Thermomechanical Determination of T_g Using a Modified Film Sample-Mounting Method

INTRODUCTION

We were interested in determining the glass transition temperatures (T_g) and, hence, the potential processability of commercially available and new experimental polymers possessing relatively high T_g values. Most of the experimental polymers were usually synthesized in quantities sufficient only to cast small films. Many of the existing methods of determining T_g required considerably larger specimens than were available from initial research studies and, generally, were too time consuming to employ for large numbers of samples. The development of a modified technique for rapid work on very small samples was therefore critical.

DISCUSSION

A du Pont Model 941 thermomechanical analyzer (TMA) was employed. In the recommended specimen-mounting procedure for this equipment, a film sample approximately 0.5 in. × 0.25 in. × 0.001 in. with a hole approximately 0.1 in. in diameter at each end is fastened between two quartz hooks by easing each holed end carefully over its respective hook. One hook is fixed, while the other is movable and is connected to the core of a linear variable differential transformer. The movement of the hook which indicates the stretching of the film under a predetermined load is recorded as the sample is heated at a predetermined rate. It was impossible to detect the T_g of our polymer film using this sample-mounting arrangement. The elongation of the sample holes was considerably greater than the stretching at T_g; also, much larger sample strips were required for this particular type of mounting.

To overcome these problems, a pair of small 17-4 PH stainless steel clamps (Fig. 1) were designed and built to slip over the quartz hooks, and the film samples in turn were secured between these clamps. Since the coefficients of thermal expansion of most polymers in the temperature range from ambient to 485°C are 5–25 times greater than that for the clamp material, the clamps were considered dimensionally stable.[1] They accommodated film samples with a nominal test area (sample area between clamps) of approximately 0.05 in. × 0.04 in. × 0.0005–0.002 in. thick and were used satisfactorily from ambient to 485°C with no apparent slippage. The nominal weight of the clamps with sample mounted was approximately 0.375 g.

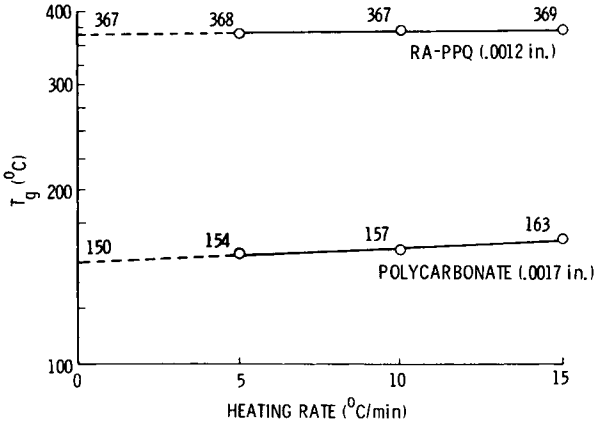

Fig. 1. Clamp assembly with mounted film sample.

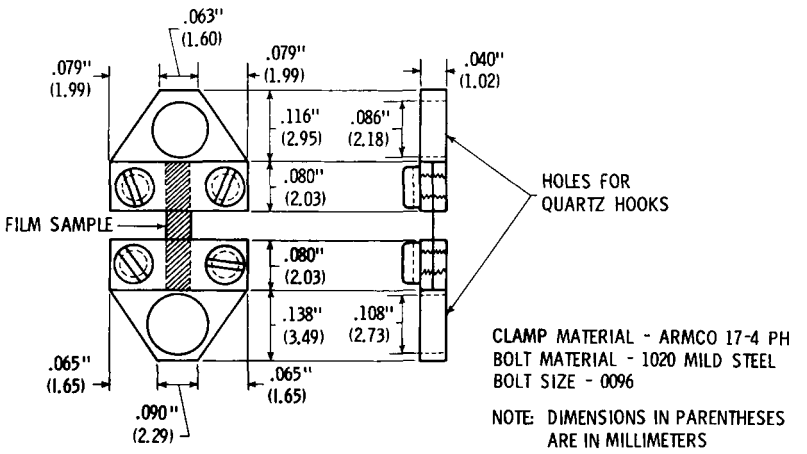

Fig. 2. Glass transition temperature (T_g) vs. heating rate.

The T_g values of two polymer films were determined using the modified sample mount in order to establish the validity of this method. A 0.0017-in.-thick sample of polycarbonate [poly(4,4'-isopropylidenediphenylene carbonate)], with a T_g of 149°C,[2] and a 0.0012-in.-thick sample of poly[2,2'-(1,4'phenylene)-6,6'-bis(3-phenylquinoxaline)], an aromatic poly(phenylquinoxaline) with a T_g of 365°C,[3] were run at heating rates of 5°, 10°, and 15°C/min with zero pan weight. Curves of T_g versus heating rate (Fig. 2) were plotted and extrapolated to a theoretical 0°C/min heating rate. This gave a T_g of 150°C for the polycarbonate, which agrees favorably with the published T_g value for this polymer. A T_g of 367°C was obtained for the poly(phenylquinoxaline) film (Fig. 2). This is within 2°C of the value Wrasidlo, using dilatometry,[3] found for the same polymer.

In practice, for well-cured samples, a single determination at 5°C/min heating rate often afforded a satisfactory T_g value at a considerable savings in time.

While this technique does indicate the softening temperature of a film, a confirming method such as the determination of the C_p or dilatometry must be used to establish that the softening temperature is indeed a T_g. Once this has been established for a particular polymer, any further T_g determinations for closely related films can be accomplished using this modified film sample mounting method.

CONCLUSIONS

A modified film sample-mounting technique used for the determination of the glass transition temperatures (T_g) of polymers by thermomechanical analysis (TMA) has been described. The technique employs a pair of small stainless steel clamps that grip a film specimen 0.05 in. × 0.04 in. × 0.0005–0.002 in. thick between the existing quartz hooks of a commercial thermomechanical analyzer. This modification permits the rapid determination of the T_g of thin films for temperatures from ambient up to 485°C. Polymers with T_g values at the extremes of the operating temperature range were analyzed using this method, and the T_g values were found to agree to within 1–2°C of the published values for the same polymers determined by alternate techniques. These clamps have been used in over 360 runs with no apparent damage due to repeated thermal cycling.

References

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2. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, J Wiley, New York, 1966, p. III-77.
3. W. Wrasidlo, *J. Polym. Sci. A-2*, **9**, 1622 (1971).

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