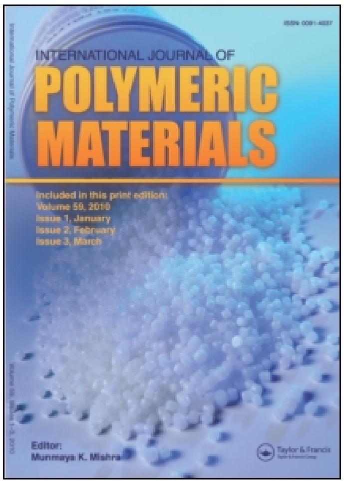

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Melt Rheology of Polymer Blends from Melt Flow Index

A. V. Shenoy[a]; D. R. Saini[a]; V. M. Nadkarni[a]
[a] National Chemical Laboratory, Polymer Science and Engineering Group, Chemical Engineering Division, Pune, India

To cite this Article Shenoy, A. V. , Saini, D. R. and Nadkarni, V. M.(1984) 'Melt Rheology of Polymer Blends from Melt Flow Index', International Journal of Polymeric Materials, 10: 3, 213 — 235

To link to this Article: DOI: 10.1080/00914038408080271

URL: http://dx.doi.org/10.1080/00914038408080271

Intern. J. Polymeric Mater., 1984, Vol. 10, pp. 213–235
0091-4037/84/1003-0213 $18.50/0

Printed in the United Kingdom

Melt Rheology of Polymer Blends from Melt Flow Index

A. V. SHENOY, D. R. SAINI, and V. M. NADKARNI

Polymer Science and Engineering Group, Chemical Engineering Division, National Chemical Laboratory, Pune 411 008 India

(*Received June 20, 1983*)

Polymer blends have received a lot of attention in recent years due to the possibility of getting compounds with novel and/or different properties through proper marriage of the properties of the respective mono-components. The flow behaviour of blends when subjected to stresses is complex and is often found not to vary monotonically with composition. Mixing rules and mixture theories have been used for estimating melt viscosity of a blend at zero shear rate. However a knowledge of the entire rheogram is desirable for process optimization, process design and trouble shooting.

In the present paper a method proposed earlier to estimate the rheograms of polymer melts through the use of the melt flow index has been extended to polyblends. A method for obtaining the melt flow index of the polymer blends at various compositions from the melt flow index of the individual components and the blend ratio has been suggested based on the altered free volume state model. Curves that are coalesced using the melt flow index of the blend at different blend ratios have been presented for a polypropylene–high density polyethylene blend, a high density polyethylene–polymethyl methacrylate blend, a polystyrene–polymethylmethacrylate blend, a polystyrene–polyacetal blend and a polymethylmethacrylate–polyacetal blend.

INTRODUCTION

Polymer blends are physical mixtures of polymers and provide a means of combining the useful properties of the constituent components to achieve an economic or property advantage. There are a

---

NCL Communication No: 3114

TABLE I

Commercial blends (Ref. 1)

Blend	Trade name	Supplier
ABS/PC	Cycoloy	Borg-Warner Chemicals
	Bayblend MC 2500	Mobay
	Bayblend MD 6500	Mobay
ABS/PVC	Abson 89129	Abtec
	Polyman 509	Schulman
	Kralastic FVJ	Uniroyal
	Cycovin KAB	Borg-Warner Chemicals
	Cycovin KAF	Borg-Warner Chemicals
PVC/acrylic	DKE 450	DuPont
	Kydex	Rohm and Haas
PPO/HIPS	Noryl	General Electric
ABS/polysulfone	Arylon	Uniroyal
SAN/polysulfone	Ucardel P-4174	Union Carbide
CPE/PVC	Hostalit	American Hoechst

number of commercial thermoplastic blends such as polyphenylene oxide/polystyrene, acrylonitrile butadiene styrene/polycarbonate, polyvinyl chloride/polymethylmethacrylate etc. currently in use as summarized in Table I.[1] In polymer blends, the individual polymers are chemically different and do not form covalent bonds as in copolymers. The blends are often characterised by their phase behaviour as being either miscible or immiscible. Certain blends are completely miscible and form a single phase while others form domains rich in one polymer dispersed within the matrix of the second polymeric component. The degree of thermodynamic compatibility[2] between the individual components of blend have implications in rheology and processing due to the possibilities of phase separation with increasing incompatibility.

During polymer processing operations like extrusion, injection molding, etc. the molten polymer blend is subjected to a series of stresses and deformation. Since these melts are highly non-Newtonian in character, a knowledge of the variation of viscosity with shear rate at each blend ratio must be known for optimizing processing conditions, for process design and troubleshooting. Further, melt rheological studies may provide useful information about the compatibility of the individual species in the molten state. However, the rheological data are generated on expensive sophisticated instruments like the Weissenberg Rheogoniometer, Instron Capillary Rheometer, Rheometrics Mechanical Spectrometer etc. which are beyond the technical and financial capabilities of most polymer processors. Moreover, experimental compilation of the necessary data with variables like viscosity, shear rate, melt temperature and blend ratio is bound to be time-consuming and expensive.

In the present paper, a method has been proposed to estimate the entire rheograms of various melt blends merely from the knowledge of the melt flow index which can be determined in a simple operation from the relatively inexpensive Melt Flow Indexer. An altered free volume state model has been used in order to develop a method for estimating the melt flow index of the blend at each blend ratio knowing the melt flow index of the individual components.

BACKGROUND

There are two extensive reviews available in recent literature on the rheology of blends, one by Van Oene[3] and the other by Plochocki.[4] This is well supplemented by the fairly comprehensive chapter on the rheology of two-phase systems by Han.[5] The various blends which have received the attention of rheologists to date have been summarized in Table II.

There have been a number of correlations used for predicting the viscosity of the blends as summarized below. Firstly, the series coupling or the inverse additivity model of Heitiller *et al.*[24] derived as the equivalent viscosity of a system of many concentric layers of two different liquids and proposed to fit those blends whose components retain their individuality and yield interactions between the different species which are weaker than those between themselves. Thus

$$\frac{1}{\eta_B}=\frac{V_1}{\eta_1}+\frac{V_2}{\eta_2} \tag{1}$$

where V is the volume fraction, η is the viscosity and subscripts 1, 2 and B stand for the two components and their blend, respectively. The viscosity calculated represents minimum values in the absence of interphase slippage[22] or other interphase phenomena.

In some systems, an equation proposed by Hayashida *et al.*[22] has

TABLE II

Investigations on the rheological properties of polymer blends

Blend systems	Investigators
high density polyethylene–low density polyethylene	Jacovic *et al.*[6] Dobrescu[7] Bersted *et al.*[8]
high density polyethylene–polymethyl methacrylate	Martinez and Williams[9]
polypropylene–high density polyethylene	Plochocki[10] Alle and Lyngaae-Jorgensen[11,12] Kasajima *et al.*[13] Noel and Carley[14]
polystyrene–high density polyethylene	Han and Yu[15] Han[16] Han and Kim[17]
polystyrene–polypropylene	Han[16]
polystyrene–polyacetal	Carley and Crossan[18]
polystyrene–Nylon 12	Carley and Crossan[18]
Nylon 12–polymethyl methacrylate	Carley and Crossan[18]
polymethyl methacrylate–polyacetal	Carley and Crossan[18]
polymethyl methacrylate–polystyrene	Carley and Crossan[18] Kasajima[19] Alle and Lyngaae-Jorgenson[20] Thornton *et al.*[21]
Nylon 6–polyethylene	Hayashida *et al.*[22]
polyethylene terephthalate–polymethyl methacrylate	Wu[23]

been found to describe the viscosity data better. This equation is similar to Eq. (1) in its form but with the weightage factors interchanged.

$$\frac{1}{\eta_B}=\frac{f_2}{\eta_1}+\frac{f_1}{\eta_2} \tag{2}$$

where f_1 and f_2 represent any type of fractions, though the use of weight fractions appears to give better interpolation.

According to Dobrescu[7] a simple additivity model could also serve the purpose when the intermolecular interactions between the two polymers are identical to the interactions among molecules of each of the polymers. Thus,

$$\eta_B = V_1\eta_1 + V_2\eta_2 \tag{3}$$

where the terminology is identical to that in Eq. (1).

In the case of high density polyethylene–low density polyethylene mixtures, it has been found that none of the above equations are able to give good estimates of the blend viscosity. Thus Dobrescu[7] proposed the following equation to describe the dependence of the blend viscosity on the viscosities of the components and composition:

$$\log \eta_B = V_1 \log \eta_1 + \lambda V_1 V_2 + \log \eta_2 \tag{4}$$

where λ stands for "packing coefficient" which can be evaluated from Eq. (4) using the viscosities of the components, their volume fractions and the experimental viscosity of just one blend 0.5/0.5. Alternatively, an empirical equation developed by Dobrescu[25] can also be used to calculate λ in terms of the component viscosities.

Bersted *et al.*[8] prefer the use of the Arrhenius[26] type of equation for estimating the viscosity of blends of high density polyethylene and low density polyethylene.

$$\eta_B = \eta_1^{w_1}\eta_2^{w_2} \quad \text{or} \quad \log \eta_B = w_1 \log \eta_1 + w_2 \log \eta_2 \tag{5}$$

where w_1 and w_2 are weight fractions of the individual components. Since the logarithmic mixing rule is the simplest method in use for estimating viscosity of mixtures,[27] it is popularly used for estimating the viscosity of blends.[12,19] Alle and Lyngaae-Jorgensen[12] prefer the use of volume fractions instead of weight fractions for estimating the viscosity of the blend of polypropylene and high density polyethylene. The utility of Eq. (5) is, however, limited to binary systems in which the actual mixture viscosities change monotonically with composition.

A slightly more complicated equation for evaluating the viscosities of blends is that of McAllister.[28]

$$\begin{aligned}\ln \nu_B = {} & x_1^3 \ln \nu_1 + x_2^3 \ln \nu_2 + 3x_1^2 x_2 \ln \nu_{12} \\ & + 3x_1 x_2^2 \ln \nu_{21} + 3x_1^2 x_2 \ln[(2M_1 + M_2)/3] \\ & + 3x_1 x_2^2 \ln[(M_1 + 2M_2)/3] + x_1^3 \ln M_1 + x_2^3 \ln M_2 \\ & - \ln(x_1 M_1 + x_2 M_2)\end{aligned} \tag{6}$$

where x is the mole fraction, M is the molecular weight, ν is the kinematic viscosity with the double subscripts indicating the interaction viscosities. This model, however, requires the knowledge of the molecular weights and densities of the individual resin as well as the viscosities of at least two mixtures for evaluating the interaction viscosities.

Despite the investigations made of mixing rules and mixture theories,[7,8,12,19,22,24,26–29] the flow mechanism of the blended polymer melts still appears to be not completely clear. The viscosity of a blend can show a monotonic change with composition or a maximum or a minimum or both between the pure-component viscosities (see Figure 1). Thus, even for a blend of two specific components, no equation for the mixture may be valid over the entire composition range. In fact, Han[15,30,31] has repeatedly demonstrated the invalidity of any simple law of additivity in terms of blending ratios and the rheological properties of the individual

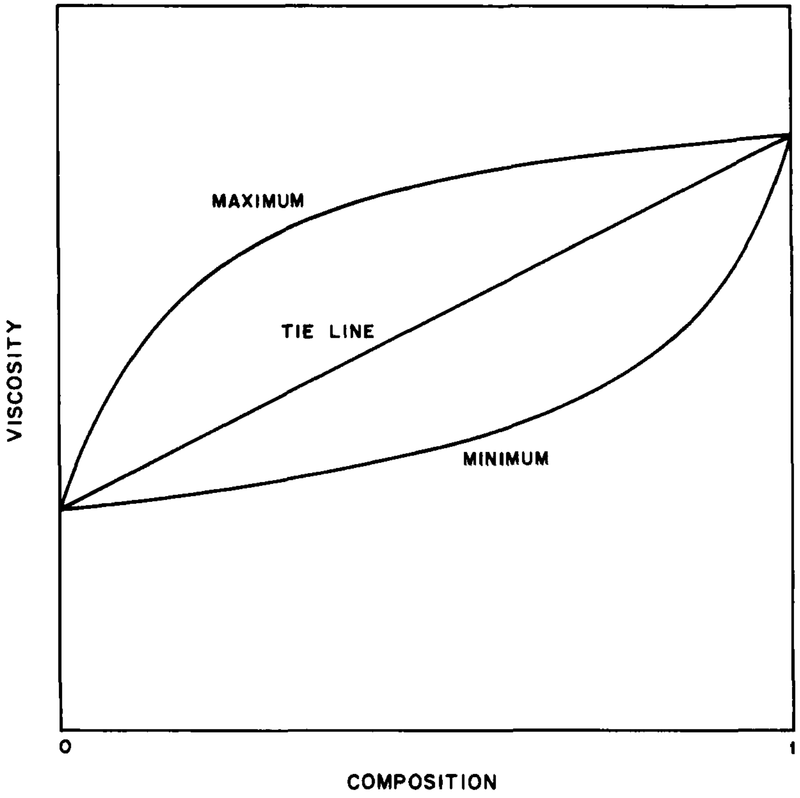

FIGURE 1 Possible viscosity–composition relationships for polymer blends

components involved. Han has attributed the occurrence of minima and maxima among blend viscosities to the formation of two phases in the molten state. This occurs because the more viscous component forming a discrete phase remains as either droplets or long fibrils and is deformable when in flow. Thus a part of the energy supplied to the bulk of the moving fluid is likely to be consumed in deforming the suspended droplets and long fibrils, resulting in a shear viscosity of the blends lower than those of the individual components. Alle and Lyngaae-Jorgensen[11,12] found that when the minor component has a higher viscosity than the major component, the minor component is coarsely dispersed. On the other hand, the minor component is finely dispersed, when it has a lower viscosity than the major component.

Available equations for evaluating the viscosity of the blends from the blending ratios and viscosities of the individual components are specifically for zero shear viscosity which is known to be a difficult parameter to determine. Thus there is a need for an alternative method to calculate blend viscosities and specifically the variation of melt blend viscosity with shear rate for each blend ratio which would be very useful for practical polymer processing.

Shenoy *et al.* have successfully demonstrated a method for estimating rheograms of polymer melts from melt flow index in the case of olefinics and styrenics,[32] cellulosics[33] and other engineering thermoplastics.[34] In the present paper, the method is extended to polymer blends. For the melt flow index of the blend at various blend ratios, a new method different from the earlier known mixture rules has been presented derived from the concepts of the altered free volume state model.[35,36]

DATA COLLECTION

Data on the melt rheology of various blend systems are compiled. These are used to determine the melt flow index values. A technique is developed to find out MFI of the blend from MFI's of the component polymers. The blend MFI value is then used to normalize the viscosity and shear rate parameters for coalescing the rheograms of each blend at different ratios of the components. A summary of the blends analyzed in the present study is given in Table III.

TABLE III

Details of the blends studied

Blend type	Composition	MFI[a] (temperature °C/ load condition, kg)	Data temp °C	No. of data points (shear rate range) sec^{-1}	Source
1	2	3	4	5	6
PP/HDPE	1.00/0.00	1.10(190/2.16)	190	3(1–100)	Ref. 11
	0.75/0.25	2.00(190/2.16)	190	3(1–100)	Ref. 11
	0.50/0.50	5.50(190/2.16)	190	3(1–100)	Ref. 11
	0.25/0.75	7.60(190/2.16)	190	3(1–100)	Ref. 11
	0.00/1.00	9.30(190/2.16)	190	3(1–100)	Ref. 11
	1.00/0.00	1.09(190/2.16)	190	8(1–350)	Ref. 10
	0.85/0.15	1.10(190/2.16)	190	9(1–700)	Ref. 10
	0.75/0.25	1.04(190/2.16)	190	9(1–700)	Ref. 10
	0.50/0.50	1.01(190/2.16)	190	9(1–700)	Ref. 10
	0.25/0.75	0.71(190/2.16)	190	9(1–700)	Ref. 10
	0.00/1.00	0.51(190/2.16)	190	8(1–350)	Ref. 10
HDPE/PMMA	1.0/0.0	1.30(160/2.16)	160	3(0.01–1)	Ref. 9
	0.9/0.1	0.78(160/2.16)	160	3(0.01–1)	Ref. 9
	0.8/0.2	0.54(160/2.16)	160	3(0.01–1)	Ref. 9
	0.7/0.3	0.34(160/2.16)	160	3(0.01–1)	Ref. 9

HDPE/PMMA	0.6/0.4	0.25(160/2.16)	160	3(0.01–1)	Ref. 9
	0.5/0.5	0.15(160/2.16)	160	3(0.01–1)	Ref. 9
	0.4/0.6	0.08(160/2.16)	160	3(0.01–1)	Ref. 9
	0.3/0.7	0.04(160/2.16)	160	3(0.01–1)	Ref. 9
	0.3/0.7	0.04(160/2.16)	160	3(0.01–1)	Ref. 9
	0.2/0.8	0.03(160/2.16)	160	3(0.01–1)	Ref. 9
	0.1/0.9	0.02(160/2.16)	160	3(0.01–1)	Ref. 9
	0.0/1.0	0.03(160/2.16)	160	3(0.01–1)	Ref. 9
PS/PMMA	1.00/0.00	112.8(220/5)	220	5(20–400)	Ref. 19
	0.75/0.25	75.8(220/5)	220	5(20–400)	Ref. 19
	0.50/0.50	41.7(220/5)	220	5(20–400)	Ref. 19
	0.25/0.75	9.8(220/5)	220	5(20–400)	Ref. 19
	0.00/1.00	1.47(220/5)	220	5(20–400)	Ref. 19
PS/PAc	1.0/0.0	5.4(210/5)	210	5(20–400)	Ref. 18
	0.9/0.1	12.3(210/5)	210	5(20–400)	Ref. 18
	0.5/0.5	22.5(210/5)	210	5(20–400)	Ref. 18
	0.2/0.8	31.4(210/5)	210	5(20–400)	Ref. 18
	0.0/1.0	39.3(210/5)	210	5(20–400)	Ref. 18
PMMA/PAc	1.0/0.0	3.6(210/3.8)	210	4(10–400)	Ref. 18
	0.8/0.2	7.6(210/3.8)	210	4(10–400)	Ref. 18
	0.5/0.5	13.2(210/3.8)	210	4(10–400)	Ref. 18
	0.2/0.8	21.1(210/3.8)	210	4(10–400)	Ref. 18
	0.0/1.0	34.3(210/3.8)	210	4(10–400)	Ref. 18

[a] MFI value read out from τ versus $\dot{\gamma}$ curve using Eqs. (9) and (10)

DATA ANALYSIS

Method to obtain coalesced viscosity versus shear rate curves through melt flow index

The melt flow index (MFI) is defined as the weight of polymer extruded in ten minutes through a capillary of specific diameter and length by pressure applied through dead weight as per ASTM 1238–73. The geometrical parameters of the apparatus for measuring the MFI and the specific test conditions for various polymers are given in Appendix I taken from ASTM 1238–73.

Since the MFI value is determined under fixed load conditions on an apparatus which is basically an extrusion rheometer, it represents a specific point on the shear stress versus shear rate curve. Thus the expressions for describing the shear stress τ and shear rate $\dot{\gamma}$ in a MFI apparatus can be written as follows

$$\tau = \frac{R_N F}{2\pi R_p^2 l} \tag{7}$$

$$\dot{\gamma} = \frac{4Q}{\pi R_N^3} \tag{8}$$

where

R_p is the piston radius

R_N is the nozzle radius

l is the nozzle length

F is the test load $L \times 9.807 \times 10^5$

Q is the flow rate $\left(= \frac{\text{MFI}}{600\rho} \text{ by definition of MFI}\right)$

Since the geometry of the melt flow indexer is fixed as indicated in Appendix I, proper substitution of the parameters in Eqs. (7) and (8) give

$$\tau = 9.13 \times 10^4 L \tag{9}$$

$$\dot{\gamma} = 1.83 \frac{\text{MFI}}{\rho} \tag{10}$$

Eqs. (9) and (10) can be used to determine the value of MFI from a known shear stress versus shear rate curve for a specific polymeric system or blend when the MFI is not reported. This method has been checked for propriety by calculating the MFI values for resins with reported MFI by Shenoy *et al.*[33,34] Further, testification of the validity of the above method can be got from Rideal and Padget.[37] They measured the viscosity on a Weissenberg Rheogoniometer at an equivalent shear stress to that in the MFI apparatus and used it to estimate the MFI of the polymers which were too low to be measured on the Melt Flow indexer.

Using the fact that $\eta = \tau/\dot{\gamma}$, the following relationship can be easily derived through Eqs. (3) and (10) as follows:

$$\mathrm{MFI} \times \eta = 4.98 \times 10^4 \rho L \tag{11}$$

$$\frac{\dot{\gamma}}{\mathrm{MFI}} = \frac{1.83}{\rho} \tag{12}$$

For a given polymeric system as the density and the testing load conditions are fixed, the right-hand sides of Eqs. (11) and (12) become constant.

Although Eqs. (11) and (12) are valid only at the particular test condition, the proportionality between MFI and $(1/\eta)$ as well as $(\dot{\gamma})$ would be valid over the entire range of the flow curve. In effect, the shear stress versus shear rate curve can be constituted by measuring the melt flow under a number of different load conditions. Each load condition can be represented in terms of Eqs. (11) and (12) but with different proportionality constant. Thus it should be possible to coalesce η versus $\dot{\gamma}$ curves by plotting $\mathrm{MFI} \times \eta$ versus $\dot{\gamma}/\mathrm{MFI}$ on a log–log scale.[32] The arguments in the foregoing analysis have been developed by Shenoy *et al.*[32] to obtain master curves for pure polymeric systems of different grades. These can be easily extended to blends of two different species provided an estimate of the MFI is available for each blend ratio at which the viscosity versus shear rate is known. Thus using the correct MFI value corresponding to each blend ratio, a master curve invarient of composition can be developed for each blend of two specific components. The present approach of coalescing the curves would work so long as the individual components of the blends have similar rates of change of viscosity with shear rate. In the specific cases investigated herein, the curves of the individual components and their blends are nearly parallel in the high shear rate region and hence a unification is possible. The method would not be effective in the case of blends produced with components whose shear-thinning behaviour changes drastically, for example, as in the case of LDPE/HDPE blends where it is known that the rate of change of viscosity with shear rate of the branched and linear polyethylene is radically different. The shear-thinning behaviour of PP and HDPE are also quite different and hence there is more scatter in Figure 7 then in all other cases. As a quick check of whether coalescence of the curves for any blend system is possible, we need to take the MFI values at two loads conditions for each of the two components and calculate the shear-thinning behaviour index n using the ratio of $(\log L_1 - \log L_2)$ to $(\log \mathrm{MFI}_1 - \log \mathrm{MFI}_2)$. If the value of n in the case of the individual components is nearly the same then one can coalesce the curves to form a unified curve.

Method to determine the Melt Flow Index of the blend knowing the Melt Flow Indices of the individual components

An approach different from the conventional mixing theories is used for obtaining the MFI values of the blends at various compositions. The altered free volume state model proposed by Kulkarni and Mashelkar[35,36] for diffusion in polymers can be extended to determine the MFI values of polyblends with varying concentrations of one of the phases.

The relationship between viscosity of a polymer melt and its free volume given by Doolittle[38] can be written in the following modified form using the inverse proportionality between viscosity and MFI given by Eq. (11) as

$$\ln \mathrm{MFI}(T, \phi) = \ln A - \frac{B}{f(T, \phi)} \tag{13}$$

where $\mathrm{MFI}(T, \phi)$ is the melt flow index of the system at temperature T and containing ϕ volume fraction of the dispersed phase

A is a constant dependent on the nature of the continuous phase

B is a constant which can be set equal to unity based on the arguments provided by Fujita and Kishimoto[39]

$f(T, \phi)$ represents the free volume of the system at temperature T and containing ϕ volume fraction of the dispersed phase

Based on the concepts of Kulkarni and Mashelkar[35,36] it is assumed that addition of another polymer to a pure homopolymer alters the free volume state of the reference medium, namely, the pure homopolymer from $f_1(T, 0)$ to $f_2(T, \phi_2)$. The melt flow index would then change from $\mathrm{MFI}(T, 0)$ to $\mathrm{MFI}(T, \phi_2)$. Thus, using Eq. (13) the following can be written

$$\ln \frac{\mathrm{MFI}(T, \phi_2)}{\mathrm{MFI}(T, 0)} = \frac{1}{f_1(T, 0)} - \frac{1}{f_2(T, \phi_2)} \tag{14}$$

As a first approximation, the free volume in the altered free volume state can be related to the free volume of the pure homopolymer through a linear function of the volume fraction ϕ_2 of the second component[39]

$$f_2(T, \phi_2) = f_1(T, 0) + \beta(T)\phi_2 \tag{15}$$

where $\beta(T)$ represents the difference between the free volumes of the two polymers.

Combining Eqs. (14) and (15) and arranging the terms gives

$$\frac{1}{\log a_{\mathrm{MFI}}} = 2.303 f_1(T, 0) + \left[\frac{2.303 f_1^2(T, 0)}{\beta(T)}\right]\frac{1}{\phi_2} \tag{16}$$

where

$$a_{\mathrm{MFI}} = \frac{\mathrm{MFI}(T, 0)}{\mathrm{MFI}(T, \phi_2)} \tag{17}$$

Eq. (16) predicts that a plot of $1/\log a_{\mathrm{MFI}}$ versus $1/\phi_2$ should be linear. The propriety of this model can be tested quantitatively using the MFI values calculated for each system as given in Table III. Note that the choice of the reference medium should be such as to have $\mathrm{MFI}(T, 0) > \mathrm{MFI}(T, \phi_2)$ in order to maintain $a_{\mathrm{MFI}} > 0$ for convenience in plotting. In case of each blend, a good linear plot is obtained as can be seen from Figures 2–6. Each plot is for a specific temperature depending on the temperature condition of the MFI values reported in Table III.

The quality of the dispersion has an effect of about ±15% on the rheology of the system. In the case of the measured MFI values, the effect of dispersion would be reflected in the measurements. However, predicted MFI values could deviate by about 15%. The method presented herein proposes to estimate the rheogram for

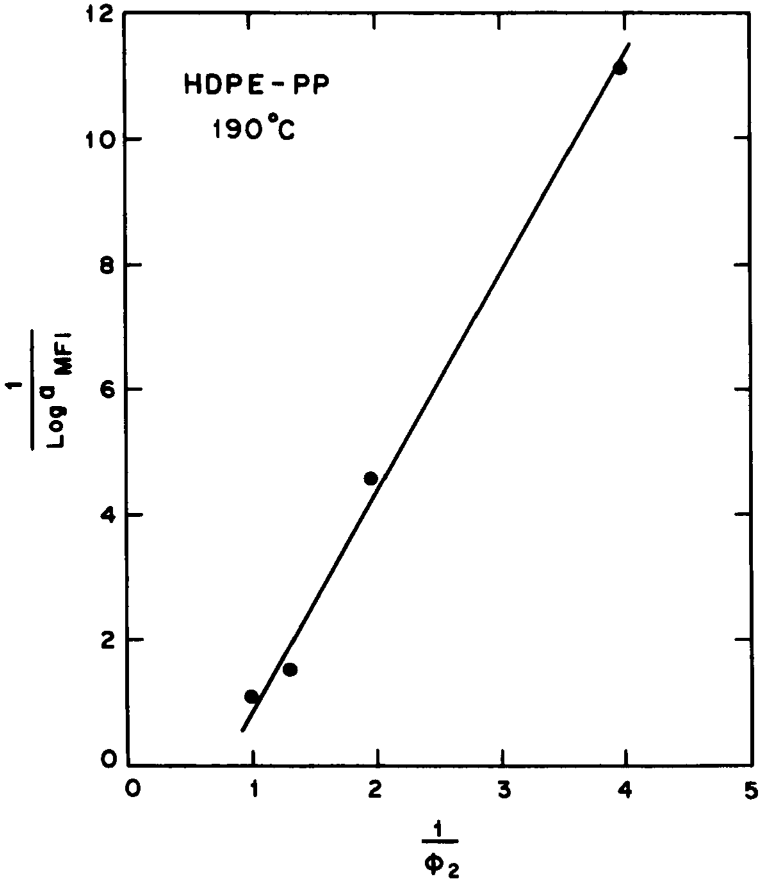

FIGURE 2 Melt Flow Index variation with blend composition for high density polyethylene/polypropylene blend at 190°C

adequate engineering calculations and does not claim accurate viscosity predictions. Hence neglecting the effect of mixing would not reduce the value of the approach.

Method to determine the Melt Flow Index of the individual components of the blend at different temperatures

Melt Flow Index obtained from the tests specified in ASTM 1238–73 would give values which may not be at the temperature of

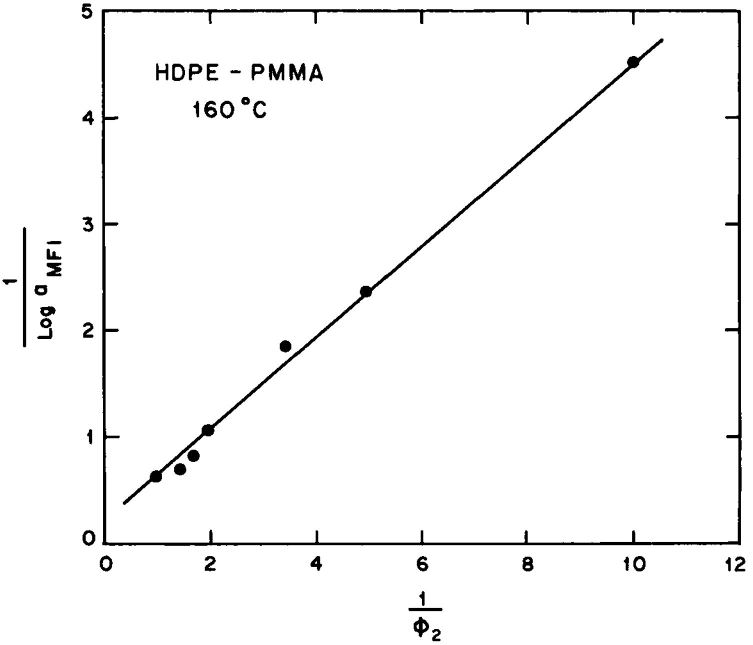

FIGURE 3 Melt Flow Index variation with blend composition for high density polyethylene/polymethylmethacrylate at 160°C

interest. In order to obtain the MFI value at the required temperature, the following modified W–L–F type equation suggested by Shenoy *et al.*[32] can be used:

$$\log\frac{\mathrm{MFI}(T_2)}{\mathrm{MFI}(T_1)}=\frac{8.86(T_2-T_s)}{101.6+(T_2-T_s)}-\frac{8.86(T_1-T_s)}{101.6+(T_1-T_s)} \qquad (18)$$

where

T_1 = temperature of MFI measurement, °K
T_2 = temperature at which MFI value is desired, °K
T_s = standard reference temperature taken as $Tg+50°K$
T_g = glass transition temperature of the polymer, °K (Table IV)

Method to determine the Melt Flow Index of the individual components of the blend at different load conditions

As can be seen from ASTM 1238–73, there are more than one test load conditions under which MFI measurements can be taken. In

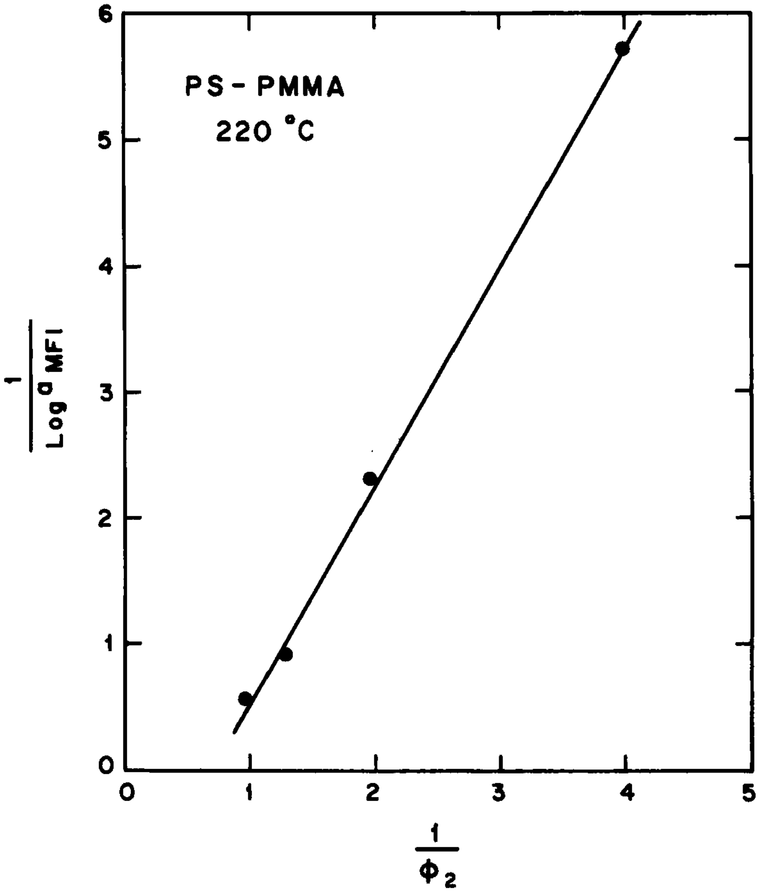

FIGURE 4 Melt Flow Index variation with blend composition for polystyrene/polymethylmethacrylate blend at 220°C

order to get estimates of MFI at different load conditions the following technique can be used.[32] The single-point measurement of MFI which gives a point on the non-Newtonian or shear-thinning portion of the shear stress versus shear rate curve is merely shifted on the curve by a change of load condition. It is known that on the non-Newtonian regime, the relationship between shear stress and shear rate can be well approximated by the following power-law

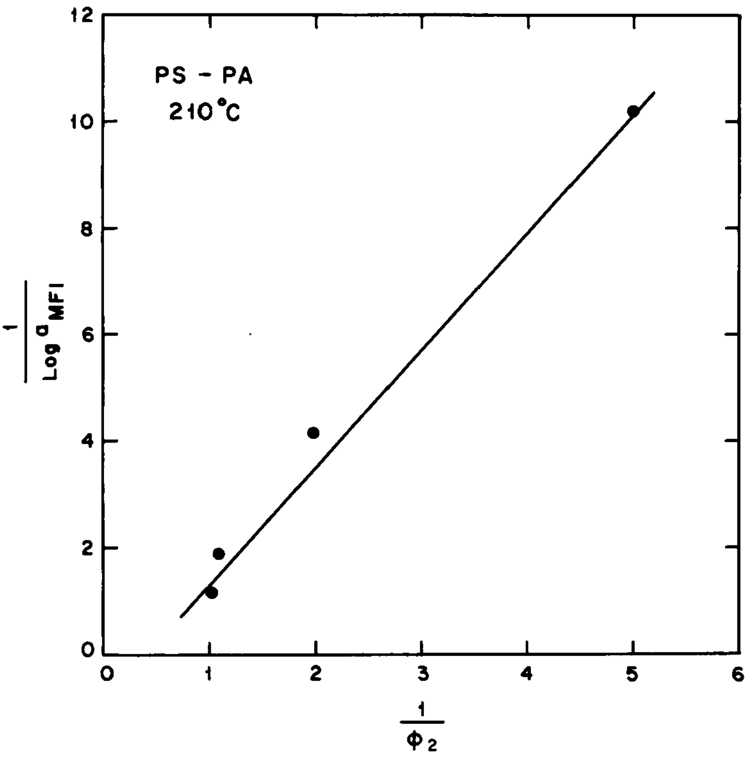

FIGURE 5 Melt Flow Index variation with blend composition for polystyrene/polyacetal blend at 210°C

model

$$\tau = K\dot{\gamma}^n \tag{21}$$

where n is defined as the pseudoplasticity index and K is the consistency index. Using Eqs. (9) and (10), the following relationship can be derived for different load conditions L_1 and L_2. Thus

$$\frac{\text{MFI}_2}{\text{MFI}_1} = \left(\frac{L_2}{L_1}\right)^{1/n} \tag{22}$$

The value of n can be obtained for a specific system from the slope of the τ versus $\dot{\gamma}$ curve on a log–log scale or calculated from the

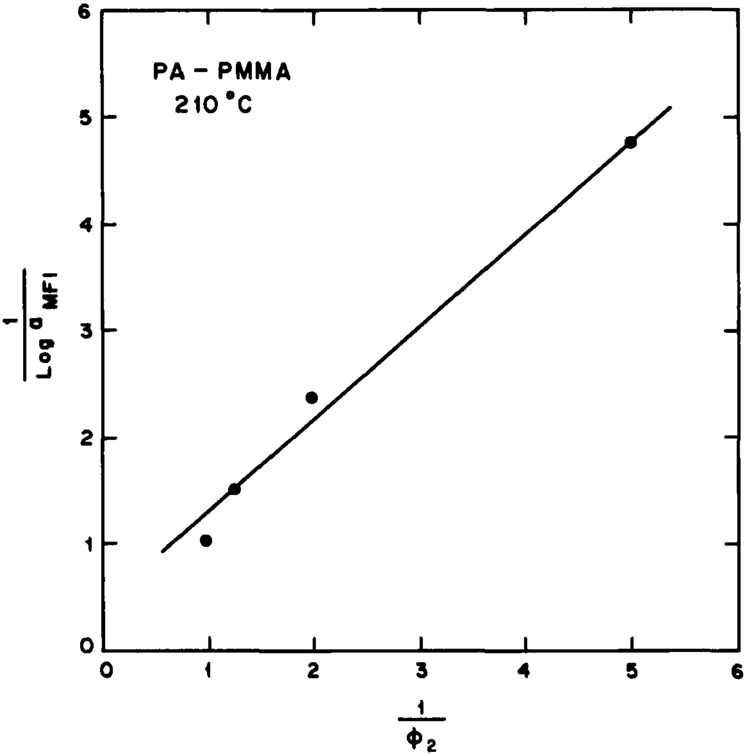

FIGURE 6 Melt Flow Index variation with blend composition for polyacetal/polymethyl methacrylate blend at 210°C

TABLE IV

Glass transition temperatures of the homopolymers involved in the blends studied

Polymer type	Tg °K
high density polyethylene	153
polypropylene	263
polyacetal	350
polystyrene	373
polymethylmethacrylate	378

TABLE V

Estimated values of n to be used in Eq. (22) for different blends studied

Blend type	n
polypropylene–high density polyethylene	0.39
high density polyethylene–polymethylmethacrylate	0.5
polystyrene–polymethylmethacrylate	0.48
polystyrene–polyacetal	0.5
polymethylmethacrylate–polyacetal	0.6

slope $(n-1)$ of the viscosity versus shear rate curve on a log–log scale. The values of n required for each of the systems studied in the present work have been calculated from the slope of the coalesced curves and tabulated in Table V.

RESULTS AND DISCUSSION

The melt rheograms of a particular polyblend at different compositions can be coalesced, when the viscosity data are plotted in terms of the modified viscosity parameter, $(\eta \cdot \text{MFI})$ and the modified shear rate parameter, $(\dot{\gamma}/\text{MFI})$. This is illustrated in Figures 7

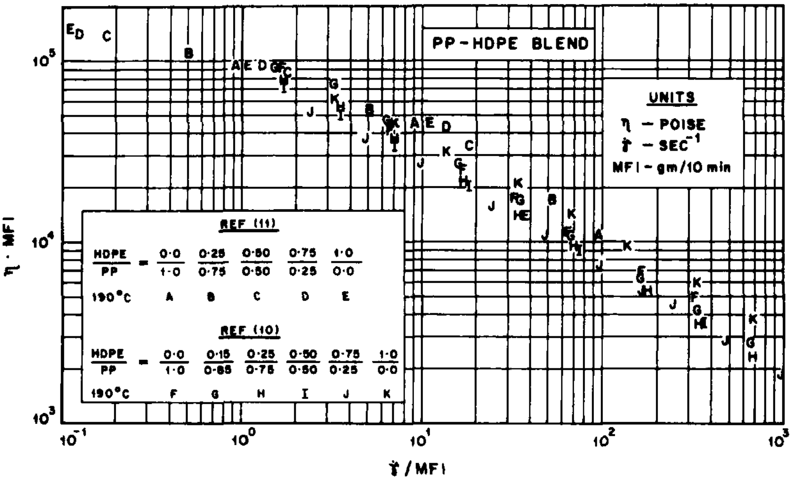

FIGURE 7 Coalesced curve for polypropylene–high density polyethylene blend at test load condition of 2.16 kg

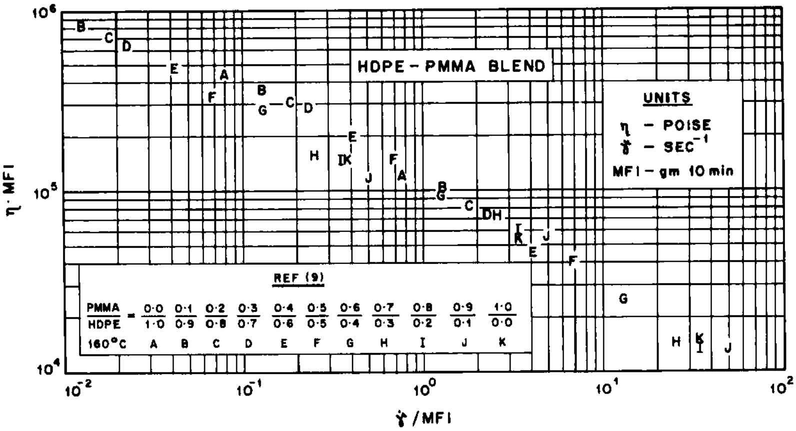

FIGURE 8 Coalesced curve for high density polyethylene–polymethylmethacrylate blend at test load condition of 2.16 kg

through 11 for various polyblends. The melt flow index of the blend can be estimated from the flow indices of the pure components and their composition in the blend as shown in Figures 2 through 6. Thus it is possible to estimate the viscosity versus shear rate curve at any composition of the blend by making use of the coalesced curve

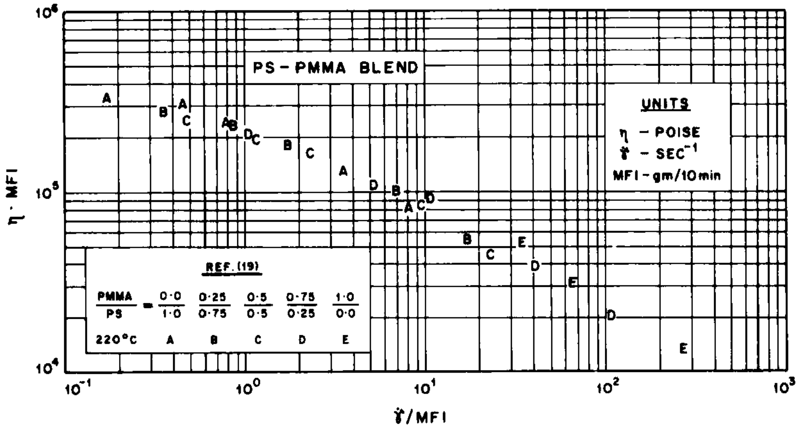

FIGURE 9 Coalesced curve for polystyrene–polymethylmethacrylate blend at test load condition of 5 kg

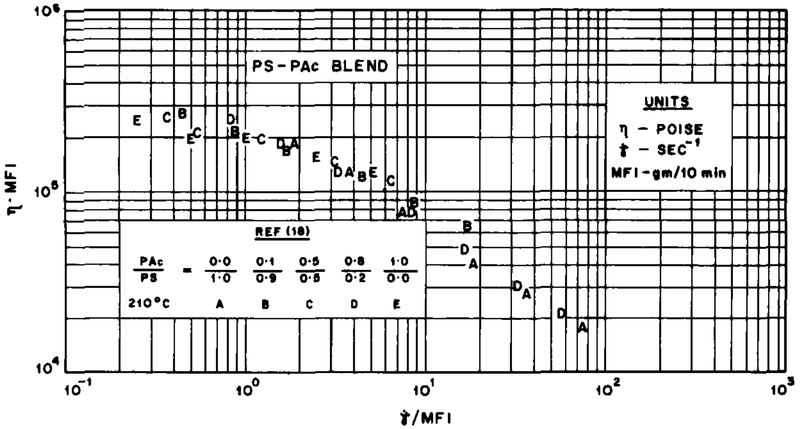

FIGURE 10 Coalesced curve for polystyrene–polyacetal blend at test load condition of 5.00 kg

for each system. It is important to note that the coalesced curves represent unification of data only at the specified temperature and load. The procedure for generating rheogram at the specified temperatures for the various blends is considerably simplified by following the proposed techniques. The steps involved in such an estima-

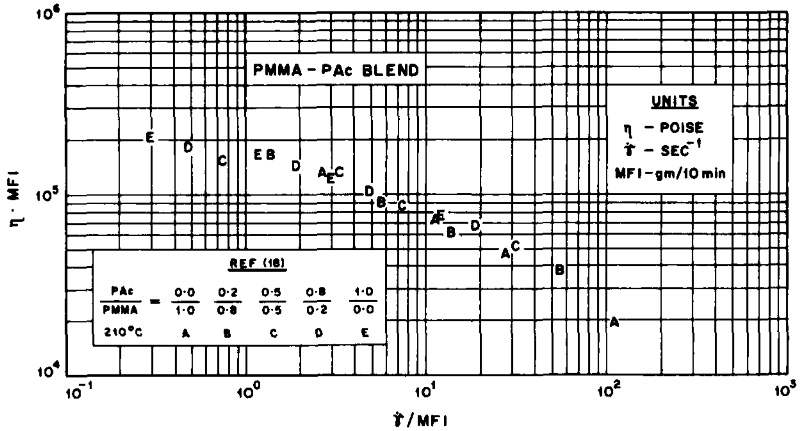

FIGURE 11 Coalesced curve for polymethylmethacrylate–polyacetal blend at test load condition of 3.8 kg

tion are given below:

- Obtain the MFI's of the pure components at the specified temperature
- Determine the MFI of the blend at the desired composition from the respective curve (Figures 2 through 6)
- Substitute this MFI in the respective coalesced rheogram (figures 7 through 11) to obtain the viscosity versus shear rate curve for the blend at the desired composition and temperature.

CONCLUSION

The technique for coalescing rheograms of polymer melts by the use of MFI has been successfully applied to polyblends. It is shown that the viscosity versus shear rate data for various compositions can be coalesced into a single curve by plotting ($\eta \cdot$ MFI) versus ($\dot{\gamma}$/MFI). This has been demonstrated for blends of polyolefins, styrenics and engineering thermoplastics such as polyacetal. The melt flow index of the blend can be determined at any desired composition from the flow indices of the pure components, and the MFI of the blend at one composition following the concepts of the altered free volume model.

References

1. J. P. Smeykal, *Modern Plastics Encyclopaedia*, p. 126 (1979–1980).
2. S. Krause, *Polymer Blends*, ed. D. R. Paul and S. Newman, (Academic Press, New York, 1978), Vol. 1, Chap. 2, p. 15.
3. H. Van Oene, *Poymer Blends*, ed. D. R. Paul and S. Newman, (Academic Press, New York, 1978), Vol. 1, Chap. 7, p. 295
4. A. P. Plochocki, *Polymer Blends*, ed. D. R. Paul and S. Newman, (Academic Press, New York, 1978), Vol. 2, Chap. 21, p. 319.
5. C. D. Han, *Rheology in Polymer Processing*, (Academic Press, New York, 1976), Chap. 7, p. 165
6. M. S. Jacovic, D. Pollock and R. S. Porter, *J. Appl. Polym. Sci.*, **23**, 517 (1979).
7. V. Dobrescu, *Proc. VIIIth Intnl. Congr. on Rheol.*, p. 555, Sept 1–5 (1980).
8. B. H. Bersted, J. D. Slee and C. A. Richter, *J. Appl. Polym. Sci.*, **26**, 1001 (1981).
9. C. B. Martinez and M. C. Williams, *J. Rheol.*, **24**, 421 (1980).
10. A. P. Plochocki, *Trans. Soc. Rheol.*, **20**, 287 (1976).
11. N. Alle and J. Lyngaae-Jorgensen, *Rheol. Acta*, **19**, 94 (1980).
12. N. Alle and J. Lyngaae-Jorgensen, *Rheol. Acta*, **19**, 104 (1980).

13. M. Kasajima, A. Suganuma, D. Kunii and K. Ito, *Rep. Progr. Polym. Physics, Japan,* XXI, 101 (1978).
14. O. F. Noel, III and J. F. Carley, *Polym. Eng. Sci.,* **15,** 117 (1975).
15. C. D. Han and T. C. Yu, *Polym. Eng. Sci.,* **12,** 81 (1972).
16. C. D. Han, *J. Appl. Polym. Sci.,* **18,** 481 (1974).
17. C. D. Han and Y. W. Kim, *J. Appl. Polym. Sci.,* **18,** 2589 (1974).
18. J. F. Carley and S. C. Crossan, *Polym. Engg. Sci.,* **21,** 249 (1981).
19. M. Kasajima, *Bulletin of the College of Engg., Hosei University,* **15,** 1 (1979).
20. N. Alle and J. Lyngaae-Jorgensen, *Proc. VIIIth Intnl. Congr. on Rheol.,* p. 521, Sept 1–5 (1980).
21. B. A. Thornton, R. G. Villasenor and B. Maxwell, *J. Appl. Polym. Sci.,* **25,** 653 (1980).
22. K. Hayashida, J. Takahashi and M. Matsui, *Proc. Fifth Intl. Congress on Rheol.,* **4,** 525 (1970).
23. S. Wu, *Polym. Engg. Sci.,* **19,** 638 (1979).
24. R. F. Heitmiller, R. Z. Naar and H. H. Zabusky, *J. Appl. Polym. Sci.,* **8,** 873 (1964).
25. V. Dobrescu, *Revista de Chimie,* in press.
26. S. Arrhenius, *Z. Phisik. Chem.,* **1,** 285 (1887).
27. L. E. Nielsen, *Polymer Rheology,* (Marcel Dekker, New York, 1977), p. 90.
28. R. A. McAllister, *AIChE J.,* **6,** 427 (1960).
29. M. Takayanagi, *Kobunshi,* **10,** 285 (1961).
30. C. D. Han, *J. Appl. Polym. Sci.,* **15,** 2579 (1971).
31. C. D. Han and T. C. Yu, *J. Appl. Polym. Sci.,* **15,** 1163 (1971).
32. A. V. Shenoy, S. Chattopadhyay and V. M. Nadkarni, *Rheol. Acta* **22,** 90 (1983).
33. A. V. Shenoy, D. R. Saini and V. M. Nadkarni, *J. Appl. Polym. Sci.* **27,** 4399 (1983).
34. A. V. Shenoy, D. R. Saini and V. M. Nadkarni, *Rheol. Acta,* **22,** 209 (1983).
35. M. G. Kulkarni and R. A. Mashelkar, *Chem. Engg. Sci.* **38,** 925, (1983).
36. M. G. Kulkarni and R. A. Mashelkar, *Chem. Engg. Sci.* **38,** 941, (1983).
37. G. R. Rideal and J. C. Padget, *J. Polym. Sci. Symposium,* **57,** 1 (1976).
38. A. K. Doolittle, *J. Appl. Phys.,* **22,** 1471 (1951), **23,** 236 (1962).
39. H. Fujita and A. Kishimoto, *J. Chem. Phys.,* **34,** 393 (1961).