Melt Rheology of Plasticized Poly(vinyl Chloride)/Epoxidized Natural Rubber Miscible Blends

K. T. VARUGHESE,* *Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India*

Synopsis

A study of the melt rheological behavior of miscible blends of plasticized poly(vinyl chloride) (PVC) and epoxidized natural rubber (ENR) was carried out with a capillary rheometer. Melt viscosity and melt elasticity behavior was determined and surface characteristics of the extrudate was examined by using a scanning electron microscope. Melt viscosity of plasticized PVC increased with ENR content at higher processing temperatures. The melt elasticity parameters such as die swell ratio, principal normal stress difference, and recoverable shear strain at a particular shear stress increased with temperature up to a 50 wt % composition of ENR in blends. For high ENR blends the die swell ratio and recoverable shear strain decreased with temperature, and the principal normal stress difference and elastic shear modulus remained independent of temperature for all values of shear stress. It was noted that the nature of deformation in the surface layer was linear for a smooth extrudate and nonlinear for a distorted extrudate. Moreover, recoverable shear strain was found to have a correlation with the extrudate distortion of the melts.

INTRODUCTION

New polymeric materials based on miscible systems of polymers often find important industrial applications because of their improved properties, ease of preparation, and economical advantage. Blends of a thermoplastic and an elastomer are specially important because they are easily processable like a thermoplastic and can be reprocessed and recycled.

The present study concerns the specific thermoplastic–elastomer blends consisting of plasticized poly(vinyl chloride) (PVC) and epoxidized natural rubber (ENR). In earlier studies,[1-3] it has been reported that ENR of 50 mol % epoxidation level is capable of mixing miscibly with rigid and plasticized PVC. A single phase behavior in their entire range of composition has been reported for both the solution-cast[1] and melt-blended[2,3] systems.

Being a new system of polymer blends and also due to its thermoplastic nature, an understanding of the melt rheology of PVC/ENR blends is essential in optimizing their processing conditions. In earlier studies,[4,5] we have experimented and reported on the melt-rheological behavior of rigid PVC/ENR systems. Important conclusions arrived at were that the melt viscosity of rigid PVC decreased significantly with the incorporation of ENR, and the anomalous melt-elasticity behavior of PVC, i.e., extrudate swell increasing with temperature at constant shear stress persisted in the blends up to the 50/50 composition of PVC/ENR.

---

*Present address: Division of Rubber Technology, Madras Institute of Technology, Anna University, Madras 600 044, India.

CCC 0021-8995/90/020205-19$04.00

The present study is directed towards the investigation of melt-rheological behavior of the melt-mixed miscible compositions of plasticized PVC and ENR. The miscibility and phase behavior of this system have been reported previously.[3] The plasticizer used, prior to blending, is dioctyl phthalate of a constant loading of 40 phr. This liquid plasticizer significantly influences the flow behavior and extrudate characteristics of PVC/ENR melts.

EXPERIMENTAL

Details of the material used and the blending procedure have been described in an earlier paper.[3] Samples are designated as PP_{100}, PP_{70}, PP_{50}, PP_{30}, and P_0, corresponding to the plasticized PVC/ENR ratios of 100/0, 70/30, 50/50, 30/70, and 0/100, respectively. PVC containing 6 phr of tribasic lead sulphate and 40 phr of dioctyl phthalate was blended with ENR of 50 mol % epoxidation level in a Brabender plasticorder (PLE 330) maintaining the rotor speed at 60 rpm and the temperature at 180°C.

Melt flow studies were carried out in a capillary rheometer (MCR 3210) attached to an Instron universal testing machine. A capillary die of length/diameter (l_c/d_c) of 40, with an angle of entry of 90° was used for this study. Melts were extruded at 160, 170, 180, and 190°C for different crosshead speeds. Apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) were calculated using eqs. (1) and (2)

$$\tau_w = \frac{F}{4A_p(l_c/d_c)} \qquad (1)$$

$$\dot{\gamma}_w = \left(\frac{3n' + 1}{4n'}\right)\frac{32Q}{\pi d_c^3} \qquad (2)$$

where in (1) F is the force on the plunger, A_p is the cross sectional area of the plunger, and l_c and d_c are the length and diameter of the capillary, respectively, and in (2) the factor $((3n' + 1)/4n')$ is the Rabinowitch correction applied to calculate the true shear rate at the wall from the apparent Newtonian shear rate at the wall

$$\dot{\gamma}_a = 32Q/\pi d_c^3 \qquad (3)$$

Q is the volumetric flow rate, and n' is the uncorrected flow behavior index

$$n' = d(\log \tau_w)/d(\log \dot{\gamma}_a) \qquad (4)$$

The n' was calculated by the regression analysis by approximating the experimental $\log \tau_w - \log \dot{\gamma}_a$ plots to straight line, i.e., taking n' as independent of τ_w.

Bagley correction[6] for the pressure losses at the capillary was not applied because this correction factor becomes negligible for capillaries with high l_c/d_c ratios. No correction was also applied for the pressure drop in the barrel, although it may become important for the low values of n'. Flow

activation energy at a constant shear stress was evaluated from the viscosity–temperature dependence using the Arrhenius–Erying equation.[7]

Extrudates emerging from the capillary were collected for die swell measurements taking maximum care to avoid any further deformations. The diameter of the extrudate was measured at several points using a traveling microscope fitted with a micrometer. Due to the severe fragmentation and spiralling of the ENR extrudates, die swell measurements for ENR could not be taken and are not included in this report. The die swell ratio (D_e/D) was calculated as the ratio of the extrudate diameter at room temperature, D_e, to the capillary diameter D.

The principal normal stress difference $(\tau_{11} - \tau_{22})$ was calculated from the die swell values and shear stress according to Tanner's equation[8]

$$\tau_{11} - \tau_{22} = 2\tau_w \left[2(D_e/D)^6 - 2 \right]^{1/2} \qquad (5)$$

Recoverable shear strain (S_R) and the apparent shear modulus (G) were calculated from the following equations[9]:

$$S_R = (\tau_{11} - \tau_{22})/2\tau_w \qquad (6)$$

$$G = \tau_w/S_R \qquad (7)$$

The distortion and surface characteristics of the extrudate were studied using a scanning electron microscope (SEM). Photomicrographs of the extrudate emerged at the apparent shear rate of 122 s^{-1} were examined along the flow direction.

RESULTS AND DISCUSSION

Melt Viscosity

Shear Stress, Composition, and Temperature Dependence

Flow curves of every composition of plasticized PVC/ENR for the temperature range 160–190°C are shown in Figures 1–4, respectively. As shear stress increases, the viscosity in all cases decreases, indicating their pseudoplastic flow behavior. A salient feature in the flow behavior of PP_{100} and PP_{70} is that their viscosity rapidly falls down as the temperature increases. The effect of temperature on the viscosity of PP_{50} and PP_{30} is relatively less. As regards P_0, this effect is almost zero. It is noted that the viscosity of P_0, instead of decreasing, slightly increases with temperature. This feature is due to the possible cyclization and crosslinking of epoxy groups through the formation of ether linkage under heat and mechanical action.[4] A similar increase in melt viscosity at higher temperature has also been reported to have taken place in 1,2-polubutadiene due to the crosslinking action of the polymer.[10]

In order to illustrate the effect of blend composition on the viscosity at a constant shear stress, 2 N/m^2 and at different temperatures, a cross plot of Figures 1–4 is shown in Figure 5. The viscosity of ENR for every temperature is much higher than that of plasticized PVC. Blends have intermediate
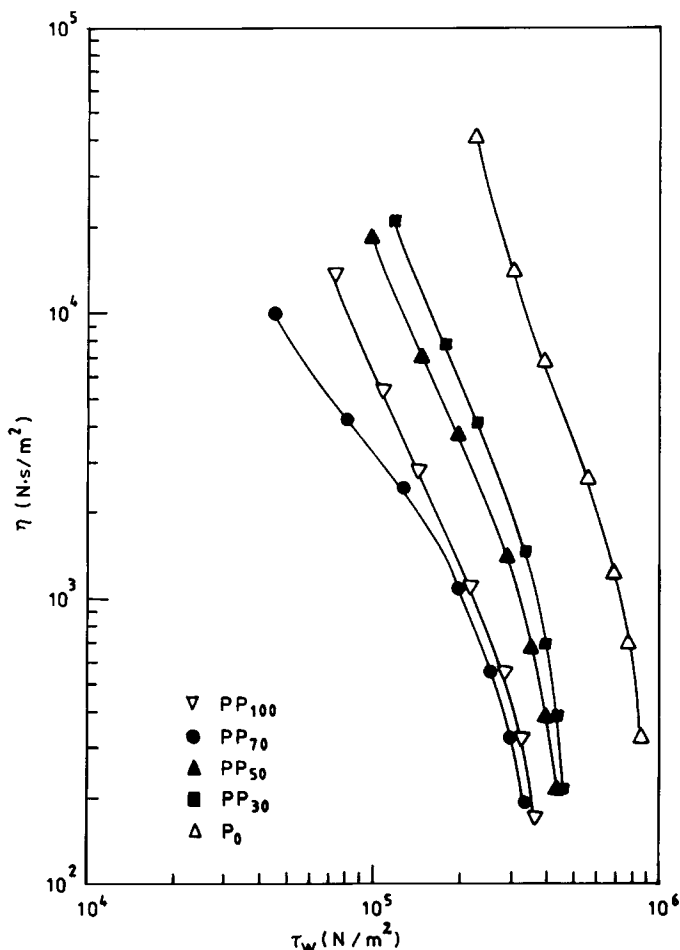
Fig. 1.   Viscosity as a function of plasticized PVC/ENR at 160°C.

viscosity behavior between the individual components except those up to a 30 wt % composition of ENR for temperatures 160 and 170°C. On the contrary, in rigid PVC/ENR systems, it has been reported[4] that the blends have lower values of viscosity at all temperatures than their individual components. A close examination in Figure 5 reveals that the viscosity of every blend at all temperatures falls below the linear additive values of plasticized PVC and ENR.

The influence of ENR in decreasing the viscosity of rigid PVC significantly[4] and plasticized PVC slightly, i.e., up to 30 wt % composition of ENR for 160 and 170°C can be understood in terms of extensive breakdown and interdiffusion of PVC particulates. These particulate structures are made up of grains 100–150 μm in size which are formed of agglomerates of 3–10 μm of 1 μm primary particles.[1-14] The interdiffusion of particles are brought about by an increase in temperature or the incorporation of plasticizers in PVC. Prior to the interdiffusion of particles, grains open up and particle aggregates rupture.
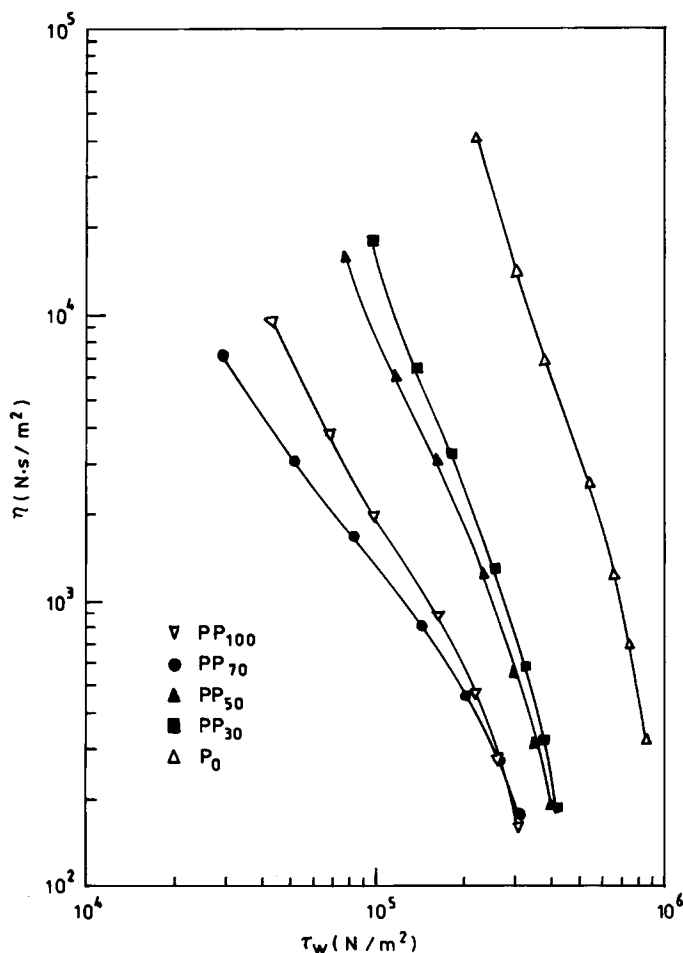
Fig. 2.   Viscosity as a function of plasticized PVC/ENR at 170°C.

Concomitantly, segmental mobility is set up in PVC chains causing rapid fall in the melt viscosity.

The molecular process associated with the particulate rupture and the subsequent setting up of segmental mobility in PVC is the dissociation of the intermolecular bonding between the C—Cl dipoles of the particulates. ENR being a compatible polymer is capable of such bond dissociation in PVC particulates. When the magnitude of this particulate dissociation is high, a rapid fall in the viscosity of PVC is noticed as in the case of rigid PVC/ENR system studied earlier.[4] The influence of PVC in ENR is to affect disentangling of ENR macromolecules, which causes a rapid fall in the melt viscosity of the ENR in blends.

The slight drop in the viscosity of plasticized PVC in blends up to the 30 wt % composition of ENR at 160 and 170°C is attributed to the effect of ENR in increasing the interdiffusion of PVC primary particles to a much greater extent than for other temperatures and compositions. At higher ENR levels,
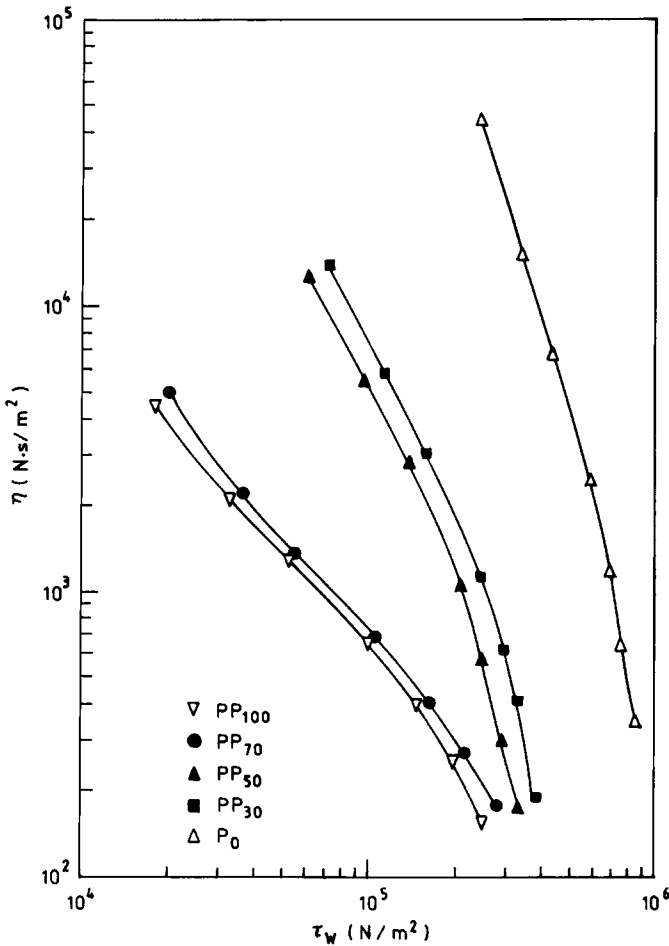
Fig. 3.   Viscosity as a function of plasticized PVC/ENR at 180°C.

the interdiffusion of primary particle due to PVC is diminished. Nevertheless, the viscosity of plasticized PVC in blends increases due to the much higher viscosity of ENR than plasticized PVC. Viscosity values of blends that are lower than their individual components indicate the improved segmental mobility in the blends of plasticized PVC and ENR.

Figure 6 is Arrhenius type plots showing viscosity–temperature dependence of plasticized PVC and plasticized PVC/ENR blends. Flow activation energies calculated from these plots are given in Table I. The flow activation energy of a polymer melt evaluated in the non-Newtonian region at a constant shear stress is important in understanding the temperature dependence.[15] the higher the flow activation energy, the more temperature sensitive is the melt. Plasticized PVC, which has the highest flow activation energy, has the highest temperature dependence of all the samples. The temperature sensitivity of plasticized PVC decreases with the addition of ENR in blends. At high ENR level the rate of decrease in temperature sensitivity is relatively negligible as understood from the flow activation energy values given in Table I. The rapid
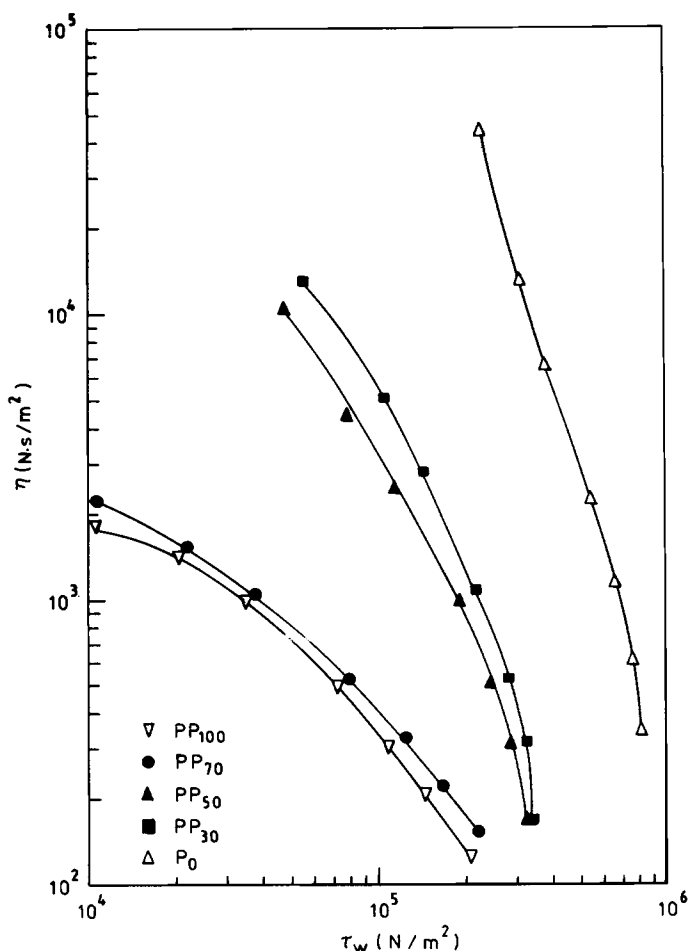
Fig. 4.   Viscosity as a function of plasticized PVC/ENR at 190°C.

fall in the viscosity of PP_{100} and PP_{70} at higher temperature as noted from their flow curves is a manifestation of their relatively higher temperature sensitivity than other samples.

In PVC, when the flow activation energy has been evaluated at a constant shear rate the existence of two types of flow has been reported by Collins and Krier.[16] At constant shear stress, they have seen only a slight evidence to such a flow behavior. The transitional flow behavior of PVC melt has also been reported by several other workers.[17-20] The transition point varies with molecular weight (K-value) temperature, shear stress, or shear rate.[16,19] In the present study, we could not observe the existence of a two type flow behavior from the Arrhenius plots made at a constant shear stress. Hence, it may be understood that the flow transition in the present PVC sample takes place at a higher temperature than the highest temperature (190°C) tested in this study. It may also be concluded that, even assuming effective distortion of the granular and aggregate structures of PVC, small primary particles still persist to an appreciable extent as reported elsewhere.[21-23]
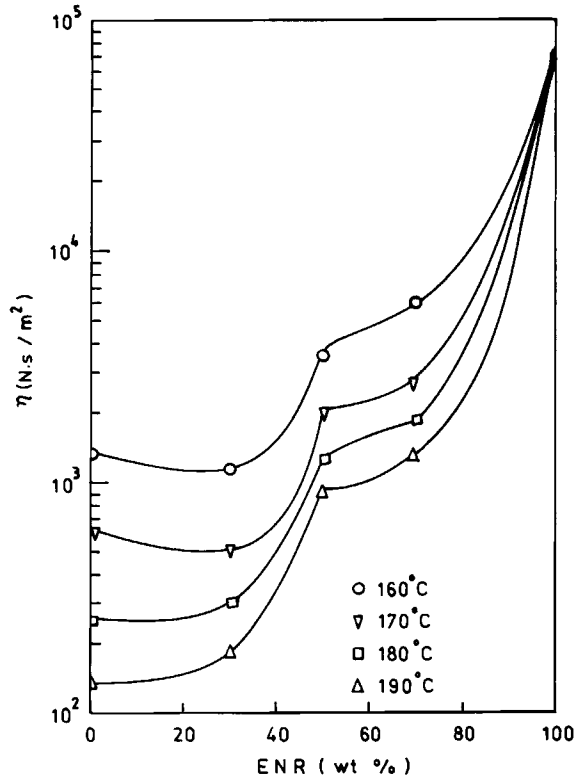
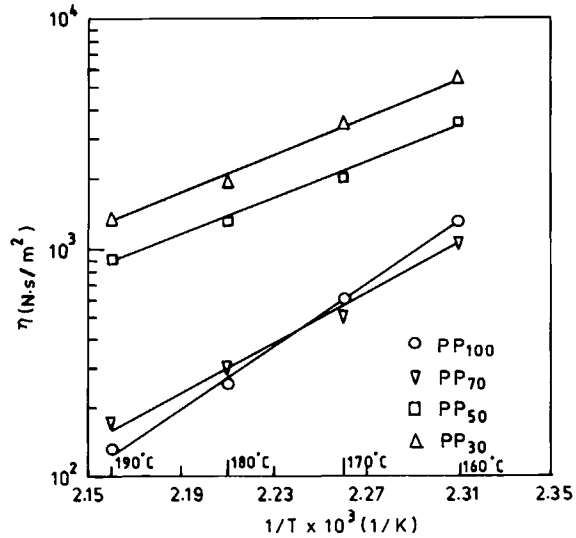Fig. 5.   Viscosity as a function of composition of PVC/ENR at a shear stress of 2×10^5 N/m^2.

Fig. 6.   Arrhenius type plots showing viscosity–temperature dependence of plasticized PVC and plasticized PVC/ENR blends at a shear stress of 2×10^5 N/m^2.

TABLE I
Flow Activation Energy of Plasticized PVC and Plasticized PVC/ENR Melts at a
Shear Stress of 2×10^5 N/m^2

Sample	PP_{100}	PP_{70}	PP_{50}	PP_{30}
Flow activation energy (kcal/mol)	31	25	19	19

Flow Behavior Index (n')

The effect of temperature and blend ratio on flow behavior index is presented in Figure 7. Non-Newtonian pseudoplastic fluids are characteristic of n' below 1. Therefore, a high value of n' indicates a low pseudoplastic or non-Newtonian nature of the polymer melt. The results indicate that the temperature effect of n' values of PP_{100} and PP_{70} are highly sensitive, PP_{50} is moderately sensitive, and PP_{30} and P_0 are relatively less sensitive. The n' of PP_{70} for temperature 160–180°C is higher and at 190°C is lower than that of PP_{100}. As the proportion of ENR increases in the blend, n' decreases as evident from the values of PP_{50}, PP_{30}, and P_0. Hence, it can be concluded that the pseudoplasticity of every PVC/ENR melt decreases with temperature, and that the high ENR blends are more pseudoplastic than the low ENR blends.

Melt Elasticity

Parameters characterizing the elasticity of polymer melts are: die swell ratio (D_e/D), which is the ratio of the extrudate diameter D_e to the capillary die diameter D; principal normal stress difference ($\tau_{11} - \tau_{22}$); recoverable shear strain (S_R); and elastic shear modulus (G). The principal normal stress difference in this study has been evaluated from values of die swell ratio and shear stress using Tanner's equation.[8] Recoverable shear strain and elastic shear modulus have been evaluated from their relations with the principal normal stress difference.[9]
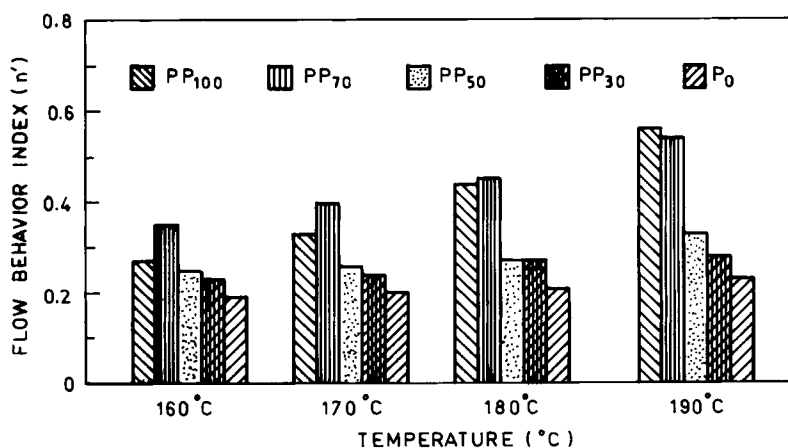

Fig. 7. Flow behavior index (n') as a function of temperature of plasticized PVC/ENR.
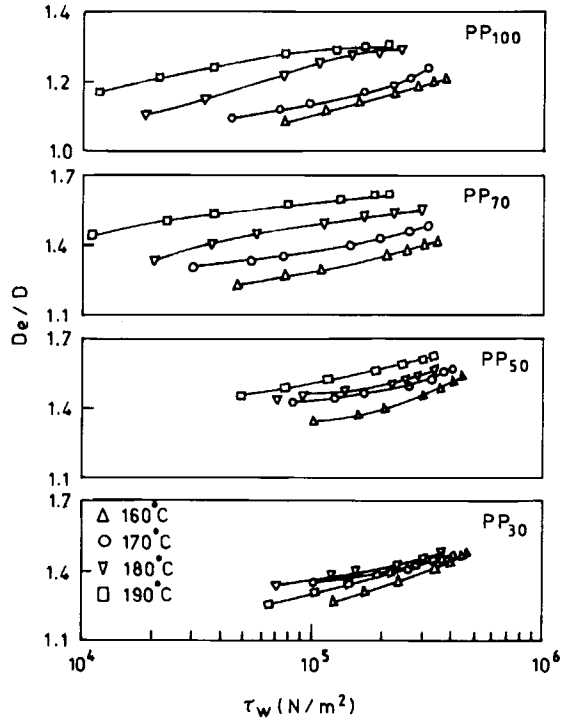
Fig. 8. Die swell ratio as a function of shear stress of plasticized PVC and plasticized PVC/ENR blends.

Die Swell Ratio

When die swell ratio is plotted against shear stress, temperature independence has been noted for several polymer melts.[24-26] On the contrary, the die swell values of rigid PVC and rigid PVC/ENR blends varied with temperature when sheer stress was held constant.[5] Similarly, plasticized PVC and plasticized PVC/ENR blends vary with temperature at a constant shear stress as evident from Figure 8. Plasticized PVC and blends up to 50 wt % composition of ENR exhibit increasing die swell ratio with increase of temperature as noted for PP_{100}, PP_{70}, and PP_{50}. In the case of PP_{30} the die swell ratio increases from 160 to 170°C followed by a decrease with further increase of temperature. This is due to the fact that the high ENR blends of plasticized PVC at higher temperatures do not have enough particulate units to undergo effective interdiffusion and cause swelling of the extrudate with increasing temperature. This was also the case for rigid PVC/ENR systems studied earlier.[5] As expected, the effect of shear stress is to increase the die swell behavior in every system.

The die swell ratio of every sample in this study is relatively less than for typical viscoelastic materials, ranging from 1.09 as minimum for PP_{100} at 160°C to 1.71 as maximum for PP_{50} at 200°C and PP_{30} at 160°C. The lowest range of die swell ratios (1.09–1.31) for the plasticized PVC does not indicate that it has a flow behavior close to Newtonian fluids, in which case the die
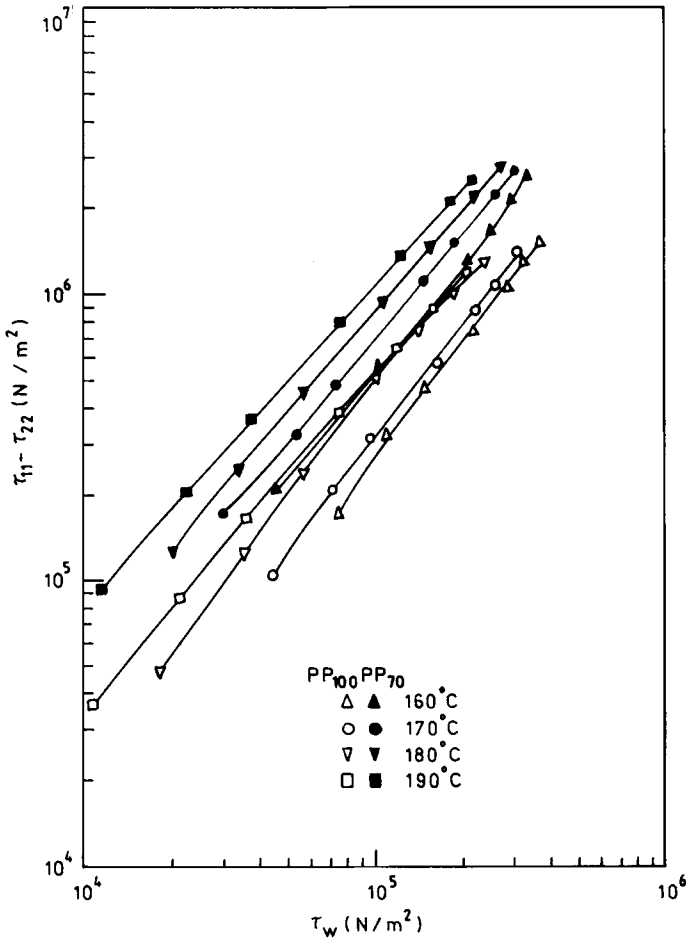
Fig. 9. Principal normal stress difference as a function of shear stress of PP_{100} and PP_{70}.

swell ratio often turns out to be 1.10. The typical non-Newtonian pseudoplastic behavior of every composition of plasticized PVC/ENR for the ranges of temperature and shear stress studied is evident from the nature of their flow curves and the lower values of flow behavior index discussed previously in this paper.

Principal Normal Stress Difference $(\tau_{11} - \tau_{22})$

Principal normal stress difference as a function of shear stress shown in Figures 9 and 10 reveal that the $\tau_{11} - \tau_{22}$ of high ENR blends at the highest temperatures are independent of temperature at any particular shear stress. PP_{100} and PP_{70}, as seen in Figure 9, exhibit an increase of normal stress difference with the rise of temperature. This trend in the case of PP_{50} continues only up to 170°C. The data points of PP_{50} above 170°C and those of PP_{30} for all temperatures fall in a single curve with the shear stress.
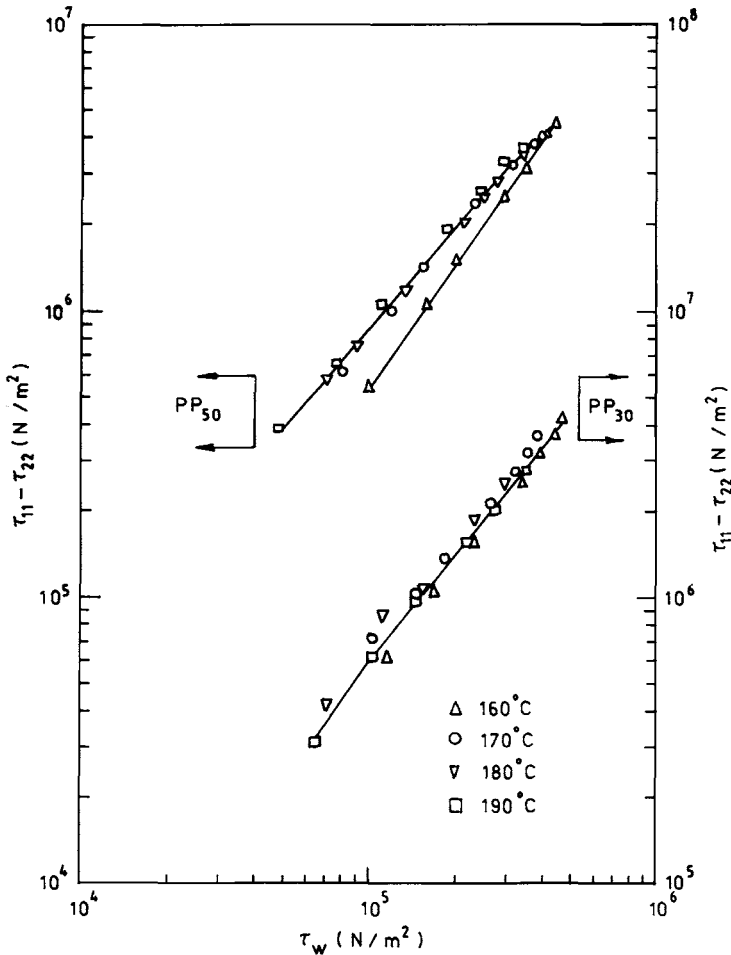
Fig. 10.   Principal normal stress difference as a function of shear stress of PP_{50} and PP_{30}.

Recoverable Elastic Shear Strain (S_R)

When the elastic shear strain energy stored in a polymer melt increases to a certain limit, the excess amount may be converted into surface free energy yielding distortion to the extrudate.[6,27,28] This limit of elastic shear strain energy is indicated by a critical value of recoverable shear strain.[28] Figures 11 and 12 are the plots of S_R as a function of shear stress. It is seen that S_R increases, with an increase of shear stress without the appearance of a critical value. However, in some cases a flex followed by a rapid increase of S_R with the shear stress is observed. The effect of temperature on S_R is similar to that of the die swell ratio. PP_{100}, PP_{70}, and PP_{50} exhibit an increase of temperature. As regards PP_{30}, S_R initially increases from 160 to 170°C and then decreases with further increase of temperature.

The rapid rise of S_R with shear stress in this study may be related to the extent of extrudate distortion of melts. This aspect will be further discussed with the results of photomicrographs of extrudates later in this paper.
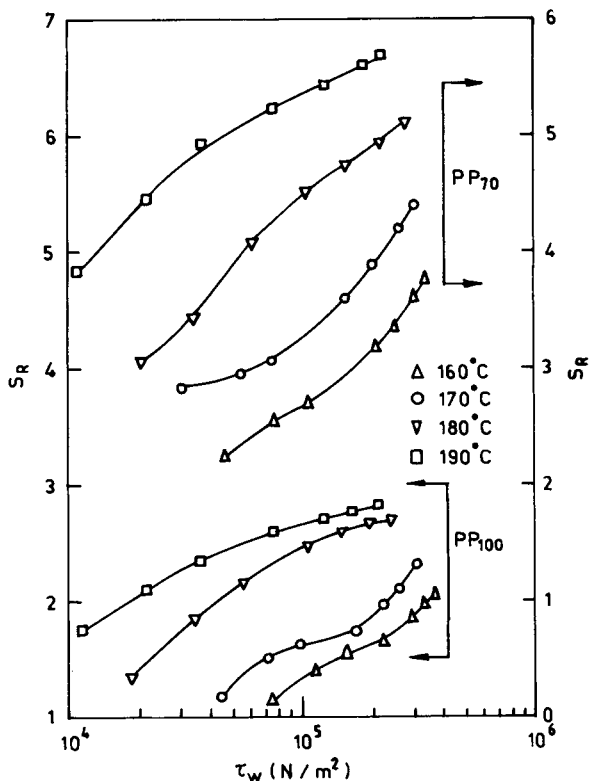
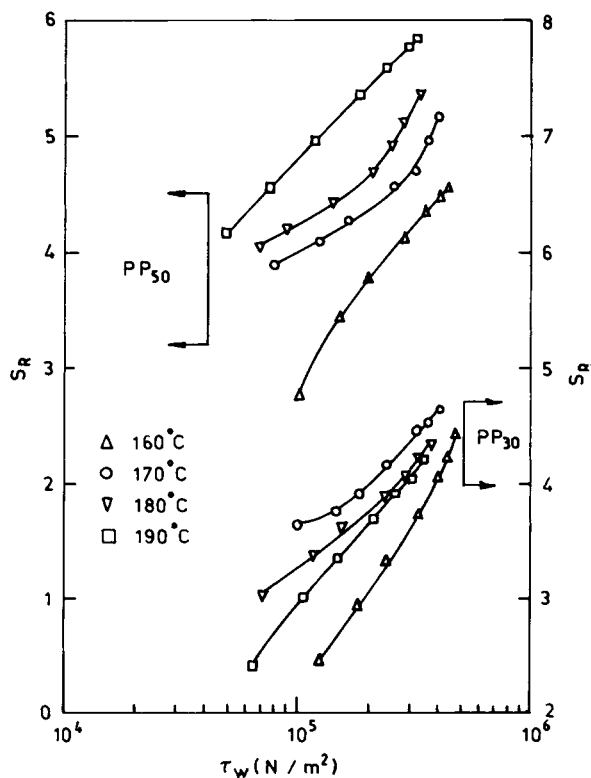Fig. 11.   Recoverable shear strain as a function of shear stress of PP_{100} and PP_{70}.

Fig. 12.   Recoverable shear strain as a function of shear stress of PP_{50} and PP_{30}.
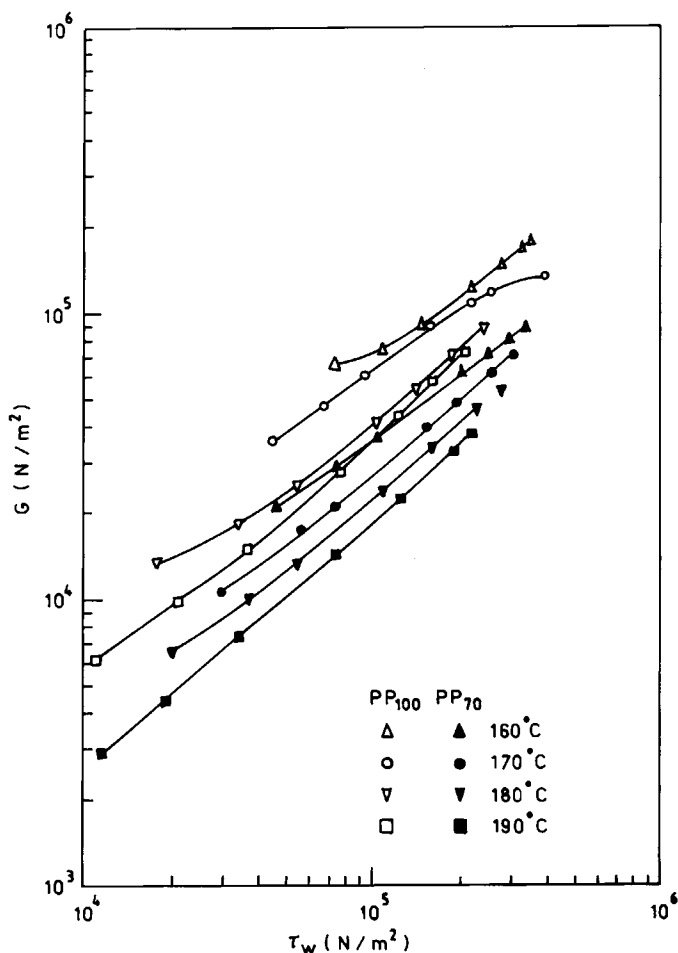
Fig. 13. Elastic shear modulus as a function of shear stress of PP_{100} and PP_{70}.

Elastic Shear Modulus (G)

As in the case of principal normal stress difference, the high ENR blends have their G values independent of temperature for every value of shear stress which is evident from the single curves of PP_{50} above 170°C and PP_{30} for all temperatures shown in Figure 14. A contrasting behavior of G from D_e/D, $\tau_{11} - \tau_{22}$, and S_R is that the former decreases with the increase of temperature and the level of ENR, as noted for PP_{100}, PP_{70}, and PP_{50} from Figures 13 and 14.

Thus we observe that the elasticity of PVC melts increases with temperature and shear stress up to a 50 wt % composition of the miscible high molecular weight substance ENR in blends, as evident from the results of die swell ratio, principal normal stress difference, and recoverable shear strain. For high ENR blends the melt elasticity becomes temperature-independent for all values of shear stress when the parameters such as principal normal stress difference and elastic shear modulus are considered.
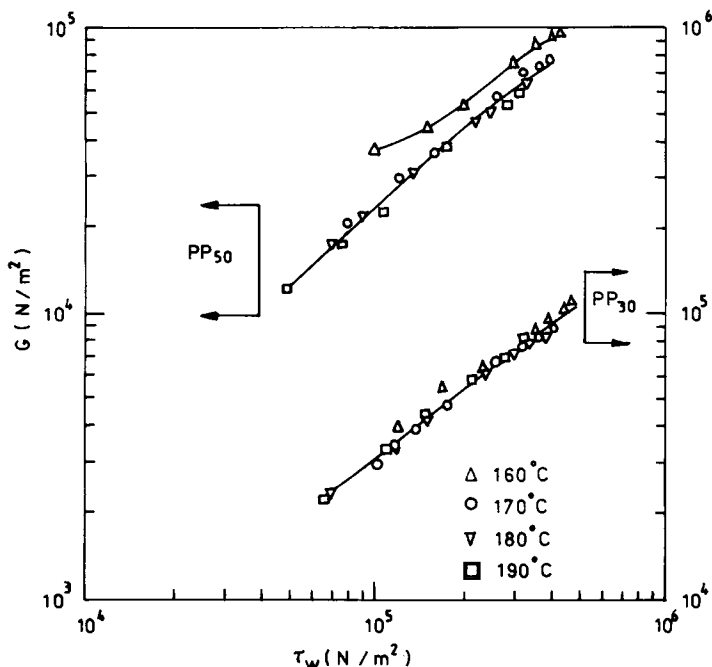
Fig. 14. Elastic shear modulus as a function of shear stress of PP_{50} and PP_{30}.

A general trend in the die swell ratio[24-26] and normal stress difference[29-31] of polymers is that these two parameters have single dependence on temperature when the shear stress is considered constant. The present study as well as our earlier observation[5] reveals that a deviation to this effect exists in PVC melts due to the particulate units influencing the rheology. Since the particulate hierarchy is diminished with the decreasing proportion of PVC in blends, a temperature-independent behavior of principal normal stress difference and elastic shear modulus for miscible blends of low PVC content is observed for any particular shear stress. Nevertheless, the die swell ratio of every composition of PVC/ENR varies with temperature and shear stress. However, it may be noted that the data points of die swell ratio of all temperatures tend to cluster with decrease of PVC content in blends at any particular shear stress.

Extrudate Characteristics

Extrudates of plasticized PVC and its blend with ENR have been tested for their surface characteristic at the $\dot{\gamma}_a$ of 122 s^{-1} by taking photomicrographs (Fig. 15–18). The extrudate deformation has been noted to increase with shear stress or shear rate. Every extrudate of plasticized PVC/ENR blends has shown surface irregularities which increases with the proportion of ENR. As regards plasticized PVC, the extrudate distortion decreases at higher temperature as evidenced from Fig. 15. It is noted that the extrudate surface of plasticized PVC appears to be distorted at 160°C and smooth at 180°C. The increasing extrudate distortion with the incorporation of ENR in plasticized PVC is attributed to the decreasing melt strength and the increasing viscosity due to the soft rubbery nature of ENR. For instance, PP_{70} (Fig. 16) exhibits a
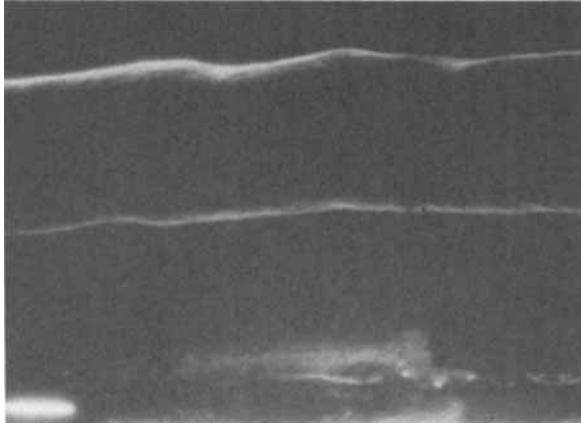
(a)
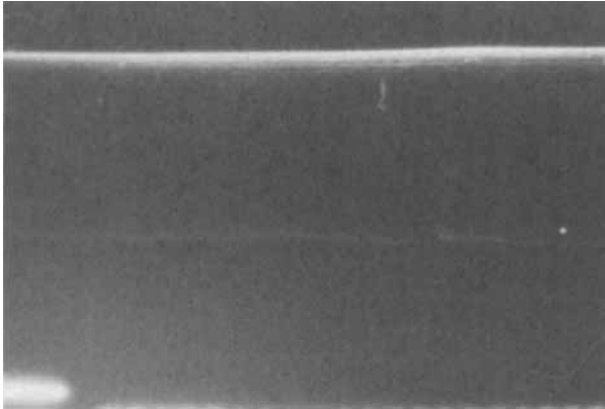
(b)

Fig. 15.   Photomicrographs of the extrudate surface of PP_{100} at: (a) 160°C ($\times 25$); (b) 180°C ($\times 25$).

higher order of extrudate distortion at 180°C, while PP_{100} [Fig. 15(b)] at the same temperature has a smooth surface.

In order to get an insight into the microstructure of the extrudate surface, photomicrographs of higher magnification have been studied in SEM. Figures 17 and 18 are the highly magnified photomicrographs of PP_{100} and PP_{50} extruded at 180°C. The microstructure of the smooth extrudate surface of PP_{100} exhibits oriented features of a smoothly flowen melt along the flow direction. For the distorted extrudate, which has higher melt viscosity than the smooth one, the microstructure reveals a randomly wrinkled surface layer as is evident for PP_{50} in Figure 18. These evidences suggest that the nature of deformation of the surface layer in polymer melts is linear for a smooth extrudate and nonlinear for a distorted extrudate.
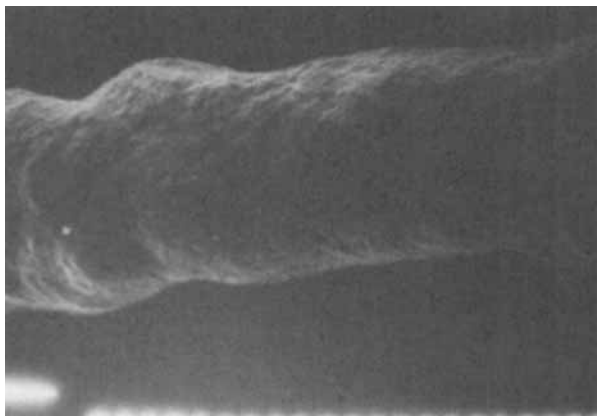
Fig. 16.   Photomicrographs of the extrudate surface of PP_{70} at 180°C (×25).

While the extrudate distortion has strong influence as viscosity and strength of melts, another feature worthy of mention in this study is an interesting dependence of the extent of extrudate distortion with the rate of rise of S_R with shear stress in Figures 11 and 12. It has been noted that a higher order in the slope or the rate of increase of S_R is accompanied by a higher degree of extrudate distortion. For instance, the smooth glossy surface characteristics of PP_{100} at 180°C shown in Figure 15(b) corresponds to a relatively slow rate of increase of S_R with shear stress in the Figure 11. On the other hand, the higher rate of increase of S_R with shear stress of PP_{100} at 160°C and blends at all temperatures is followed by a higher order in surface irregularities. A detailed mechanism of the extrudate distortion of melts, at present, from this study is not clear due to the lack of information of their melt–metal adhesion and wall slip characteristics. Failure of melt–metal adhesion and wall slip are closely related to surface irregularities of the extrudate as are evident from the recent studies.[32, 33]
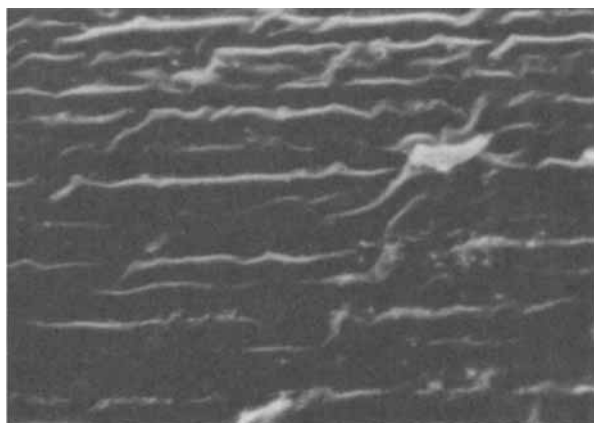

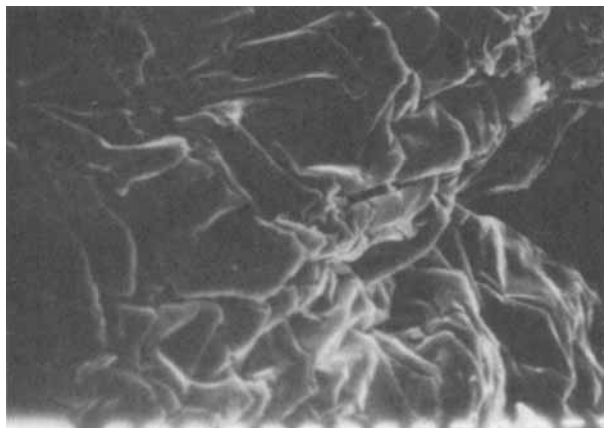Fig. 17.   High magnification photomicrograph of the extrudate surface of PP_{100} at 180°C (×400).

Fig. 18. High magnification photomicrograph of the extrudate surface of PP_{50} at 180°C ($\times$400).

CONCLUSIONS

Melt viscosity of plasticized PVC increases with the increase of ENR content in blends at higher processing temperatures. The higher melt viscosity of blends than plasticized PVC suggests better melt processability of the latter than the former. This was in contrast to the rigid PVC/ENR system studied earlier,[4] in which the processability improved in blends. As in agreement with the rigid PVC/ENR systems,[5] the melt elasticity of plasticized PVC/ENR blends at a particular shear stress increases with temperature up to the 50 wt % composition of ENR in blends, as evident from the results of die swell ratio, principal normal stress difference and recoverable shear strain. For high-ENR blends, the melt elasticity becomes temperature-independent for any value of shear stress when the parameters such as principal normal stress difference and elastic shear modulus are considered. In plasticized PVC, as the temperature increases, the extrudate surface becomes smooth. In blends, the surface irregularity was noted at all temperatures. This is because ENR decreases the melt strength and increases the melt viscosity of the extrudate. The photomicrographic study reveals that the nature of deformation in the surface layer is linear for a smooth extrudate and nonlinear for a distorted extrudate. Finally the nature of recoverable shear strain has a correlation with the extent of extrudate distortion of melts.

References

1. A. G. Margaritis and N. K. Kalfoglau, *Polymer*, **28**, 497 (1987).
2. K. T. Varughese, G. B. Nando, P. P. De and S. K. De, *J. Mater. Sci.*, **23**, 3894 (1988).
3. K. T. Varughese, P. P. De, S. K. Sanyal, and S. K. De, *J. Appl. Polym. Sci.*, **37**, 2537 (1989).
4. K. T. Varughese, P. P. De, G. B. Nando, and S. K. De, *J. Vinyl, Technol.*, **9**(4), 161 (1987).

5. K. T. Varughese, P. P. De, and S. K. Sanyal, *J. Vinyl Technol.*, **10**(4), 166 (1988).
6. E. B. Bagley, *Trans. Soc. Rheol.*, **5**, 355 (1961).
7. H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).
8. R. I. Tanner, *J. Polym. Sci.*, *A-2*, **14**(8), 2067, (1970).
9. C. D. Han, *Rheology in Polymer Processing*, Academic, New York, 1976, p. 115.
10. B. Kuriakose, *Kautschuk Gummi Kunststoffe*, **37**, 1044 (1984).
11. H. T. Kau and F. E. Filisko, *Macromolecules*, **12**, 479 (1979).
12. F. R. Kulas and N. P. Thorshang, *J. Appl. Polym. Sci.*, **23**, 1781 (1979).
13. J. A. Davidson and D. E. Witenhafer, *J. Polym. Sci.*, *Polym. Phys. Ed.*, **18**, 51 (1980).
14. J. W. Summers, J. D. Isner, and E. B. Rabinovitch, *Polym. Eng. Sci.*, **20**, 155 (1980).
15. R. S. Porter, J. Whan, and F. Johnson, *J. Polym. Sci.*, **C15**, 365 (1966).
16. E. A. Collins and C. A. Krier, *Trans. Soc. Rheol.*, **11**, 225 (1967).
17. C. L. Sieglaff, *Polym. Eng. Sci.*, **9**, 81 (1969).
18. E. A. Collins and A. A. Metzger, *Polym. Eng. Sci.*, **10**, 57 (1970).
19. L. A. Utracki, Z. B. Bakerdjain, and M. R. Kamal, *Trans. Soc. Rheol.*, **19**, 173 (1975).
20. J. J. Pena, A. Santamaria, and G. M. Guzman, *Eur. Polym. J.*, **20**, 49 (1984).
21. A. R. Berens and V. L. Folt, *Trans. Soc. Rheol.*, **11**, 95 (1967).
22. A. R. Berens and V. L. Folt, *Polym. Eng. Soc.*, **9**, 27 (1969).
23. G. Menges and N. Berndsten, *Pure Appl. Chem.*, **49**, 597 (1977).
24. D. Romanini and G. Pezzin, *Rheol. Acta*, **21**, 699 (1982).
25. J. W. Teh, A. Rudin and H. P. Schreiber, *Plast. Rubber Process. Appl.*, **4**, 149 (1984).
26. K. J. Wang and L. J. Lee, *J. Appl. Polym. Sci.*, **33**, 431 (1987).
27. J. P. Tordella, *Rheol. Acta*, **1**, 216 (1958).
28. C. D. Han and R. R. Lamonte, *Polym. Eng. Sci.*, **12**, 77 (1972).
29. K. J. Wang and L. J. Lee, *J. Appl. Polym. Sci.*, **33**, 431 (1987).
30. H. K. Chuang and C. D. Han, *J. Appl. Polym. Sci.*, **29** 2205 (1985).
31. C. D. Han and H. H. Yang, *J. Appl. Polym. Sci.*, **33**, 1199 (1987).
32. A. V. Ramamurthy, *J. Rheol.*, **30**, 337 (1986).
33. D. S. Kalika and M. M. Denn, *J. Rheol.*, **31**, 815 (1987).