

# Rheograms of Cellulosic Polymers from the Melt Flow Index

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## Synopsis

Data on the variation of melt viscosity over a wide range of shear rates and temperatures are necessary in the processing of cellulosic polymers. An effective method has been proposed to estimate the viscosity vs. shear rate flow curves of a cellulosic resin at temperatures relevant to the processing conditions, from its melt flow index and glass transition temperature. The method involves the use of a master curve obtained by coalescing the rheograms of various grades in terms of a modified viscosity,  $\eta$ -MFI, and a modified shear rate,  $\dot{\gamma}$ /MFI. Master curves have been reported for cellulose esters and ethers.

## INTRODUCTION

Chemical modification of the naturally occurring, highly crystalline polyether available from wood pulp and cotton linters, namely, cellulose, reduces the structural order by disrupting the molecular packing, thereby producing thermoplastic materials termed as cellulosics. In the course of the chemical reactions to produce cellulosics, some degradation occurs in the chain length of the cellulose polymer. The highest molecular weight of cellulose, found in cotton, is about 570,000 corresponding to a degree of polymerization of 3500. The degree of polymerization of wood cellulose is about 1000, whereas that of the cellulosic derivatives is usually below 500.<sup>1</sup> Cellulosic polymers include cellulose nitrate, three organic esters cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate, and one ether-ethyl cellulose.

The property features and applications of the various cellulosic polymers are summarized in Table I.<sup>2</sup> The major processing methods, used in converting cellulosic plastics into the various products listed in Table I, include extrusion, injection molding, compression molding, and thermoforming. In all these processes, the molten polymer is subjected to shearing flows. The range of shear rates encountered is quite wide, and the temperatures of flow deformation also vary with the process. A knowledge of the melt viscosity of the plastics over a wide range of shear rates at temperatures relevant to processing is therefore essential for process design, optimization, and trouble shooting.

The rheological data necessary to generate rheograms depicting the variation of melt viscosity with shear rate at various temperatures are obtained on sophisticated instruments such as the Weissenberg Rheogoniometer, Instron Capillary Rheometer, Rheometrics Mechanical Spectrometer, etc. These instruments are expensive, costing about \$25,000–120,000, and require trained operators. The data collection is quite cumbersome and time-consuming, particularly if the viscosity behavior over the entire range of relevant temperatures

TABLE I

Cellulosic type	Special advantageous features	End applications
Cellulose nitrate	Good dimensional stability Low water absorption Toughness	Hollow objects like rods and tubings Sheets Casings for personal accessories and toileteries Base for lacquers, binders, and coatings
Cellulose acetate	Good surface lustre Pleasant touch Color stability Toughness	Extruded tapes Premium toys Tool handles Audio tape base Write-on pressure sensitive tapes Eyeglass frames
Cellulose propionate	Good surface luster Good clarity High shock resistance	Blister packages Lighting fixtures Safety goggles Face shields Motor covers Steering wheels
Cellulose acetate butyrate	Good clarity Weatherability Toughness	Curtain walls Weather shelters Pen and pencil barrels Decorative plaques
Ethyl cellulose	Good impact strength Moderately flexible Toughness at low temperatures Heat resistance	Flashlight cases Fire extinguisher components Electrical appliance parts

and shear rates is to be investigated for each of the various grades of a thermoplastic material. Thus the collection of the necessary rheological data is beyond the financial and technical means of most plastics processors. It is therefore desirable to have a procedure for estimating the rheograms of the polymer melts from a readily available engineering flow parameter like the melt flow index (MFI). Shenoy et al.<sup>3,4</sup> have successfully developed a method to estimate the rheogram from MFI. Their unifying approach has been found to be valid for polyolefins and styrenics,<sup>3</sup> and also for a number of engineering thermoplastics.<sup>4</sup> The unifying method involves generation of a master curve by coalescing rheograms of various grades of a resin at various temperatures. In the present paper, the method is extended to cellulosic plastics, including cellulose acetate, cellulose acetate butyrate, cellulose propionate, and ethyl cellulose.

### DATA COLLECTION

A series of flow curves for different grades of cellulosic polymers at various temperatures have been compiled by Westover.<sup>5</sup> These data were used for generation of the master curves. A summary of the systems analyzed in the present study is given in Table II.

TABLE II

Cellulose type	Grade	MFI (temp, °C) C/load condition, kg	Data temp (°C)	No. of data pts (shear rate range, s <sup>-1</sup> )	Source (Ref. no.)
Cellulose acetate	Tenite 036-H2	0.7 <sup>a</sup> (190/2.16)	190	3 (10-100)	5
		3.6 <sup>b</sup> (210/2.16)	210	5 (10-5000)	5
	Tenite 036-MS	4.8 <sup>a</sup> (190/2.16)	190	3 (100-5000)	5
		24.5 <sup>b</sup> (210/2.16)	210	3 (100-5000)	5
Cellulose propionate	Tenite 307-H	3.7 <sup>a</sup> (190/2.16)	190	3 (300-5000)	5
		19.0 <sup>b</sup> (210/2.16)	210	3 (300-5000)	5
	Tenite 307-H5	68.8 <sup>b</sup> (230/2.16)	230	3 (300-5000)	5
		1.3 <sup>a</sup> (210/2.16)	210	3 (100-1000)	5
		4.7 <sup>b</sup> (230/2.16)	230	3 (100-1000)	5
Cellulose acetate butyrate	Tenite 205-H2	0.25 <sup>a</sup> (190/2.16)	190	3 (30-500)	5
		1.3 <sup>b</sup> (210/2.16)	210	4 (30-500)	5
	Tenite 205-MS	4.7 <sup>b</sup> (230/2.16)	230	4 (30-500)	5
		2.5 <sup>a</sup> (190/2.16)	190	3 (100-5000)	5
		13.0 <sup>b</sup> (210/2.16)	210	3 (100-5000)	5
Ethyl cellulose	Unknown CAB	5.0 <sup>c</sup> (230/2.16)	230	4 (1-1000)	7
		1.3 <sup>c</sup> (170/2.16)	170	3 (10-100)	5
	Ethocel 856	4.4 <sup>c</sup> (190/2.16)	190	3 (10-300)	5
		14.2 <sup>c</sup> (210/2.16)	210	3 (20-1000)	5
		31.0 <sup>c</sup> (230/2.16)	230	3 (50-900)	5

<sup>a</sup> MFI given under standard test conditions.

<sup>b</sup> MFI calculated by WLF type eq. (7).

<sup>c</sup> MFI calculated from the read out method at constant shear stress.

## DATA ANALYSIS

The melt flow index (MFI) is defined as the weight of polymer (g) extruded in 10 min under the application of a dead weight through a melt flow apparatus. The geometrical parameters of the melt flow apparatus and the testing conditions specific to cellulose as stated in ASTM D1238-73 are given in Tables III. Since the melt flow apparatus is an extrusion rheometer and the melt flow index is basically a flow rate parameter, we can use the conventional expressions for shear stress  $\tau$  and shear rate  $\dot{\gamma}$  to get the relationship between MFI and viscosity as well as shear rate. Thus

$$\tau = R_N F / 2\pi R_p^2 l \quad (1)$$

$$\dot{\gamma} = 4Q / \pi R_N^3 \quad (2)$$

where piston radius  $R_p = 0.4737$  cm, nozzle radius  $R_N = 0.105$  cm, nozzle length  $l = 0.8$  cm, force  $F =$  test load  $L(\text{kg}) \times 9.807 \times 10^5$  dyn, flow rate  $Q = \text{MFI}/600$  cc/s. Equations (1) and (2) can be simplified through proper substitution of the fixed geometric parameters of the melt flow apparatus to give

$$\tau = 9.13 \times 10^4 L \quad (3)$$

$$\dot{\gamma} = 1.83 \text{ MFI}/\rho \quad (4)$$

As the MFI value is generated at a fixed temperature and a fixed load, a single point on the shear stress vs. shear rate curve at that specific temperature can be obtained through eqs. (3) and (4). This fact is useful for calculating the value of MFI from a known shear stress vs. shear rate curve when the MFI is not reported. This was the case with ethyl cellulose wherein no MFI value under standard test conditions was reported.<sup>5</sup> However, the shear stress vs. shear rate curve was available. For a load condition of 2.16 kg, the constant shear stress in the melt flow apparatus from eq. (3) is equal to  $1.95 \times 10^5$ . Thus reading out the value of shear rate  $\dot{\gamma}$  for this constant shear stress at a specific temperature, a value of MFI could be calculated using eq. (4). The propriety of this method for obtaining MFI from a shear stress vs. shear rate curve has been tested for different polymers with reported MFI.<sup>4</sup>

Using the fact that  $\eta_a = \tau/\dot{\gamma}$ , the following relationship can be easily derived through eqs. (3) and (4) as follows:

$$\text{MFI} \times \eta_a = 4.98 \times 10^4 \rho L \quad (5)$$

TABLE IIIA  
Standard Test Conditions for Cellulose Derivatives

MFI test temperature (°C)	Total test load including piston (kg)
190	0.325
190	2.16
190	21.6

TABLE IIIB  
Geometric Parameters of the Melt Flow Indexer

	Piston	Die/nozzle
Diameter (cm)	0.94742 ± 0.0008	0.20955 ± 0.0005
Length (cm)	0.635 ± 0.013	0.8 ± 0.0025

$$\dot{\gamma}/\text{MFI} = 1.83/\rho \quad (6)$$

For a given cellulose polymer, the density and the testing load conditions are fixed, thus indicating that the MFI of the 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 prescribed in the test. Although eqs. (5) and (6) 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  $\eta_a$  vs.  $\dot{\gamma}$  curves of cellulosic grades with different MFI by plotting  $(\text{MFI} \times \eta_a)$  vs.  $(\dot{\gamma}/\text{MFI})$  in a log-log scale independent of temperature if the correct MFI value corresponding to the temperature of measurement of  $\eta_a$  vs.  $\dot{\gamma}$  is used. The coalescence would be governed by the shape of the original  $\eta_a$  vs.  $\dot{\gamma}$  curve. 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. 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 regimes. 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 the processors.

Within the melt flow indexer die, capillary entrance effects are important as  $L/D = 3.8$ . These have not been accounted for during the derivation of eqs. (5) and (6). However, from the above discussion it is clear that MFI would be used merely as a normalizing factor to obtain reduced viscosity vs. 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 master plots would have the capillary entrance effects implicit in them and hence would annul each other.

A further rationale for obtaining a master curve can be derived from Vinogradov and Malkin,<sup>6</sup> who have shown that the viscosity data for a number of polymers like polyethylene, polypropylene, polystyrene, and polyisobutylene fall within an acceptable bandwidth when  $\log \eta/\eta_0$  vs.  $\log \eta_0 \dot{\gamma}$  is plotted. Taking note of the fact that the zero shear viscosity  $\eta_0$  is only a special case of  $\eta_a$  for  $\dot{\gamma} \rightarrow 0$ , from eq. (5) the inverse relationship between MFI and  $\eta_0$  is evident. Thus a master curve should be possible by replacing  $\eta_a$  by the reciprocal of MFI in the master curve function suggested by Vinogradov and Malkin.<sup>6</sup>

Master curves for three cellulosic esters and one cellulosic ether have been obtained from the apparent viscosity vs. apparent shear rate curve at different temperatures. MFI reported by Westover<sup>5</sup> has been used for obtaining the  $\eta \times \text{MFI}$  vs.  $\dot{\gamma}/\text{MFI}$  curve when the viscosity vs. shear rate curve was given at the temperature of MFI measurement, namely, 190°C. For MFI values at other temperatures, the modified WLF-type equation suggested earlier by Shenoy et al.<sup>3</sup> has been used:

$$\log \frac{\text{MFI}[T_2]}{\text{MFI}[T_1]} = \frac{8.86[T_2 - T_s]}{101.6 + [T_2 - T_s]} - \frac{8.86[T_1 - T_s]}{101.6 + [T_1 - T_s]} \quad (7)$$

when  $T_1$  = temperature of MFI measurement (°K), which in the present case

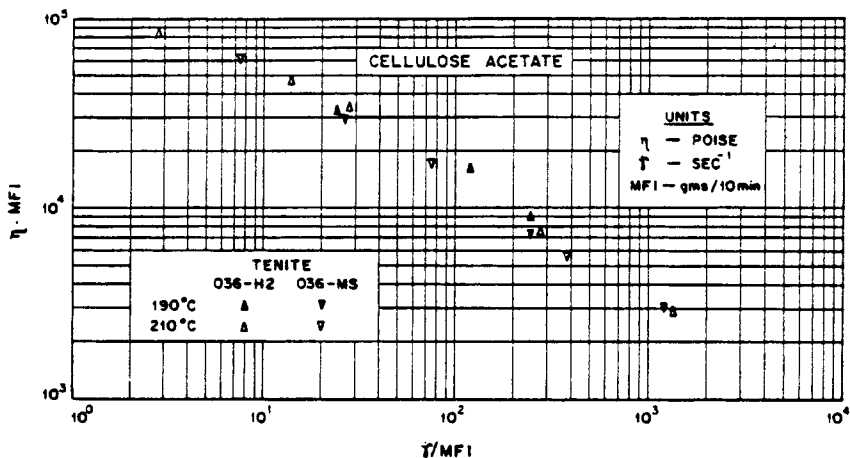


Fig. 1. Master curve for cellulose acetate at 2.16-kg test load condition.

is 463°K,  $T_2$  = temperature at which MFI value is desired,  $T_s$  = standard reference temperature taken as  $T_g + 50^\circ\text{K}$ , and  $T_g$  = glass transition temperature taken as 365°K for cellulose esters.

As can be seen from Table IIIA, there is more than one test load condition under which MFI measurement can be taken. MFI values obtained under the 2.16-kg load condition have been used in the present work. In cases when the load condition is different, the following technique is suggested. The single-point measurement of MFI gives a point on the non-Newtonian (shear-thinning) portion of the shear stress vs. shear rate curve. At different load conditions, the point is merely shifted on this portion of the curve. In the non-Newtonian regime, the relationship between shear stress and shear rate can be well approximated by the following power-law model:

$$\tau = K\dot{\gamma}^n \quad (8)$$

where  $n$  is defined as the pseudoplasticity index and  $K$  is the consistency index. Using eqs. (3) and (4) under different load conditions of  $L_1$  and  $L_2$ , we get the following relationship from eq. (8):

$$\text{MFI}_2/\text{MFI}_1 = (L_2/L_1)^{1/n} \quad (9)$$

$n$  can be obtained as the slope of the  $\tau$  vs.  $\dot{\gamma}$  curve on a log-log scale or calculated from the slope ( $n - 1$ ) of the viscosity vs. shear rate curve on a log-log scale. In the case of cellulotics, a value of  $n = 1/3$  for cellulosic esters and  $n = 1/2$  for cellulosic ether has been found to be a good conservative estimate. Thus

$$\text{MFI}_2/\text{MFI}_1 = (L_2/L_1)^3 \quad \text{for cellulosic esters} \quad (10)$$

and

$$\text{MFI}_2/\text{MFI}_1 = (L_2/L_1)^2 \quad \text{for cellulosic ethers} \quad (11)$$

## RESULTS AND DISCUSSION

The cellulose derivatives investigated include cellulose acetate, cellulose propionate, cellulose acetate butyrate, and ethyl cellulose. In all cases, except ethyl cellulose, plots have been generated using at least two grades of the par-

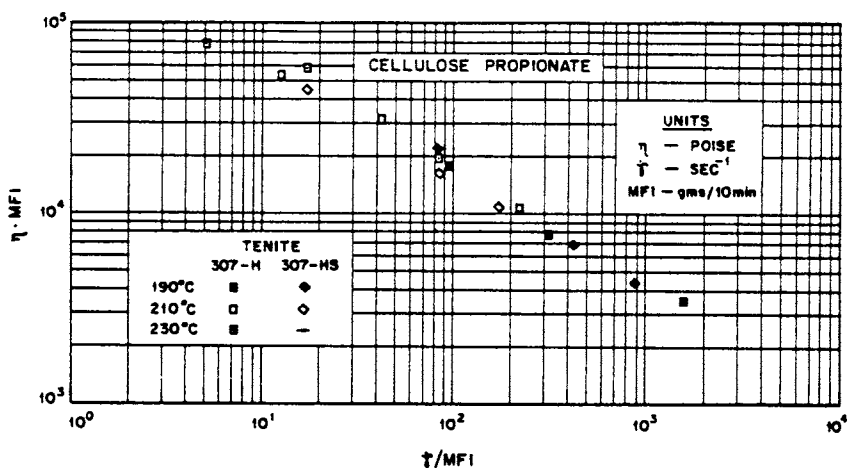


Fig. 2. Master curve for cellulose propionate at 2.16-kg test load condition.

ticular resin at two or three different temperatures. The only available data on ethyl cellulose were for a single grade at four different temperatures.

In the case of each type of cellulose derivative, it was found that a master curve could be generated by plotting  $MFI \times \eta$  vs.  $\dot{\gamma}/MFI$  on a log-log scale. These are shown for cellulose acetate, cellulose propionate, and cellulose acetate butyrate in Figures 1, 2, and 3, respectively. It is interesting to note that all the three curves could be superimposed on one single curve given in Figure 4. However, the master curve for ethyl cellulose did not fit within the band of this curve, suggesting the existence of a unique master curve for cellulose esters and a separate master curve for cellulose ethers.

The fact that the curves for cellulose acetate, cellulose propionate, and cellulose-acetate-butyrate coalesce into a unique curve is to be expected, since the degree of chemical modification in these various resins is comparable, in the range of 40–50% as given in Table IV. The molecular sizes of the different pendant groups are also not very different, the shortest chain being the two carbon acetate and the longest being the four carbon butyrate chain. The disruption in the packing ability, which would influence the intermolecular interactions and hence the viscosity,<sup>4</sup> is therefore comparable in all the ester derivatives.

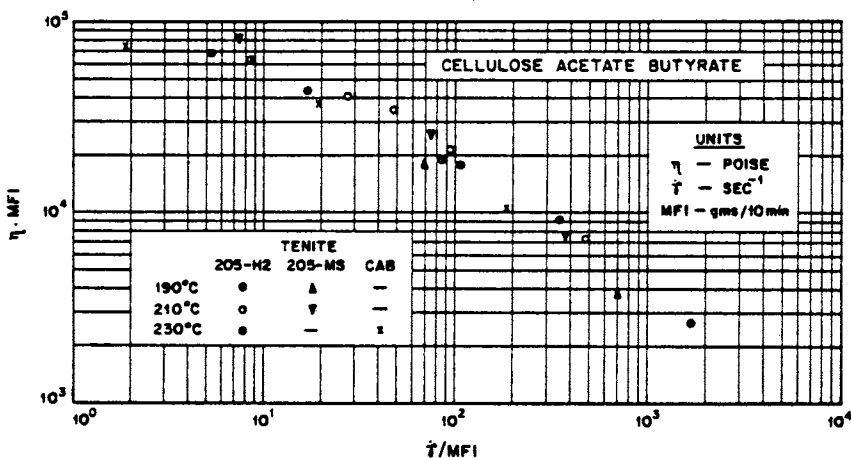


Fig. 3. Master curve for cellulose acetate butyrate at 2.16-kg test load condition.

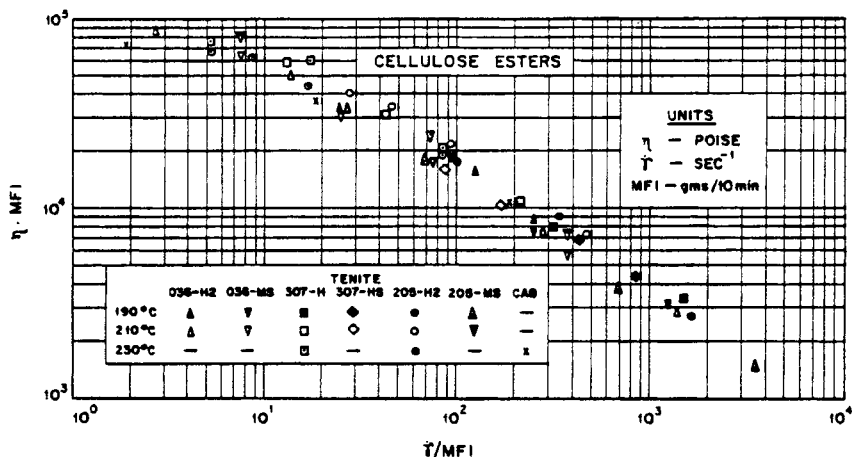


Fig. 4. Master curve for cellulose esters at 2.16-kg test load condition.

At a given shear rate and temperature, the ester derivatives exhibit a higher viscosity than that of the ether derivatives. The reason for this behavior is related to the polar character of the carbonyl group in the ester linkage. The carbonyl oxygen atoms in the cellulose esters can enter into hydrogen bonds with hydroxyl groups on the cellulose chain. This results in higher intermolecular forces relative to the cellulose ethers, which have a nonpolar ether linkage, leading to higher viscosity.

Figures 4 and 5 thus provide sufficient information to generate rheograms for the cellulose derivatives from the knowledge of MFI, which is either provided by the manufacturer or can be easily measured using a standard MFI apparatus. The steps involved in generating such rheograms are as follows:

1. Obtain the MFI under ASTM-specified temperature and loading conditions.
2. In cases when the loading condition is different from that specified in the master curve, obtain a new value of MFI using eq. (7) for cellulose esters and eq. (8) for cellulose ethers at the required loading condition of 2.16 kg.
3. If the specified temperature condition, too, is different from the condition at which the rheogram is desired, then eq. (3) ought to be used for calculating the effective MFI value.
4. Using the correct value of effective MFI in the master curve, the viscosity vs. shear rate curve can be generated by mere substitution.

TABLE IV  
Extent of Chemical Modification in Cellulosic Polymers<sup>2</sup>

Cellulosic polymer	Extent of modification
Cellulose nitrate	11% Nitrogen (about 45% nitrate)
Cellulose acetate	38–40% Acetyl
Cellulose acetate-propionate	39–47% Propionyl and 2–9% acetyl
Cellulose acetate-butyrate	26–39% Butyryl and 12–15% acetyl
Ethyl cellulose	44–48% Ethoxyl



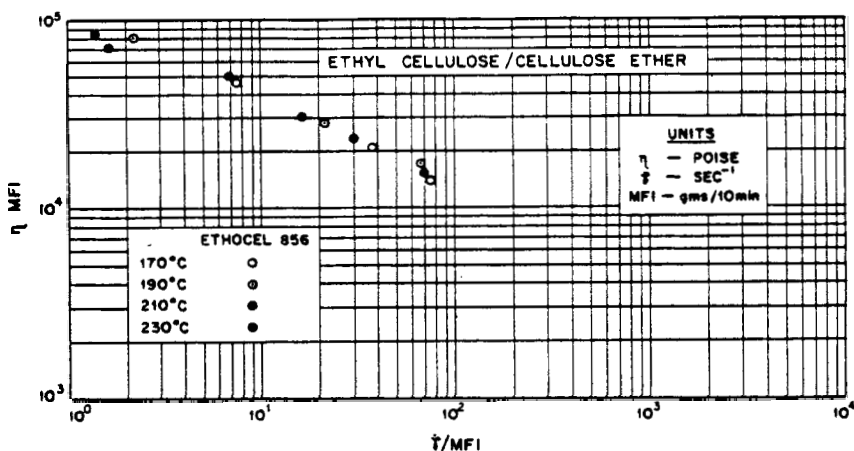


Fig. 5. Master curve for ethyl cellulose/cellulose ether at 2.16-kg test load condition.

## CONCLUSION

The unifying approach for coalescing rheograms of various grades of a resin at different temperatures, in terms of a modified viscosity,  $\eta$ -MFI, and a modified shear rate,  $\dot{\gamma}$ /MFI, is applicable to the cellulosic plastics. Unique master curves are obtained for cellulose esters and cellulose ethers, which can be used to estimate complete flow curves of a resin at relevant processing temperatures, from a knowledge of its melt flow index, and glass transition temperature. The master curve for the cellulose esters exhibits higher viscosity than that for the cellulose ethers, at a given shear rate. This observation can be accounted for in terms of the greater intermolecular interactions in the cellulose esters resulting from hydrogen bonding of the carbonyl oxygen atoms with hydroxyl groups of the cellulose.

The rheograms obtained by using this method would give an order of magnitude information on viscosity, adequate for most exercises in process design, optimization, and trouble shooting. However, subtle differences in the low and high shear viscosities of the cellulosics arising from variable molecular weight distribution cannot be elucidated. This limitation of the method is to be expected, since the rheograms are generated using MFI as a normalizing factor, which itself is insensitive to the effects of molecular parameters such as branching and molecular weight distribution. Nevertheless, it is to be noted that 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.

## NOMENCLATURE

$F$	force due to the weight of piston and load
$K$	consistency index
$l$	length of nozzle
$L$	weight of piston and load (kg)
$n$	pseudoplasticity index given by the slope of the shear stress vs. shear rate curve on log-log scale
$Q$	flow rate

$R_N$	radius of nozzle
$R_p$	radius of piston
$T_1$	temperature at condition 1
$T_2$	temperature at condition 2
$T_g$	glass transition temperature
$T_s$	standard reference temperature equal to $T_g + 50^\circ\text{K}$
$\dot{\gamma}$	shear rate
$\rho$	density of the polymer
$\eta_a$	apparent viscosity
$\tau$	shear stress

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Received December 16, 1981

Accepted June 7, 1982