

Influence of Molecular Weight Distribution on the Elasticity and Processing Properties of Polypropylene Melts

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Synopsis

In a study of the flow behavior of polymer melts a semi-empirical viscometric equation has been used which contains an elasticity parameter relating the shear dependence of the viscosity to the normal-stress effect. The way in which both these effects are influenced by the molecular weight distribution of the polymers investigated is shown, and the influence of melt elasticity on polymer processing behavior is discussed. From previously published viscosity data the elasticity parameter has been determined for a number of polypropylene grades, and the possibility of classifying these grades according to a characteristic time constant is indicated.

Introduction

In the development of new polymers and the improvement of existing grades there is a steadily increasing need to relate the properties of the polymers to their molecular structure. As nearly all polymers have to be processed in some way to be made into useful products, flow behavior is of special interest in this respect.

Clearly, in trying to relate flow properties to molecular structure, it would help if we knew more precisely what was meant by the as yet rather vague concepts of flow behavior and molecular structure. Before specifying our own views on the matter, however, we should like to make our particular approach quite clear. Generally speaking, two extreme approaches appear possible;^{1,2} either one starts with an assumed molecular structure and constructs a molecular theory^{1a, 1b} which explains observed phenomena, or one starts with a continuum theory^{1c} which enables a rigorous description of the flow behavior and subsequently tries to introduce statistical or molecular arguments. Owing to the complexity of both the deducible molecular structure and the observable flow behavior, these two approaches are still rather far apart, although of course they may or even must come together in the end.* This means that to obtain results which have direct practical

* It should be made clear that we do not want to suggest that nothing has been done in this direction (see for instance ref. 2), nor are the references cited by any means exhaustive; they are given only by the way of illustration.

significance, it is still necessary to put up with a certain amount of arbitrariness. The procedure thus followed is mainly concerned with the finding and subsequent correlation of parameters which are thought to characterize the molecular structure and the flow behavior. This is what we therefore have attempted.

One way in which the steady laminar shear flow of linear bulk polymers can be characterized has been discussed by us elsewhere.³ We proposed a viscometric equation relating the viscosity η to the shear stress σ_t as follows:

$$\eta = \eta_0/[1 + (\sigma_t/\sigma_c)^n]^{1.7} \quad 0 < n \leq 2$$

The special feature of this equation is that the parameter σ_c (together with the index n) not only expresses the shear dependence of the viscosity as indicated but also is a measure of the melt elasticity. Following the ideas of Weissenberg⁴ as interpreted by Philippoff,⁵ we consider melt elasticity to give rise to the occurrence of the so-called recoverable strain S_R , which is thought to be responsible for the normal stress[†] σ_n , so that:

$$\sigma_n = \sigma_t S_R$$

and a modulus of elasticity μ can be introduced:

$$\mu \equiv \sigma_t/S_R = \sigma_t^2/\sigma_n.$$

Furthermore we showed that the normal stress-shear stress relation appears to follow a power law:

$$\sigma_n/\sigma_t^m = \text{constant}$$

with $m = 1 + \frac{1}{2}n$, and that up to a constant numerical factor, the parameter σ_c can be identified with μ_1 , i.e., the value of the modulus of elasticity at which $S_R = 1$.

As regards molecular characteristics we restrict ourselves to the molecular weight distribution of linear polymers (polypropylene) in the hope of specifying it by two parameters, viz., one for (some average) molecular weight and another for the width (or form) of the distribution. Our main concern will be the possible correlations between the various parameters proposed, but some attention will also be paid to the role of melt elasticity in processing, with specific reference to injection molding.

Experimental Results

The results we are about to discuss (see Table I) were obtained from rheogoniometer⁷ and/or capillary rheometer measurements on a number of polypropylene melts. The way in which the rheological parameters were derived from the experimental results is discussed in detail in our other article.³ In cases where both rheogoniometer and capillary rheometer

† In the general three-dimensional description of simple-shear flow of incompressible media⁸ (1 = direction of flow, 2 = direction of velocity gradient, 3 = neutral direction) two normal-stress differences have to be considered, viz., $\sigma_{11} - \sigma_{33}$ and $\sigma_{22} - \sigma_{33}$, σ_{33} being unknown in the case of incompressibility. We only consider $\sigma_{11} - \sigma_{22} = \sigma_n$.

results are given, the measurements are our own, while the molecular weight distribution was known, having been determined by a column fractionation⁸ technique, followed by calculation of the various molecular weight averages by Mussa's⁹ method of graphical integration. In all other cases, the rheological parameters have been derived from capillary rheometer measurements reported by Van der Vegt,¹⁰ the molecular weight distribution being estimated later from the relation found for the other samples.

But for some apparent scatter, the zero shear viscosity results are in agreement with the well-known exponential relation¹¹ generally found¹² with the weight-average molecular weight \bar{M}_w . This is illustrated in Figure 1, where results of measurements at 200°C, not given in Table I, are also included. When judging these results one should bear in mind that values of η_0 presented here were obtained by fitting the capillary rheometer data to the viscometric function presented in the introduction. Although the same overall picture is obtained when the rheogoniometer data are used, direct comparison between the two types of results for individual samples shows discrepancies on account of the viscosity being very sensitive to slight differences in temperature and/or molecular weight. For instance, slight differences in molecular weight may be found as a result of having to press the nibs, used for the capillary rheometer experiments, into plates for the rheogoniometer measurements.

Fortunately, the other rheological parameters, i.e. the index n and the elasticity parameters σ_c and μ_1 , did not show any significant dependence on or correlation with temperature or any of the (average) molecular weights. However, one of the parameters characterizing the width of the molecular weight distribution did appear to affect the melt elasticity, and that was \bar{M}_z/\bar{M}_w . This is illustrated in Figures 2, 3, and 4 for n , σ_c and μ_1 respectively, where it can be seen that n decreases with \bar{M}_z/\bar{M}_w whereas σ_c and μ_1 decrease with $(\bar{M}_z/\bar{M}_w)^2$.

That melt elasticity is independent of molecular weight has in fact been pointed out previously,^{13,14} and has been supported recently^{15,16} with experimental evidence relating to anionic polystyrenes. Mieras and Van Rijn¹⁵ showed that the theoretically expected¹⁷⁻¹⁹ molecular weight dependence virtually disappeared at molecular weights above 160000, and Akovali¹⁶ showed that in the blending of monodisperse samples no significant correlation could be detected with the parameter \bar{M}_{z+1} (\bar{M}_z/\bar{M}_w), considered by Ferry¹⁷ to be the one determining the melt elasticity. Thus the absence of any dependence of melt elasticity on molecular weight would seem to be quite well established experimentally, and consequently the observed influence of the molecular weight distribution remains quite incomprehensible from a theoretical point of view.^{18,19}

Discussion

Let us now consider the practical implications, if any, of the following statement, which is clearly supported by the data presented here.

TABLE I
Rheological and Molecular Characteristics of Various Polypropylene Grades

| Polypropylene | $\eta_0 \times 10^{-5}$, P at 250°C, P | $\sigma_c \times 10^{-5}$, dyne/cm ^{2a} | n^a | τ_{c1} sec | $\mu_1 \times 10^{-5}$, dyne/cm ^{2b} dg/min, | MI, 230°C | $\bar{M}_w \times 10^{-5}$ | \bar{M}_z/\bar{M}_w | $\bar{M}_w \times 10^{-5}$ (estimated) ^d | \bar{M}_z/\bar{M}_w (estimated) ^d |
|---------------|--|--|-------|--------------------|---|--------------|----------------------------|-----------------------|--|---|
| A 1 | 1.3 | 3.8 | 1.5 | 0.35 | | 0.2 | | 5.0 | | 1.9 |
| 2 | 1.4 | 3.1 | 1.6 | 0.45 | 0.66 | 0.5 | 5.7 | 2.0 | | |
| 3 | 0.88 | 2.7 | 1.4 | 0.32 | | 0.8 | | 4.5 | | 2.2 |
| 4 | 0.30 | 1.8 | 1.2 | 0.17 | 0.26 | 2.6 | 3.5 | 2.9 | | |
| 5 | 0.26 | 1.5 | 1.1 | 0.17 | 0.18 | 3.7 | | 3.2 | | 3.0 |
| 6 | 0.18 | 1.2 | 1.0 | 0.14 | | 6.3 | | 2.9 | | 3.3 |
| 7 | 0.23 | 1.4 | 1.1 | 0.17 | | 5.3 | | 3.0 | | 3.1 |
| 8 | 0.17 | 1.4 | 1.1 | 0.12 | | 4.2 | | 2.8 | | 3.1 |
| 9 | 0.20 | 1.6 | 1.1 | 0.12 | | 5.1 | | 2.9 | | 2.9 |
| B 1 | 0.51 | 6.0 | 1.8 | 0.10 | 1.0 | 1.2 | 3.5 | 1.7 | | |
| 2 | 0.11 | 4.5 | 1.5 | 0.025 | | 5.2 | | 2.5 | | 1.7 |
| 3 | 0.28 | 2.0 | 1.4 | 0.14 | | 2.7 | | 3.2 | | 2.5 |
| 4 | 0.07 | 6.8 | 1.9 | 0.01 | 1.0 | 7.9 | 2.2 | 1.4 | | |
| 5 | — | 6.5 | 1.8 | — | 1.0 | 1.2 | 3.6 | 1.5 | | |
| C 1 | 1.15 | 3.0 | 1.5 | 0.39 | | | | | 4.9 | 2.1 |
| 2 | 0.31 | 1.8 | 1.2 | 0.17 | | 3.0 | | 3.3 | | 2.7 |
| 3 | 0.36 | 1.7 | 1.2 | 0.21 | | 2.5 | | 3.5 | | 2.8 |
| 4 | — | 2.0 | 1.3 | — | 0.25 | 7.0 | 3.5 | 2.7 | | |
| 5 | 0.22 | 2.0 | 1.2 | 0.11 | | 3.0 | | 3.0 | | 2.5 |

| | | | | | | | | | | | | | |
|---|---|------|-----|-----|------|--|------|--|----------|--|-----|-----|-----|
| D | 1 | 1.9 | 4.0 | 1.6 | 0.48 | | | | 0.3 | | | 5.7 | 1.8 |
| | 2 | 0.68 | 1.9 | 1.2 | 0.36 | | | | 1.1 | | | 4.2 | 2.6 |
| | 3 | 0.30 | 2.0 | 1.2 | 0.19 | | 0.25 | | 3.4 | | 2.9 | | |
| | 4 | 0.19 | 1.7 | 1.1 | 0.11 | | | | 4.3 | | | 2.9 | 2.8 |
| E | 1 | 1.06 | 3.1 | 1.4 | 0.34 | | 0.45 | | 0.4 | | 2.0 | | |
| | 2 | 0.32 | 1.7 | 1.2 | 0.19 | | | | 3.3 | | | 3.4 | 2.7 |
| | 3 | 0.24 | 1.5 | 1.2 | 0.16 | | | | 6.1 | | | 3.1 | 3.0 |
| | 4 | 0.16 | 1.5 | 1.1 | 0.11 | | | | 4.0 | | | 2.8 | 3.0 |
| F | 1 | 0.22 | 2.0 | 1.2 | 0.19 | | 0.26 | | 5.0 | | 2.5 | | |
| | 2 | 1.55 | 2.6 | 1.3 | 0.60 | | | | 0.4 | | | 5.3 | 2.2 |
| G | 1 | 0.25 | 2.1 | 1.3 | 0.12 | | 0.35 | | 5.1(3.8) | | 2.3 | | |
| | 2 | 1.06 | 2.9 | 1.4 | 0.37 | | | | 0.6 | | | 4.7 | 2.1 |
| H | | 0.21 | 2.2 | 1.3 | 0.10 | | 0.35 | | 3.9 | | 2.4 | | |
| I | | 0.27 | 1.1 | 1.2 | 0.23 | | | | 5.4 | | | 3.2 | 3.4 |
| K | | 0.13 | 1.0 | 0.9 | 0.13 | | | | 11.5 | | | 2.6 | 3.6 |
| L | | 0.16 | 1.5 | 1.1 | 0.10 | | 0.15 | | 9.7 | | 2.5 | | |
| | | | | | | | | | | | | | 3.1 |

^a Temperature-independent parameters derived from viscosity-shear stress data.

^b Temperature-independent parameters derived from normal stress-shear stress data.

^c Obtained by fractionation.

^d Estimated from rheological data by using relations reported here (Figs. 1-4).

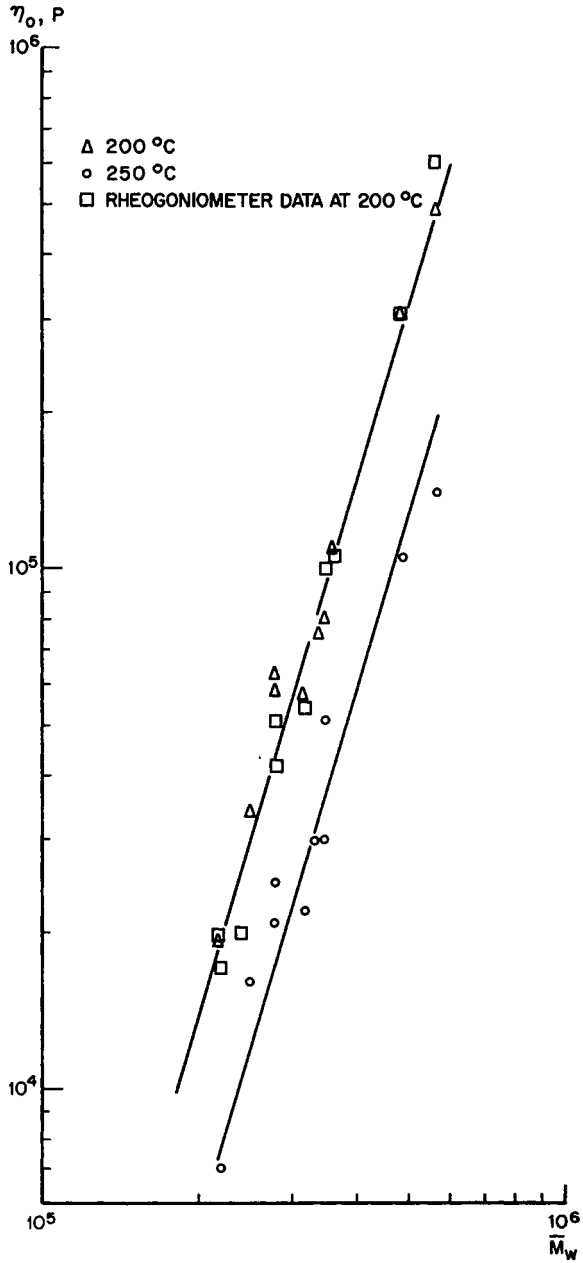


Fig. 1. Zero shear viscosity η_0 vs. weight-average molecular weight \bar{M}_w at 200°C and 250°C.

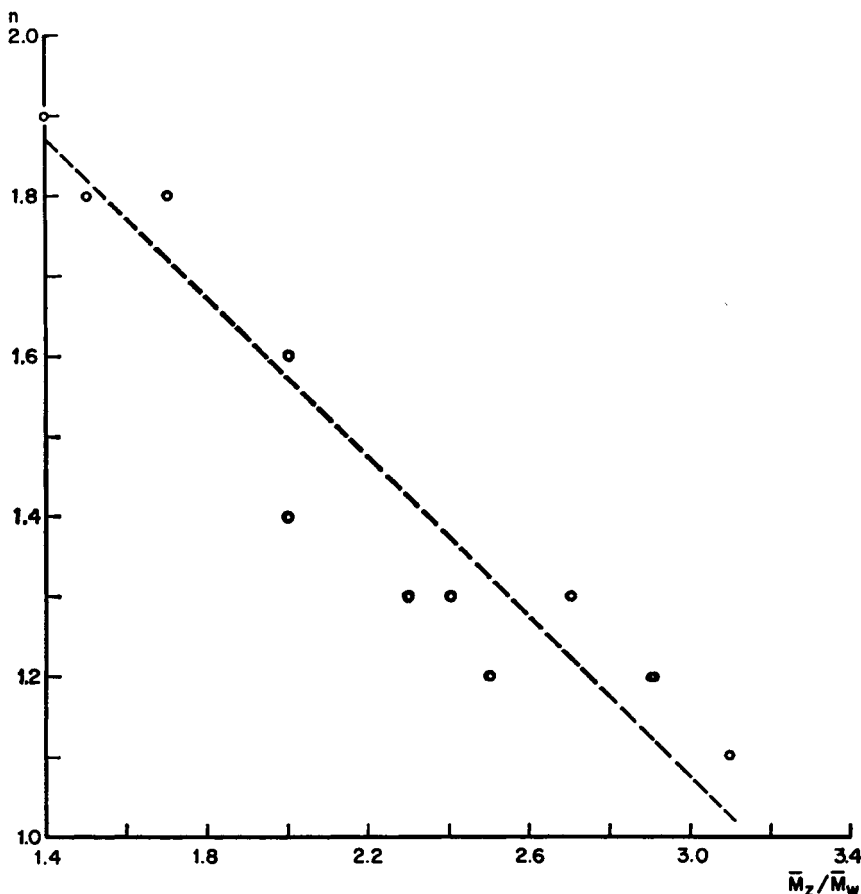


Fig. 2. Index n vs. \bar{M}_z/\bar{M}_w .

Observed differences in the shear dependence of the viscosity (i.e., differences in σ_c) allow one to make sensible guesses about differences in normal-stress behavior (this being of special interest in cases where this behavior cannot be or is not directly determined.) We consider this to be important because we believe that normal-stress effects play a predominant role in the processing of polymers. Usually this processing involves a compromise between the opposing demands of, for instance, time, energy consumption, and quality. This invariably leads to processing conditions which involve such high rates of shear that (appreciable) elastic strains are introduced. The stresses accompanying these strains will differ substantially according to the type of material and the conditions used, but they always need time to relax. So if they are still partially present (frozen-in) in a finished product, they may affect its properties. That the normal stresses play a predominant part in this may be inferred, in our opinion, from the fact that: (a) they are usually much higher than shear stresses, (b) they relax more

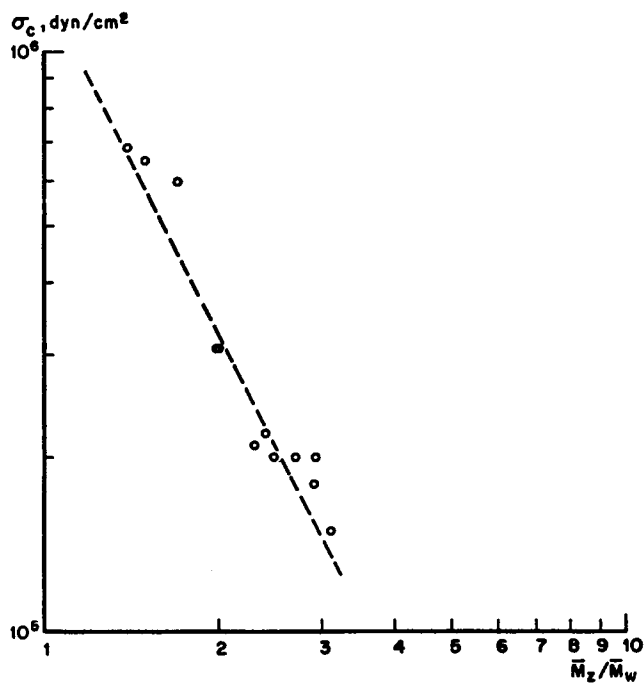


Fig. 3. Elasticity parameter σ_c vs. \bar{M}_z/\bar{M}_w .

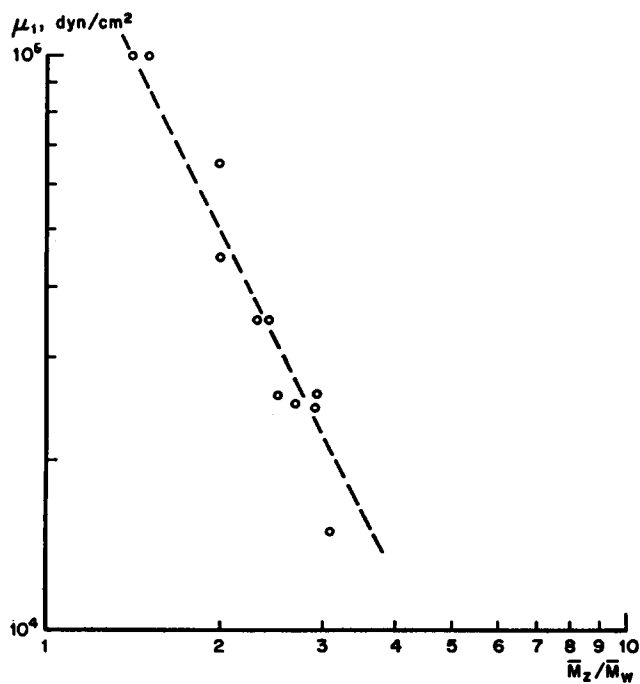


Fig. 4. Elasticity modulus at $S_E = 1$ vs. \bar{M}_z/\bar{M}_w .

slowly, and (c) they may give rise more readily to shear-induced nucleation²⁰ and/or crystallization²¹ due to their tensile nature.

We can best illustrate this with a specific example, viz., the high-temperature form stability of injection-molded dishes. Following the procedure outlined in Table II, we tried to correlate a likely measure of the normal-stress effect during molding with the high-temperature form stability. Although, as indicated in Table II, the two factors in question are expressed in rather arbitrarily chosen terms, the correlation of the average results for the three processing temperatures (Fig. 5) is quite significant.

Obviously it would be valuable if now a single parameter could be found to classify polymer melts with regard to their processability. In view of the diversity of processing techniques, if nothing else, any such proposition will be either restrictive or fictitious or even both. Bearing in mind our remarks about the effect of unrelaxed stresses, however, we would consider a characteristic time measure:

$$\tau_c = \eta_0 / \sigma_c$$

(η_0 here being the zero shear viscosity at, say, the processing temperature and σ_c , the elasticity parameter, being independent of temperature within processing temperature range) to be a rheologically more significant processing parameter than, for instance, the well-known melt index MI.²²

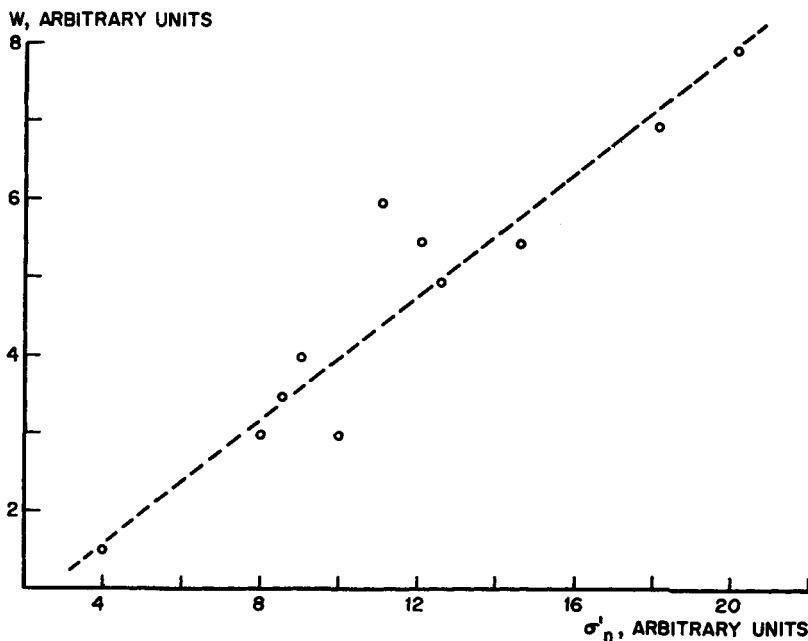


Fig. 5. High-temperature form stability (specified as the tendency to warp W) vs. the normal-stress effect, σ'_n (see Table II)

TABLE II
Relation between Rheological Behavior and Product Properties of Injection-Molded Plates^a

| | Processing temp 210°C | | | | Processing temp 240°C | | | | Processing temp 270°C | | | |
|----|----------------------------|--------------------|----------------------|-------------|---------------------------|--------------------|--------------------|-----|---------------------------|--------------------|--------------------|-----|
| | OP, kg/cm ^{2b} | σ_t° | $\sigma_n^{\circ d}$ | W° | OP, kg/cm ² | σ_t° | σ_n° | W | OP, kg/cm ² | σ_t° | σ_n° | W |
| A2 | — | — | — | — | 1010 | 1.89 | 20.0 | 6 | 670 | 1.61 | 16.0 | 8 |
| A4 | 600 | 0.88 | 16.0 | 8 | 430 | 0.80 | 12.0 | 5 | 390 | 0.94 | 16.0 | 3.5 |
| B4 | 570 | 0.84 | 4.0 | 2. | 400 | 0.75 | 4.0 | 1 | 340 | 0.82 | 4.0 | 1.5 |
| B5 | 940 | 1.38 | 6.0 | 4 | 690 | 1.29 | 11.0 | 4.5 | 520 | 1.25 | 10.0 | 3.5 |
| C4 | 600 | 0.88 | 10.0 | 4 | 400 | 0.75 | 7.0 | 2.5 | 290 | 0.70 | 6.0 | 2 |
| D3 | 760 | 1.12 | 20.0 | 8 | 550 | 1.03 | 20.0 | 9 | 400 | 0.96 | 20.0 | 7 |
| E1 | — | — | — | — | 740 | 1.39 | 12.0 | 6 | 540 | 1.30 | 10.0 | 6 |
| F1 | 570 | 0.94 | 13.0 | 5.5 | 400 | 0.75 | 11.0 | 5.5 | 340 | 0.82 | 13.0 | 4 |
| G1 | 610 | 0.90 | 9.0 | 4 | 440 | 0.82 | 8.0 | 3 | 350 | 0.85 | 8.0 | 3.5 |
| H | 640 | 0.94 | 11.0 | 4 | 450 | 0.84 | 9.0 | 2.5 | 350 | 0.85 | 10.0 | 2 |
| L | 450 | 0.66 | 10.0 | 5.5 | 350 | 0.65 | 10.0 | 5 | 350 | 0.85 | 15.0 | 6 |

^a Injection-molding conditions. Machine: conventional plunger Netstal SM 60/40 V, shot capacity: 60 g. Mold: single-cavity center-gated small-plate mold, shot volume 40 cm³. Product: small dish, diameter 150 mm, wall thickness 2 mm. Machine conditions: cycle time 65 seconds, divided into: injection + after-pressure time (20 sec), cooling time (20 sec), operation of machine + interval (25 sec). Mass temperature 210, 240, and 270°C; mould temperature 50°C; injection pressure intermediate between short-shot and flash pressure.

^b Injection pressure in kg/cm².

^c Arbitrary measure of the shear stress in kg/cm², $\sigma_t^{\circ} = OP/\overline{OP}$ (actual injection pressure divided by average injection pressure).

^d Arbitrary measure of the normal stress σ_n° belonging to σ_t° as follows from our data.

^e High-temperature form stability, given by the degree of warping after 1 hr at 170°C according to a relative visual rating scale running from 0 (no warping) to 10 (severe warping).

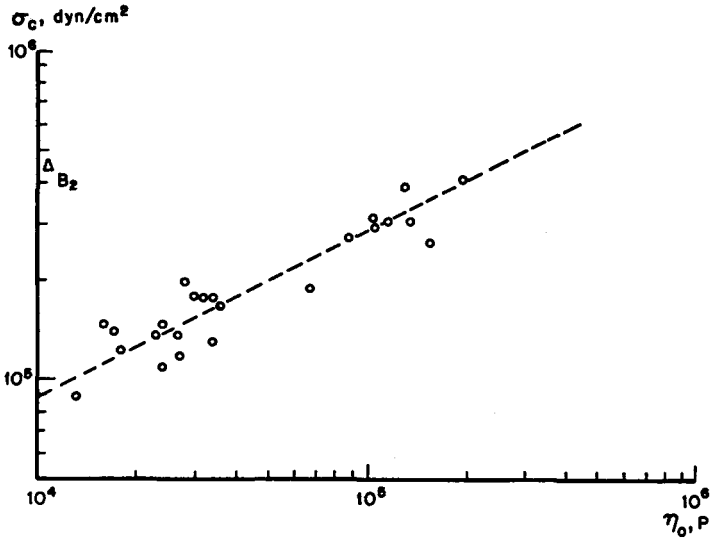


Fig. 6. Elasticity parameter σ_c vs. zero shear viscosity η_0 at 250°C.

To try this idea out we considered van der Vegt's measurements, i.e., the samples in Table I for which the molecular weight distribution parameters have had to be estimated. Unfortunately, however, it appeared that in most cases here there is a marked interdependence between η_0 and σ_c (Fig. 6). As η_0 is known to increase with \bar{M}_w and σ_c is known to decrease with \bar{M}_z/\bar{M}_w , this would suggest that the polypropylene grades concerned are manufactured in such a way that a decrease in molecular weight is accompanied by a broadening of the molecular weight distribution (Fig. 7). This, in

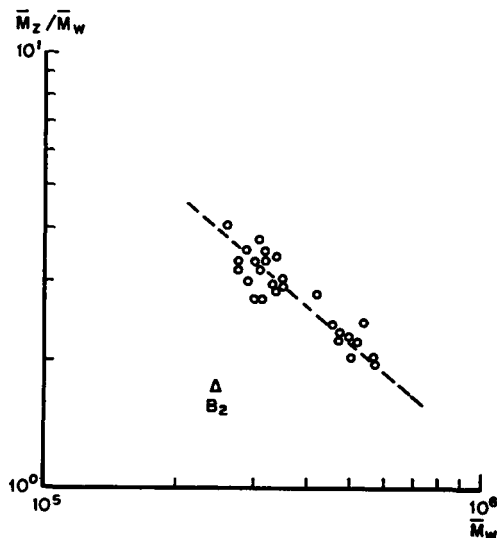


Fig. 7. \bar{M}_z/\bar{M}_w vs. \bar{M}_w

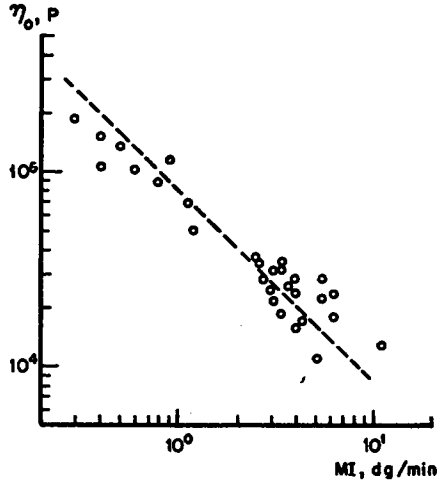


Fig. 8. Zero shear viscosity η_0 at 250°C vs. melt index (MI).

turn, could explain why the melt index, which is in fact a rough measure of the zero shear viscosity (Fig. 8), has been so useful as a classifying parameter, giving as it does more or less the same information in most cases as does τ_c (Fig. 9).

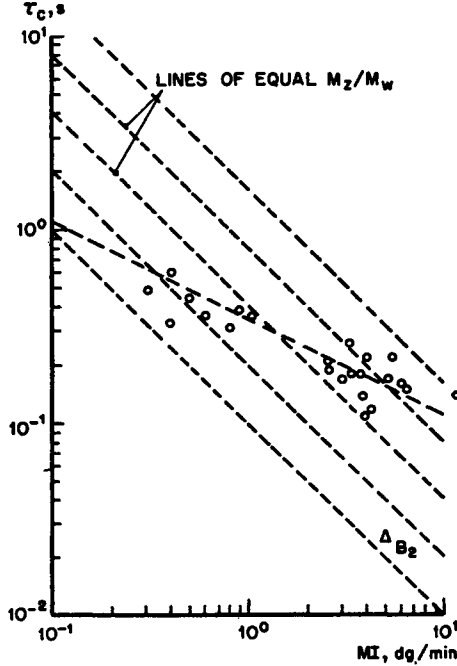


Fig. 9. Characteristic time τ_c at 250°C vs. MI.

At the same time it would appear that optimum performance in a particular application can be expected in some extreme cases, viz., (a) a combination of low \bar{M}_w (η_0 , MI) and narrow distribution (\bar{M}_z/\bar{M}_w) would lead to the lowest possible time-constant, which would be beneficial for injection molding (see, for instance, B4), whereas (b) a combination of high \bar{M}_w (η_0 , MI) and wide distribution (\bar{M}_z/\bar{M}_w) would lead to the highest possible time constant, which could well be preferable in extrusion applications. However, with the notable exception of the grades B2 and B4, no such extremes appear to exist. None are commercially available.

Conclusion

It has been shown that the elasticity of polymer melts, which is responsible for the shear dependence of the viscosity and for the normal-stress effect, is solely determined by the width of their molecular weight distribution.

The influence of melt elasticity on the processing behavior of polymers has been stressed and illustrated by demonstrating the effect on the high-temperature form stability of injection-molded plates.

A characteristic time measure has been proposed as an improved means of classifying polymers as far as their processability is concerned. The advantages of this approach were partly obscured, however, by the fact that most of the polypropylene grades investigated appeared to have been manufactured in such a way that a decrease in molecular weight was coupled with a widening of the distribution.

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