

Effect of Rheology on Melt-Spinning of Polymer Blends

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The rheology of blends of polypropylene and high-density polyethylene (HDPE) was measured at 185, 200 and 215°C using Weissenberg cone and plate rheogoniometer. Fibres were spun from these blends at 200°C and the mechanical properties of these fibres were measured using Instron tensile strength meter. The addition of small amounts of HDPE to polypropylene improved the tenacity considerably.

Keywords: Melt-spinning, Polymer blends, Rheology

1 Introduction

The rheology plays a very important role in processing operations such as spinning of polymers¹. Most polymers show a non-Newtonian flow behaviour and possess significant elasticity². The fibre spinning process involves extrusion of polymer melt at a given rate followed by controlled cooling and then stretching (drawing). The die swell and orientation of molecules depend largely on the velocity profile, which, in turn, is influenced by the rheological properties of the polymer³. A brief review of rheological principles is given below.

The relationship between shear stress (τ) and shear rate ($\dot{\gamma}$) is known as a rheogram. For Newtonian fluids, such a relationship is linear and is given by the equation

$$\tau = \mu \dot{\gamma} \quad \dots (1)$$

For Newtonian fluids, the viscosity (μ) is independent of shear rate. For non-Newtonian fluids, the viscosity depends upon the shear rate and, therefore, the ratio of $\tau/\dot{\gamma}$ is termed as apparent viscosity (μ_a). For shear thinning or pseudoplastic fluids the apparent viscosity decreases as the shear rate increases, while for shear thickening or dilatant fluids the apparent viscosity increases with the increase in shear rate (Fig. 1).

The shear thinning or shear thickening behaviour is most commonly expressed by a power law model,

$$\tau = K(\dot{\gamma})^n \quad \dots (2)$$

where K is the consistency index and n , the power law index. Thus, $n < 1$ indicates the shear thinning behaviour, $n = 1$ the Newtonian behaviour, and $n > 1$ the shear thickening behaviour.

Although mathematically the power law is a simple model yet it has inherent limitations as it predicts either a decrease or increase in the apparent viscosity in a monotonic manner. Practically, most fluids show a Newtonian behaviour at low shear rates as well as at very high shear rates. Therefore, it is necessary to use other models which include the Newtonian behaviour at these two extreme conditions. Such models have been discussed and reviewed by Skelland². The limiting viscosity at low shear rates is called zero shear viscosity (μ_0) and the limiting viscosity at high shear rates is called infinite shear viscosity (μ_∞). Due to high viscosities of polymers, very high shear rates, where the infinite shear viscosity may be observed, are not encountered. Hence, models using zero shear viscosity are very commonly used. One such model, the Ellis model, is given as

$$\dot{\gamma} = \frac{1}{\mu_0} \left[1 + \left(\frac{\tau}{A} \right)^{a-1} \right] \tau \quad \dots (3)$$

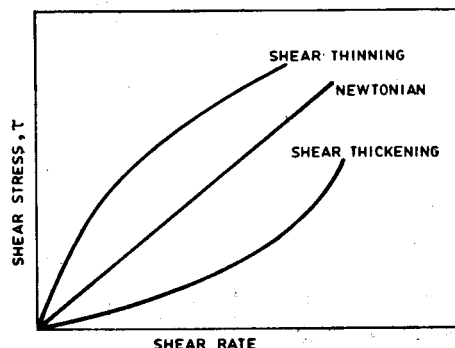


Fig. 1 - A class of non-Newtonian behaviour

where A and α are constants. At low shear rates the term $(\tau/A)^{\alpha-1}$ is small compared to 1 and hence a Newtonian behaviour with constant viscosity of μ_0 is predicted. As the shear rate increases the numerical value of $(\tau/A)^{\alpha-1}$ becomes much larger in comparison to 1 and a non-linear behaviour is predicted. $\alpha > 1$ indicates a shear thinning behaviour.

Most of the polymers show visco-elastic properties also. This visco-elastic behaviour is described by a simple Maxwell model.

$$\tau + \lambda \frac{D\tau}{Dt} = \mu \dot{\gamma} \quad \dots (4)$$

where λ is the relaxation time relating to elastic properties of polymer; μ , the viscosity; and D/Dt , a convected Oldroyd derivative⁴.

For many polymers, however, more complex rheological equation must be used. In Maxwell model, both viscosity (μ) and relaxation time (λ) are constant but for many polymers they are functions of shear rates. The theoretical equations become too complex to be used in the analysis. A good account of such models is given by Han⁴. A commonly used model is the modified Rivlin Ericksen model.

$$\tau = \mu(\hat{\Pi}) A_1 + W(\hat{\Pi}) A_2 - \lambda(\hat{\Pi}) A_2 \quad \dots (5)$$

where $\mu(\hat{\Pi})$, $W(\hat{\Pi})$ and $\lambda(\hat{\Pi})$ are the functions of second invariant, and A_1 and A_2 , the Rivlin Ericksen tensors of first and second order. Since $\mu(\hat{\Pi})$, $W(\hat{\Pi})$ and $\lambda(\hat{\Pi})$ are functions of second invariant, one may use any empirical relationship which fits the experimental data. Many such empirical forms have been reported in the literature and used in engineering analysis of non-Newtonian fluids⁵.

The elasticity of fluids is exhibited through the normal stress difference, $\tau_{11} - \tau_{22}$. Similar to Eq. (3), one may write

$$\dot{\gamma}^2 = \frac{1}{G_0} \left[1 + \left(\frac{\tau_{11} - \tau_{22}}{B} \right)^{C-1} \right] (\tau_{11} - \tau_{22}) \quad \dots (6)$$

where G_0 , B and C are constants.

As viscosity is defined as the ratio of $\tau/\dot{\gamma}$, the coefficient of normal stress is defined as $(\tau_{11} - \tau_{22})/\dot{\gamma}^2$. Eq. (6) is a numerical expression analogous to Ellis model. Thus, at low shear rates the numerical value of the term $[(\tau_{11} - \tau_{22})/B]^{C-1}$ is much smaller than 1 and it may be neglected in which case one may obtain $(\tau_{11} - \tau_{22}) = G_0 \dot{\gamma}^2$, yielding a constant coefficient of normal stress difference. Similarly, as shear rate increases the term $[(\tau_{11} - \tau_{22})/B]^{C-1}$ may be much larger than 1 and hence a linear variation in normal stress coefficient is predicted. The variation of normal stress

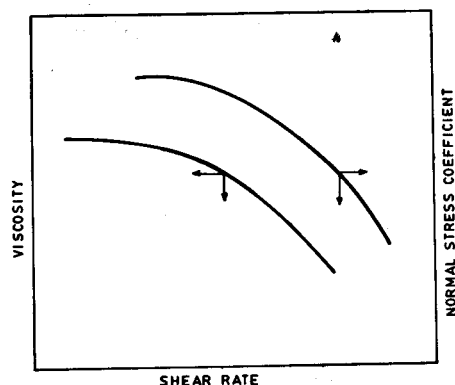


Fig. 2—Usual variation of viscosity and normal stress difference coefficient for polymer melt

with $(\dot{\gamma})^2$ is predicted from Eq. (5) when the functions $\mu(\hat{\Pi})$, $W(\hat{\Pi})$ and $\lambda(\hat{\Pi})$ are constants and not the variable functions of shear rate⁴. This point has been explained and discussed in a simple manner by Middleman³. Eq. (6) is empirical and has been used in the engineering analyses⁵. A general variation of viscosity and normal stress coefficient is shown in Fig. 2. The relaxation time (λ) is related to the normal stress difference and shear stress as

$$\lambda = \frac{\tau_{11} - \tau_{22}}{\tau \dot{\gamma}} \quad \dots (7)$$

Thus, the relaxation time also should approach a limiting value at lower shear rates.

Since both viscosity and relaxation time change with shear rate, their relative rates of change become significant. Thus, if viscosity decreases more rapidly the elastic effects would predominate and if the relaxation time decreases more rapidly the viscous effects would predominate. There are many analyses which qualitatively account for the viscous and elastic effects to some extent^{6,7}. The exact nature of rheology on the stress involved in and the stability of the spinning operation is not fully understood.

The blends often alter the properties of polymers. Therefore, it was thought to blend the polypropylene (PP) and high-density polyethylene (HDPE) and to study their rheology, spin the fibres and test the tensile strength of these fibres.

2 Materials and Methods

Polypropylene (Koylene, YF81, IPCL, Baroda, India) and HDPE (GF 7750 M, Polyolefin Industries, Bombay, India) were blended in different proportions using a two-roll compounding mill. The temperature of the rolls was set at 140°C.

The following compositions were obtained: (i) 100% PP, (ii) 80% PP+20% HDPE, (iii) 60% PP+40% HDPE, (iv) 40% PP+60% HDPE, (v) 20% PP+80% HDPE, and (vi) 100% HDPE. The pellets of each polymer were weighed appropriately to obtain total weight of each blend as 300 g. The polymers were blended into a homogeneous mass for 40 min. At the end of the homogenization process, a thin sheet of the blend was obtained. The sheet was cooled to room temperature and cut into small pieces of 2×2 mm using a shear cutter. To keep the same thermal history of all the samples, the pure PP and HDPE samples were also homogenized in the same way and cut into small pieces.

The rheological properties of the samples were measured at 185, 200 and 215°C using a Weissenberg rheogoniometer (model R-19) employing a cone and plate assembly. The shear rate range was $1\text{--}56 \text{ sec}^{-1}$. Fibres were spun using Fuji mini melt-spinning apparatus at 200°C.

The mechanical properties of fibres were determined using Instron (1026) tensile strength meter. The creep tests were carried out on ten specimens of fibres from each of the six blends with a pre-calibrated load of 100 g. The average of these values was taken as the representative value.

3 Results and Discussion

The flow behaviour of all the blends at 200°C is shown in Fig. 3. The rheogram shows a highly non-linear behaviour. Fig. 4 shows the variation of apparent viscosity (μ_a) with shear rate. It is observed that all these blends show a limiting viscosity at low shear rates. Also, all the samples show a shear thinning behaviour. Fig. 5 shows normal stress difference of melts of these blends. The rheological data of the blends at 185°C and 215°C are not given here. The trend of variation of viscosity and normal stress difference was similar. The data at 200°C are reported here since fibres were drawn at 200°C only. The zero shear viscosity was generally found to decrease when

temperature was increased. All these data including the viscous and elastic properties of the samples at 185°C and 215°C have been reported by Bopardikar⁸. The viscous and elastic behaviour were correlated by Eqs (3) and (6) respectively. Table 1 gives the values of the model parameters at 200°C.

The zero shear viscosity of a given blend is an important parameter. Table 2 shows its variation with temperature. A semi-empirical relation-

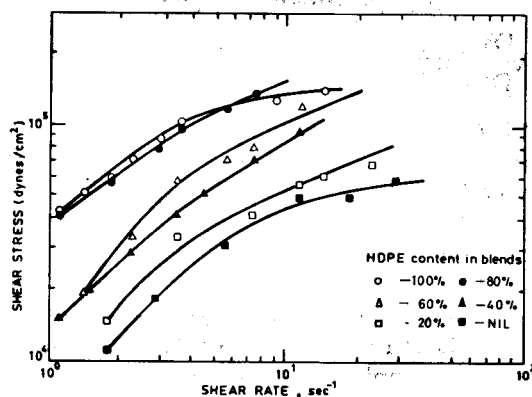


Fig. 3 – Rheograms of PP/HDPE blends at 200°C

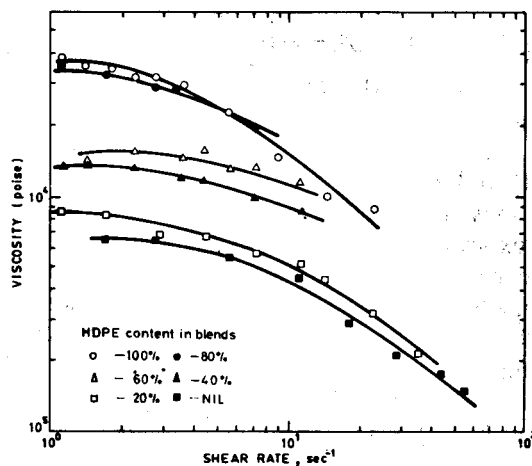


Fig. 4 – Variation of apparent viscosity at 200°C for PP/HDPE blends

Table 1 – Values of Model Parameters (Eqs 3 and 6) at 200°C

HDPE content in blend %	$\mu_0 \times 10^{-4}$ poise	$A \times 10^{-5}$ dyne/cm ²	α	$G_0 \times 10^{-5}$ dyne sec ² /cm ²	$B \times 10^{-5}$ dyne/cm ²	C
100	3.70	1.33	6.18	1.14	4.2	3.27
80	3.30	1.57	3.32	1.29	4.6	2.57
60	1.50	0.83	1.97	0.65	3.0	3.88
40	1.35	0.42	1.28	0.63	1.5	3.96
20	0.85	0.61	1.82	0.47	2.0	3.01
0	0.64	0.53	2.69	0.82	1.7	1.86

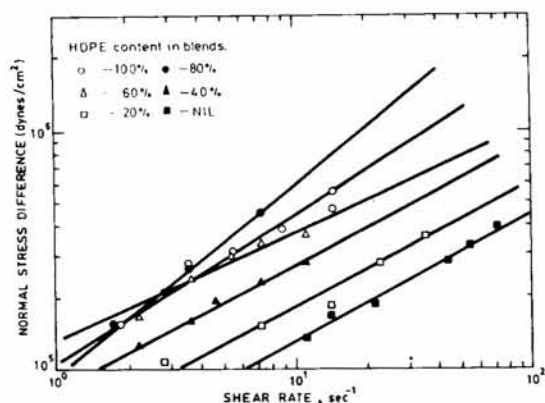


Fig. 5 - Variation of normal stress difference with shear rate at 200°C for PP/HDPE blends

Table 2 - Variation of Zero Shear Viscosity with Temperature and Blend Composition

HDPE content in blend %	Temperature °C	Zero shear viscosity (μ_a), poise
100	185	4.50×10^4
100	200	3.75×10^4
100	215	2.90×10^4
80	185	4.70×10^4
80	200	3.30×10^4
80	215	2.90×10^4
60	185	2.40×10^4
60	200	1.80×10^4
60	215	1.35×10^4
40	185	2.00×10^4
40	200	1.40×10^4
40	215	1.10×10^4
20	185	1.30×10^4
20	200	8.50×10^3
20	215	5.10×10^3
0	185	1.00×10^4
0	200	6.40×10^3
0	215	4.20×10^3

ship^{9,10} correlates the viscosity of a fluid with the free volume (V_F). Thus,

$$\ln \mu_0 = \ln P + S \left(\frac{V - V_F}{V_F} \right) \quad \dots (8)$$

where P and S are constants and V and V_F are total volume and free volume respectively. Eq. (8) can be rearranged as

$$\ln \mu_0 = \ln P + S \left(\frac{1}{f} - 1 \right) \quad \dots (9)$$

where $f = V_F/V$, called as fractional free volume. The constant P is thus an intrinsic parameter.

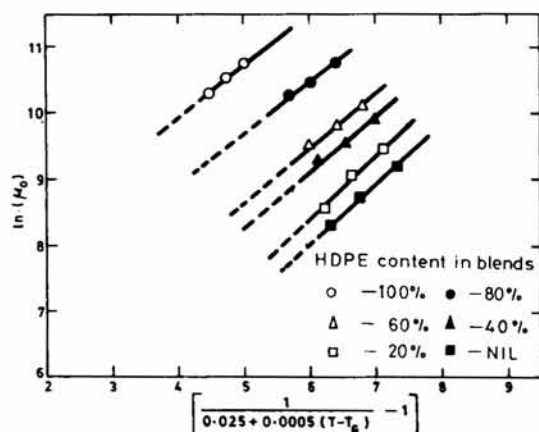


Fig. 6 - Variation of zero shear viscosity with temperature and free volume for PP/HDPE blends

Table 3 - Values of Parameters P and S (Eq. 9)

HDPE content in blend %	P	S
100	6.25	0.90
80	6.05	0.74
60	5.75	0.64
40	4.44	0.78
20	2.91	0.91
0	2.36	0.96

The fractional free volume may be correlated with temperature through glass transition temperature T_G . Thus,

$$f = f_g + \alpha_F (T - T_G), \quad T \geq T_G \quad \dots (10)$$

where α_F is thermal coefficient of expansion of free volume. For most polymers, $f_g = 0.025$ and $\alpha_F = 5 \times 10^{-4}/^\circ\text{C}$. One can rearrange Eq. (9) as

$$\ln \mu_0(T) = \ln P + S \left[\frac{1}{0.025 + 5 \times 10^{-4}(T - T_G)} - 1 \right] \quad \dots (11)$$

Thus, a plot of $\ln \mu_0(T)$ vs

$\left[\frac{1}{0.025 + 5 \times 10^{-4}(T - T_G)} - 1 \right]$ should result into a straight line giving $\ln P$ as an intercept and S as the slope. The glass transition temperature of the blend may be estimated from

$$\frac{1}{T_{G \text{ blend}}} = \frac{W_1}{T_{G_1}} + \frac{W_2}{T_{G_2}} \quad \dots (12)$$

where W_1 and W_2 are weight fractions of two polymers. Glass transition temperatures of 173°K and 263°K for HDPE and PP respectively were used. Fig. 6 shows these results. The values of P and S are given in Table 3. The intrinsic param-

Table 4 - Variation of Mechanical Properties with Blend Composition

HDPE content in blend %	Denier of fibre	Tenacity g/den	Elongation %
100	62.5	1.36	644
80	65.0	0.48	656
60	62.5	0.61	464
40	62.5	0.70	604
20	57.5	0.68	498
0	62.5	0.61	445

ter P varies systematically and the slope S does not show any particular trend but decreases as % PP is increased. Indeed, the data over a wider range of temperature would be most revealing and an estimation of zero shear viscosity at any temperature may be very easy.

Table 4 gives the values of denier, tenacity and % elongation for all the six samples. The tenacity of HDPE reduces considerably if polypropylene is added to HDPE. The % elongation does not change by small additions of polypropylene, whereas the viscosity of HDPE reduces if polypropylene is added. If HDPE is added in small quantities (up to 20%) to polypropylene, the viscosity and tenacity do not change significantly but average % elongation increases fairly. Thus, the addition of other polymers may be used to advantage.

4 Conclusions

The flow behaviour of blends of HDPE and PP shows shear thinning characteristics with a limit-

ing zero shear viscosity. The behaviour can be correlated well by Ellis model. The variation of zero shear viscosity with temperature can be correlated with free volume theory. All the samples studied show significant elastic effects. The tenacity and % elongation can be altered by blending the two polymers.

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