# From melt flow index to rheogram\*)

### A. V. Shenoy, S. Chattopadhyay, and V. M. Nadkarni

Polymer Science and Engineering Group, Chemical Engineering Division, National Chemical Laboratory Pune (India)

*Abstract:* A knowledge of the complete flow curve or rheogram of a polymeric melt depicting the variation of the melt viscosity over industrially relevant range of shear rate and temperature is essential in the design of polymer processing equipment, process optimization and trouble-shooting. These data are generated on sophisticated rheometers that are beyond the financial and technical means of most plastics processors. The only flow parameter available to the processor is the melt flow index of the material.

In the present work, a method has been proposed to estimate the rheograms of a melt at temperatures relevant to its processing conditions with the use of a master curve, knowing the melt flow index and glass transition temperature of the material. Master curves that coalesce rheograms of different grades at various temperatures have been generated and presented for low density polyethylene, high density polyethylene, polypropylene, polystyrene and styrene-acrylonitrile copolymer.

Key words: Melt flow index, rheogram, master curve, polymeric melt

Nomenclature

- diameter of the tube (cm) D K, K'constants length of the tube (cm) 1 L weight of piston and load (kg) MFI melt flow index (g/10 min) pressure drop through tube (dynes/cm<sup>2</sup>)  $\Delta P$ volumetric flow rate (cm<sup>3</sup>)  $Q T_1 T_2 T_g T_s V$ temperature at condition 1 (K) temperature at condition 2 (K) glass transition temperature (K) standard reference temperature (K) (=  $T_q$  + 50 K) average velocity (cm/s) W weight rate of flow (g) ў Уа shear rate  $(s^{-1})$ apparent shear rate  $(s^{-1})$ viscosity at condition 1 (poise)  $\eta_1$ apparent viscosity (poise)  $\eta_a$ viscosity at standard temperature (poise)  $\eta_s$ density (g/cm<sup>3</sup>) ρ
- $\tau$  shear stress (dynes/cm<sup>2</sup>)

## **1. Introduction**

Shearing flow of polymeric fluids is encountered in a number of polymer processing operations. The vis-

cosity under simple shear is an important material parameter used for determining the pumping efficiency of an extruder, the pressure drop through a die, designing balanced flow runner systems in multiple cavity injection molding, computing the temperature rise due to viscous heat generation during processing etc. The viscosity of polymeric melts is dependent on both the temperature and shear rate. Therefore, knowledge of the complete flow curve or rheogram depicting the variation of the melt viscosity over industrially relevant range of shear rates and temperature is essential in the design of polymer processing equipment, process optimization and trouble-shooting.

The rheological data needed for constructing a rheogram are obtained on sophisticated scientific instruments such as the Weissenberg Rheogoniometer, the Instron Capillary Rheometer, Rheometrics Mechanical Spectrometer, etc. These instruments are very expensive and require trained operators. Thus collection of the necessary flow data is beyond the financial and technical capabilities of most processors of polymeric materials.

The only flow parameter the processor has ready access to is the melt flow index (MFI). The MFI is

<sup>\*)</sup> NCL Communication Number 2903.

either specified by the material supplier or can be easily measured using a relatively inexpensive apparatus. MFI is defined as the weight of the polymer in grams extruded in ten minutes through a capillary of specific diameter and length in a melt flow indexer by pressure applied through dead weight under prescribed temperature conditions as specified by ASTM D 1238. Although MFI is a good indicator of the most suitable end use for which the particular grade can be used [1], it is not a fundamental polymer property. It is an empirically defined parameter critically influenced by the conditions of measurement, besides the physical properties and molecular structure of the polymer. It is a single point viscosity measurement at relatively low shear rate and temperature. Since the values of temperature and shear rate employed in the MFI test differ substantially from those encountered in actual large-scale processes, the results do not correlate directly with processing behaviour. This point has been well illustrated by Shida and Cancio [2] and Smith [3]. The latter has also shown the insensitivity of MFI to the effects of molecular-weight distribution. This is due to the fact that variation in molecular-weight distribution would normally affect the flow behaviour at very low  $(10^{-1} \text{ s}^{-1})$  and very high  $(10^4 \text{ s}^{-1})$  shear rates, whereas MFI is measured at an intermediate shear rate. The effect of molecular weight distribution on processibility and insensitivity of the MFI measurement to these effects have also been described by Borzenski [4]. Despite all these limitations, MFI still remains to be a simple, easily obtainable viscosity parameter from a relatively inexpensive apparatus within the technical and financial means of plastics processors.

In the present paper, a method has been proposed for estimating the rheogram of a polymeric material from its MFI knowing the conditions of the MFI test and the glass transition temperature of the resin. Menges et al. [5] have suggested a mathematical equation as a universal viscosity function based on the zero-shear viscosity, and had shown that the function can be used to estimate the rheogram from a knowledge of zero-shear viscosity and glass-transition temperature. The zero-shear viscosity is a difficult parameter to obtain experimentally. The method proposed in the present paper uses the melt flow index as a normalizing parameter. Therefore the technique is more convenient for the processor since the MFI can be very easily measured. The polymer systems included in the present investigation are low density polyethylene, high density polyethylene, polypropylene, polystyrene and styrene-acrylonitrile copolymers. Based on the available data on consumption

patterns [6], these polymers constitute about 55% of the total sales of polymers, thus rendering the results of the present work useful to a large number of plastics processors.

### 2. Data Collection

Data collection has been done in three ways. Viscosity versus shear rate data were generated on the above mentioned polymer systems with our own laboratory facilities. The data were taken on the Weissenberg rheogoniometer R19 in the lower shear rate region  $(10^{-1} \text{ to } 10^2 \text{ s}^{-1})$  and on the Instron Capillary Rheometer Model 3211 in the higher shear rate region  $(10-10^3 \text{ s}^{-1})$ . All the data were analysed to give master curves which are independent of the polymergrade measuring temperature and load in MFI measurements. For each of the studied systems, data from published literature were also collected to confirm the master curves. As a further check, data were obtained on viscosity versus shear rate curves directly from manufacturers of the various polymers along with details of MFI values and measurement conditions. All this was done in order to consolidate the findings of the master curves and eliminate any dependence these might have on the measuring techniques, equipment or operator. A summary of the systems analysed in the present study is given in table 1.

#### 3. Data Analysis

The flow of the polymer melt through the capillary die of the MFI apparatus is a simple shear flow in laminar region. The volumetric flow rate of the fluid through a circular tube is given by the Hagen-Poiseuille law:

$$Q = \frac{\pi \Delta P D^4}{128\eta_a l} \tag{1}$$

where D are the diameter and l the length of the tube,  $\Delta P$  the pressure drop through the tube, Q the volumetric flow rate and  $\eta_a$  the apparent viscosity of the fluid.

Within the melt flow indexer die, capillary entrance effects are important as L/D = 3.8. However, from the subsequent analysis it will be clear that MFI would be used merely as a normalising factor to obtain reduced viscosity shear rate curves. The MFI values used in generating the plots as well as those which would be used for obtaining the rheograms from the

Table 1

Polymer	Grade	MFI (Temperature, °C/Load Condition, kg)	Temperature at which data generated, °C	No. of data points (shear rate range, $s^{-1}$ )	Source
1	2	3	4	5	6
LDPE	Indothene 22FA002	0.16 <sup>a</sup> ) (175/2.16)	175	9(0.01 - 1000)	This work
	- do -	$0.2^{\circ}$ ) (190/2.16)	190	9(0.01 - 1000)	- do
	- do -	0.25 <sup>a</sup> ) (205/2.16)	205	9(0.01 - 1000)	— do —
	Indothene 24MA040	$3.0^{\rm a}$ ) (175/2.16)	175	10(0.01 - 1000)	— do —
	- do -	$4.0^{\circ}$ ) (190/2.16)	190	10(0.01 - 1000)	- do
	-do -	$5.0^{a}$ ) (205/2.16)	205	10(0.01 - 1000)	– do –
	Indotnene 24FS040	$3.0^{\circ}$ (1/5/2.16)	175	10(0.01 - 1000)	- do
	- do -	$4.0^{\circ}$ (190/2.16)	190	10(0.01 - 1000)	- do
	-00 - Indothene 26MA 200	(205/2.16)	205	10(0.01 - 1000)	- do
	-do -	(175/2.16) (190/2.16)	1/3	10(0.01 - 1000) 10(0.01 - 1000)	- do -
	-do	$25^{a}$ (205/2.16)	205	10(0.01 - 1000) 10(0.01 - 1000)	- u0
	LDPE-B	(1207/2.10) (190/2.16)	190	4(0.01 - 1000)	$-u_0 -$
	LDPE-C	$2.1^{\text{b}}$ (190/2.16)	190	4(0.01 - 1000) 4(0.01 - 1000)	-do -
	LDPE-D	$6.9^{b}$ (190/2.16)	190	4(0.01 - 1000)	- do -
HDPE	GD 6260	$2.34^{a}$ ) (175/2.16)	175	6(2-700)	This work
	- do -	3.6 <sup>b</sup> ) (190/2.16)	190	6(2 - 700)	- do
	- do -	$3.17^{b}$ ) (205/2.16)	205	6(2 - 700)	- do
	GF 5740	0.35 <sup>a</sup> ) (175/2.16)	175	6(2-700)	- do
	- do -	0.45 <sup>b</sup> ) (190/2.16)	190	6(2 - 700)	— do —
	- do -	$0.57^{a}$ ) (205/2.16)	205	6(2-700)	— do —
	Marlex EHM-606	$0.54^{a}$ ) (170/2.16)	170	18(0.01 - 1000)	Ref. [10]
	- do -	$0.64^{\circ}$ (180/2.16)	180	18(0.01 - 1000)	– do –
	- do -	$0.75^{\circ}$ (190/2.16)	190	18(0.01 - 1000)	- do
	- d0 -	(200/2.16)	200	17(0.01 - 500)	- do -
	- do -	(210/2.16) (220/2.16)	210	18(0.01 - 1000) 18(0.01 - 1000)	- do
	HDPE 4	(1.2) $(220/2.10)(190/2.16)$	190	10(0.01 - 1000) 5(0.01 - 1000)	$-u_0 -$ Ref [0]
РР	Koylene EB 0730	(100/2.10)	200	17(0.005 - 700)	This work
	-do-	$(0.5^{a})$ $(215/2.16)$	215	16(0.005 - 700)	-do -
	- do -	(230/2.16)	230	16(0.005 - 700)	- do
	Koylene 1730	$0.75^{a}$ ) (200/2.16)	200	12(0.03 - 700)	This work
	- do -	1.2ª) (215/2.16)	215	13(0.05 – 700)	- do
	- do -	(230/2.16)	230	13(0.05 - 700)	do
	Koylene 3030	1.3 <sup>a</sup> ) (200/2.16)	200	16(0.03 - 700)	— do —
	-do-	$2.0^{a}$ ) (215/2.16)	215	13(0.1 - 700)	— do —
	- do -	(230/2.16)	230	13(0.1-700)	- do
	Moplen 015	(230/2.16)	230	4(20 - 1000)	Ref. [12]
	Moplen 040	(230/2.16)	230	7(20 - 1000)	- do
	PP 10 1046	$(2.0^{\circ})$ $(2.0/2.10)$	230	4(20 - 1000)	-00 -
	- do -	(210/2.16) $(3^{b})$ $(230/2.16)$	210	6(10 - 500) 6(10 - 500)	do -
	- do -	(250/2.10) 10 0 <sup>a</sup> ) (250/2.16)	250	6(10 - 500)	-do -
	PP 10-6016	(210/2.16) (210/2.16)	210	6(10 - 500)	- do
	- do -	(230/2.16)	230	6(10-500)	- do
	- do -	10.3ª) (250/2.16)	250	6(10-500)	- do -
PS	Styrene 666 U	7.5 <sup>b</sup> ) (200/5)	200	10(5-5000)	Ref. [14]
	- do -	$37.0^{\rm a}$ ) (220/5)	220	10(5 - 5000)	- do
	- do -	$130.0^{a}$ ) (240/5)	240	10(5 - 5000)	- do
	XP 6065.00	8.0°) (200/5)	200	10(5 - 5000)	Ref. [14]
	- do	$42.0^{a}$ ) (220/5)	220	10(5 - 5000)	- do
	- do -	$139.0^{\circ}$ ) (240/5)	240	10(3 - 5000)	- do
	Styrene 000	9.4°) (200/5)	200	/(0.01 - 0.55)	Kei. [11]

92

Table 1 (C	(ontinued)
------------	------------

Polymer	Grade	MFI (Te °C/Loa kg)	MFI (Temperature, °C/Load Condition, kg)		No. of data points (shear rate range, s <sup>-1</sup> )	Source
1		3		4	5	6
	Polysar 201	1.5 <sup>b</sup> )	(200/5)	200	1(100)	Ref. [15]
	- do -	7.4ª)	(220/5)	220	1(100)	- do -
	Polysar 205	0.9ª)	(180/5)	180	1(100)	— do —
	- do -	6.8 <sup>b</sup> )	(200/5)	200	1(100)	- do
	- do -	33.5ª)	(220/5)	220	1(100)	- do -
	Polysar E 520	2.4 <sup>b</sup> )	(200/5)	200	1(100)	- do
	- do -	12.0ª)	(220/5)	220	1(100)	- do -
	Polysar M 520	0.7 <sup>a</sup> )	(180/5)	180	1(100)	- do -
	- do	5.4 <sup>b</sup> )	(200/5)	200	1(100)	- do
	— do —	26.5ª)	(220/5)	220	1(100)	- do -
	H 5M	15.4ª)	(210/5)	210	6(10-500)	Ref. [13]
	- do	47.7 <sup>a</sup> )	(230/5)	230	5(20-500)	- do
	- do -	121.0ª)	(250/5)	250	6(10 - 500)	- do -
	G 2	27.4ª)	(210/5)	210	6(10-500)	Ref. [13]
	- do -	85.1ª)	(230/5)	230	6(10 - 500)	- do -
	- do -	215.0ª)	(250/5)	250	6(10-500)	-do -
SAN	Tyril 860B	1.0 <sup>a</sup> )	(200/3.8)	200	10(20-600)	Ref. [14]
	- do -	3.4ª)	(215/3.8)	215	10(20 - 600)	- do -
	- do	9.5 <sup>b</sup> )	(230/3.8)	230	10(20 - 600)	- do -
	- do -	29.5 <sup>a</sup> )	(250/3.8)	250	10(20 - 600)	- do -
	Tyril 867B	0.5ª)	(200/3.8)	200	10(20-600)	- do
	- do -	1.6 <sup>a</sup> )	(215/3.8)	215	10(20-600)	- do -
	- do -	4.5 <sup>b</sup> )	(230/3.8)	230	10(20 - 600)	- do -
	- do -	14.0 <sup>a</sup> )	(250/3.8)	250	10(20 - 600)	- do

<sup>a</sup>) MFI value calculated from eq. (15) knowing the MFI as per B and  $T_a$  from table 2.

<sup>b</sup>) MFI value given by manufacturer under ASTM testing conditions.

master plots would have the capillary entrance effects implicit in them and hence would annul each other.

From the definition of MFI

$$MFI = 10 \times 60 \times W \tag{2}$$

where W is the weight rate of flow in  $g/cm^3$ 

$$W = Q\rho . (3)$$

Combining eqs. (1), (2) and (3) we obtain

MFI = 
$$(14.13\rho) \frac{D^4}{l} (\Delta P) \frac{1}{\eta_a}$$
. (4)

[Note – all parameters are in c.g.s. units.]

For a given polymer melt,  $\rho$  can be assumed constant. The geometric parameters D and l are fixed as per the ASTM test specifications. Once a test condition is prescribed, the load is specified thereby fixing  $\Delta P$ . Thus, in the ASTM test measurement of the melt flow index, eq. (4) reduces to

$$(MFI)(\eta_a) = K \tag{5}$$

where the constant K is determined by the test conditions and the density of the polymer.

The apparent shear rate,  $\dot{\gamma}_a$ , is given by

$$\dot{\dot{\gamma}}_a = \bar{K} \frac{V}{D} \tag{6}$$

where V is the average velocity through the capillary of diameter D;  $\overline{K}$  is a function of the pseudoplasticity index n for a structurally complex power-law fluid and takes a value of 8 for a Newtonian fluid. Now

$$V = \frac{Q}{\left(\pi/4\right)D^2} \,. \tag{7}$$

Therefore, from eqs. (1) and (5-7) we obtain

$$\frac{\dot{\gamma}}{\mathrm{MFI}} = K' \tag{8}$$

where the constant

$$K' = \frac{\bar{K}}{K} \frac{\Delta P}{32} \frac{D}{l}.$$
(9)

As per eqs. (5) and (8), the MFI of a material is directly proportional to the apparent shear rate and inversely proportional to the apparent viscosity of the material under the conditions of temperature and pressure percentage prescribed in the test. Although eqs. (5) and (8) are valid only at the particular MFI test condition, in effect the validity of these equations over the entire flow curve can be constituted by a change of dead-weight condition and hence the proportionality constant. It should, therefore, be possible to coalesce the  $n_a$  vs.  $\dot{\gamma}_a$  rheograms of polymer grades of different MFI by plotting (MFI  $\times \eta_a$ ) versus ( $\dot{\gamma}_a$ /MFI) on log-log scale at a given temperature and pressure. The coalescence would be governed by the shape of the original  $n_a$  versus  $\dot{\gamma}_a$ . Similar shaped curves would, undoubtedly, coalesce better. Shapes of the rheograms are known to vary with regard to molecular parameters like long-chain branching and molecular-weight distribution. This explains why the master curves of LDPE (branched PE) and HDPE (linear PE) do not coalesce into a single master curve. In arriving at the master curves, the viscosity and shear rate are normalized via the melt-flow index. As melt-flow index is itself insensitive to subtle changes in molecular parameters, this limitation would be expected to be present even in the master curves. The limitation of molecular-weight distribution would be more critical in the very low and very high shear rate regions. However, the working ranges for most polymer processing operations fall in the intermediate shear rate region and therefore, the master curves would still be effective for use as a handy tool for polymer processors.

The correlation suggested by Boenig [7] between MFI and melt viscosity of polyethylene at  $190^{\circ}$ C appears to be a specific case of eq. (5):

$$\log MFI = Constant - \log \eta_0.$$
 (10)

Vinogradov and Malkin [8] have proposed a universal viscosity function at a constant temperature. Viscosity data for a number of polymers such as polyethylene, polypropylene, polystyrene and poly-

isobutylene were reported to fall within a band on a master curve of  $\log(\eta/\eta_0)$  vs.  $\log\eta_0\dot{\gamma}$ . Combination of this reported observation and the inverse dependence of  $\eta_0$  on MFI also suggests that a master curve should be possible by replacing  $\eta_0$  with reciprocal of MFI. The arguments used in arriving at eqs. (5) and (8) are based on flow equations, which appear to be supported by the empirical correlations put forth in the prior literature.

The temperature dependence of the master curve can be eliminated by using a relationship derived from the WLF equation:

$$\ln \frac{\eta_s}{\eta_1} = \frac{8.86 \left(T_1 - T_s\right)}{101.6 + \left(T_1 - T_s\right)} \tag{11}$$

where  $T_1$  is the temperature at which viscosity is to be determined,  $T_s$  the reference temperature related to the glass transition temperature,  $\eta_1$  the viscosity at  $T_1$ , and  $\eta_s$  the viscosity at  $T_s$ . The latter quantity is defined as

$$T_s = T_q + 50 \,\mathrm{K} \tag{12}$$

where  $T_g$  is the glass transition temperature of the material. From eq. (5) we have

$$\frac{\eta_1}{\eta_2} = \frac{(\text{MFI})_2}{(\text{MFI})_1},$$
 (13)

$$\frac{\eta_1}{\eta_2} = \frac{\eta_1}{\eta_s} \cdot \frac{\eta_s}{\eta_2} \,. \tag{14}$$

Combining eqs. (11), (13) and (14), we obtain

$$\ln \frac{(\text{MFI})_2}{(\text{MFI})_1} = \frac{8.86 (T_2 - T_s)}{101.6 + (T_2 - T_s)} - \frac{8.86 (T_1 - T_s)}{101.6 + (T_1 - T_s)}.$$
 (15)

The effective MFI of a polymer at processing temperature can be readily estimated from the MFI reported as the ASTM test temperature using eq. (15).

From ASTM 1238-73, it is clear that MFIs are determined under different test load conditions and hence it is necessary to eliminate the MFI test load dependency of the master curve. In order to do this, it is essential to first appreciate that the melt flow measurement is done under constant shear stress which is directly proportional to the combined weight of the piston and the load on it. Thus

$$\tau \propto L$$
 (weight of piston: load) (16)

or

$$\eta_a \propto \frac{L}{\dot{\gamma}} \,. \tag{17}$$

Since MFI is nothing but a flow rate, it can be directly related to shear rate through the geometry of the melt flow apparatus, and the following proportionality can easily be established

$$MFI \propto \dot{\gamma} . \tag{18}$$

MFI values obtained under ASTM testing conditions give apparent shear rates which are larger than the critical shear rate at which the polymer starts behaving as a shear-thinning system. Within this portion of the curve the apparent viscosity can be characterized by a power-law model as follows

$$\eta_a \propto \dot{\gamma}^{(n-1)} \tag{19}$$

where (n - 1) would be the slope of the viscosity versus shear rate curve. Combining eqs. (17), (18) and (19) gives the following relationship

MFI 
$$\propto L^{\frac{1}{n}}$$
 (20)

or

$$\frac{\mathrm{MFI}_2}{\mathrm{MFI}_1} = \left(\frac{L_2}{L_1}\right)^{\frac{1}{n}}.$$
(21)

For a given polymer grade at a given temperature, there is only one viscosity versus shear rate curve and hence the master curve can be generated using the MFI at some standard loading condition (say 2.16 kg) if known or calculated from eq. (21) when the loading is different.

#### 4. Results and discussion

The polymer systems investigated include LDPE, HDPE, PP, PS and SAN, and the plots generated for these are illustrated in figures 1-9.

Figure 1 shows a plot of viscosity versus shear rate for three grades of LDPE with MFI's of 0.2, 4 and 10 at a temperature of 190 °C. The curves were generated from data taken on the Weissenberg Rheogoniometer and Instron Capillary Rheometer. Unification of the three curves was attempted through the use of a plot



Fig. 1. Viscosity versus shear rate curve for three different grades of LDPE with different MFI at 190 °C



Fig. 2. Master curve for three different grades of LDPE with different MFI at 190 °C

of  $\eta$ . MFI versus  $\dot{\gamma}$ /MFI and the resulting curve is shown in figure 2. This curve is now grade-independent but dependent on the MFI test conditions of 190 °C/2.16 kg load.

96

Figure 3 shows a plot of viscosity versus shear rate at three different temperatures 175 °C, 190 °C and 205 °C for one grade of LDPE, namely, 24FS040 with a MFI of 4 (190 °C/2.16 kg). In order to obtain a unified master curve of  $\eta \cdot$  MFI versus  $\dot{\gamma}$ /MFI, it is essential to obtain MFI values at different temperatures but same loading conditions, namely, 175 °C/ 2.16 kg and 205 °C/2.16 kg. Eq. (15) was then used to obtain these effective MFI values at 175 °C and 205 °C, knowing the MFI at 190 °C and the glass transition temperature of the polymer (table 2). Using the appropriate MFI values with each of the curves in

Table 2. Polymer glass transition temperatures used for computation

Polymer type	Glass transition temperature		
Polyethylene	153 K		
Polypropylene	263 K		
Polystyrene	373 K		
Styrene acrylonitrile	388 K		

figure 3, a plot of  $\eta$  · MFI versus  $\dot{\gamma}$ /MFI was generated as shown in figure 4. This unified curve is then temperature independent but dependent only on the testing load condition of 2.16 kg. When a plot of  $\eta$  · MFI versus  $\dot{\gamma}$ /MFI is to be generated at a different load condition, eq. (21) is used to obtain the MFI at the required load condition. Thus, for example, knowing the MFI of LDPE 24FS 040 at 190 °C for a load of 2.16 kg to be 4, the value of MFI under 5 kg load at the same temperature is calculated to be 21 from eq. (21) using a value of 0.5 for *n* determined from the slope of the viscosity vs. shear rate curve.

Under the fixed loading condition of 2.16 kg, curves in figures 2 and 4 can be plotted together in figure 5 to give a master curve independent of polymer grade and temperature. The number of data points included in this curve and their sources are summarized in table 1. Master plots similar to figure 5 have been generated for HDPE, PP, PS and SAN and are given in figures 6, 7, 8 and 9 respectively. The internal data and the data from outside sources are found to fit very well considering the variation in measurement techniques and the varied element of human error during measurement.

Figures 5-9 thus represent the master curves for LDPE, HDPE, PP, PS and SAN from which the



Fig. 3. Viscosity versus shear rate curves for one grade of LDPE at three different temperatures



Fig. 4. Master curve for one grade of LDPE at three different temperatures



Fig. 5. Master curve for LDPE



Fig. 6. Master curve for HDPE





Fig. 7. Master curve for PP



Fig. 8. Master curve for PS



Fig. 9. Master curve for SAN

entire viscosity versus shear rate curves can be generated at any temperature simply through the knowledge of MFI. The MFI is either given by the manufacturer or obtained from a standard MFI apparatus under ASTM conditions. The steps involved in generating such rheograms are the following:

- Obtain MFI value under standard specified temperature and loading conditions.
- If the loading condition is different from the one used in generating the master curve, obtain value of MFI at the loading condition of the master curve by using eq. (21) and calculating n from the value of the slope of the master curve in the non-Newtonian region.
- If the specified temperature condition of MFI is also different from the temperature of interest at which viscosity versus shear rate curve is to be generated, then calculate a new value of MFI using eq. (15) and the correct determined value of  $T_g$  for the specific polymer under consideration.
- Knowing the effective MFI at the temperature of interest the rheogram can be generated by simply substituting the value in the master curve.

It is to be noted that the value of an effective MFI for a resin at a temperature other than the ASTM test

temperature, computed using eq. (15) is very sensitive to the value of the glass transition temperature used. Since the glass transition temperature of various grades of an amorphous polymer could vary over a broad range of 10-15 °C, it is recommended that the actual glass transition temperature of the particular resin be determined whenever possible.

The values of the heat distortion temperatures of various grades of polystyrene are reported in table 3. The heat distortion temperature, being a thermomechanical property of a resin, is qualitatively related to the glass transition temperature. Therefore, for these grades, the glass transition would also vary over about 8 °C. The sensitivity of the effective MFI value to the glass transition temperature is illustrated in the last two columns of table 3. In formulating the master curve for polystyrene (figure 8), a single value of 100 °C was used for the glass transition temperature, whereas the glass transition temperature of an impact polystyrene is expected to be lower than that of the general purpose crystal grade. The rheograms of the various grades at different temperatures would coalesce in a narrower band, if the correct glass transition temperatures for the grades were available.

Even with a semi-crystalline polymer like high density polyethylene, where the density could vary

Grade	Heat Distoration Temp. °F (264 lbf/in <sup>2</sup> )	Reported MFI at ASTM conditions of 200 °C/ 5.00 kg	Computed values of effective MFI for 50 kg at different temperatures					
			$T_g = 80 ^{\circ}\mathrm{C}$	$T_g = 100 ^{\circ}\mathrm{C}$				
			°C	°C				
			160 180 210 220 230 240 250	160 180 210 220 230 240 250				
Amoco G2	185	14.1	27.4 - 85.1 - 215	33.0 - 135 - 415				
Amoco H5M	190	7.9	15.4 - 47.7 - 121	18.4 - 75.6 - 239				
Polysar 205	193	6.8	0.17 1.4 - 24.0	$0.05\ 0.85\ -\ 33.5\ -\ -\ -$				
Styron 666U	197	7.5	26.4 - 73.5 -	37.0 - 130 -				

Table 3. Sensitivity of the effective MFI to the glass transition temperature for polystyrene resins

from 0.940 to 0.965, the glass transition temperature would be different for different grades. The range of this variation in the semi-crystalline polymers is generally narrower than that in amorphous polymers.

#### 5. Conclusion

An effective method has been proposed to estimate the viscosity versus shear rate flow curves of a resin at temperatures relevant to the processing conditions from its melt flow index and glass transition temperature. The rheograms obtained by using the method would give an order of magnitude information on viscosity, adequate for most exercises in process design, optimization and trouble shooting. However, the flow curves so generated cannot be used for material quality control purposes. Therefore, for example, subtle differences in the low and high shear viscosities of the resin arising from variable molecular weight distribution cannot be elucidated. This limitation of the method is to be expected, since the rheograms are generated using a value of MFI measured under ASTM test conditions that are insensitive to the effects of the molecular-weight distribution, as illustrated by Smith [3]. The proposed method has been introduced as a handy aid to the plastics processor in the event of his having no other rheological data on the material besides the melt flow index.

#### Acknowledgements

The authors are thankful to IPCL, Baroda (India) for supplying free samples of LDPE and PP of different grades used for our experimental data, USS Novamont Inc. (USA) for supplying viscosity versus shear rate data for PP with known MFI values, Amoco Chemicals Corporation (USA) for supplying viscosity versus shear rate data for HDPE, PP and PS with known MFI values and Polysar Inc. (USA) and Dow Chemicals (USA) for supplying viscosity versus shear rate data for PS of different grades with known MFI.

### References

- 1. Van Krevelan, D. W., Properties of Polymers, p. 488, Elsevier Scientific Publishing Company (Amsterdam 1976).
- Shida, M., L. V. Cancia, Polym. Engg. Sci. 11, 124 (1971).
- 3. Smith, D. J., TAPPI 60, 131 (1977).
- 4. Borzenski, F. J., Plastics Compounding 25 (Sept./Oct. 1978).
- 5. Menges, G., J. Wortberg, W. Michaeli, Kunststoffe 68, 47 (1973).
- 6. Plastics Engineering 7, 18 (1979).
- 7. Boenig, H. V., Polyolefins, p. 262, Elsevier Scientific Publishing Company (Amsterdam 1966).
- Vinogradov, G. V., A. Ya. Malkin, J. Polym. Sci. A2, 4, 135 (1966).
- 9. Mendelson, R. A., Trans. Soc. Rheol. 9, 3 (1965).
- 10. Dutta, A., Ph. D. Thesis, S.U.N.Y. Buffalo (1981).
- Kataoka, T., T. Kitano, M. Sasahara, K. Nishijima, Rheol. Acta 17, 149 (1978).
- 12. Private Communication with G. A. Vaughan, Technical Service Engineer, USS Novamont, Inc., West Virginie (USA).
- 13. Private Communication with J. P. Whelan, Senior Divisional Engineer, Amoco Chemicals Corporation, Illinois (USA).
- 14. Private Communication with Dow Chemicals, Michigan (USA).
- 15. Private Communication with H. A. Biletech. Manager, LTDC, Polysar Inc., Massachusetts (USA).

(Received May 3, 1982; in revised form July 2, 1982)

Authors' address:

Dr. A. V. Shenoy, S. Chattopadhyay, V. M. Nadkarni Chemical Engineering Division National Chemical Laboratory Pune 411008 (India)