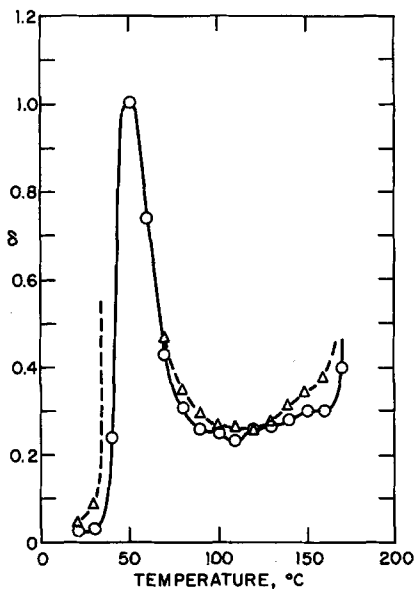
Fig. 10. Temperature dependence of the logarithmic decrement for tetrafluoroethylene–
isobutylene copolymer: (O) annealed; (Δ) conventionally molded.

the specimens of tetrafluoroethylene–isobutylene copolymer (Figs. 9 and
10). As the conventionally molded specimen was warmed and the tem-
perature approached 40°C., the modulus dropped abruptly. Then, as the
temperature continued to rise, the modulus recovered to about 3×10^8
dyne/cm.², remained fairly constant between the temperatures of 70 and
125°C., then subsided again gradually as the melting point was approached.
To explain this behavior, we postulate that the copolymer is crystalline
in its equilibrium state at room temperature, but is easily supercooled.
Thus, the conventionally molded film was largely amorphous and under-
went a pronounced glass transition at 40°C. As the temperature con-
tinued to rise, conditions became more favorable for crystallization. As
the copolymer crystallized, a structure was developed which could support
stresses elastically, and the modulus increased.

The annealed specimen gave results which were in harmony with this
explanation. Its modulus decreased monotonically with increasing tem-
perature, although even this presumably well-crystallized specimen ex-
hibited a distinct glass transition.

CONCLUSIONS.

The experiments with poly(methyl methacrylate) and polystyrene sug-
gest that thermal history will have only moderate effects on the dynamic
mechanical properties of amorphous polymers. In the absence of further
information, one could use the curves shown in Figures 1–4 to estimate the

direction and magnitude of these effects in an uncharacterized amorphous polymer for which the glass temperature is known.

The situation for crystalline polymers is more complicated. For polymers which do not easily supercool, the curves in Figures 5–8 probably indicate the kind and degree of the effects which may be expected. However, in characterizing a crystalline polymer, one must recognize the possibility that it may be a polymer which readily supercools. In such cases, as Figures 9 and 10 show, variations in thermal history can have a profound effect on dynamic mechanical properties.

References

1. L. E. Nielsen, *Mechanical Properties of Polymers*, Reinhold, New York, 1962, pp. 251–253.
2. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, p. 118.
3. Y. Inoue and Y. Kobatake, *Kolloid-Z.*, **160**, 44 (1958).
4. R. P. Porter, unpublished results.

Résumé

Un pendule de torsion a été utilisé pour comparer des échantillons refroidis et recuits de polymères représentatifs en rapport avec leurs propriétés mécaniques dynamiques. Parmi les polymères amorphes, les effets de l'histoire thermique apparaîssent à la fois comme modérateurs et semblables pour divers polymères. Pour certains polymères cristallins, les effets de l'histoire thermique sont de nouveau modérés. Toutefois, les effets sont très grands dans un des polymères cristallins choisis, probablement par suite de ce qu'il est facilement sur fondu en-dessous de son point de fusion.

Zusammenfassung

Ein Torsionspendel wurde zum Vergleich abgeschreckter und getemperter Polymerer in Bezug auf ihre dynamisch mechanischen Eigenschaften verwendet. Bei den amorphen Polymeren scheint der Einfluss der thermischen Vorgeschichte gering und für verschiedene Polymere ähnlich zu sein. Für einige kristalline Polymere ist der Einfluss der thermischen Vorgeschichte ebenfalls gering. Bei einem der ausgewählten kristallinen Polymeren ist der Einfluss, vermutlich wegen seiner leichten Unterkühlung unter den Schmelzpunkt, jedoch sehr gross.