Flow Behavior of LDPE and Its Blends with LLDPE I and II: A Comparative Study

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SYNOPSIS

Studies on melt rheological properties of blends of low density polyethylene (LDPE) with selected grades of linear low density polyethylene (LLDPE), which differ widely in their melt flow indices, are reported. The data obtained in a capillary rheometer are presented to describe the effects of blend composition and shear rate on flow behavior index, melt viscosity, and melt elasticity. In general, blending of LLDPE 1 that has a low melt flow index (2 g/10 min) with LDPE results in a decrease of its melt viscosity, processing temperature, and the tendency of extrudate distortion, depending on blending ratio. A blending ratio around 20–30% LLDPE I seems optimum from the point of view of desirable improvement in processability behavior. On the other hand, blending of LLDPE II that has a high melt flow index (10 g/10 min) with LDPE offers a distinct advantage in increasing the pseudoplasticity of LDPE/LLDPE II blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In recent years, blends of various polyolefins have received more attention for two main reasons. Firstly, polyolefins form most of the plastic waste, and their recycling leads to mixtures without separation.[1] Secondly, blends of polyolefins provide new materials with tailored properties for specific end-use applications.[2-4] Several studies have been performed to investigate the main properties of such blends.[5-12]

The introduction of a new class of polyethylene, linear low density polyethylene (LLDPE), gives the possibility of obtaining a new class of blends (LDPE/LLDPE) that are easily processable with good mechanical properties.

The objective of this study is to present a set of data on the melt rheological properties of blends made from one LDPE sample and two selected grades of LLDPE samples differing widely in molecular weight. Melt rheology data obtained on a piston type capillary rheometer are used to obtain shear–stress versus shear rate relationship, melt viscosity, and melt elasticity parameters of the two series of blend at various blend compositions.

EXPERIMENTAL

Materials

The materials used were commercially available thermoplastics with the following characteristics.

Low Density Polyethylene (LDPE)

Indothene FS 300 was supplied by IPCL, Baroda, with its density (g/cm^3) = 0.922 and its melt flow index (g/10 min) = 6.

Linear Low Density Polyethylene (LLDPE I)

Ladene 218 W was supplied by IPCL, Baroda, with its density (g/cm^3) = 0.918 and its melt flow index (g/10 min) = 2.

Linear Low Density Polyethylene (LLDPE II)

Ladene 118 W was supplied by IPCL, Baroda, with its density (g/cm^3) = 0.918 and its melt flow index (g/10 min) = 10.
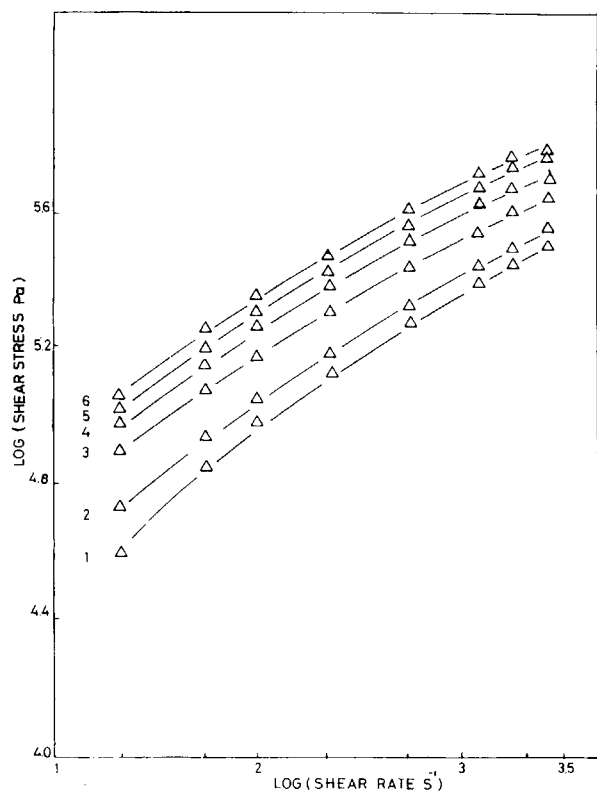
Figure 1   Flow curves of LDPE/LLDPE I blends at 180°C: 1, LDPE; 2, LDPE/LLDPE (80/20); 3, LDPE/LLDPE (60/40); 4, LDPE/LLDPE (40/60); 5, LDPE/LLDPE (20/80); 6, LLDPE I.
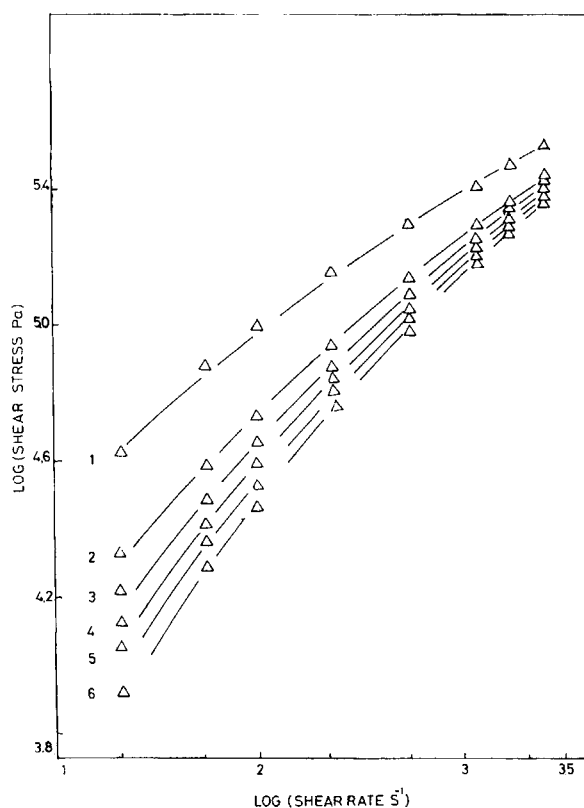

Figure 2   Flow curves of LDPE/LLDPE II blends at 180°C: 1, LDPE; 2, LDPE/LLDPE (80/20); 3, LDPE/LLDPE (60/40); 4, LDPE/LLDPE (40/60); 5, LDPE/LLDPE (20/80); 6, LLDPE II.

Preparation of Blends

The blends were prepared by melt blending in a Brabender plasticorder model PS 3S under identical conditions of the experiment in each case at 180°C and 30 rpm for 20 min. The pure polymers were also subjected to the same procedure in order to make the data comparable to those of the blends. The investigated compositions were 0, 20, 40, 60, 80, and 100 wt %, respectively, of LLDPE.

Melt Rheological Measurements

Melt rheological measurements were made on a piston type capillary rheometer (Goettfert viscotester model 1500), using circular die (L/R = 60), flat at the entrance region. Measurements were carried out using the fixed temperature method to obtain flow curves using constant pressure. Additional information on the experimental procedure is provided in the following section.

RESULTS AND DISCUSSIONS

Flow Curves

Volumetric flow rate measurements at a constant temperature (180°C) and varying pressures were used to evaluate the shear stress and shear rate relationships in the samples.

Shear stress at wall $(\tau_w)_{app}$, was calculated using the following expression neglecting the end correc-

Table I   Values of Power-Law Exponent for LDPE/LLDPE Blends

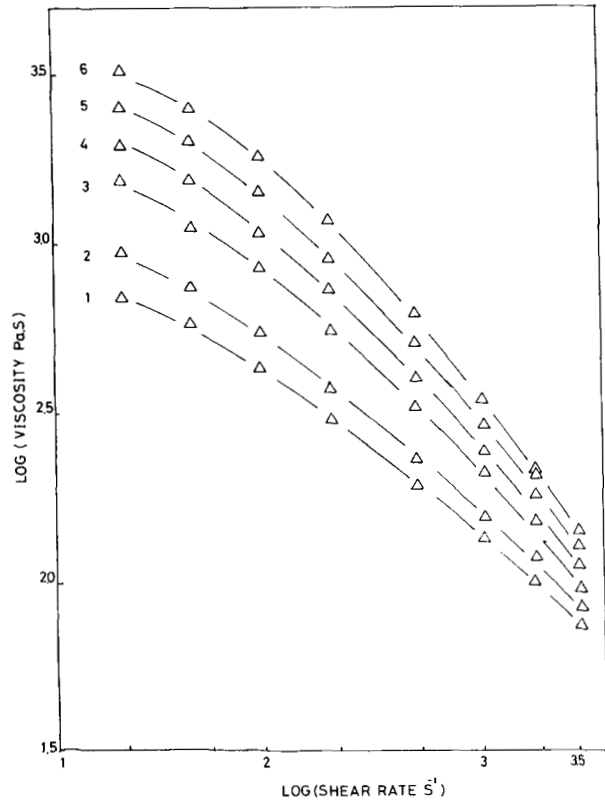| LDPE Content (Wt %)	n	
	LDPE/LLDPE I	LDPE/LLDPE II
0	0.35	0.53
20	0.35	0.53
40	0.42	0.46
60	0.42	0.46
80	0.42	0.41
100	0.39	0.39

Figure 3 Variation of viscosity with shear rate of LDPE/LLDPE I blends at 180°C: 1, LDPE; 2, LDPE/LLDPE (80/20); 3, LDPE/LLDPE (60/40); 4, LDPE/LLDPE (40/60); 5, LDPE/LLDPE (20/80); 6, LLDPE I.

tion term for these data at a constant L/R ratio of the die

$$(\tau_w)_{\text{app}} = \Delta P/2 \cdot L/R \tag{1}$$

where ΔP is the pressure difference between the entrance and exit of the capillary.

Shear rate was determined according to the expression

$$\dot{\gamma}_{\text{app}} = 4Q/\pi R^3 \tag{2}$$

where Q is the volumetric flow rate and R is the radius of the capillary. From the log $(\tau_w)_{\text{app}}$ versus log $\dot{\gamma}_{\text{app}}$ plots (shown in Figs. 1 and 2), values of power law exponent n were calculated in accordance with the following power law[13]:

$$(\tau_w)_{\text{app}} = K(\dot{\gamma}_{\text{app}})^n \tag{3}$$

where K is a constant.

The values of n, between 0.35 and 0.53, being lower than unity, indicate pseudoplastic nature[14] of

the melts of all the samples. The value of n is of comparable magnitude to that reported in literature for LDPE (0.398).[15] Differences in the values of n for the various samples shown in Table I may imply differences in the ease of flow in these samples, but no definite comment as to their origin is possible from these data alone. The insignificant variation of n in in the case of LDPE/LLDPE I blends indicates that the pseudoplasticity is more or less unchanged with blend composition. On the other hand, a systematic decrease in the value of n from 0.5 to 0.4 with increasing LDPE content indicates the role of LDPE in increasing the pseudoplasticity in the case of LDPE/LLDPE II blends.

Melt Viscosity

Apparent melt viscosity η_{app} (referred to hereafter as melt viscosity) was calculated using the following expression:

$$\eta_{\text{app}} = (\tau_w)_{\text{app}}/\dot{\gamma}_{\text{app}} \tag{4}$$
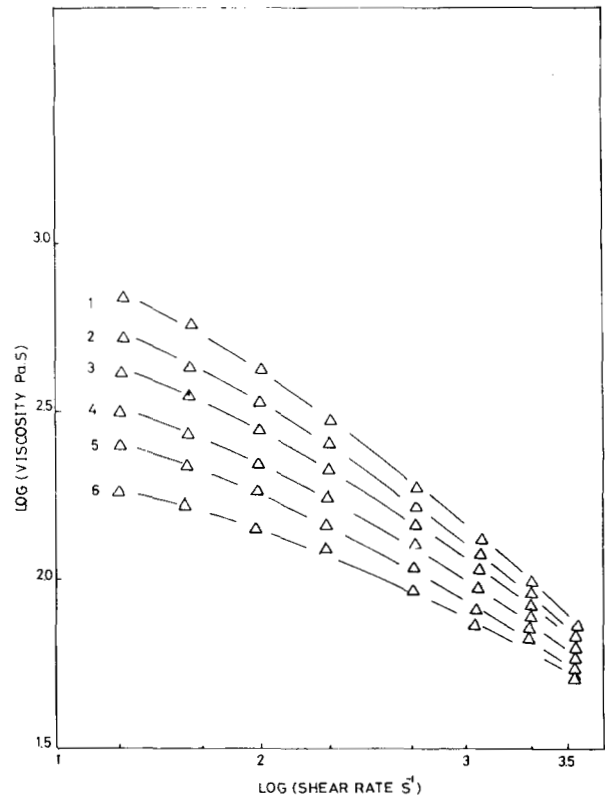

Figure 4 Variation of viscosity with shear rate of LDPE/LLDPE II blends at 180°C: 1, LDPE; 2, LDPE/LLDPE (80/20); 3, LDPE/LLDPE (60/40); 4, LDPE/LLDPE (40/60); 5, LDPE/LLDPE (20/80); LLDPE II.
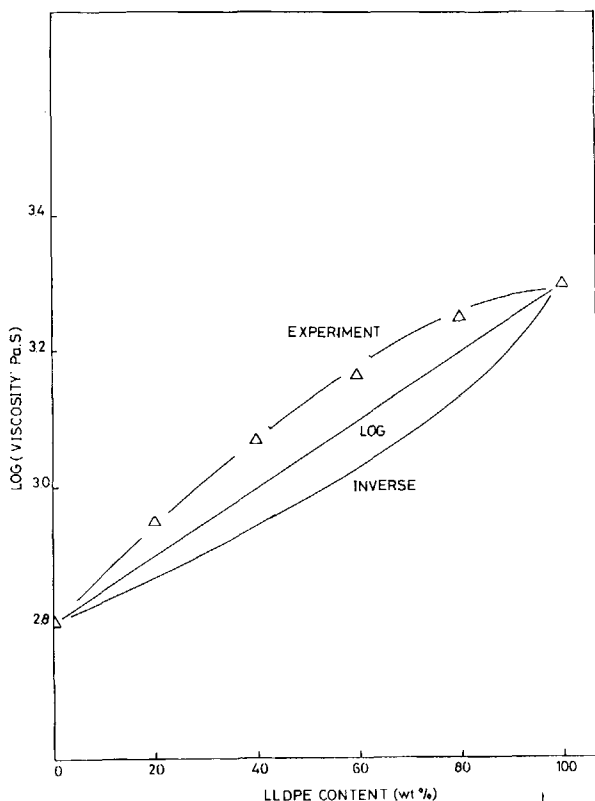
Figure 5   Variation of viscosity with blend composition of LDPE/LLDPE I blends at 180°C, with a shear rate of 10^2 S^{-1}.

Variation of melt viscosity with shear rate is shown in Figures 3 and 4 for LDPE/LLDPE I and LDPE/LLDPEII blends. Melt viscosity decreases with increasing shear rate and is almost linear over the entire range of measurements. The power law fitting these viscosity curves (Figs. 3 and 4) may be written as follows:

$$\eta = A\dot{\gamma}^a \qquad (5)$$

Variations of melt viscosity as a function of blend composition at a fixed shear rate is shown in Figures 5 and 6 for the two series of blends. Also shown in the figures are viscosities of the blend predicted from simple mixing rules.

$$\ln(\eta_{app})_{blend} = \sum_i w_i \ln(\eta_{app})_i \qquad (6)$$

$$1/\ln(\eta_{app})_{blend} = \sum_i w_i/\ln(\eta_{app})_i \qquad (7)$$

where w_i is the weight fraction of the ith component of the blend.

In a recent review entitled "Melt Flow of Polymer Blends," Utracki[16] showed that the positive or negative deviation of measured viscosity from that calculated from log additivity rule [such as, for example, (eq. 6)], is indicative of strong or weak interactions between the phases of the blend. As shown in Figures 5 and 6, the measured melt viscosity is higher than $(\eta_{app})_{blend}$ calculated by the log additivity rule [eq. (6)], indicating the positive deviation blend (PDB) character of all the blends. According to Utracki, immiscible blends show negative deviation, while the positive deviation is expected for miscible liquids with high solubility and homologous polymer blends.

Temperature dependence of melt viscosity is represented in Figures 7 and 8 for the two series of blends as the Arrhenius plots, log η_{app} versus $1/T$. Activation energy (ΔE) calculated from the slopes of these plots using Arrhenius expression

$$\eta = Ae^{E/RT} \qquad (8)$$

is shown in Table II.

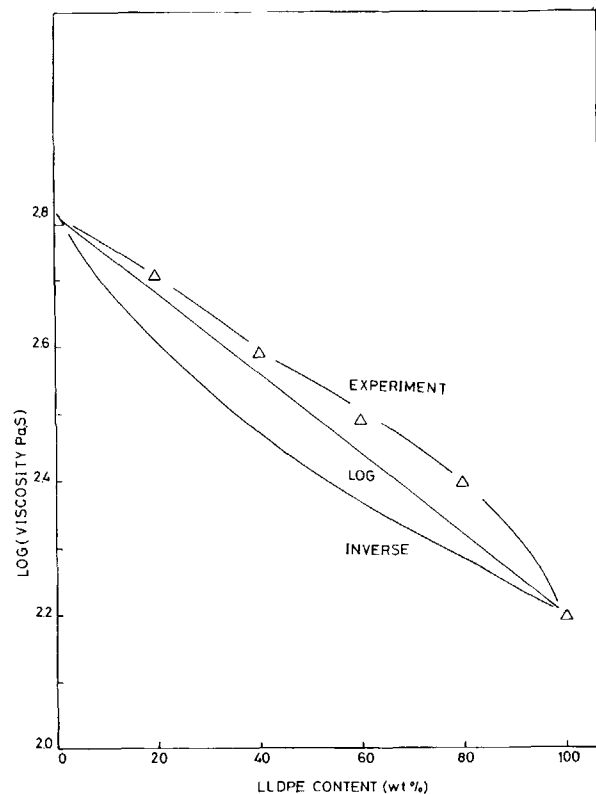Activation energy for viscous flow of the melt remains unchanged; for all compositions of the blend

Figure 6   Variation of viscosity with blend composition of LDPE/LLDPE II blends at 180°C, with a shear rate of 10^2 S^{-1}.
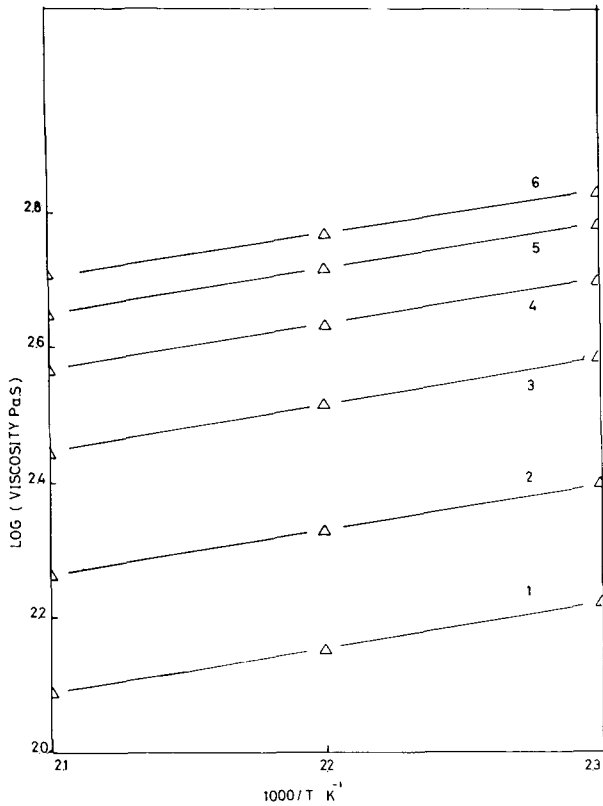
Figure 7 Variation of viscosity with reciprocal absolute temperature of LDPE/LLDPE I blends, with a shear rate of 10^2 S^{-1}: 1, LDPE; 2, LDPE/LLDPE (80/20); 3, LDPE/LLDPE (60/40); 4, LDPE/LLDPE (40/60); 5, LDPE/LLDPE (20/80); 6, LLDPE I.
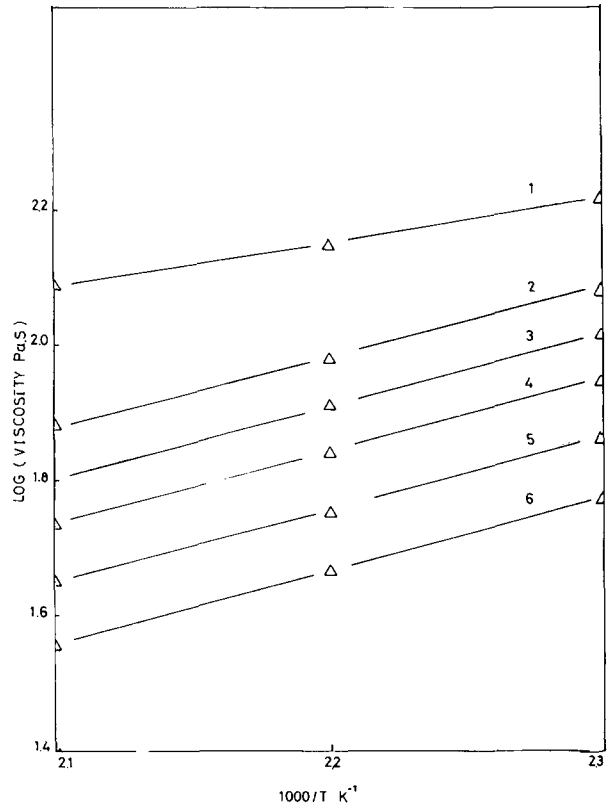

Figure 8 Variation of viscosity with reciprocal absolute temperature of LDPE/LLDPE II blends, with a shear rate of 10^2 S^{-1}: 1, LDPE; 2, LDPE/LLDPE (80/20); 3, LDPE/LLDPE (60/40); 4, LDPE/LLDPE (40/60); 5, LDPE/LLDPE (20/80); 6, LLDPE II.

in either case, the values being correspondingly higher for LDPE/LLDPE II blends.

Melt Elasticity

A property of non-Newtonian viscoelastic fluids important in the choice of their processing parameters is their melt elasticity behavior, which causes expansion of the fluid on its exit from the die, known as die-swell. Such an effect arises due to the recovery of the elastic deformation imposed in the capillary.[13,17-20] Die-swell ratio D_e/D, where D_e, and D are, respectively, the diameters of extrudate and die determined at various shear rates, are shown in Figures 9 and 10 for the two series of blends.

Die-swell ratio increases gradually with LLDPE content at low levels of shear and rapidly with LLDPE content at relatively high levels of shear. Higher values of die-swell ratio imply greater elastic recoverability or, in other words, higher melt elasticity. Pure LLDPE has the highest value of melt

elasticity, which decreases substantially on blending with LDPE. This indicates a significant role of LDPE in the reduction of melt elasticity in the case of LDPE/LLDPE I blends. Die swell ratio was too small in the case of LDPE/LLDPE II blends to give

Table II Activation Energy for Viscous Flow (ΔE) of LDPE/LLDPE Blends at a Constant Shear Rate (10^2 s^{-1})

LDPE Content (Wt %)	ΔE(kcal/Mol)	
	LDPE/LLDPE I	LDPE/LLDPE II
0	15.2	22.0
20	15.2	22.0
40	15.2	22.0
60	15.2	21.7
80	15.2	21.7
100	15.2	15.2

any significant variation with composition, owing to the low average molecular weight of LLDPE in the second case.

CONCLUSIONS

1. LDPE and LLDPE blends are sufficiently compatible in the melt, and, hence, proper grades of the polymers can be chosen to optimize rheological properties.
2. Compatibility of polymers can be improved by choosing a low viscosity grade LLDPE (large MFI).
3. Pseudoplasticity increases (power law exponent decreases) with increasing LDPE content in the case of LDPE/LLDPE II blends and shows insignificant variation in the case of LDPE/LLDPE I blends.
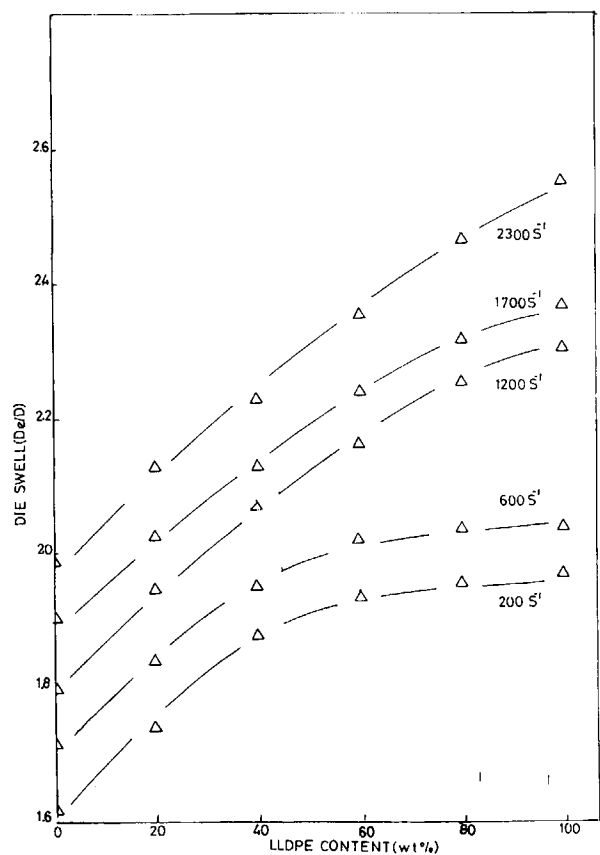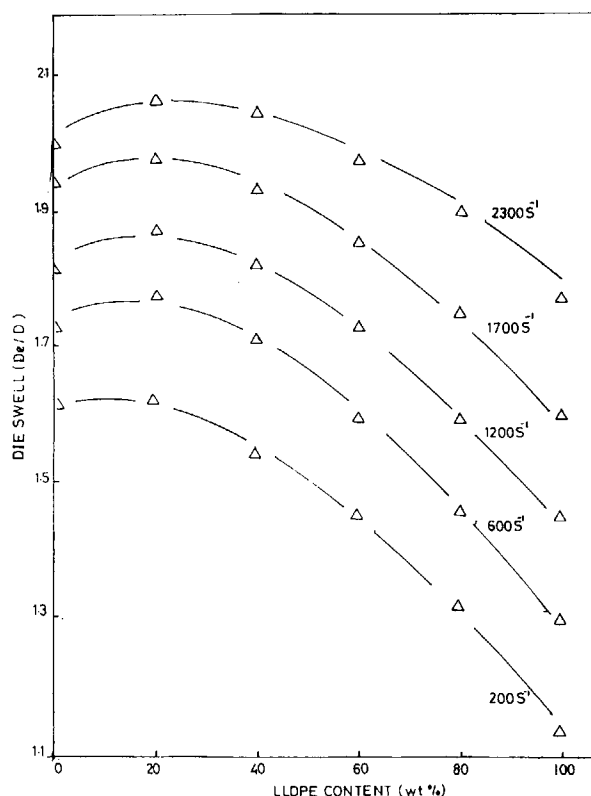4. Activation energy is constant for all compositions of the blend in either case.

Figure 10   Variation of die-swell ratio with blend composition of LDPE/LLDPE II blends at 180°C and various shear rates.

5. While the melt elasticity of blends decreases substantially with an increase in LDPE content in the case of LDPE/LLDPE I blends, it shows insignificant variation in the case of LDPE/LLDPE II blends.

REFERENCES

1. I. Leidner, *Plastic Waste*, Marcel Dekker, New York, 1981.
2. J. A. Manson and L. H. Sperling, *Polymer Blends and Composites*, Plenum Press, New York, 1976.
3. D. R. Paul and S. Newmann, *Polymer Blends*, Academic Press, New York, 1978.
4. O. Olabisi, L. M. Robeson, and T. H. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979.
5. A. P. Plochocki, *J. Appl. Polym. Sci.*, **16**, 987 (1972).
6. L. A. Utracki and M. R. Kamal, *Polym. Eng. Sci.*, **22**, 96 (1982).
7. D. Curto, F. P. La Mantia, and D. Acierno, *Rheol. Acta*, **22**, 197 (1983).
8. M. M. Dumoulin, C. Farha, and L. A. Utracki, *Polym. Eng. Sci.*, **24**, 1319 (1984).

Figure 9   Variation of die-swell ratio with blend composition of LDPE/LLDPE I blends at 180°C and various shear rates.

9. F. P. La Mantia, D. Acierno, and D. Curto, *Rheol. Acta,* **21,** 452 (1982).
10. S. K. Bhateja and E. H. Andrews, *Polym. Eng. Sci.,* **23,** 888 (1983).
11. A. Siegmann and Y. Nir, *Polym. Eng. Sci.,* **27,** 1182 (1987).
12. N. K. Dutta and A. W. Birley, *Plast. Rubber Proc. Appl.,* **3,** 237 (1983).
13. C. D. Han, *Rheology in Polymer Processing,* Academic Press, New York, 1976, Chap. 5.
14. R. S. Lenk, *Polymer Rheology,* Applied Science, London, 1978, Chap. 1.
15. C. D. Han, *J. Appl. Polym. Sci.,* **15,** 2591 (1971).
16. L. A. Utracki, *Polym. Eng. Sci.,* **23,** 602 (1983).
17. O. Truesdell, *Trans. Soc. Rheol.,* **4,** 9 (1960).
18. S. L. Green, S. Middleman, and J. Gavis, *J. Appl. Polym. Sci.,* **3,** 367 (1960).
19. S. Middleman and J. Gavis, *Phys. Fluids,* **4,** 355 (1961).
20. J. Gavis and S. Middleman, *J. Appl. Polym. Sci.,* **7,** 493 (1963).