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Characterization of Polypropylene According to Steady-State Flow Behavior

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Synopsis

Commercial samples of polypropylene were characterized in respect to their molecular weight and molecular weight distribution on the basis of quantitative information gained from their steady-state flow behavior. The information obtained from this analysis was used to interpret the results of extrudate swelling, reinforcement of impact strength, and lowering of brittleness temperature. Manners of thermal and shear degradation were also studied.

INTRODUCTION

The measurement of steady-state viscosity is a widespread practice among those who are concerned with thermoplastic materials. This is because a knowledge of the flow properties of a polymer is of great importance in two aspects: namely, it indicates how the polymer behaves during melt processing such as extrusion, injection molding, and other fabrications. At the same time it reflects molecular structure of the polymer, especially the molecular weight and the molecular weight distribution. The purpose of this paper is to demonstrate the latter aspects in detail with variety of commercial polypropylene samples.

The steady-state flow behavior of thermoplastics is, in general, a pseudoplastic type; the observed flow at the low shear rates is either Newtonian or often asymptotically approaching the Newtonian behavior with the decrease of the shear rate. When the shear rate is increased, the viscosity decreases, giving a curve. From the viewpoint of molecular relaxation mechanism, this flow behavior may be interpreted as a response of the distribution of the relaxation times. Namely, the decrease of viscosity with the increase of shear rate arises from the fact that the viscous response corresponding to the longer relaxation time ceases. The viscous response of a given polymer chain consists of motions of the whole chain as well as the segments of the chain. There, the longest relaxation time belongs to the motion of the whole chain.[1] With the increase of shear rate the viscosity decrease can be interpreted as the successive removal of the viscous contribution from the longest relaxation time. In the polydispersed system this is analogous to the fractionation, which begins from the high end

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of the molecular weight distribution. Therefore, the steady-state flow behavior is a quantitative expression of the molecular weight distribution.

CONSIDERATIONS ON FLOW CURVE AND MOLECULAR WEIGHT DISTRIBUTION

A most widely used technique of the flow measurement is to obtain the viscosities (or fluidities) at two arbitrarily chosen stress levels, for example, a measurement of two melt indices.[2] The ratio of the two fluidities, the so-called shear sensitivity, is taken as a characteristic of a given sample. Often the attempt is made to relate the shear sensitivity to the molecular weight distribution. However, this approach has only very limited significance, because no reference is made to the curve to which these points belong. Normally, a power-law type of flow behavior is assumed, and therefore the two points can provide two constants for the power-law equation. This method is valid for a narrow range of the shear rate, to which the power-law relation is applicable. In turn, the information obtainable is also limited to the narrow range of the shear rate; the observed flow behavior is, then, a manifestation of primarily a limited portion of the molecular weight distribution.

A more fruitful approach is to measure viscosity in a wider range of shear rate. This is done usually with the use of a single viscometer, which covers two to at most three decades of shear rate. Data obtained do not obey the power law in most cases; the logarithm of viscosity plotted against the logarithm of shear rate is not linear. Such a plot varies from the obvious curve to a slight but undisputable deviation from a straight line. The curve is concave downward and sometimes includes the low shear Newtonian region, depending upon the sample and the shear rate range of observation. The examples of such flow curves are numerous and readily found in the literature.

For a variety of polyethylene samples the flow data were obtained by the gas pressure capillary rheometer (CIL), and it was shown that flow curves could be summarized into one master curve by the use of reduced variables.[3,4] It was assumed that a flow behavior of any polyethylene could be expressed with the same curve, i.e. $\eta/\eta_0 = f(\dot{\gamma}/\dot{\gamma}_0)$, where (η/η_0) and $(\dot{\gamma}/\dot{\gamma}_0)$ are the reduced viscosity and reduced shear rate, respectively. One of the authors[4] derived an empirical function for this curve having the form:

$$\log(\eta/\eta_0) = [(\eta/\eta_0) - a] \log [1 + (\dot{\gamma}/\dot{\gamma}_0)^b] \tag{1}$$

where $a = 2$ and $b = {}^1/_3$.

Although this approach was quite successfully demonstrated, it presented questions of both experimental and theoretical nature. With the increasing variety of commercial polyethylene, the flow curves began to show a slight but noticeable deviation from the master curve, even within three decades of shear rate observed with the CIL viscometer.

Since the flow curve is a quantitative expression of the molecular weight and its distribution, an analogy may be taken between the expressions for the flow curve and the fractionation data. Widely known facts are that the fractionation data of polyethylene often show the log-normal type of distribution. If this were generally true, one mathematical function and two constants could provide the expression for any fractionation data. The situation is analogous to the expression for the flow curve, where one master curve and two constants were thought to be sufficient. On closer examination, however, the fractionation data often deviated in various manner from the log-normal function.[5] Therefore, the method of one function with two material constants is not satisfactory as a general expression for the varieties of molecular weight distribution nor for representing their flow curves.

Indeed, it was shown by several workers that the flow curves of narrow molecular weight fractions have quite a different shape from the flow curves of polydispersed materials. The polymers treated were linear high-density polyethylene,[6] polyisobutene–cetane,[7] and polystyrene.[8]

In a previous paper[9] we presented flow curves of linear high-density polyethylene covering six decades of shear rates. There, we demonstrated that a considerable variation exists in the shape of the flow curves and a single master curve is not sufficient. Then, our question can be summarized essentially in two points: (*1*) how sensitively the shape of the flow curve is affected by the molecular weight distribution and (*2*) is there a general function (expression) for the flow curve, and, if so, how many material constants are involved in the expression.

The molecular weight distribution of commercial polyethylene often extends over three to four decades in molecular weight. Therefore, infinite combinations can be made to include all possible imaginary distributions. For this situation, it appears to be impossible to have one general expression for all types of distribution. In practice, however, most commercial products have an approximately log-normal type of distribution, and the deviations occur at both high and low end of the distribution. Therefore, several synthetic blends were prepared from the commercial products, the amount of the high molecular weight fraction and the low molecular weight fraction being varied. The flow curves of these blends were found to obey eq. (1) if a and b were made variable. In most cases the products ab were constant and equal to $^2/_3$. Therefore, the flow curves could be represented by the general expression, eq. (1), with three material constants, η_0, $\dot{\gamma}_0$, and a.

In the present work a similar approach is used to analyze molecular weight distribution of commercial polypropylenes through the interpretation of their flow curves. Also, in the previous work[9] the effect of gel particles on the shape of flow curve was studied. The curve showed an inflection at low shear rate and kept rising as the shear rate was further decreased. Here, this observation is applied to the interpretation of flow curves of some modified polypropylenes.

EXPERIMENTAL TECHNIQUE

The steady-state melt flow data of polypropylene were obtained from two instruments. The Kepe's cone-and-plate consistometer[10] measured viscosities at low shear rate in the range from 10^{-3} to 1 sec.$^{-1}$. High shear data were obtained from a capillary gas extrusion rheometer.[11] For capillary rheometer data, appropriate corrections were applied to obtain shear stress at the capillary wall[11] and the corresponding shear rate.[12] After these corrections, the viscosity data from the two instruments agree very closely with each other. All measurements were made at 190°C. under nitrogen. Additional stabilizers were added to ensure the stability of samples during the measurement.

EQUATION AND PARAMETERS FOR FLOW CURVES

As in the case of polyethylene,[9] the quantitative expression of the flow curves is made by the empirical equation:[4]

$$\log (\eta/\eta_0) = [(\eta/\eta_0) - a] \log [1 + (\dot{\gamma}/\dot{\gamma}_0)^b] \tag{1}$$

When shear rate approaches zero, the eq. (1) gives η approaching η_0 asymptotically. At very high shear rate, eq. (1) approaches a power law form:

$$\eta/\eta_0 = (\dot{\gamma}/\dot{\gamma}_0)^{-ab}$$

The value $-ab$ is the limiting slope of the flow curve when the plot is made with log (η/η_0) versus log $(\dot{\gamma}/\dot{\gamma}_0)$. For most of the polypropylene samples examined here, we have found that the limiting slope seldom exceeds $-^4/_5$ at the highest shear rate obtainable from our instruments. By

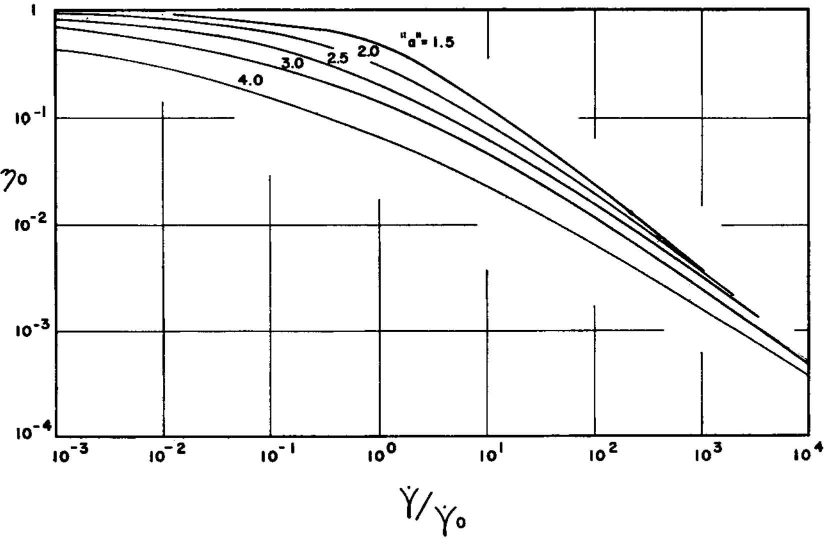

Fig. 1. Empirical flow curves for polypropylene.

varying a and keeping ab constant, we are able to construct a family of curves which fit the observed flow curves of polypropylene. Figure 1 shows the calculated flow curves with different values of a.

RESULTS

Characterization of Polypropylene Homopolymers

Several commercial samples having a range of melt index 1–3 were selected for study. Their flow parameters are listed in Table I. Also, the flow curves of some of the samples are shown in Figures 2–4.

TABLE I
Flow Parameters of Polypropylene Homopolymers

Sample	a	$\eta_0 \times 10^{-5}$	$\dot{\gamma}_0$
Escon CD76-314[a]	2.3	2.64	1.46
Escon 302M[a]	2.3	2.47	1.37
Chemore 9025L[b]	2.3	2.4	1.93
Avisun TD-160[c]	2.0	1.3	4.20
Profax 6523[d]	1.9	1.05	2.67
Profax 6726[d]	1.8	3.50	0.96
Tenite 066E[e]	1.4[f]	1.53	0.44

[a] Product of Enjay Chemical Company.
[b] Product of Chemore Corporation.
[c] Product of Avisun Corporation.
[d] Product of Hercules Powder Company.
[e] Product of Eastman Kodak Company.
[f] The limiting slope is $ab = {}^2/_3$.

With a number of polyethylene samples it was shown that the flow parameter a was particularly sensitive to the very high molecular weight

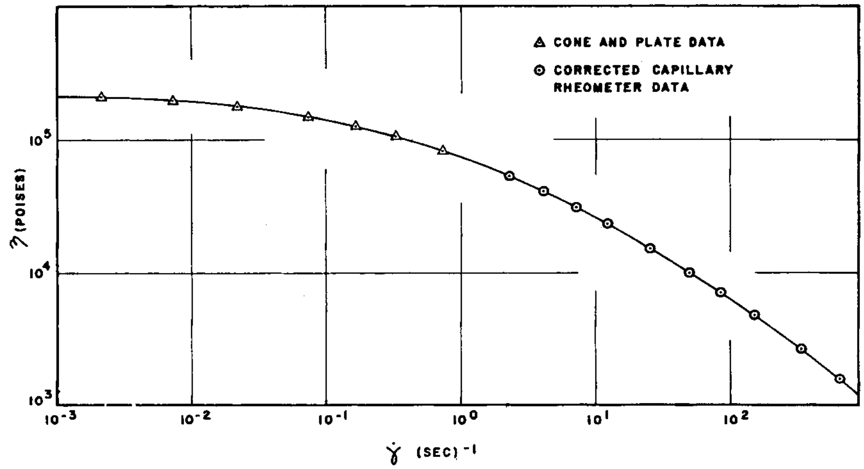

Fig. 2. Flow curve of Chemore 9025L.

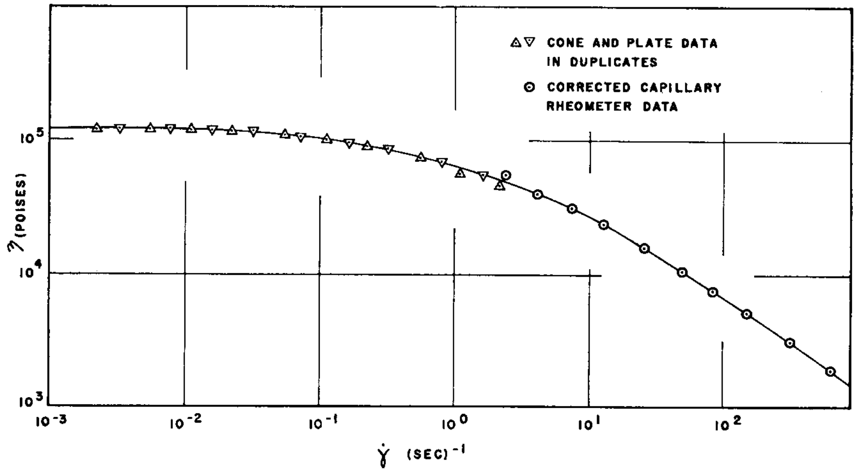

Fig. 3. Flow curve of Avisun TD 160.

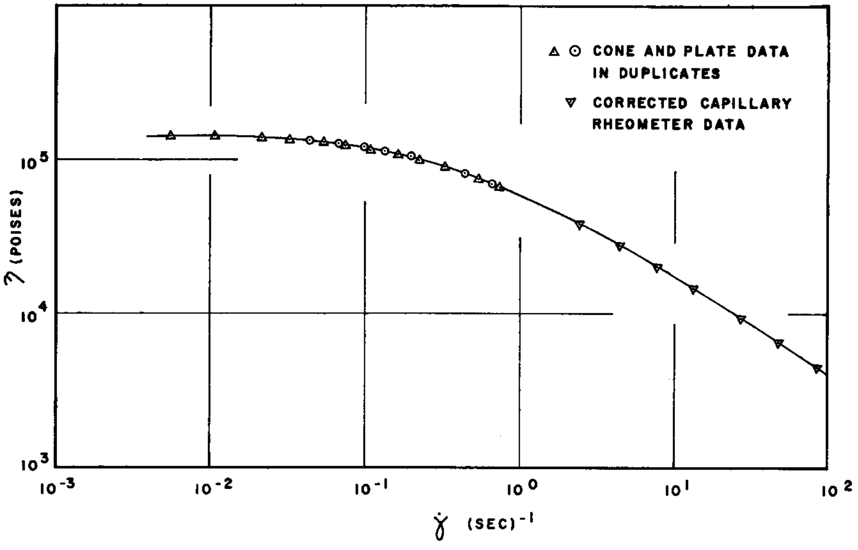

Fig. 4. Flow curve of Tenite 006E.

component.[9] In Table II we show the relationship between extrudate swelling and flow parameters. The swelling data were obtained with a die having streamlined entry, and a capillary of 33 mils diameter and a length-to-diameter ratio of 20. The apparent shear rate of extrusion was 5000 sec^{-1} and the temperature was 200 or 240°C. The extrudates were allowed to crystallize in room temperature. Therefore, the swelling was not completed and the data were for the relative comparison only.

The swelling ratios relate very well with the a values, but do not seem to have any direct relation to η_0 and $\dot{\gamma}_0$. The swelling data indicate that

TABLE II
Extrudate Swelling of Polypropylene

	Flow parameters			Swelling ratios[a]	
Sample	a	$\eta_0 \times 10^{-5}$	$\dot{\gamma}_0$	200°C.	240°C.
Escon CD76-314	2.3	2.64	1.46	2.42	1.73
Profax 6726	1.8	3.50	0.96	2.06	1.18
Profax 6523	1.9	1.05	2.67	2.12	1.27

[a] Ratio of the extrudate diameter to the die diameter.

the phenomenon is markedly influenced by the presence of very high molecular weight fraction. The fact emphasizes the importance of the evaluating a.

Characterization of Modified Polypropylene

In order to lower the brittleness temperature and improve the impact strength, ethylene units may be incorporated into polypropylene. This

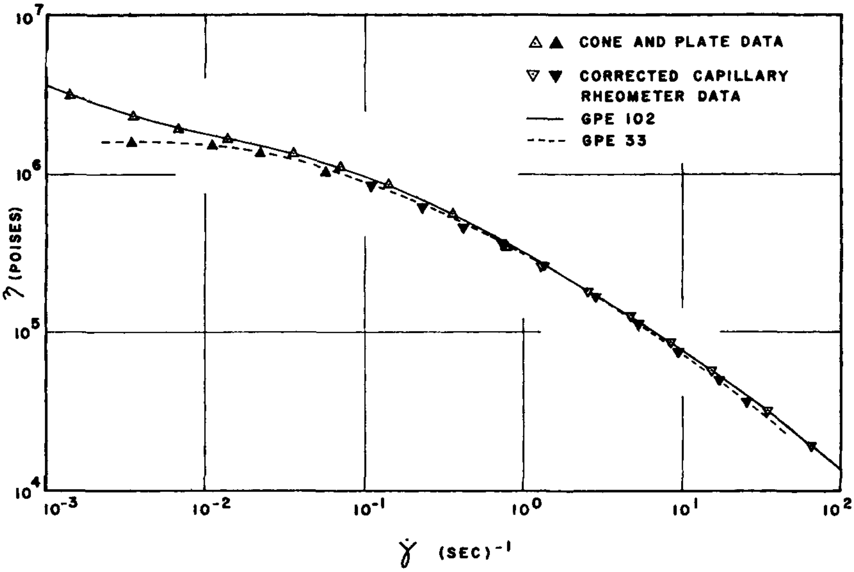

Fig. 5. Flow curves of Propathene GPE 33 and GPE 102.

may result in random or block copolymer, a blend of polyethylene and polypropylene, and a mixture of any or all combinations of the above. Two commercial grades of such modified polypropylene were selected and their flow behavior was compared to the unmodified polypropylene of equivalent melt indices. The flow curves of these resins are shown in Figures 5 and 6. In Table III the flow parameters of these samples are presented together with the ethylene content, the impact strength, and the brittleness temperature.

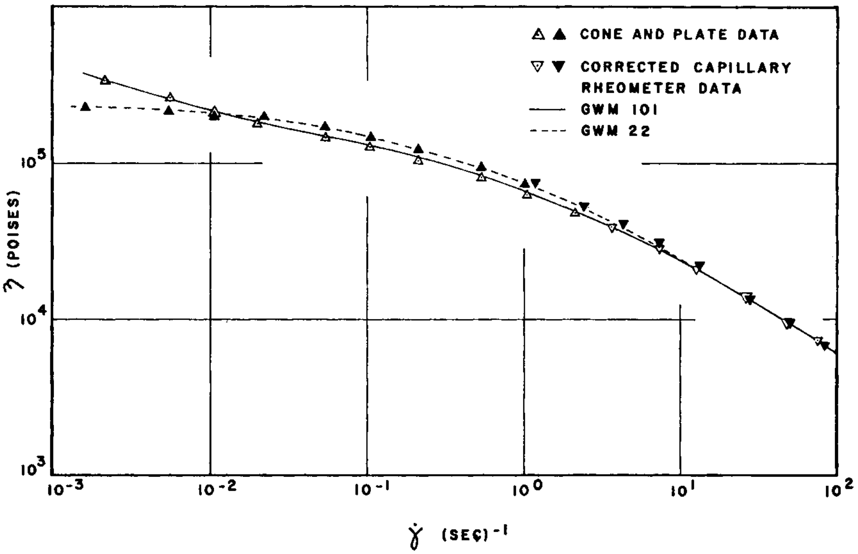

Fig. 6. Flow curves of Propathene GWM 22 and GWM 101.

The infrared analyses on these samples show that GPE 102 and GWM 101 contain approximately about 10% of ethylene block. The ethylene block may be blended polyethylene or short and long sequences of ethylene block copolymerized with propylene. However, the estimated amount may not include an isolated ethylene unit randomly copolymerized with propylene. With GPE 33 and GWM 22 a presence of ethylene block is not detected.

The flow curves of GPE 33 and GPE 102 are practically identical except at very low shear rate, where the viscosity of GPE 102 rises as the shear rate is decreased. Again, the flow curves of GWM 22 and GWM 101 are practically identical except at very low shear rate, where the viscosity of GWM 101 rises in a very similar manner as the viscosity of GPE 102. This viscosity rise of GPE 102 and GWM 101 is due to the presence of

TABLE III
Properties of Modified Polypropylene

Sample	Flow parameters			Ethylene block content (by infrared), %	Tensile impact strength, in.-lb./in.^{2}	Brittleness temperature, °C.
	a	$\eta_0 \times 10^{-5}$	$\dot{\gamma}_0$			
Propathene GPE 33[a]	1.9	20	0.22	0	1900	16
Propathene GPE 102[a]	1.9	(21)	0.22	ca. 10	2570	−1.5
Propathene GWM 22[a]	2.3	2.73	1.33	0	240	<20
Propathene GWM 101[a]	2.3	(2.03)	2.2	ca. 10	1160	2

[a] Product of Imperial Chemical Industries, Ltd.

small amounts of component having very long relaxation times. Previously, it was shown that gel containing polyethylenes showed very similar flow behavior.[9] In GPE 102 and GWM 101 there seems to be a small amount of finely dispersed particles of polyethylene, which may consist of whole chains or long blocks which are joined to polypropylene. These polyethylene particles are expected to have gellike behavior, even though they may not be crosslinked.[13] The values of η_0 listed for GPE 102 and GWM 101 are extrapolated from the master curves. Therefore, they are lower than the observed values. However, the extrapolated values give estimates of η_0 for the gel-free portion of the polymers.

The tensile impact test was performed according to ASTM D1822-61T at room temperature. Type L (long) specimen was used. The values are averages obtained on ten specimens. It is clearly shown that the incorporation of ethylene block improves the impact strength remarkably. Besides, the impact strength is closely related to the η_0 value, which is a measure of the weight-average molecular weight. There are two types of fracture mechanism; one involves slight elongation at the smallest cross section, and subsequent whitening at the torn region. Another is a brittle fracture involving no elongation. Only GWM 22, which has the lowest molecular weight and no reinforcement, showed the brittle fracture; the others showed the elongation failure.

The brittleness temperature test was performed according to ASTM D746-57T with the following modifications: (a) the sample was a rectangular strip with $1^1/_2$ in. in length, $^1/_4$ in. in width, and 0.075 in. thick; (b) a sharp notch, 20 mil deep, was sliced out of the $^1/_4$-in. width with a razor blade on one side of the strip 1 in. from the clamping end; (c) six samples were tested simultaneously. Again, the brittleness temperature is markedly lowered with the incorporation of ethylene block, but the effect of the molecular weight is not very significant.

Approximate Treatment of Flow Behavior

In order to obtain as complete information as possible on the molecular weight distribution, it is necessary to measure the viscosity at as wide range of shear rate as possible. In the present work we have covered six decades in shear rate with the use of two instruments: the cone-and-plate and CIL viscometers. With the CIL viscometer alone only three decades of shear rate can be covered. However, if we do not expect any anomaly in the molecular weight distribution such as a presence of gel particles, it may be possible to predict a flow curve for a wider range of shear rate with the CIL data and an appropriate choice of a master curve. Moreover, it would be very convenient if the CIL data could be processed according to the Poiseuille equation without applying elaborate corrections.[11,12] Such tests were made by fitting the flow curves of apparent viscosity versus apparent shear rate to one of the master curves by an appropriate choice of the parameter a.

TABLE IV
Approximate Treatment of Flow Curve

	CIL data without corrections				Corrected CIL data and cone-plate data			
Sample	$\eta_0 \times 10^{-5}$	$\dot{\gamma}_0$	a	ab	$\eta_0 \times 10^{-5}$	$\dot{\gamma}_0$	a	ab
Elrex 51H3[a]	1.52	4.4	2.2	0.8	1.53	3.0	2.2	0.8
Elrex 51H2[a]	3.4	2.0	2.3	0.8	3.6	1.8	2.3	0.8
Chemore 9040L[b]	2.0	4.1	2.6	0.8	1.8	4.0	2.6	0.8
Avisun 116[c]	2.8	2.7	2.6	0.8	2.5	2.3	2.6	0.8

[a] Product of Rexall Chemical Company.
[b] Product of Chemore Corporation.
[c] Product of Avisun Corporation.

The choice of the master curve, then, enables us to determine the values of η_0 and $\dot{\gamma}_0$. The results of the evaluation are presented in Table IV together with the results of more exact treatment involving the two instruments and the corrections.

When there is no anomalous distribution of molecular weight, the uncorrected CIL data are sufficient to give a choice of the master curve; namely, the values of a and ab found from the uncorrected data are the same as those from more exact evaluation. The values of η_0 and $\dot{\gamma}_0$ evaluated from the exact method and approximate one, show that η_0 is in good agreement within the experimental error but $\dot{\gamma}_0$ is sometimes overestimated by the approximate method.

Analysis of Thermal and Shear Degradation

The stability of polypropylene is very sensitively affected by the shear at elevated temperatures. Therefore, it is very important to analyze the manner of the degradation for a given processing condition. Table V gives an example of such analysis on the monofilament process. The flow parameters were obtained from uncorrected CIL data.

TABLE V
Analysis of Degradation in Processing

Sample	$\eta_0 \times 10^{-5}$	$\dot{\gamma}_0$	a	Melt index
Original pellets	1.27	7	2.3	4.45
Monofilament 1	0.78	9.6	2.2	9.41
Monofilament 2	0.58	11.9	2.0	10.7

It is interesting to note that monofilament 2 had undergone more severe degradation than the monofilament 1, resulting in the more extensive reduction of the weight-average molecular weight. This is shown by the extent of decrease in η_0 and increase in the melt index. However, monofilament 1 has preserved a general pattern of the molecular weight distribution in respect to the high molecular weight fraction. This is indicated by only slight change in the parameter a. On the other hand, monofilament 2 lost the very high molecular weight fraction, which is shown by the decrease in a. Although the increase of melt index values indicates degradation during the process, it fails to distinguish the difference between monofilaments 1 and 2 in respect to the manner of degradation.

SUMMARY

Commercial samples of polypropylene were characterized according to their steady-state flow behavior. The quantitative expression of the flow behavior was made through the empirical equation:

$$\log (\eta/\eta_0) = [(\eta/\eta_0) - a] \log [1 + (\dot{\gamma}/\dot{\gamma}_0)^b]$$

With homopolymer samples having melt indices in the range 1–4, it was shown that flow curves can be represented by the equation and independent material parameters, η_0, $\dot{\gamma}_0$, and a. In most cases the product ab was found to be a constant and equal to $^4/_5$. The parameter a, which is very sensitive to the presence of very high molecular weight fraction, is shown to relate the extrudate swelling.

Modified polypropylenes containing about 10% of polyethylene block are found to show the reinforcement of impact strength and the lowering of brittleness temperature. The flow curves of these polymers deviated at very low shear rate from the master curve represented by the empirical equation. The manner of deviation implied the presence of a component having very long relaxation times. This component is most likely to be finely dispersed particles of polyethylene. It was also shown that the impact strength depends strongly on weight-average molecular weight, but the brittleness temperature does not.

When a polymer has no such anomaly in the molecular weight distribution as a presence of gellike particle, the apparent flow curve may be used to select appropriate master curve. The parameters a and b selected this way are in good agreement with the values by the more exact method. Once a and b are determined, the corresponding master curve provides the remaining parameters, η_0 and $\dot{\gamma}_0$. Again, the values of η_0 and $\dot{\gamma}_0$ are in agreement with those obtained by the exact method, but the $\dot{\gamma}_0$ value is sometimes overestimated.

It was shown that the difference of the flow parameters η_0 and a before and after the melt processing of a polymer can be used to study the manner of the thermal and shear degradation. The increase of melt index alone could not distinguish the difference between the general decrease of molecular weight and the loss of very high molecular weight fraction.

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Résumé

Des échantillons commerciaux de polypropylène ont été caractérisés en ce qui concerne leurs poids moléculaires et la distribution de leurs poids moléculaires en se basant sur des informations quantitatives obtenues à partir de leur comportement d'écoulement à l'état stationnaire. On a employé les informations obtenues par cette analyse pour interpréter les résultats du gonflement de l'extrudat, du renforcement de la force d'impact et de l'abaissement de la température de cassure. On a également étudié les méthodes de dégradation thermique et de dégradation par cisaillement.

Zusammenfassung

Handelsübliche Polypropylenproben wurden auf Grundlage der aus ihrem stationären Fliessverhalten gewonnenen quantitativen Information in Bezug auf ihr Molekulargewicht und ihre Molekulargewichtsverteilung charakterisiert. Die Ergebnisse dieser Analyse wurden zur Interpretation von Resultaten bei der Extrusionsquellung, bei der Verstärkung der Stossfestigkeit und bei der Erniedrigung der Sprödigkeitstemperatur herangezogen. Weiters wurde der Wärme- und Scherungsabbau untersucht.

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