

# Rheological Properties, Shrinkage and Melt Spinning Instability of Blends of Linear Polyolefins with Low Density Polyethylene

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## Synopsis

A comparative study is presented of the influence of addition of a long chain branched low density polyethylene LDPE on the rheological and processing characteristics of a high density polyethylene (HDPE), a polypropylene (PP), and a polybutene-1 (PB). The influence of the LDPE on the PP and PB are most striking. Substantial increases in normal stresses, "shrinkage" of extruded filaments, and melt spinning stability are observed. The effects are much smaller for the HDPE blends.

## INTRODUCTION

Blends of polyolefins have drawn considerable attention in the literature<sup>1-12</sup> from academic and industrial laboratories. However, no general perspective has developed from these papers. Most commercially available linear polyolefins are broad molecular weight linear polymers and exhibit basically similar rheological characteristics. This is emphasized in recent papers from our laboratories.<sup>13-16</sup> Long chain branched low density polyethylenes exhibit somewhat different flow properties. These are especially striking in elongational flows. Filaments stretch out more uniformly and exhibit much greater elongations to break.<sup>17,18</sup> The elongational viscosity is a strong rising function of stretch rate.<sup>17,18</sup> Spinlines are more stable,<sup>18,19</sup> and vortices are observed in the entrance region to dies.<sup>20-22</sup> In the present paper we investigate the influence of the addition of low density polyethylene on several rheological and processing characteristics of linear polyolefins. We consider blends with high density polyethylene, polypropylene, and polybutene-1. This paper continues research programs by the authors on the rheological and structure development characteristics on polymer blend systems.<sup>12,23-25</sup>

## EXPERIMENTAL

### Materials

The low density polyethylene (LDPE) used in this study was a Chemplex 1009 with a density of 0.919 and a melt index of 3.5. The high density polyethylene (HDPE) was a Chemplex 6109 with a density of 0.96 and a

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melt index of 0.9. The polypropylene was an experimental polymer supplied by Diamond Shamrock. It has a melt index of 5. The polybutene-1 was a Shell 1600.

The blends were prepared as follows: Pellets of the appropriate plastics were blended using a 3/4 in Brabender screw extruder with a Koch static mixer at 190°C. The blend compositions prepared are summarized in Table I.

The phase morphologies of the blends were not investigated. Previous experience had shown scanning electron microscopy and phase contrast microscopy not truly capable of distinguishing the individual phases.<sup>12</sup>

### Rheological Measurements

Shear viscosities were measured as a function of shear rate using both a Rheometrics Mechanical Spectrometer in the cone-plate mode and in Instron (Merz-Colwell) Capillary Rheometer. Principal normal stress differences  $N_1$  were measured in a Rheometrics Mechanical Spectrometer.

### Shrinkage

Filaments formed from the Brabender extruder with a static mixer at 190°C were placed in a hot silicone oil bath and allowed to shrink. The length of the filaments was measured at various times up to 4000 s.

### Melt Spinning

The various polymers and blends were melt spun from the Instron capillary rheometer through an isothermal chamber into a water quench bath. The filaments were extruded at 0.35 cm/s (0.21 m/min) and taken up on a rotating roll. A Rothschild tensiometer was used to determine the onset of the draw resonance instability.

## RESULTS

### Shear Viscosity

The shear viscosities  $\eta$  of the LDPE, HDPE, PP, and PB melts are shown in Figure 1. It may be seen that in general the viscosity tends to a constant

TABLE I  
Blend Compositions Investigated in This Study

10 LDPE/90 HDPE
30 LDPE/70 HDPE
50 LDPE/50 HDPE
75 LDPE/25HDPE
10 LDPE/90 PP
30 LDPE/70 PP
50 LDPE/50 PP
75 LDPE/25 PP
20 LDPE/90 PB
30 LDPE/70 PB
50 LDPE/50 PB

TABLE II  
Estimated Steady State Compliances and Mean Relaxation Times for Blends

Sample	(1) AT $\sigma_{12} = 10^4$ dyn/cm <sup>2</sup>		(2) AT $\sigma_{12} = 5 \times 10^4$ dyn/cm <sup>2</sup>		$\gamma$
	$J_e(1)$ (cm <sup>2</sup> /dyn)	$J_e(2)$ (cm <sup>2</sup> /dyn)	$\bar{\tau}(1)$ (s)	$\bar{\tau}(2)$ (s)	
LDPE	$9 \times 10^{-5}$	$8.9 \times 10^{-5}$	7	1.4	1
HDPE	7.5	1.8	25	1.6	0.9
PP	2.5	1.5	1.8	0.8	1
PB	2.3	1.4	8.5	0.9	0.5
10 LDPE/90 HDPE	7.7	1.9	25	1.8	0.9
30 LDPE/70 HDPE	5.8	2.4	20	1.9	0.9
50 LDPE/50 HDPE	6	1.2	12.5	1	0.9
10 LDPE/90 PP	2.8	1.8	1.5	0.4	1
30 LDPE/70 PP	7	1.9	1.8	0.5	3
50 LDPE/50 PP	7	2	2.5	0.7	3.4
10 LDPE/90 PB	2.5	0.9	3.5	0.4	0.9
30 LDPE/70 PB	8	1.9	8	0.8	2.5
50 LDPE/50 PB	8	1.7	7	0.6	2.5

value at low shear rates and decreases at higher shear rates. Only the PB does not reach a clear low shear rate constant asymptote.

The viscosities of the LDPE, HDPE, and blends are shown as a function of shear rate in Figure 2. Similar plots for the PP/LDPE and PB/LDPE systems are shown in Figures 3 and 4. Plots of  $\eta$  as a function of composition at specific shear stresses are shown in Figures 5-7 for the HDPE/LDPE, PP/LDPE, and PB/LDPE systems respectively. A monotonic variation of  $\eta$  with composition is found for the HDPE-LDPE, but maxima and minima are found for the other systems.

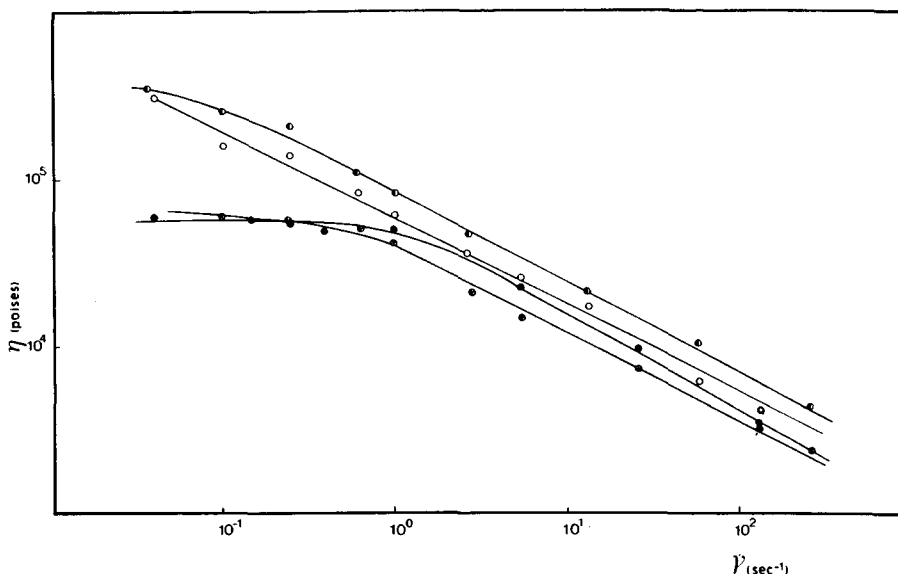


Fig. 1. Shear viscosity  $\eta$  of LDPE (⊙), HDPE (●), PP (●) and PB (○) vs. shear rate.

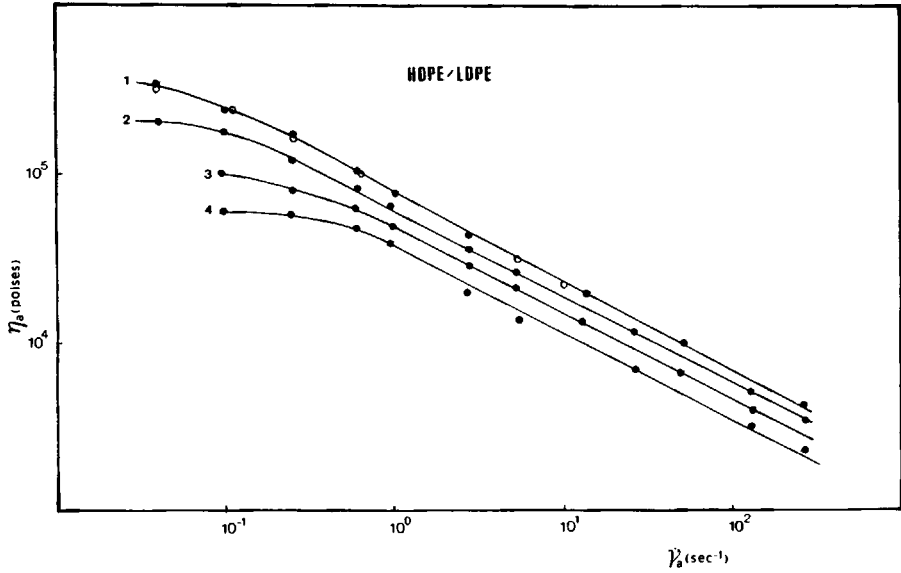


Fig. 2. Shear viscosity  $\eta$  of LDPE (4), HDPE, and their blends (HDPE/LDPE) as a function of shear rate: (1) (●) 90/10; (○) 70/30; (2) 50/50; (3) 25/75.

### Principal Normal Stress Difference

The principal normal stress differences for the four melts LDPE, HDPE, PP, and PB are shown as a function of shear stress in Figure 8. The data order as:

$$\text{LDPE} > \text{HDPE} > \text{PP} > \text{PB}$$

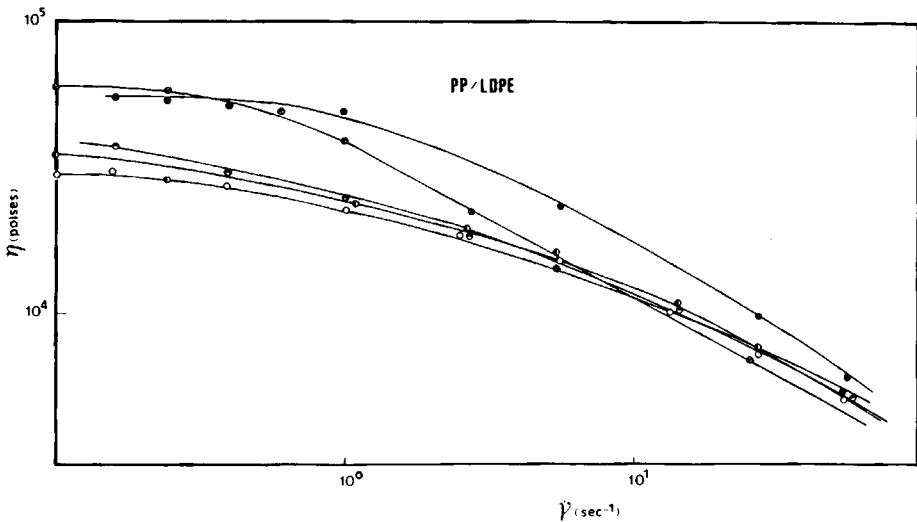


Fig. 3. Shear viscosity  $\eta$  of LDPE (⊗), PP (●), and their blends (PP/LDPE) as a function of shear rate: (●) 50/50; (●) 30/70; (○) 10/90.

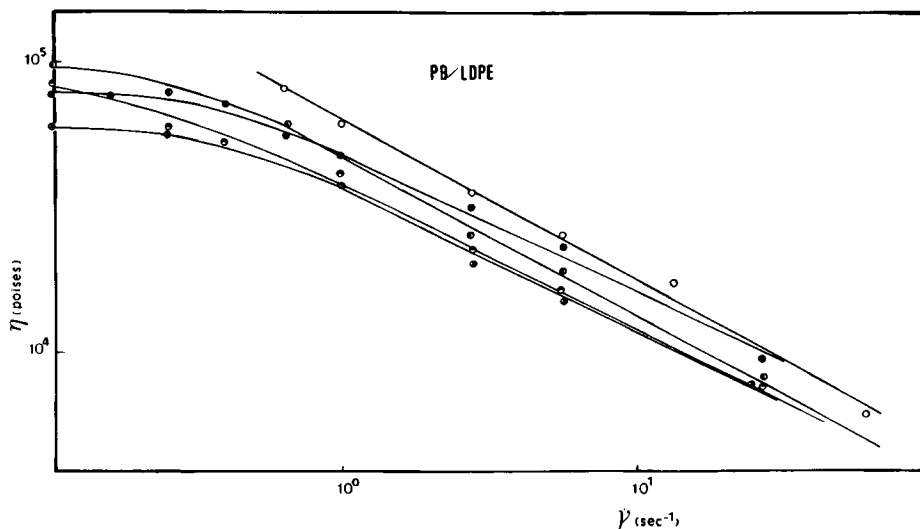


Fig. 4. Shear viscosity  $\eta$  of LDPE ( $\otimes$ ), PB ( $\circ$ ), and their blends (PB/LDPE) as a function of shear rate: ( $\bullet$ ) 50/50; ( $\circ$ ) 30/70; ( $\bullet$ ) 10/90.

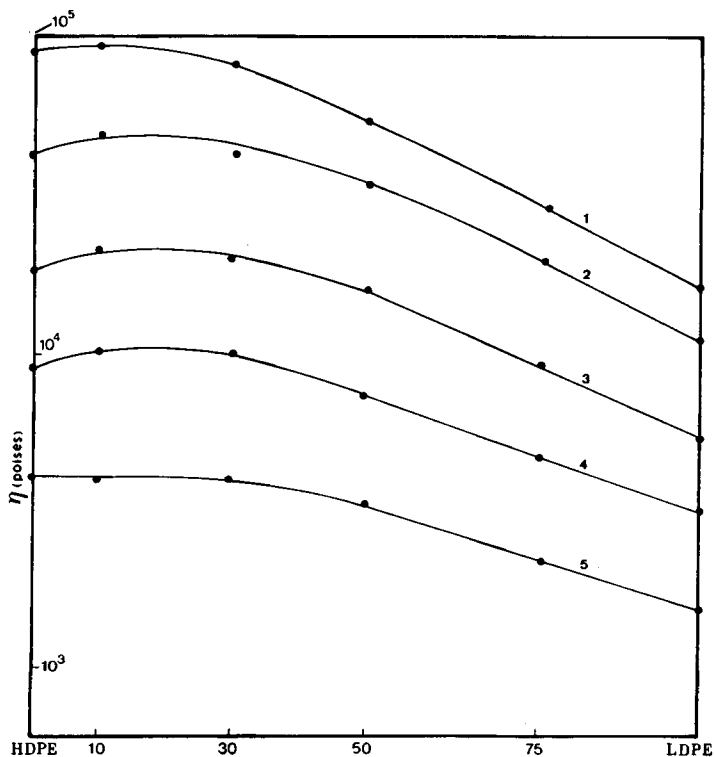


Fig. 5. Shear viscosity  $\eta$  of LDPE-HDPE blends at various shear stresses: ( $\text{dyn/cm}^2$ ): (1)  $\sigma_{12} = 0.5 \times 10^6$ ; (2)  $1 \times 10^6$ ; (3)  $2.5 \times 10^6$ ; (4)  $5 \times 10^6$ ; (5)  $10 \times 10^6$ .

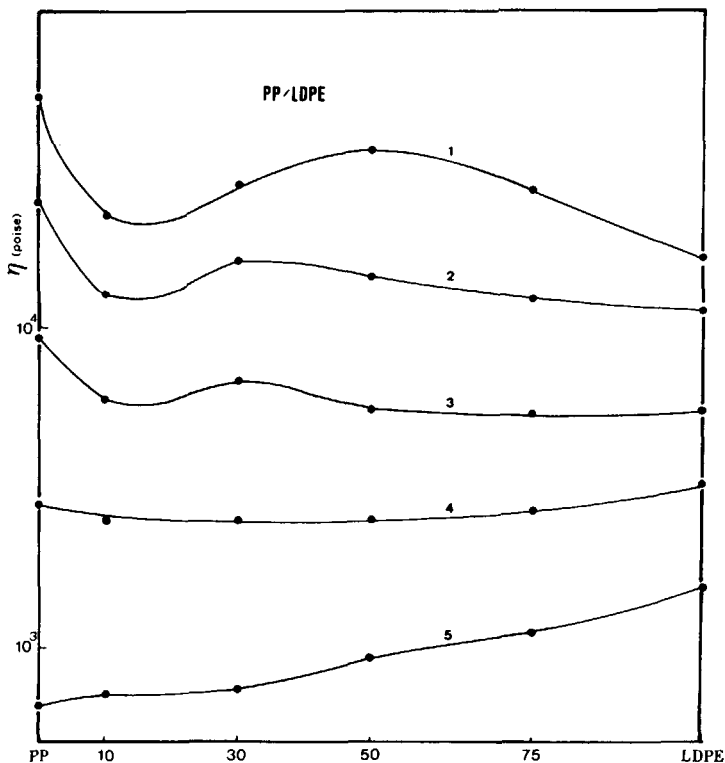


Fig. 6. Shear viscosity  $\eta$  of LDPE-PP blends at various shear stresses ( $\text{dyn}/\text{cm}^2$ ): (1)  $\sigma_{12} = 0.5 \times 10^5$ ; (2)  $1 \times 10^5$ ; (3)  $2.5 \times 10^5$ ; (4)  $5 \times 10^5$ ; (5)  $10 \times 10^5$ .

We plot  $N_1$  vs.  $\sigma_{12}$  for the HDPE/LDPE blends in Figure 9. Similar plots for the PP/LDPE and PB/LDPE systems are shown in Figures 10 and 11. The data roughly order monotonically with composition, with  $N_1$  increasing with LDPE content.

### Shrinkage

The shrinkage of extruded filaments in hot silicone oil baths has been represented in terms of Hencky measure of strain

$$\gamma = \ln \frac{L(0)}{L(t)} \quad (1)$$

This is plotted in Figure 12 for the different homopolymer and blend systems for various compositions as a function of time.

The shrinkage of the pure LDPE, HDPE, PP, and PB thermoplastics are similar, having values of  $\gamma$  less than unity.

The shrinkage of the blends may be seen to rise rapidly with addition of LDPE. This is most striking for the PP and PB blends. Figure 13 plots shrinkage  $\gamma$  for large times vs. composition. Striking maxima are observed. The values of asymptotic shrinkage  $\gamma$  are also listed in Table II.

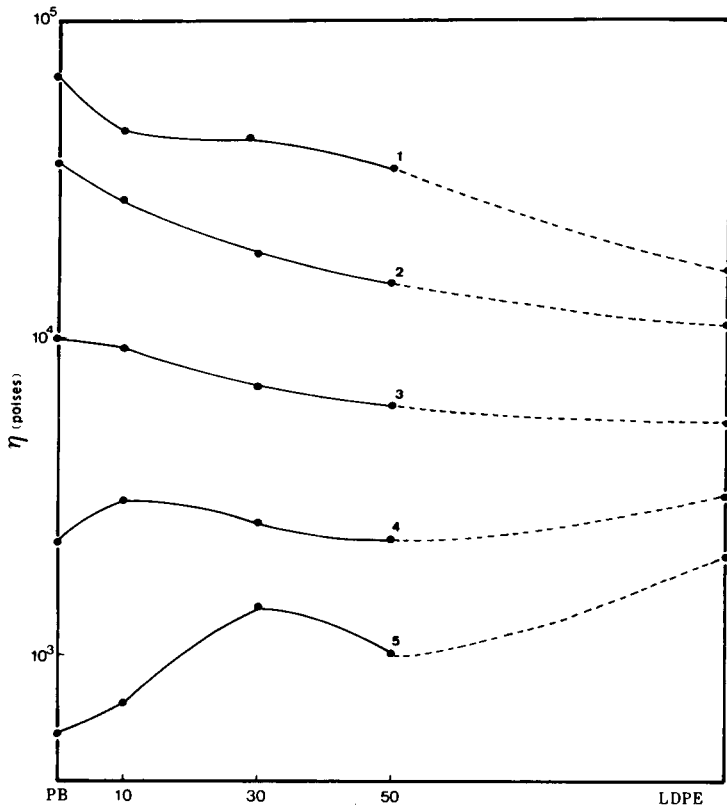


Fig. 7. Shear viscosity  $\eta$  of LDPE-PB blends at various shear stresses ( $\text{dyn}/\text{cm}^2$ ): (1)  $\sigma_{12} = 0.5 \times 10^5$ ; (2)  $1 \times 10^5$ ; (3)  $2.5 \times 10^5$ ; (4)  $5 \times 10^5$ ; (5)  $10 \times 10^5$ .

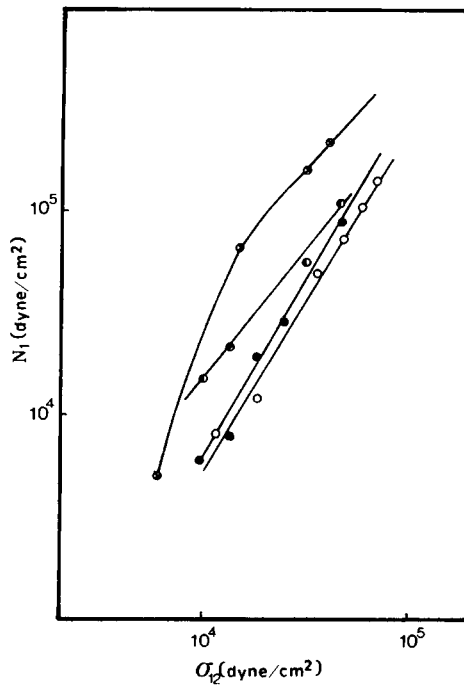


Fig. 8. Principal normal stress difference  $N_1$ -shear stress  $\sigma_{12}$  plot for the LDPE (⊗), HDPE (⊙), PP (●) and PB (○) melts.

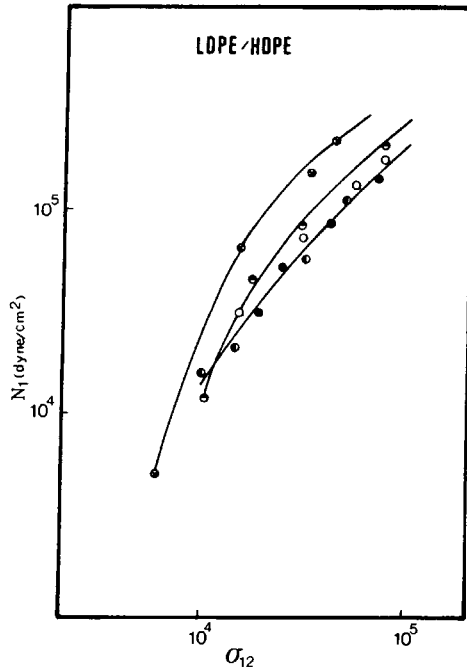


Fig. 9. Principal normal stress difference  $N_1$ -shear stress  $\sigma_{12}$  plot for LDPE ( $\otimes$ ), HDPE ( $\bullet$ ), and their blends (LDPE/HDPE): ( $\bullet$ ) 10/90; ( $\circ$ ) 30/70; ( $\ominus$ ) 50/50.

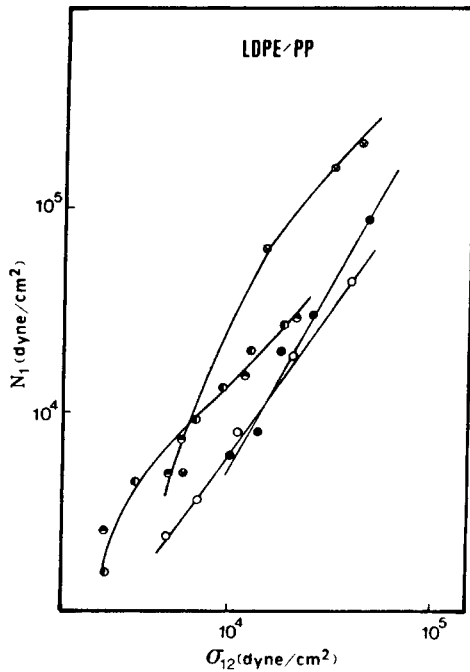


Fig. 10. Principal normal stress difference  $N_1$ -shear stress  $\sigma_{12}$  plot for LDPE ( $\otimes$ ), PP ( $\bullet$ ), and their blends (LDPE/PP): ( $\circ$ ) 10/90; ( $\ominus$ ) 50/50; ( $\bullet$ ) 30/70.



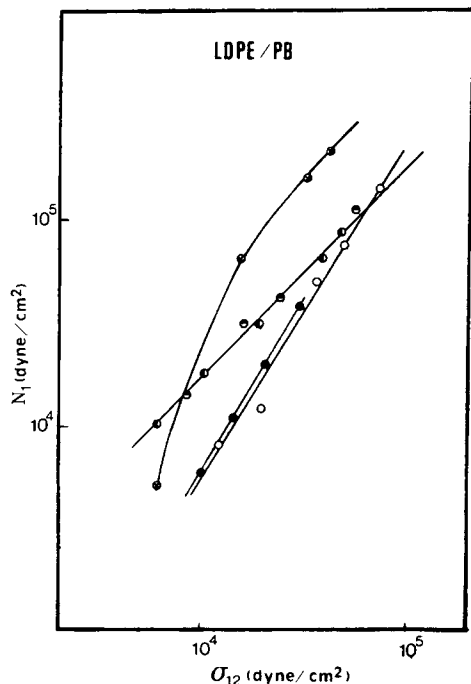


Fig. 11. Principal normal stress difference  $N_1$ -shear stress  $\sigma_{12}$  plot for LDPE (●), PB (⊗) and their blends (LDPE/PB): (⊙) 50/50; (⊚) 30/70; (●) 10/90.

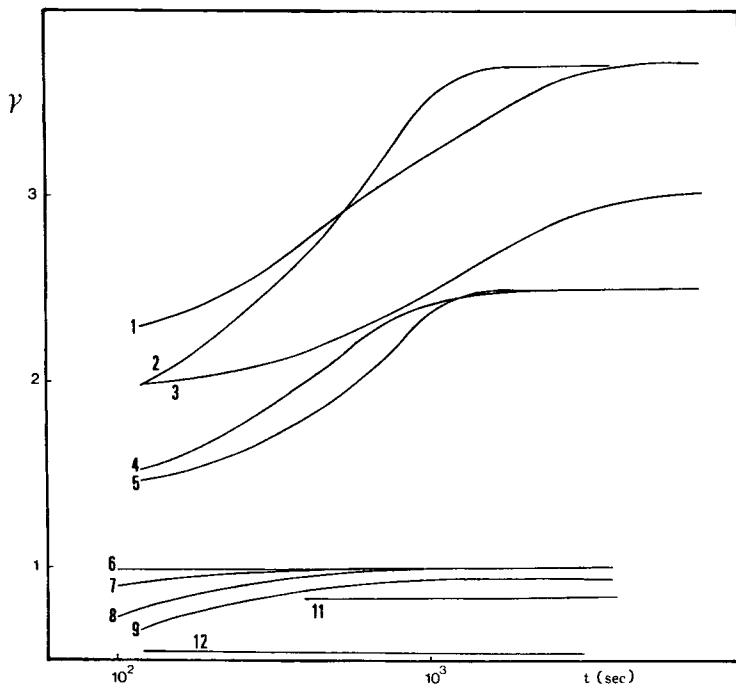


Fig. 12. Shrinkage  $\gamma = L(0)/\ln L(t)$  as a function of time for LDPE-HDPE, LDPE-PP, and LDPE-PB blends: (1) 75 LDPE/25PP; (2) 50 LDPE/50PP; (3) 30 LDPE/70 PP; (4) 30 LDPE/70 PB; (5) 50 LDPE/50 PB; (6) 10 LDPE/90 PP; (7) LDPE; (8) PP; (9) 10 LDPE/90 PB; (11) HDPE; (12) PB.

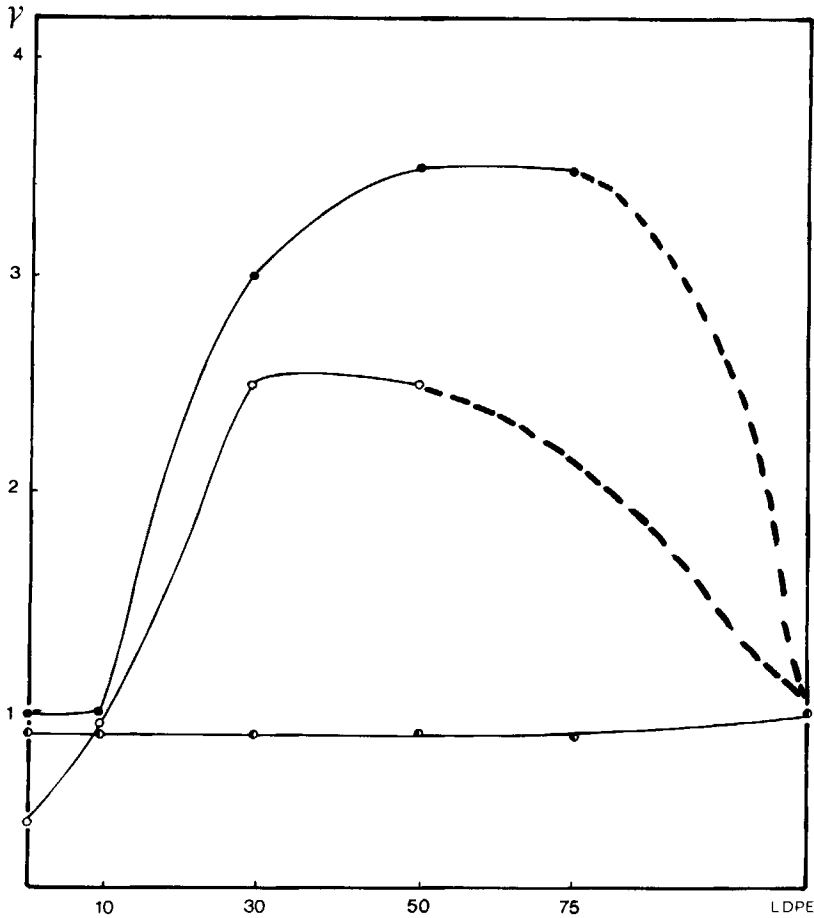


Fig. 13. Shrinkage  $\gamma = L(0)/\ln L(t)$  as a function of composition for large time  $t_*$  for LDPE-HDPE (●), LDPE-PP (●) and LDPE-PB-1 (○) blends.

### Melt Spinning Stability

At low drawdowns  $v_L/v_0$ , uniform filaments are obtained or at least filaments with a low amplitude random disturbance (compare Minoshima et al.<sup>14</sup> and Yamane and White<sup>16</sup>). At higher drawdowns the disturbances increase in amplitude and become periodic in character. It is this phenomenon which is known as draw resonance. It has been reported by numerous earlier investigators<sup>14,16,18,19,26-29</sup> of the melt spinning process.

The HDPE, PP, and PB are all rather unstable exhibiting the onset of draw resonance at drawdown  $v_L/v_0$  ratios less than 10. The addition of LDPE increases  $v_L/v_0$ . The critical  $v_L/v_0$  is plotted in Figure 14 as a function of weight fraction LDPE. The increases for the PP and PB are much greater than for the HDPE blends.

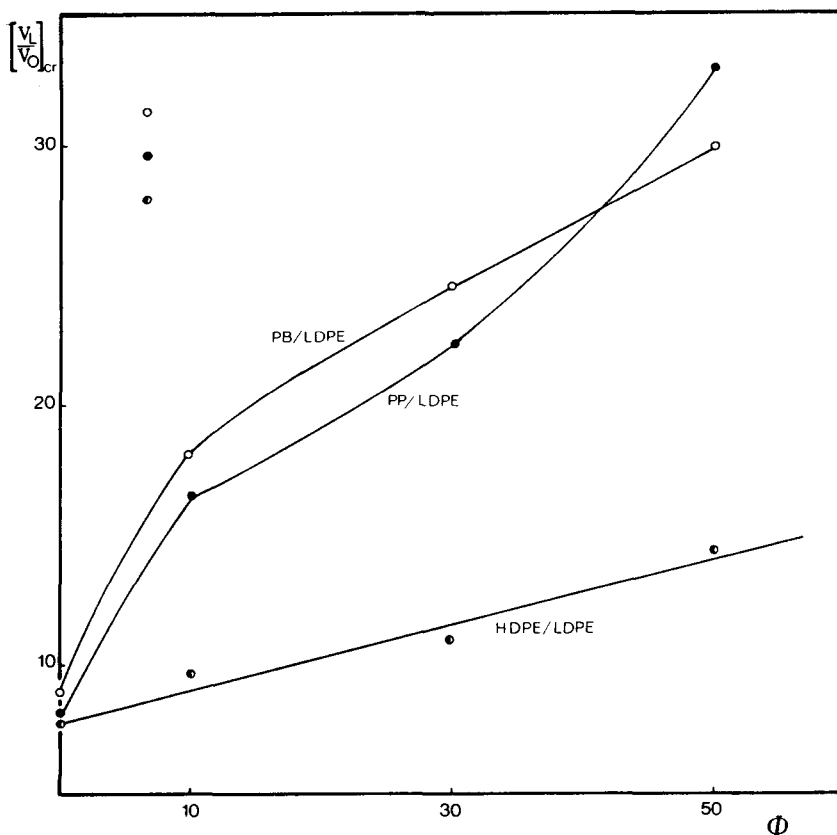


Fig. 14. Critical draw ratio  $v(L)/v(0)$  for the onset of draw resonance in LDPE-HDPE, LDPE-PP, and LDPE-PB-1 blends as a function of composition

## DISCUSSION

### Rheological Properties

The influence of LDPE on the rheological properties of PP and PB is striking.  $N_1$  increases with LDPE content in a roughly monotonic manner. The effect on shrinkage is striking, with blends exhibiting strong maxima as a function of composition. Indeed it had been our original intention to study the elongational viscosity of the blend system but the shrinkage effects were so large that this was not possible.

The rheological properties of molten polymer blends are complex and unless there is compatibility on the molecular level, or nearly so, we should not expect continuum theories of flow to be valid. As shown by Shimomura et al.'s<sup>12</sup> wide angle X-ray diffraction results polyethylene is incompatible with polypropylene and undoubtedly polybutene-1 in the crystalline state. The situation in the melt state is not so clear.

If we do consider the blends' rheological properties to satisfy the theory of nonlinear viscoelastic fluids, we may seek to show consistency of the

normal stress and shrinkage results. As first clearly shown by Coleman and Markovitz,<sup>30</sup> the principal normal stress difference  $N_1$  is related to the shear stress  $\sigma_{12}$  at low deformation rates where second-order fluid theory is valid through

$$N_1 = 2 J_e \sigma_{12}^2 \quad (2)$$

where  $J_e$  is the steady state compliance

$$J_e = \frac{\int_0^\infty sG(s) ds}{[\int_0^\infty G(s) ds]^2} \quad (3)$$

Here  $G(s)$  is the linear viscoelastic relaxation modulus.

We have computed  $J_e$  from eq. (2) using the data of Figures 10 and 11 at shear stresses of  $10^4$  and  $5 \times 10^4$  dyn/cm<sup>2</sup>. Results for the original LDPE, HDPE, PP, PB, and the blends with LDPE are summarized in Table II and plotted in Figure 15. It may be seen that  $J_e$  sharply rises with LDPE content

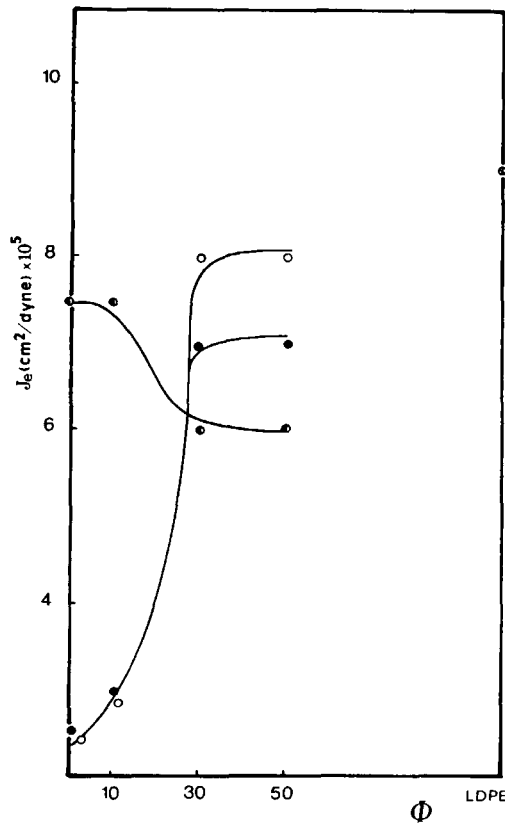


Fig. 15. Steady state compliance  $J_e$  estimated from  $N_1 - \sigma_{12}$  data at shear stress of 10 dyn/cm for LDPE-HDPE (○), LDPE-PP (●), and LDPE-PB-1 (○) blends as a function of composition.

for the PP and PB blends but is roughly independent of composition for the HDPE blends.

We may express eq. (2) in terms of a characteristic relaxation time  $\bar{\tau}$  through

$$N_1 = 2\bar{\tau} \eta \dot{\gamma}^2 \quad (4)$$

where

$$\bar{\tau} = \frac{\int_0^{\infty} sG(s) ds}{\int_0^{\infty} G(s) ds} \quad (5a)$$

$$J_e = \frac{\bar{\tau}}{\eta} \quad (5b)$$

$\bar{\tau}$  was determined from eq. (5b) using the calculated  $J_e$  values and  $\eta$  at  $\sigma_{12}$  of  $10^4$  and  $5 \times 10^4$  dyn/cm<sup>2</sup>.  $\bar{\tau}$  at  $10^4$  dyn/cm<sup>2</sup> actually decreases with increasing LDPE for the blends with HDPE but is roughly independent of composition for the others. At  $5 \times 10^4$  dyn/cm<sup>2</sup>, little dependence on composition exists for any of the blends. The reason for  $\bar{\tau}$  being constant or decreasing is that as  $J_e$  increases, the shear viscosity  $\eta$  decreases.

### Shrinkage

The quantity  $J_e$  is the steady state shear compliance usually associated with recoil  $\gamma_r$ :

$$\gamma_r = J_e \sigma_{12} \quad (6)$$

$\gamma$  for the blends in Figures 12 and 13 is generally significantly higher than for the pure PP and PB. Similar behavior is shown by  $J_e$  and  $\gamma_r$ . If we consider the shrinkage in the various blend extrudates to be recovery from identical (shear) stress states, then  $\gamma$  should correlate with  $J_e$  and  $\gamma_r$ . We make such a plot in Figure 16 taking  $\sigma_{12}$  as  $10^4$  dynes/cm<sup>2</sup>. The data may only be correlated using a very broad band. Generally the trend for the systems orders as

$$\text{PP/LDPE} > \text{PB/LDPE} > \text{HDPE/LDPE}$$

### Melt Spinning Stability

The draw resonance results are also striking in character. The LDPE substantially increases the stability. If we may presume the blends to behave as a viscoelastic continuum, this result may also be traced to the viscoelastic characteristics through the theory of Fisher and Denn.<sup>31</sup> These authors consider the melt spinning stability of a nonlinear viscoelastic "convected" Maxwell model. Fisher and Denn find melt elasticity through the Weissenberg number acts to stabilize the spinline.

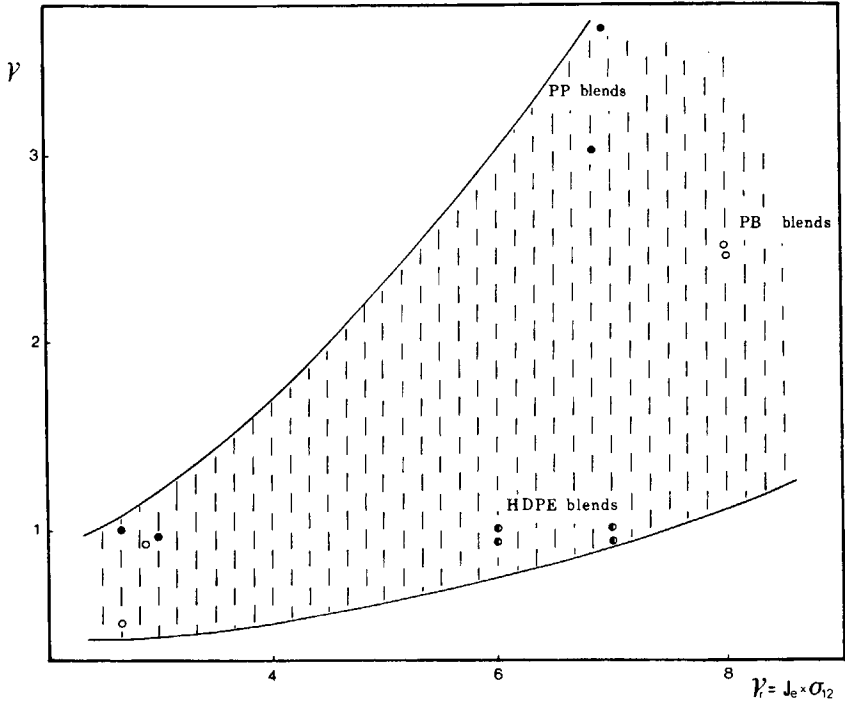


Fig. 16. Plot of shrinkage  $\gamma_s$  vs.  $\gamma_r$ .

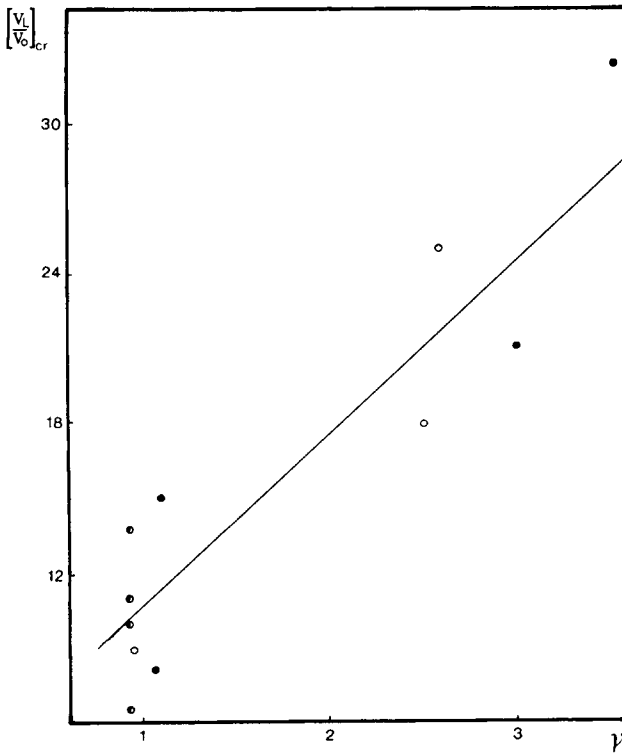


Fig. 17. Critical drawdown ratio  $(v_L/v_o)_{crit}$  as a function of shrinkage: (○) PB blends; (●) PP blends; (●) HDPE blends.

If we relate the critical drawdown ratio  $(v_L/v_0)_{crit}$  to the shrinkage which is an elastic recovery and a Weissenberg number according to Weissenberg's original concept,<sup>†</sup> we find the results plotted in Figure 17 are obtained. A monotonic correlation is found. However, this correlation is not completely in the spirit of the Fisher–Denn theory based on a convected Maxwell model. Their development leads to a Weissenberg number of  $\tau v_0/L$ , where  $L$  is the spinline length and  $\tau$  the Maxwell relaxation time. The quantity  $\tau$  has been estimated from the  $\bar{\tau}$  of eq. (5). We plot  $(v_L/v_0)_{crit}$  as a function of  $\bar{\tau} v_0/L$  in Figure 19. No real correlation is obtained, but there is a broad increasing trend for the PP blends and PB-1 blends but not for the HDPE blends. White and Ide,<sup>19</sup> Minoshima et al.,<sup>14</sup> and Yamane and White<sup>16</sup> have found in polyolefins that deformation rate softening, as shown by the elongational viscosity function, strongly influences melt spinning stability. This is not obviously helpful here, because of the inability to make elongational flow studies on the blends.

INTERPRETATION

There are fundamental differences in these characteristics of the systems studied. The addition LDPE exhibits a much more pronounced effect on the rheological and processing characteristics of the PP and PB-1 than the

<sup>†</sup> See the discussions of Weissenberg,<sup>32</sup> Shite,<sup>33</sup> and Metzner, White, and Denn<sup>34</sup> which relate various definitions.

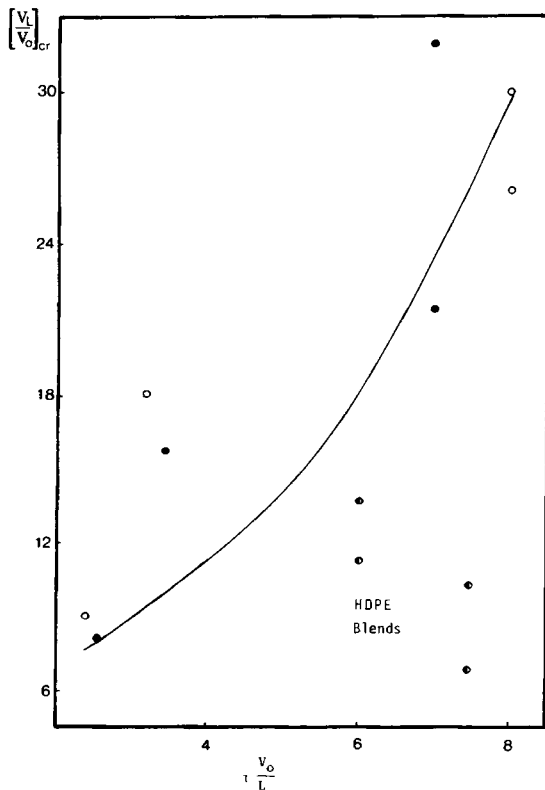


Fig. 18. Critical drawdown ratio  $(v_L/v_0)_{crit}$  as a function. Symbols are the same as in Figures 16 and 17.

HDPE. Melt elasticity and spinline stability are greatly enhanced. Shrinkage and melt spinning stability correlations with rheological properties do not seem to exist in these systems. This suggests that there may be fundamental differences in the materials themselves. This might mean a greater level of incompatibility in the PP and PB blends. It is known that melt solidified blends of polyethylene and polypropylene are incompatible. However, the level of segregation is not really known especially in the melt state. Certainly on the basis of superficial structural characteristics (all are aliphatic hydrocarbons) and interfacial tension, compatibility in the melt state is suggested.

We would like to thank Dr. K. Min for her help and constructive comments during the course of this research.

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