Effect of EPDM rubber on melt rheology, morphology and mechanical properties of polypropylene/HDPE (90/10) blend. 2

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Melt rheology and morphology of ternary blends of polypropylene/high density polyethylene (PP/HDPE) (90/10) and ethylene–propylene–diene (EPDM) terpolymer were investigated using an Instron capillary rheometer and Weissenberg rheogoniometer. The effect of temperature and shear rate or stress on melt viscosity was also investigated. A non-Newtonian flow behaviour was observed in all the samples in the shear rate range 40–1600 s^{-1}, whereas at shear rates in the range 0.01–10 s^{-1} a Newtonian flow behaviour was observed. The morphology of the extrudates examined by scanning electron microscopy revealed the formation of agglomerates at higher concentrations of elastomer in PP/HDPE (90/10) binary blend. Impact strength of the ternary blends increased with an increase in EPDM content up to an optimum concentration ($\sim$20% w/w) of rubber.

(Keywords: melt rheology; morphology; mechanical properties; blends)

INTRODUCTION

Blends of polyolefins with ethylene–propylene–diene (EPDM) terpolymer and ethylene–propylene rubber have been extensively investigated primarily with the aim of improving tensile and impact properties[1–8]. Addition of rubber to polypropylene (PP) or high density polyethylene (HDPE) may affect crystallization behaviour and hence can affect mechanical properties. Studies on crystallization behaviour of PP and HDPE in the presence of EPDM were therefore carried out[9–11]. Addition of EPDM to HDPE resulted in an increase in nucleation, crystallization rate, percentage crystallinity and heat of crystallization whereas blending of EPDM with PP resulted in a delayed nucleation and did not influence the heat of crystallization. The observed difference in the crystallization behaviour of these two commercially important polymers (PP and HDPE) in the presence of EPDM may be attributed to the low C_3 content in EPDM. In blends of PP/HDPE, addition of EPDM only marginally affected the crystallization behaviour of PP, whereas nucleation was observed for HDPE crystallization[11]. The variation in crystallinity on addition of EPDM may affect the mechanical properties of these blends and will also affect the melt rheology which is an important parameter from the processing point of view. Therefore, in the present work, a systematic study has been carried out to investigate the effect of the incorporation of varying amounts of EPDM on morphology, melt rheology and mechanical properties of the PP/HDPE binary blend.

EXPERIMENTAL

Isotactic PP (Koylene M 3030) was obtained from the Indian Petrochemical Corporation Ltd (melt flow index 3.0 g per 10 min) and HDPE (Hostalene GD-7250, melt flow index 6.5 g per 10 min) and EPDM rubber (NORDEL-1560) were obtained from DuPont. The ethylene content of the rubber was $\sim$80 wt% and a small amount of 1,4-hexadiene was also present.

Preparation of blends

A Betol single screw extruder (length/diameter = 19.47) was used for melt blending the binary PP/HDPE (90/10) blend containing different weight percentages of EPDM: 0 (sample A′), 5 (sample A), 10 (sample B), 15 (sample C), 20 (sample D) and 25% (sample E) (w/w). The detailed conditions used for blending have been described elsewhere[11].

The chopped granules obtained after blending were dried in a vacuum oven at 70°C for 4 h and then stored in plastic bags in a desiccator containing anhydrous $CaCl_2$. The samples were then used for melt flow measurements.

Flow behaviour of blends at 180, 200 and 215°C was investigated using a MCR capillary rheometer attached to an Instron model 1112 having a capillary length/diameter ratio = 20 at shear rates ranging from 40 to 1600 s^{-1}. A Weissenberg rheogoniometer (model R-18) was used for shear rates in the range 0.01–10 s^{-1}. The true shear stress at the wall (τ_w), true shear rate at the wall ($\dot{\gamma}_w$) and melt viscosity (η) were calculated using standard procedures[12].

Extrudates of the polymer blends exiting out of the capillary (length/diameter = 20) at a shear stress of $\sim 6 \times 10^4$ N m^{-2} and 200°C were investigated to study the state of dispersion of the rubber phase using a Stereoscan S4-10 scanning electron microscope. The cryogenically fractured extrudates were etched in cyclohexane for 1 h at room temperature and then sprayed with fresh cyclohexane to remove the EPDM inclusions. These samples were then mounted on a base

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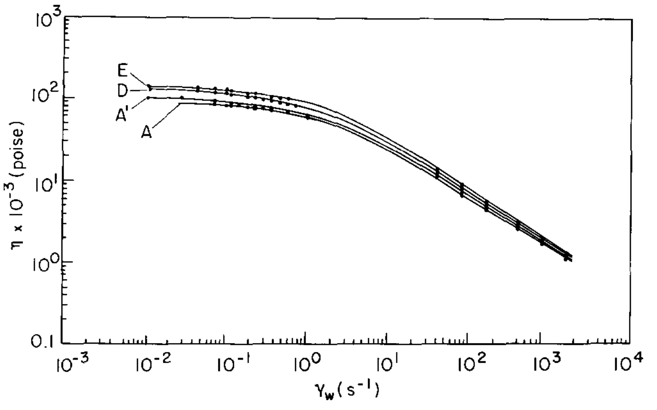

Figure 1 Variation of melt viscosity, η, with shear rate at 215°C for samples A', A, D and E

Table 1 Results of melt viscosity of PP, HDPE and ternary PP/HDPE/EPDM blends at 200°C (length/diameter = 20)

Sample designation	Shear stress, τ_w ($\times 10^{-4}$) (N m^{-2})	Shear viscosity, η ($\times 10^{-3}$) (poise)	Theoretical viscosity, $\ln \eta_b = \sum w_i \ln \eta_i$
PP	8	3.75	–
	14	1.50	
	22	0.70	
HDPE	8	5.60	–
	14	3.54	
	22	2.48	
A'	8	5.10	3.90
	14	2.00	1.63
	22	0.94	0.85
A	8	4.50	4.52
	14	1.80	1.92
	22	0.85	0.94
B	8	5.00	5.23
	14	2.00	2.26
	22	0.99	1.12
C	8	6.00	6.64
	14	2.30	2.66
	22	1.10	1.33
D	8	6.10	7.03
	14	2.30	3.14
	22	1.07	1.58
E	8	6.60	8.14
	14	2.50	3.70
	22	1.15	1.89

plate and coated with silver by using the vapour deposition technique prior to scanning.

The tensile and impact properties of various injection-moulded samples were determined using an Instron tensile tester (model 1121) and Izod impact tester (model IT-0.42, Fuel Instruments & Engineers Pvt Ltd), respectively. The detailed conditions of testing the mechanical properties have been described elsewhere[10].

RESULTS AND DISCUSSION

Variation of η with shear rate at 215°C for various polymer samples is shown in *Figure 1*. The results of η obtained at 200°C for different values of shear stress are summarized in *Table 1*. Similar behaviour was observed at different temperatures. At any given temperature, η decreased linearly with increasing shear rate, i.e. 40–1600 s^{-1}. However, at lower shear rates, i.e. in the range 0.01–10 s^{-1}, only a marginal change in η was observed (*Figure 1*). Thus in these samples, a non-Newtonian flow behaviour was observed in the shear stress range studied of $\sim 8 \times 10^4$–22×10^4 N m^{-2} (*Table 1*).

A linear relationship between the shear stress (τ_w) and shear rate ($\dot{\gamma}_a$) was observed in the shear rate range 40–1600 s^{-1}, thereby confirming the validity of the power law relationship. Values of the power law exponent (n) of ternary blends were in the range 0.27–0.52 indicating pseudoplastic behaviour of the melt at these temperatures (*Table 2*). The blend composition had an insignificant effect on the value of n. The activation energy for viscous flow was calculated from $\log \eta$ *versus* the reciprocal of temperature, T^{-1}, plots and the values are given in *Table 2*. No systematic variation in activation energy with blend composition was observed.

Zero shear viscosity of ternary blends could be obtained from Weissenberg rheogoniometric data at 215°C as shown in *Figure 2*. It is clear from this plot that up to an addition of 15% rubber to the PP/HDPE (90/10) blend, the viscosity of the ternary blend was lower than that of the binary PP/HDPE blends.

The effect of blend composition on η at different temperatures and shear stresses is shown in *Figure 3*. Addition of 5% rubber to binary PP/HDPE blend (sample A') resulted in a decrease in η in the shear stress range $\sim 6 \times 10^4$–14×10^4 N m^{-2}. However at higher shear stress, i.e. 14×10^4 N m^{-2} no decrease in η of

Table 2 Values of power law exponent, n, and activation energy of viscous flow for various samples

Sample designation	Power law exponent, n			Activation energy (kJ mol^{-1})	
	180°C	200°C	215°C	$\tau_w = 6 \times 10^4$ N m^{-2}	$\dot{\gamma}_w = 40$ s^{-1}
PP	0.29	0.37	0.39	50.49	42.16
HDPE	0.54	0.54	0.44	24.49	12.89
A'	0.24	0.40	0.34	106.34	70.00
A	0.26	0.38	0.38	72.01	68.87
B	0.28	0.40	0.39	69.08	49.90
C	0.27	0.37	0.40	80.80	56.85
D	0.27	0.36	0.38	69.08	52.46
E	0.27	0.36	0.35	87.08	58.19

the binary blend was observed on addition of EPDM. Increase in rubber content from 10 to 25% resulted in an increase in viscosity of these blends at all shear stresses.

Theoretical values of viscosity at a constant shear stress were evaluated for various blends using the log additivity principle[13] and the values are given in *Table 1*. In the concentration range 5–15%, the calculated and observed values were similar whereas at higher rubber concentration (> 15%), a negative deviation from the log additivity rule was observed indicating a phase separation of these blends.

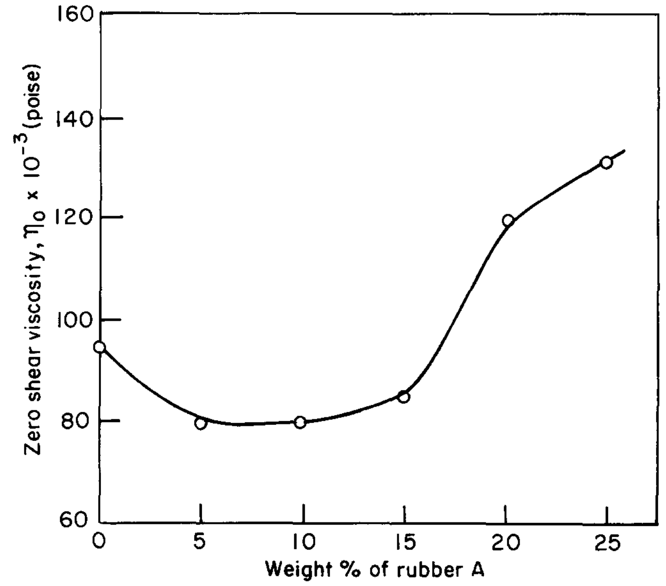

Figure 2 Composition dependence of zero shear viscosity, η_0, of ternary blends at 215°C (Weissenberg rheogoniometric data)

These results indicate that the EPDM at low concentration acts as a compatibilizer for the binary PP/HDPE (90/10) blend. When small amounts of EPDM and HDPE are added to PP, it is possible that EPDM functions as an emulsifier at the surface of HDPE particles[6] and the two additives have a tendency to form composite EPDM–HDPE particles in the PP matrix[14]. At higher concentration, (samples D and E) agglomerates of EPDM may be formed leading to separate phases.

The effect of shear rate on η of various samples was also investigated. However, these results were not a true replica of shear stress data. It is well established that shear stress should be used as a parameter instead of shear rate in correlating viscoelastic properties of polymer fluids, at least over certain ranges of conditions. This is because in two- or three-phase flow, shear rate may not be continuous whilst shear stress may be continuous at the phase interface[15].

Extrudate distortion in ternary blends was investigated at different shear stresses at 200°C (length/diameter = 20). Extrudates exiting out of the capillary at different shear stresses are shown in *Figure 4*. In sample A, as the shear stress was increased above $\sim 18 \times 10^4$ N m^{-2}, the melt fracture or extrudate

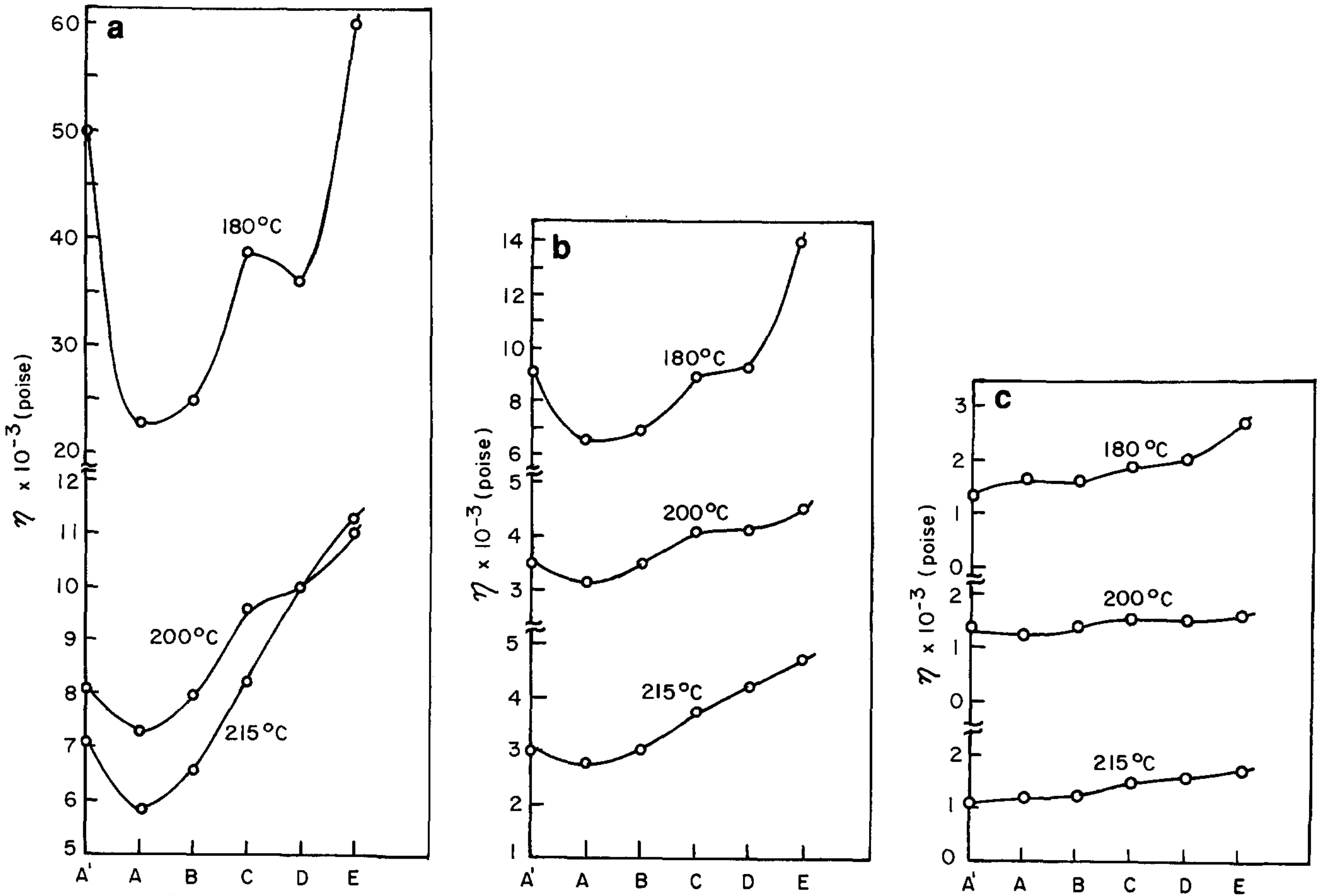

Figure 3 Variation of melt viscosity, η, with blend composition at different shear stresses and temperatures. Shear stress (N m^{-2}): (a) 6×10^4; (b) 10×10^4; (c) 18×10^4

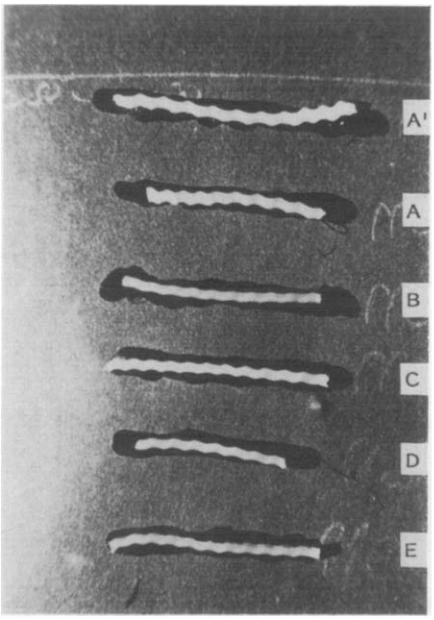

Figure 4 Effect of rubber concentration on extrudate distortion in ternary blends ($\tau_w \sim 22 \times 10^4$ N m^{-2}, 200°C, length/diameter = 20)

distortion began appearing (*Figure 4*). On increasing the rubber content from 5 to 25% in ternary blends at a shear stress of $\sim 22 \times 10^4$ N m^{-2}, the severity of extrudate distortion and the diameter of the extrudate decreased, but even at a level of 25% rubber (sample E), extrudate distortion did not disappear completely. Tendency to melt fracture decreased as the temperature was increased from 180 to 215°C at a fixed composition and shear stress in ternary blends.

Scanning electron micrographs of the cryogenically fractured and etched surfaces of the extrudates obtained at a shear stress of $\sim 6 \times 10^4$ N m^{-2} and at 200°C were examined (*Figure 5*). The micrographs of the binary PP/HDPE blend show the occurrence of a discrete phase of HDPE as droplets sticking to the surface of the PP matrix. These droplets are quite uniformly distributed inside the PP matrix. On addition of EPDM to the binary blend, EPDM and HDPE form composite EPDM–HDPE particles within the PP matrix[14]. This gives a very characteristic morphology to the ternary PP/HDPE/EPDM blends.

There are both empty holes and partly filled holes in the micrographs. Partly filled holes are due to HDPE which remained attached to the PP matrix even after etching of the rubber shell enveloping the HDPE component. The micrographs of the ternary blends, especially those containing a large EPDM content, are conspicuous by the absence of discrete HDPE droplets. It was observed that the size and number of these droplets increases on increasing the percentage of EPDM in the blends.

The effect of blend composition on the tensile and impact properties of ternary (PP/HDPE/EPDM) blends is shown in *Figure 6*. Young's modulus and tensile strength at yield decreased with increasing concentration of EPDM in PP/HDPE blends (*Table 3*). A significant improvement in Izod impact strength and percentage elongation was observed. Such an effect may be related to the fact that the overall morphology[6] as well as mechanism and mode of fracture were greatly modified by the presence of such an additive. Since PP/HDPE blends are incompatible, addition of a compatibilizer such as EPDM is expected to improve the performance characteristics.

Incorporation of 5% rubber to binary blend resulted in a decrease in the percentage elongation at break (*Table 3*). Further addition of rubber to binary blend increased the percentage elongation at break. A significant improvement ($\sim$620%) in impact strength was observed upon addition of $\sim$20% of EPDM to binary blend. Further addition resulted in a decrease in the impact strength.

CONCLUSIONS

On the basis of this study, it can be concluded that EPDM in the concentration range 5–10% (w/w) helps in the

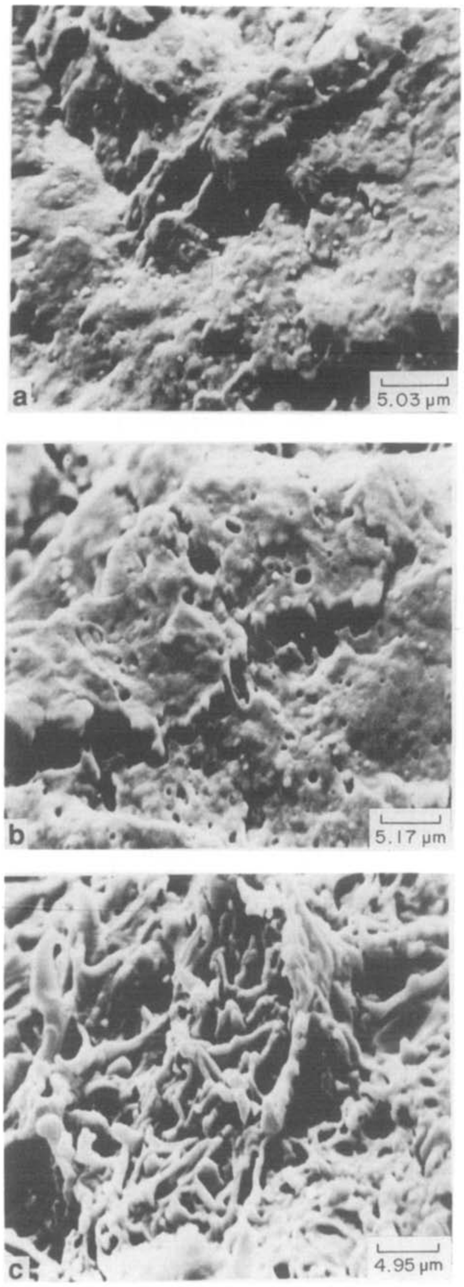

Figure 5 Scanning electron micrographs of etched extrudate surfaces of binary PP/HDPE (90/10) and ternary PP/HDPE/EPDM blends. (a) Sample A'; (b) sample B; (c) sample D

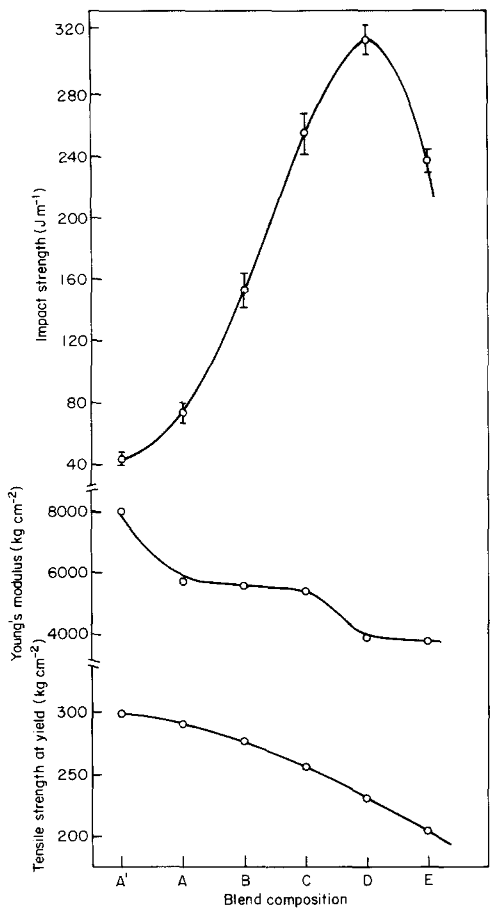

Figure 6 Composition dependence of mechanical properties of ternary blends

Table 3 Results of tensile mechanical and impact properties of ternary PP/HDPE/EPDM blends

Sample designation	Young's modulus $(kg\,cm^{-2})$	Tensile strength $(kg\,cm^{-2})$	Elongation at break (%)	Izod impact $(J\,m^{-1})$
PP	6500	318	372	25
HDPE	4100	197	612	84
A'	8000	298	354	44
A	5700	289	294	74
B	5600	276	320	153
C	5400	256	424	256
D	3900	231	618	316
E	3800	202	800	238

compatibilization of isotactic PP/HDPE (90/10) binary blends as is reflected from viscosity data and scanning electron microscope studies. However at higher EPDM concentrations, agglomerates of EPDM lead to the formation of larger domains thereby increasing the viscosity of the blend.

A significant improvement in the impact strength was observed on addition of EPDM rubber.

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