

LETTERS TO THE EDITORS

Apparent Increase in Melt Index during Measurement

The recent letter by Skinner¹ 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 1957³ 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:

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

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 wall² and later (b) by a pressure transducer in a similar location (Lamb and Benbow⁴). 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

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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 testing² 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 properties³ 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.

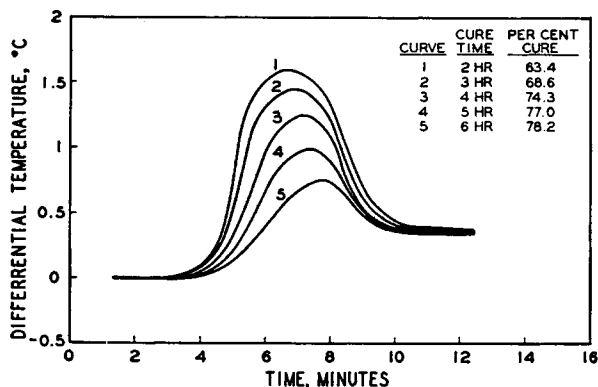


Fig. 1. DTA cure exotherms for unsaturated polyester-styrene copolymer cured at ambient temperature.

Polymerization, in general, is an exothermic process. When addition copolymerization occurs in an unsaturated polyester-styrene system, an amount of heat will be given off which is proportional to the extent of the polymerization. If a method were available for measuring the heat evolved by a curing resin system in a period of time, it would be possible to assign a relative degree of cure to the system at that time. In view of the previous work with DTA,¹ we felt that differential thermograms of the resins might provide the necessary information.

The unsaturated polyester used to study this possible application for DTA was prepared in the following manner. Isophthalic acid was reacted with propylene glycol to form the bis ester. This bifunctional ester was then reacted with maleic anhydride to form the unsaturated polyester.^{4,5} The reactant ratios were 1 mole isophthalic acid to 1 mole maleic anhydride to 2.1 moles propylene glycol. A 50% (by weight) solution of this unsaturated polyester in styrene was then prepared for use in the investigation. The polymerization initiator was a 60% solution of methyl ethyl ketone peroxide in dimethyl phthalate; the promoter, a commercial 6% cobalt naphthenate solution.

Test castings $\frac{1}{8}$ in. by $\frac{1}{2}$ in. by 6 in. were prepared by pouring the catalyzed polyester-styrene solution into finger molds sealed between glass plates. After gelation, the glass plates were removed and the finger molds, containing the sample bars, were wrapped in cellophane to exclude air. Subsequently, at definite time intervals, the cellophane cover was peeled back to permit removal of a sample bar from the mold. A small portion of material was cut from the bar for determination of the degree of cure in the casting.

Degree of cure of the resin samples was determined by DTA. The small portion of the sample bar was frozen with solid carbon dioxide, then ground to 40 mesh or finer in a Wiley Laboratory Mill, Intermediate Model. Dry Ice was removed by evaporation. Weighed portion of the ground copolymer was then subjected to DTA, using isophthalic acid as the reference material. The heating rate was adjusted to give a temperature increase of about 10°C./min. The quantity of heat given off in the postcuring of the sample during the DTA run is proportional to the area under the curing exotherm of the DTA thermogram.⁶ These area values, when compared to the exotherm area for the polymerization of the uncured polyester-styrene solution, were taken as a measure of the relative cure of the system. Relative percentage of cure data for the ambient-cured resin are given in Table I.

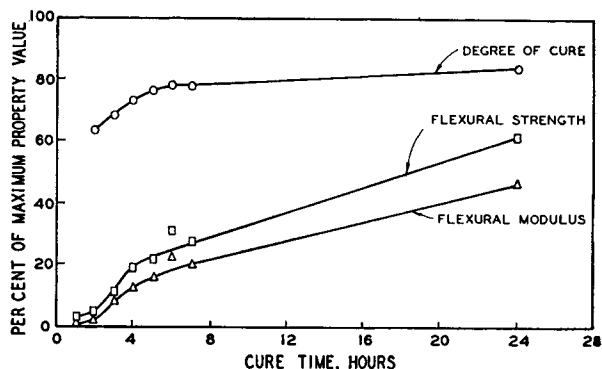


Fig. 2. Relative flexural strength, flexural modulus, and degree of cure versus time of ambient-temperature cure of an unsaturated polyester-styrene copolymer.

That DTA cure data are consistent is illustrated by Figure 1, which shows the area reduction the curing exotherm undergoes with increasing cure time, and Figure 2, which shows the agreement of the degree of cure values with a smooth curve. From these results it appears that DTA is a simple, precise method for the determination of relative degree of cure in unsaturated polyester-styrene systems and undoubtedly could be used in other systems where curing is involved (as pointed out by Bhaumik et al.,⁷ who applied DTA to hard rubber reactions).

Degree of cure as measured by DTA was also correlated with degree of cure as measured by change in flexural strength and flexural modulus. The major portion of each test casting was cut in half to provide samples for duplicate determination of the flexural properties.³ These analyses were performed with the aid of an Instron testing machine.

Oven-cured samples of the unsaturated polyester-styrene solution were also prepared in finger molds, and the flexural properties of these cured samples were taken to be the maximum values obtainable for the copolymer. Flexural properties data for ambient- and oven-cured samples are listed in Table I. Data relating degree of cure, flexural strength, and flexural modulus for this unsaturated polyester-styrene system are illustrated in Figures 2 and 3. These figures show that the relationships between degree of cure and flexural properties are definitely nonlinear and that the resin is about 75% cured before any appreciable flexural value is evidenced.

TABLE I
Relative Degree of Cure and Flexural Data for an Ambient-Cured Unsaturated Polyester-Styrene Copolymer

Cure time, hr.	Relative % cure	Flexural strength		Flexural modulus	
		psi	% Max.	psi	% Max.
1	—	180	1.3	0.2×10^4	0.4
2	63.4	649	4.7	0.9×10^4	1.7
3	68.6	1,650	11.9	4.0×10^4	7.7
4	74.3	2,690	19.5	7.1×10^4	13.6
5	77.0	2,960	21.4	8.0×10^4	15.4
6	78.2	4,250	30.8	12.1×10^4	23.2
7	78.3	3,750	27.2	10.3×10^4	19.8
24	82.8	8,350	60.5	24.6×10^4	47.3
48	—	10,500	76.0	31.8×10^4	61.2
Oven-cured	100	13,800	100	52.0×10^4	100

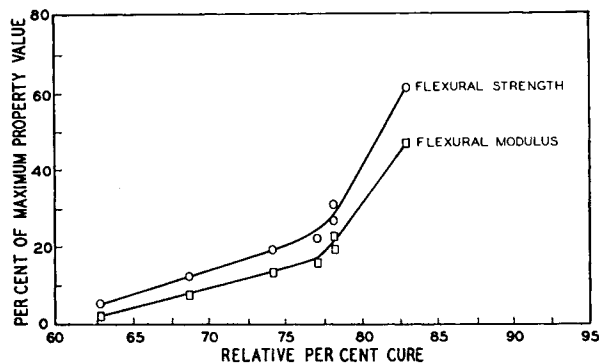


Fig. 3. Relative flexural strength and flexural modulus versus relative degree of cure of an ambient-temperature-cured unsaturated polyester-styrene copolymer.

Differential thermal analysis determinations were found to be much simpler to perform than the flexural properties determination, in respect of both the time of the determination and the sample preparation. (The casting of resin bars was necessary for the flexural determinations. Any shape casting is suitable as a sample for DTA, since these samples are powdered.) Since the degree of cure data, as determined by DTA, was found to be more consistent in fitting a smooth curve than the flexural values, and since the DTA data have been found to be more reproducible than the flexural data, it would also seem that the DTA determinations are more precise (if not more accurate) than the flexural property determinations.

This investigation is continuing, and results in greater detail will be submitted for publication at a later date.

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Stress Relaxation in Molten Polymers

As a result of extensive experimental work on stress relaxation of molten polymers of the linear and branched type (with few or no crosslinks), our attention was drawn to the following phenomenon which was shown more or less clearly in all the instances of the investigation.

The relaxation times tend to be independent on the initial value \mathcal{T}_{ss} of the stress (namely, of the shear stress following cessation of the steady-state flow). This occurs particularly at the higher values of \mathcal{T}_{ss} , and is better verified when the values attained by the relaxation stresses \mathcal{T} are low.

The phenomenon will be called here *relaxation isochronism*. It was thought to be a consequence of the nonlinearity (non-Hookeanity) of the elasticity of molten polymers. Indeed, when the strains γ are extremely large, as they are in the case of stress relaxation following cessation of a steady-state viscous flow at high steady-state stresses, a linear (Hookean) stress-strain relationship cannot be assumed.

It can be shown that a stress-strain *asymptotic* relationship is a sufficient condition for "isochronic" relaxation; "asymptotic" means that as the stress \mathcal{T} increases toward infinity the corresponding strain γ tends toward an asymptotic value γ_m .

The general differential equation of the stress relaxation, $\mathcal{T} = -\eta d\gamma/dt$, was integrated, with the aim of obtaining the stress-time equation $\mathcal{T} = f(t)$ which is valid within the whole range of the investigated values of the initial stress, and which is in agreement with the actual stress-time relationships experimentally found.

This integration was done under the assumption that the internal friction η which is effective in the stress relaxation phenomena (not to be confused with the measured melt viscosity of the bulk polymer) is a constant, namely, that it depends only on the structure and temperature of the polymer, and not on the stress or the time.

Furthermore, some different nonlinear stress-strain relationships have been assumed, as: Asymptotic-exponential:

$$\gamma = \gamma_m \left[1 - \exp \left\{ -\frac{\mathcal{T}}{\mathcal{T}_k} \right\} \right] \quad (1)$$

Asymptotic-hyperbolic:

$$\gamma = \gamma_m \mathcal{T} / (\mathcal{T} + \mathcal{T}_k) \quad (2)$$

Nonasymptotic logarithmic:

$$\gamma = \gamma_c [\ln(\mathcal{T} + \mathcal{T}_k) / \mathcal{T}_k] \quad (3)$$

Here γ_m , γ_c , and \mathcal{T}_k are constants characterizing the elastic features of any given polymer sample at a given temperature. Such constants are defined and calculated from the experimental data of the stress relaxation.

The stress-time relationships resulting from such integrations fulfill more or less strictly the condition of relaxation isochronism.

Models consisting of linear elastic elements coupled with nonlinear ones, characterized by eqs. (1)-(3), can be defined, giving stress-time relationships which are in agreement with the experimentally recorded ones, within the limits of experimental accuracy.

Details of the calculations and applications to experimental instances will be given in subsequent work.

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