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Melt Flow Behaviour of Liquid Crystalline Polymer†

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The method proposed earlier to estimate complete flow curves depicting the variation of melt viscosity over industrially relevant shear rate and temperature through the melt flow index has been extended to liquid crystalline polymer melts. The present work considers the study of the thermotropic system of the copolymer of poly(ethylene terephthalate) and p-hydroxybenzoic acid with different ratio of the components. A master curve is shown to exist for the system when modified viscosity function is plotted against modified shear rate. A new rheological model has been suggested to fit the master curve adequately as the curve is different from the conventional form.

During recent years, liquid crystalline polymers have attained immense commercial importance due to the possibility of producing ultrahigh strength and modulus fibers and plastics[1-8] from them. The exceptional physical properties of these uniquely structured systems are a direct consequence of the morphology and orientation induced into the polymers due to the flow history during processing. Therefore, an understanding of the rheology of these systems is extremely important.

Rheology of liquid crystalline polymers has received a great deal of attention in recent literature adjudging from the publication of reviews and key articles[9-22] on the subject. Rheological studies have been performed for both lyotropic systems (liquid crystals which exist in solution) as well as thermotropic systems (liquid crystalline order which exists in polymer melts or undiluted polymers). There is a considerable degree of similarity between the rheological properties

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of lyotropic and thermotropic systems. The most distinguishing feature of lyotropic and thermotropic systems is the sharp decrease in viscosity with the onset of liquid crystalline order.[9,12,18,19] In fact, it has been postulated[19,20] that the shear rate dependence of viscosity of such systems shows three distinct regions: a shear-thinning region at very low shear rates, a plateau region of nearly constant viscosity and another shear thinning region at high shear rates. Viscosity is also dependent on temperature and hence, a knowledge of the complete flow curve or rheogram depicting the variation of viscosity over industrially relevant range of shear rates and temperature is essential in the design of processing equipment, process optimization and trouble-shooting. The rheological data for constructing the rheogram are generally obtained on sophisticated scientific instruments such as the Weissenberg Rheogoniometer, the Instron Capillary Rheometer, Rheometrics Mechanical Spectrometer, etc. which are very expensive and require trained operators. Recently, Shenoy et al.[23-31] have suggested a method for obtaining an adequate estimate of the flow behaviour of polymer melts merely from the knowledge of the Melt Flow Index (MFI). Their method involves the generation of unified curves by coalescing rheograms of various grades of a resin at various temperatures. Unified curves have been provided for a large number of homopolymer types such as polyolefins and styrenics,[23] cellulosics,[24] vinyls,[25] engineering thermoplastics[26] and some speciality polymers.[27] From these unified curves, rheograms of the polymer melts can be easily estimated from readily available or easily determinable flow parameter, namely, the MFI. The technique has been shown to be effectively applicable to filled polymers,[28,29] polymer blends[30] and copolymers.[31]

In the present paper, the unifying approach is extended to liquid crystalline melts. For thermotropic systems, there are three reports[10,18,19] giving the viscosity of copolymers of polyethylene terephthalate (PET) modified with varying amounts of p-hydroxybenzoic acid (HBA). It will be shown in the following that all the viscosity versus shear rate curves for these systems can be coalesced into a single curve independent of the mole percentage composition of the PET and HBA.

DATA ANALYSIS

The melt flow is a flow parameter obtained from an extrusion rheometer. It is defined as the weight of the polymer in grams extruded in ten minutes through a capillary of specific diameter and length by

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pressure applied through dead weight as per ASTM 1238–73. MFI truly represents a single point on the viscosity versus shear rate curve. The expressions for the shear stress τ and the shear rate $\dot{\gamma}$ corresponding to the MFI determination can be obtained from the conventional equations used for flow through a capillary. Hence

$$\tau = \frac{R_N F}{2\pi R_P^2 \ell} \tag{1}$$

$$\dot{\gamma} = \frac{4Q}{\pi R_N^3} \tag{2}$$

where R_P is the piston radius (0.4737 cm), R_N is the nozzle radius (0.105 cm), ℓ is the length (0.8 cm), F is the test load L in kg $\times$ 9.807 $\times$ 10^5 (dynes), Q is the flow rate = MFI/600ζ (cc/sec) and ζ is the polymer melt density (gm/cc).

Since the geometric parameters of the melt flow indexer are fixed as per ASTM 1238–73, equations (1) and (2) reduce to

$$\tau = 9.13 \times 10^4 L \tag{3}$$

$$\gamma = \frac{1.83\, MFI}{\zeta} \tag{4}$$

Using the fact that

$$\eta = \tau/\gamma \tag{5}$$

equations (3) and (4) can be rearranged to give the following form.

$$\eta\,.MFI = 4.98 \times 10^4 \zeta L \tag{6}$$

$$\frac{\dot{\gamma}}{MFI} = \frac{1.83}{\zeta} \tag{7}$$

For a given polymer since the density and *MFI* load conditions are fixed, the right hand side of equations (6) and (7) are both constant. This suggests that a master curve independent of polymer grade and temperature can be obtained by plotting $\eta.MFI$ versus $\dot{\gamma}/MFI$ as has been shown by Shenoy et al.[23–31] The method should be applicable to thermotropic liquid crystalline polymers as well, provided the ap-

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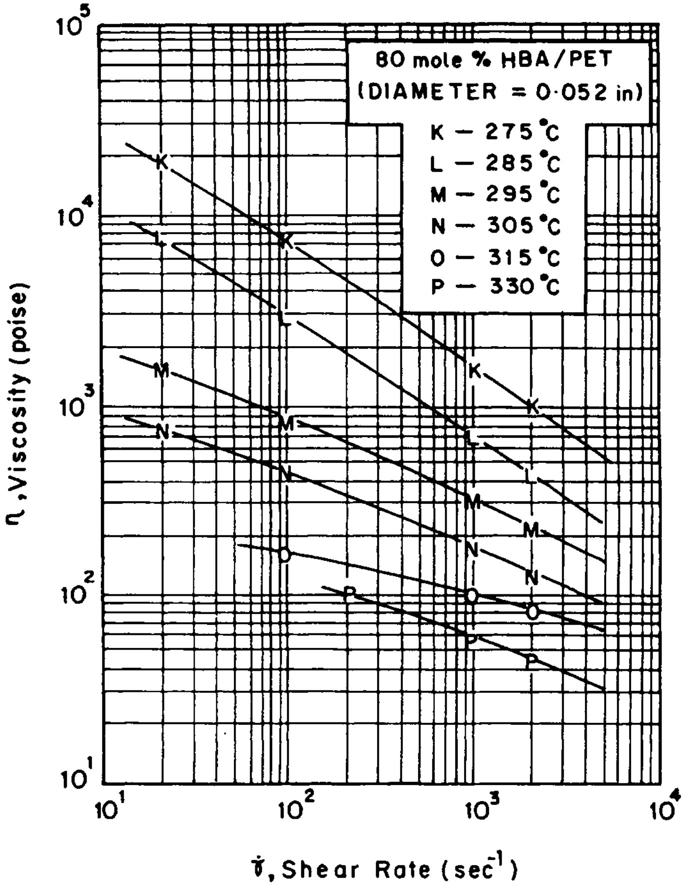

FIGURE 1 Viscosity versus shear rate curve for 80 mole percent of HBA at six different temperatures (taken from Wissburn 18).

propriate value of *MFI* is used. Specific test conditions for most common polymers are given in ASTM 1238–73. However, for thermotropic systems of the type studied in the literature[10,16,13,19] there are no specifications given. Since the studied systems are copolyesters, it would be appropriate to choose test load conditions akin to those of poly(ethylene terephthalate) namely, 2.16 kg.

MASTER CURVE GENERATION

Figures 1–4 are viscosity versus shear rate curves for different compositions of HBA/PET at various temperatures. Two particular com-

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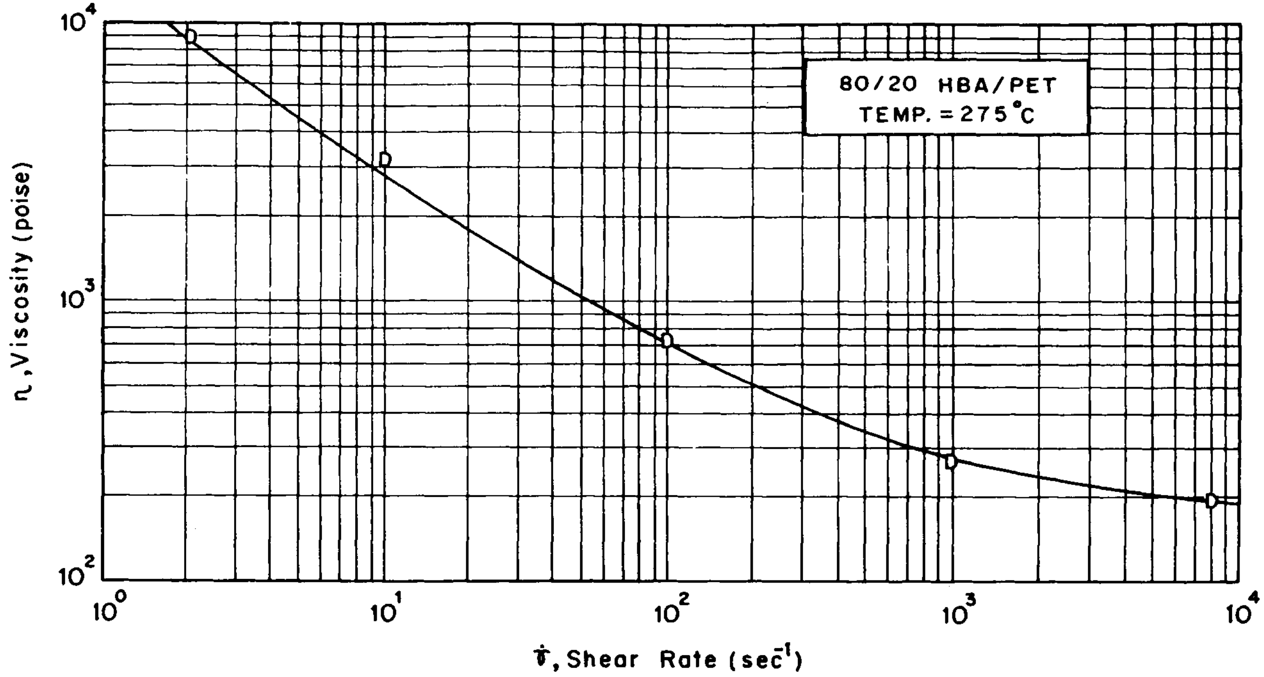

FIGURE 2 Viscosity versus shear rate curve for 80 mole percent of HBA at 275°C (taken from Baird 17).

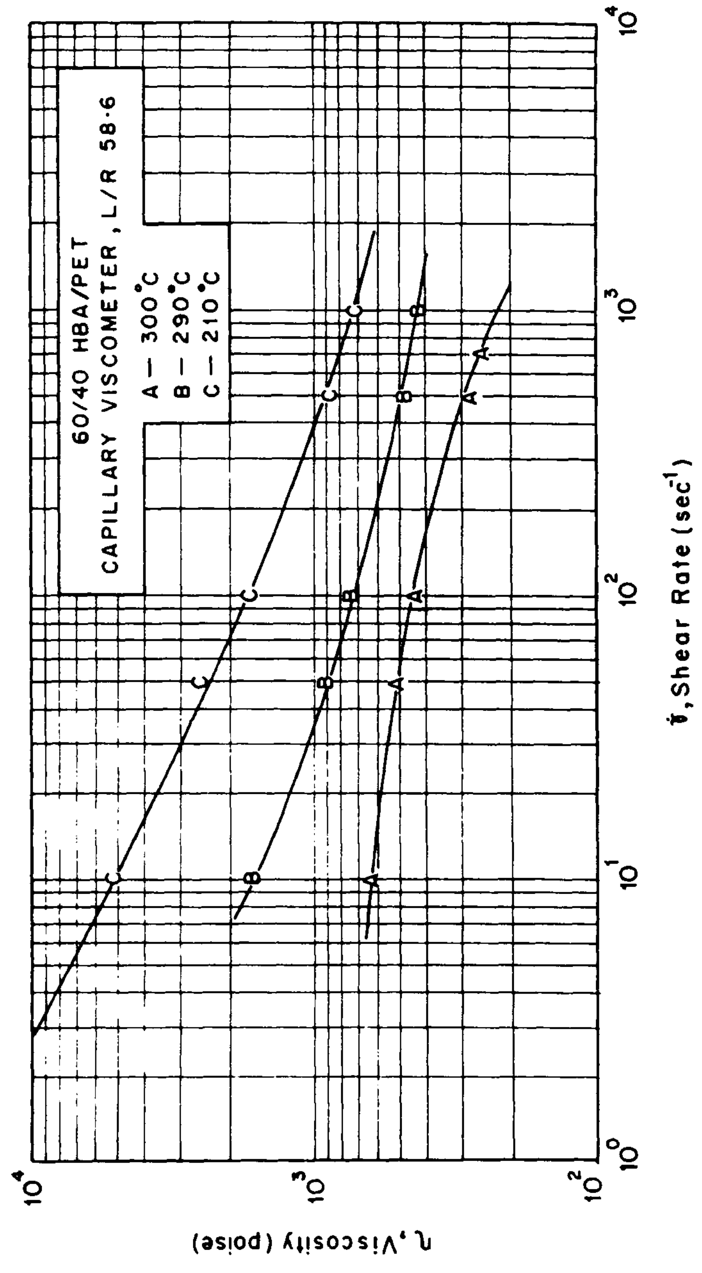

FIGURE 3 Viscosity versus shear rate curve for 60 mole percent of HBA at three different temperatures (taken from Wissburn 16).

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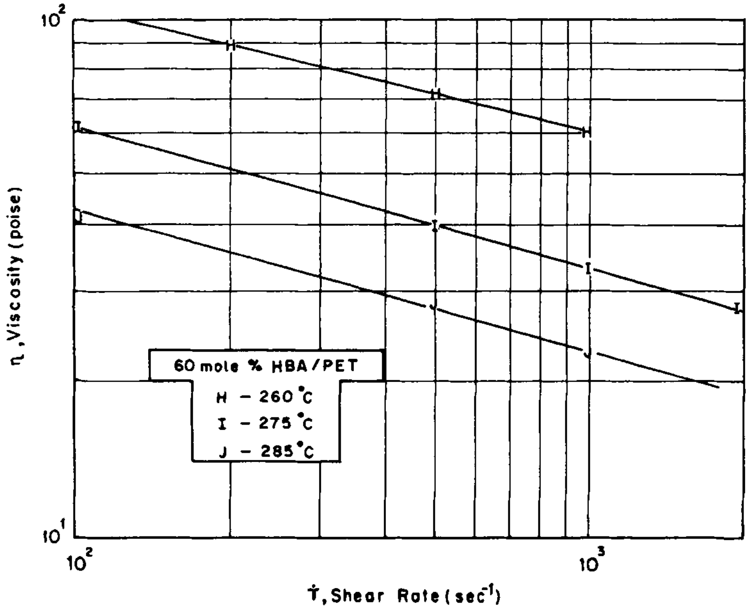

FIGURE 4 Viscosity versus shear rate curve for 60 mole percent of HBA at three different temperatures (taken from Jerman and Baird 18).

positions, namely, 80 mole percent and 60 mole percent of hydroxy benzoic acid have been chosen. Figure 1 gives the viscosity versus shear rate curve for 80 mole percent of hydroxy benzoic acid at six different temperatures ranging from 275–230°C. This data is taken from Wissbrun.[16] In order to consolidate our findings and eliminate the operator or interlaboratory errors, it was decided to use data from another source[17] for the same composition at one temperature. Figure 2 shows the viscosity versus shear rate data for 80 mole percent of HBA at 275°C. The other composition of HBA/PET chosen was 60 mole percent and again from two different sources.[16,18] Figure 3 gives the viscosity versus shear rate data for 60 mole percent of HBA at three temperatures between 210–300°C, while Figure 4 gives the viscosity data at three different temperatures between 260–285°C. Figure 1–4 give different viscosity-shear rate relationships, not only in the magnitude of η at a given shear rate but also in the shape of the curve. For example, the curve "*K*" in Figure 1 is a straight line whereas curve "*D*" in Figure 2 shows a near-Newtonian plateau above $\sim 3 \times 10^3$ sec^{-1}. It is known that the shapes of the curves are dependent largely on the molecular weight distribution.[24] The coalescence of these curves by the method of Shenoy et al.[23–31] is governed to a certain extent by the shape of the curves. Similar shaped curves

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would definitely coalesce better. This can be seen from Figure 5 wherein the coalescence is excellent in the lower to middle shear rate region where the original curves had similar shapes. At higher shear rate, there is a noticeable degree of scatter. The method for coalescence used in the present case has been outlined below.

Each of the curves in Figures 1–4 were transformed into shear stress versus shear rate curves (not shown here) in order to estimate the *MFI* value corresponding to each curve. This was done by substituting the value of the load condition 2.16 kg in equation (3) in order to get the value of shear stress corresponding to the *MFI* test. The shear rate corresponding to this shear stress value was found from the curves and an estimate of the *MFI* value was estimated from equation (4). This method of estimating *MFI* from known shear stress versus shear rate curves has been used successfully by Shenoy et al.[23–31] and Rideal and Padget[32] when the *MFI* of the polymer is not known through the manufacturer or too low to measure on the melt flow indexer. Details of the *MFI* values calculated are given in Table I.

Using the appropriate values of *MFI*, each of the curves in Figures 1–4 were replotted as $\eta.MFI$ versus $\dot{\gamma}/MFI$. It was found that a unique curve resulted as can be seen from Figure 5. This coalesced curve contains data from thirteen different curves and the coalescence can be seen to be reasonably good. Figure 5 therefore represents the master curve for the liquid crystalline copolyester system HBA/PET. The master curve can now be used for generating the rheograms at any required temperature using the following steps.

Obtain the *MFI* value for the system under load condition of 2.16 kg at the temperature of interest.

If the *MFI* value cannot be determined from the melt flow indexer at the temperature of interest, the *MFI* value may be generated at any other temperature and then an estimate of *MFI* at the temperature of interest may be calculated through the procedure given by Saini and Shenoy.[33] The following equation may then be used

$$\frac{MFI(T_2)}{MFI(T_1)} = \exp \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{8}$$

Using the correct value of the effective *MFI*, the viscosity versus shear rate curve can be obtained by mere substitution in the master curve. This step can be eliminated if the curve is fitted through a rheological model and the parameters of the model given as has been done by Shenoy and Saini[34] for their unified curves. This would con-

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TABLE I

Details of the systems used for master curve generation

HBA/PET	*MFI*[a] (Temperature °C/ Load condition, kg)	Data temperature (°C)	Number of data points (Shear rate range (sec^{-1}))	Source
80/20	0.10 (275/2.16)	275	4(20–2000)	Ref. (16)
	0.44 (285/2.16)	285	4(20–2000)	-do-
	6.86 (295/2.16)	295	4(20–2000)	-do-
	19.1 (305/2.16)	305	4(20–2000)	-do-
	63.7 (315/2.16)	315	3(10–2000)	-do-
	122.5 (330/2.16)	330	3(20–2000)	-do-
	4.9 (275/2.16)	275	5(2–8000)	Ref. (17)
60/40	1.7 (210/2.16)	210	5(10–1000)	Ref. (16)
	8.4 (240/2.16)	240	5(10–1000)	-do-
	21.6 (300/2.16)	300	5(10–700)	-do-
	142.2 (260/2.16)	260	3(100–1000)	Ref. (18)
	294.1 (275/2.16)	275	3(100–1000)	-do-
	539.2 (285/2.16)	285	3(100–1000)	-do-

[a] *MFI* values read out from shear stress versus shear rate curves using equations 3 and 4.

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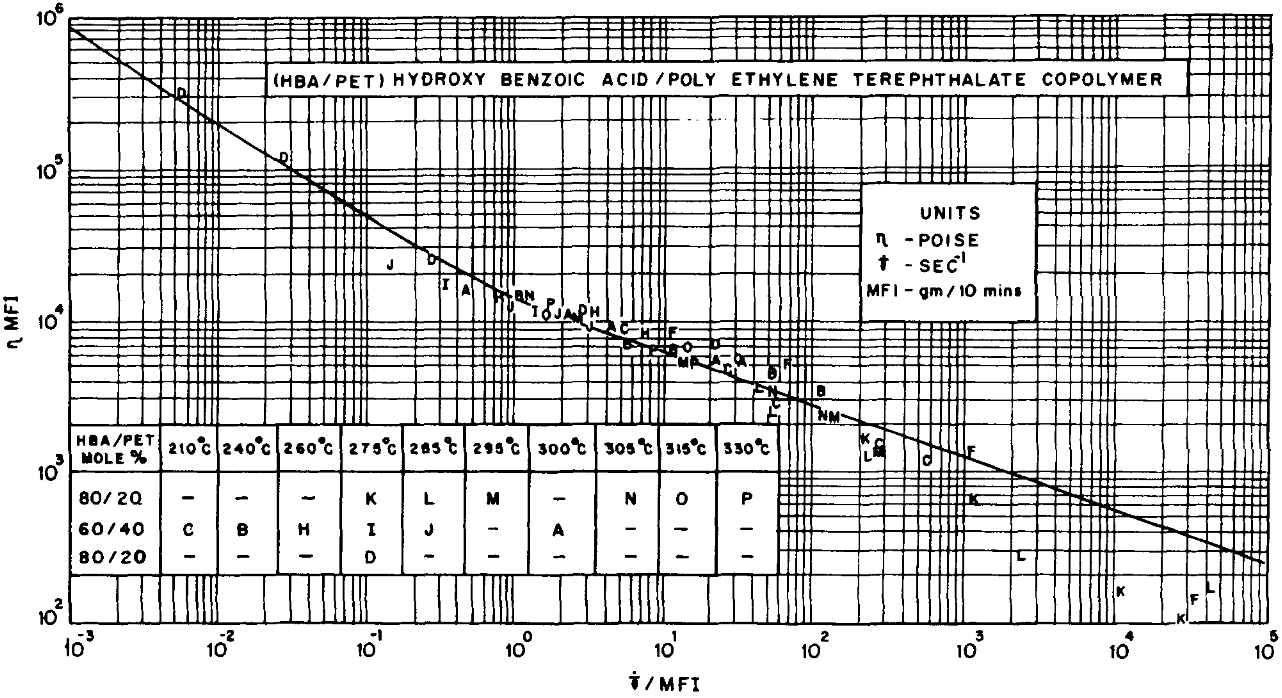

HBA/PET MOLE %	210°C	240°C	260°C	275°C	285°C	295°C	300°C	305°C	315°C	330°C
80/20	–	–	–	K	L	M	–	N	O	P
60/40	C	B	H	I	J	–	A	–	–	–
80/20	–	–	–	D	–	–	–	–	–	–

FIGURE 5 Unified curve of modified viscosity function versus modified shear rate for different mole percent HBA at various temperatures.

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siderably simplify the procedure for generating rheograms and also provide equation for use in design.

Shenoy and Saini[34] used well-known models such as the Carreau,[35] Ellis[36] and Ostwald-de Waele power-law[36] appropriately modified to fit their unified curves. The same approach cannot be used here as the shape of the unified curve in the present case is radically different from those obtained for other thermoplastics.[34] There are two shear-thinning regions separated by a short plateau as can be seen in Figure 5. It was thus decided that a new equation of the following form be tried.

$$\eta.MFI = \frac{K_1\left(\dfrac{\dot{\gamma}}{MFI}\right)^{n_1}}{\left[1+\left(\dfrac{K_1}{K_2}\right)^{\frac{1}{n_1-n_2}}\left(\dfrac{\dot{\gamma}}{\mathrm{MFI}}\right)\right]^{n_1-n_2}} \tag{9}$$

where $\eta.MFI$ is the modified non-Newtonian viscosity function, $\dot{\gamma}/MFI$ the modified shear rate function, n_1 the slope of the linear portion in the low shear rate region (10^{-3} to 10^{0} sec^{-1}), n_2 the slope of the linear portion in the medium shear rate region (10^{0} to 10^{2} sec^{-1}), K_1 the viscosity function value at $\dot{\gamma}/MFI = 1.0$ based on the initial linear portion of the curve and K_2 the viscosity function value at $\dot{\gamma}/MFI = 1.0$ based on the second linear portion of the curve. From Figure 5, it can be seen that in the medium to higher shear rate regions, the slope of the curve is continuously changing. Hence, the determination of K_2 and n_2 based on a linear correlation is not truly correct over the entire range. Hence, there has to be a restriction imposed on the upper limit of the shear rate. In the present case, the parametric values of the suggested rheological model have been determined to be equal to the following.

$$K_1 = 10^4, \qquad n_1 = -0.65, \qquad K_2 = 1.5 \times 10^4, \qquad n_2 = -0.35.$$

Using these values in equation (9), the theoretical predictions of $\eta.MFI$ for various values of $\dot{\gamma}/MFI$ were made. The solid line in Figure 5 gives the theoretical curve which can be seen to give reasonable accuracy at least in the region of 10^{-3} to 10^{3} values of $\dot{\gamma}/MFI$. Knowing the model parameters as given above, the generation of the rheograms from MFI values is considerably simplified and so also are all engineering design calculations which could now need only a desk calculator.

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