



Fig. 2. Composites of melt fracture data.

small, no cycle occurs, as is the case of resin E. A correlation among the diameter of the extrudate, the molecular weight, and the molecular weight distribution is indicated by the data presented here.

References

1. Bagley, E. B., I. M. Cabott, and D. C. West, *J. Appl. Phys.*, **29**, 109 (1958).
2. Sabia, R., *J. Appl. Polymer Sci.*, in press.
3. Clegg, P. L., *Brit. Plastics*, **30**, 535 (1957).

R. SABIA
M. E. MULLIER

W. R. Grace & Company
Polymer Chemicals Division
Clifton, New Jersey

A Simple Method for the Determination of Glass Temperatures of Amorphous Polymers

The glass temperature of an amorphous polymer is of some significance in that it is the temperature at which a marked increase in molecular movement gives rise to an incipient change from glasslike to rubberlike properties. It is commonly obtained from an inflection in the temperature-dependence curve of some physical property such as specific volume¹ or refractive index,² measured under standardized conditions of rate of heating.

In the course of a preliminary investigation of the properties of amorphous polymers obtained as fibers (radius < 0.01 cm.) drawn from the "melt," it appeared that a relatively simple method is available for the determination of glass temperatures. A polarizing microscope and the use

of a retardation technique reveal the presence of birefringence, the optical axes coinciding with the extinction position of the crossed Nicols. If such a fiber is periodically immersed in a heated bath containing an inert liquid (e.g., aq. KCl solution, so that temperatures in excess of 100°C. may be realized), above a certain critical temperature, which is reproducible to 0.5°C., the fiber rapidly develops a permanent spiral form. It is believed that the phenomenon is due to a differential stress relaxation effect, possibly related to one described in an investigation into the influence of shearing stress on melt extrudates:³ as the temperature of the bath reaches the glass temperature, enough mobility of the polymer chains is afforded for the fiber to develop spirality. That relaxation has occurred is confirmed by a decrease in the magnitude of the birefringence (Table I).

TABLE I
Birefringence and Glass Temperatures of Drawn Amorphous Fibers

Polymer	Birefringence		Glass temp., °C.
	Before treatment	After treatment	
Polyvinyl acetate	0.001	<0.001	28
Polystyrene	0.010	0.001	95
Polymethyl methacrylate	0.001	<0.001	75

The values of the glass temperatures of polyvinyl acetate and polystyrene obtained in this way agree quite well with other published data, but assessment in the case of polymethyl methacrylate is more difficult, owing to a diversity in such information.⁴ In conclusion, it should be emphasized that the technique, as described, is apparently inapplicable to semicrystalline polymers, probably because of crystallite stabilization, although reference has been made to a method for the measurement of contraction temperatures in synthetic fibers.⁵

References

1. Boyer, R. F., and R. S. Spencer, *Advances in Colloid Science*, Vol. 2, Interscience, New York-London, 1946.
2. Wiley, R. H., *J. Polymer Sci.*, **2**, 10 (1947).
3. Spencer, R. S., and R. E. Dillon, *J. Colloid Sci.*, **4**, 241 (1949).
4. See, e.g.; Billmeyer, F. W., *Textbook of Polymer Chemistry*, Interscience, New York-London, 1957; Gaylord, N. G., and H. F. Mark, *Linear and Stereoregular Addition Polymers*, Interscience, New York-London, 1959; Tobolsky, A. V., *Properties and Structure of Polymers*, Wiley, New York, 1960.
5. Preston, J. M., *J. Textile Inst.*, **40**, T767 (1949).

R. P. SHELDON

Polymer Research Laboratories
Department of Chemical Technology
Institute of Technology
Bradford, England

Received June 4, 1962