LETTERS TO THE EDITORS

Apparent Increase in Melt Index during Measurement

The recent letter by Skinner[1] draws attention to two features of capillary rheometry which are not often appreciated in routine viscometric measurements. One of these effects has received considerable attention in these laboratories in connection with the flow of molten polypropylene and the establishing of a melt flow index test method for that material.[2]

Skinner shows that with the standard melt indexer there may be a 50% increase in flow rate during the complete extrusion of a full charge of polythene, assuming a power law of flow, and making no capillary end connection. It is, of course, a prerequisite that for a standardized test method, the measured quantity shall respond to the test conditions in the same way for all materials tested—in this case that the flow rate shall be constant at all points during the extrusion. It is clear from Skinner's example, that this is not true in the case quoted: whether or not this has been experimentally observed during routine measurements of melt index in the United States or Canada is not known but as the ASTM test method requires only one sample of extrudate to be cut, it is unlikely that changes in rate would be noticed: on the other hand, the B.S.I. method includes, in its procedure, a check on the constancy of flow rate.

With polypropylene, the position becomes much worse, for the index n may be as much as 2.5, and the consequent increase in flow rate is by a factor of 3.6 in the course of a run. It was the direct observation of such an increase that initiated work on this problem, which showed that the pressure gradient in the barrel, or "reservoir effect," was responsible.

Oakes and Peover in 1946 and Clegg in 1957[3] considered the Melt Indexer as a system of two extruders in series, and showed that the barrel pressure gradient was only of the order of a few percent for most polythenes at grading stress (1.7×10^5 dynes/cm.^{2}). Clegg showed, however, that for materials with $n > 2$ (e.g., P.V.C.) the effect was very great, and could not be ignored in the measurement of melt indices.

His treatment gives an expression for the output rate:

$$Q = \text{const.} \left[\frac{1}{1 + \dfrac{L}{l}\left(\dfrac{r}{R}\right)^{1+3/n}} \right]^n$$

where L = length of polymer column between die and piston, l = length of die, r = radius of die, R = radius of barrel, and n = flow power law exponent. This result can also be derived from the equation given by Skinner.

In the Melt Indexer, with $n = 2$, Q increases by 100% between the beginning and end of the run, and attains the value equivalent to that due to the whole pressure on the piston only at the end of the run.

Measurements of the pressure in the melt near the die entry were made (a) by the deflection of a diaphragm in the barrel wall[2] and later (b) by a pressure transducer in a similar location (Lamb and Benbow[4]). A parallel register of the rate of flow was also made and both showed an increase as the piston descended. Values of apparent viscosity

calculated from the rate alone and assuming full pressure to be operative at the die entry showed a decrease by a factor of 2 in the course of the run, whereas those using the pressure indicated at die entry were constant.

In comparing the fluidities of different propylene polymers it is necessary to do so at the same shear stresses: since the barrel pressure gradient is different for different polypropylenes, a fair comparison can only be made at the end of the run when the barrel is nearly empty. To enable this to be done simply, a recorder has been constructed which monitors the motion of the piston. From a record of this motion the flow rate at the end of the run, i.e., under a known shear stress, is easily calculated.

References

1. Skinner, S. J., J. Appl. Polymer Sci., 5, 14 (1961).
2. Charley, R. V., Brit. Plast. 38, 9 (1961).
3. Oakes, W. G., and C. Peover, and P. L. Clegg, unpublished information.
4. Benbow, J. J., and P. Lamb, unpublished information.

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Relative Degree of Cure in Unsaturated Polyester–Styrene Copolymer as Determined by Differential Thermal Analysis

Differential thermal analysis (DTA) has been used for many years to study the changes which a substance undergoes when heated. Early applications of DTA were in the ceramics and metallurgy fields. In recent years, this technique has been applied to a variety of arts, including the study of polymers. Some of the aspects of polymeric systems which have been investigated with the aid of DTA are qualitative analysis (identification of a polymer from its unique thermogram), degree of cure (qualitative), heat of polymerization, glass transition temperature, and the effect of irradiation on polymers.[1]

During our investigation of unsaturated polyester–styrene copolymer systems, we found that no adequate method was available for the determination of degree and rate of cure of these resins. The SPI exotherm methods of testing[2] provide some information about the overall curing properties of thermosetting systems, but these accelerated curing tests give no data relating degree of cure to time. ASTM methods for determining flexural properties[3] would provide data for flexural strength and flexural modulus of the copolymer with respect to curing time, but the time required, the poor reproducibility, and nonlinearity of flexural properties and degree of cure, make this method of following cure cumbersome.