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Rheological behaviour and extrudate morphology of thermoplastic elastomers from natural rubber and high density polyethylene

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Abstract. The rheological behaviour of blends of high density polyethylene and natural rubber has been examined with reference to the effect of blend ratio, dynamic crosslinking and carbon black filler. The dependence of shear viscosity, flow behaviour index (n') and extrudate deformation of the blends on temperature and shear rate has been studied. The shear viscosity of these blends is influenced more by shear rate than by temperature. Processing temperatures are not critical, particularly in the lower ranges, as can be seen from n' values (flow behaviour index) up to 160°C; n' increases with increase in temperature. The morphology of the extrudates of the blends has been examined by scanning electron microscopy at different shear rates at 150°C. The morphology was found to depend on the blend ratio and the shear rate.

1 Introduction

Thermoplastic elastomers are gaining industrial importance because such blends combine the ease and economy of processing of thermoplastic resins with the mechanical properties of vulcanized rubbers. They are prepared by melt mixing of a thermoplastic and an elastomer under high shearing action. Systematic melt flow studies of such materials are necessary for optimizing the processing conditions and for developing suitable equipment. Since these blends can be injection moulded or extruded their melt viscosity, melt fracture and extrudate deformation also need to be examined as functions of (1) shear stress, (2) temperature and (3) composition.

Some studies on the rheological behaviour of blends of thermoplastics and elastomers have been reported.[1-6] This paper examines the rheological characteristics of natural rubber (NR)–high density polyethylene (HDPE) blends by capillary rheometry. The effects of dynamic crosslinking, blend ratio and addition of carbon black have been studied. In addition, the morphology of the extrudates has been examined in order to understand how the blend morphology is influenced by rheological parameters.

2 Experimental

Formulations of the blends are given in Table 1. Blends of NR and HDPE were prepared in a Brabender Plasticorder model PLE 330, using a cam-type mixer with a rotor speed of 60 rpm and the mixer temperature set at 150°C. HDPE was melted in the mixer for 2 min and then NR, as such or in a masterbatch, was added and the mix was allowed to blend for 4 min. At the end of 6 min curative (DCP) in the form of a masterbatch was added and the mixing continued for 2 more min. The mix was then taken out and sheeted through a laboratory mill at 2 mm nip setting. The sheeted out stock was cut into small pieces and re-mixed in the plasticorder at 150°C for 1 min and then finally sheeted out on the

Table 1. Formulations of the mixes

Mix	A	B	C	C_c	C_b
HDPE[a]	70	50	30	30	30
NR[b]	30	50	70	70	70
DCP[c]	—	—	—	1·0	—
HAF[d]	—	—	—	—	40

[a] Hostalen GA 7260, obtained from Polyolefin Industries Limited, Bombay.

[b] Crumb rubber ISNR 5 grade, obtained from the Rubber Research Institute of India, Kottayam.

[c] Di-cumyl peroxide (40%), supplied by Bengal Waterproof Limited, Panihati. DCP loading was based on the rubber phase only.

[d] High abrasion furnace black (N330), obtained from Phillips Carbon Black Limited, Durgapur. HAF loading was based on the rubber phase only.

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mill once again. This second step was found necessary for uniform dispersion of the ingredients.

The melt flow measurements were carried out using a capillary rheometer MCR 3210 attached to an Instron Universal Testing Machine model 1195 and a capillary of length to diameter ratio (l_c/d_c) 40 with an angle of entry of 90°. The sample for testing was placed inside the barrel of the extrusion assembly and forced down to the capillary with the plunger attached to the moving crosshead. After a warming-up period of 5 min the melt was extruded through the capillary at pre-selected speeds of the crosshead which varied from 0·5 to 500 mm min^{-1}. The melt height in the barrel before extrusion was kept the same in all the experiments and the machine was operated to give five different plunger speeds from lower to higher speed, with a single charge of the material. Forces corresponding to specific plunger speeds were recorded using a strip chart recorder assembly. The force and crosshead speed were converted into apparent shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) at the wall by using the following equations involving the geometry of the capillary and the plunger:

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

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

where F is the force applied at a particular shear rate, A_p is the cross-sectional area of the plunger, l_c the length of the capillary, and d_c the diameter of the capillary. Q, the volume flow rate, was calculated from the velocity of the crosshead and the diameter of the plunger. n' is the flow behaviour index defined by $n' = \mathrm{d}(\log \tau_w)/\mathrm{d}(\log \dot{\gamma}_{wa})$ and was determined by regression analysis of the values of τ_w and $\dot{\gamma}_{wa}$ obtained from the experimental data. $\dot{\gamma}_{wa}$ is the apparent wall shear rate calculated as $32Q/\pi d_c^3$. The shear viscosity, η was calculated from τ_w and $\dot{\gamma}_w$.

The extrudates were fractured under liquid nitrogen and the morphology of the extrudate cross-section was examined with the help of scanning electron microscopy after removing the rubber phase with nitric acid; this did not affect the thermoplastic phase.

3 Results and discussion

Figure 1 shows the viscosity versus shear stress curves for HDPE, NR and their blends at 150°C. The viscosity of all the blends decreases monotonically with increasing shear stress, showing the pseudoplastic behaviour of the blends. Although at low shear stresses the viscosity of the blend increases with increasing proportion of rubber in the blend, at high shear stresses the curves converge as the difference in the viscosities of the blends decreases. This is true for all blend ratios.

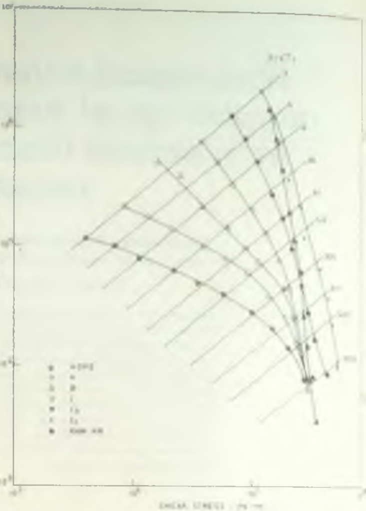

Fig. 1 Viscosity shear stress plots for NR–HDPE blends at 150°C.

The effect of polyethylene content on the viscosity is shown in Fig. 2. It can be seen that up to a shear rate of 30 s^{-1}, the viscosity of the blend decreases with increasing HDPE content. However, at a shear rate of 120 s^{-1} the viscosity of HDPE exceeds that of NR and the curves show a maxima at a 70 NR–30 HDPE blend ratio. At 3 000 s^{-1} the trend is completely reversed as compared to that at 3 s^{-1}. Another feature which can be seen from Fig. 2 is that at most shear rates the viscosity of the blend appears to be a non-additive function of the viscosity of the homopolymers. Only at a shear rate of 30 s^{-1} do the experimental viscosity values coincide with those predicted by simple linear additivity. It has been reported earlier that the viscosity of polyisoprene–polybutadiene (rubber–rubber) blends and polystyrene–polyethylene (plastic–plastic) blends cannot be predicted by simple linear additivity. In general, the viscosity of NR–HDPE blends also does not follow this principle. Figure 3 shows the viscosity as predicted by Hashin's model.[9] Hashin, using variational principles similar to those used successfully for the prediction of limits for the modulus

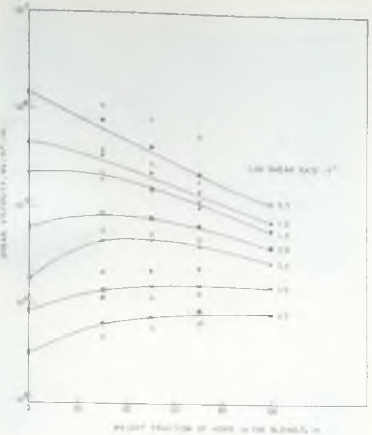

Fig. 2 Shear viscosity versus HDPE content in the blends at different shear rates at 150°C. ●, ▲, ▼, ■, ×, ◐ and ◆ are experimental values and ○, △, ▽, □, *, ⊙ and ◇ are calculated.

of elasticity of composite materials, obtained the viscosity of Newtonian fluid mixtures. The limits are as follows

$$\text{Upper limit } \eta_{\max} = \eta_2 + \frac{\phi_1}{1/(\eta_1 - \eta_2) + 2\phi_2/5\eta_2}$$

$$\text{Lower limit } \eta_{\min} = \eta_1 + \frac{\phi_2}{1/(\eta_2 - \eta_1) + 2\phi_1/5\eta_1}$$

where η_1 and η_2 are the viscosities of the two components of a blend and ϕ_1 and ϕ_2 their weight fractions respectively. For non-Newtonian fluids the coefficient 2/5 in the denominator is replaced by 1/2. We tested Hashin's model for NR–HDPE blends at a shear stress = $1{\cdot}5 \times 10^7$ Pa at 150°C and found that the experimental values lie exactly on the lower limit of the Hashin model. It is interesting to note that the curve corresponding to the expression derived from inverse additivity lies much below while that predicted by linear additivity lies above the experimental points.

Figure 4 shows the effect of temperature on the shear viscosity of NR–HDPE blends at different shear rates. The viscosity of all the blends drops with increasing temperature; at low shear rates the high rubber blends have higher viscosities. At high shear rates the blends display the same viscosity values at all temperatures irrespective of the blend ratio and pure HDPE shows higher viscosity than pure NR. At low shear rates both NR and black filled high rubber blend show similar viscosity values, but at high shear rates the black filled high rubber blend shows higher viscosity than NR at all temperatures. At all shear rates the black filled blend shows a higher viscosity

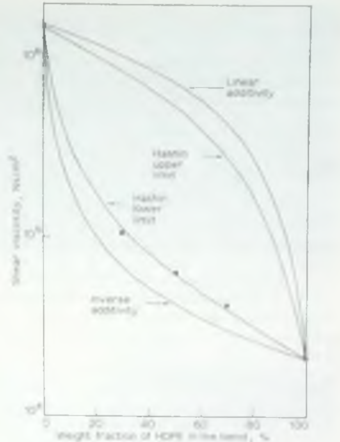

Fig. 3 Shear viscosity as predicted by Hashin's model versus weight fraction of HDPE in the blend at 150°C at a shear stress of 1.5×10^7 Pa.

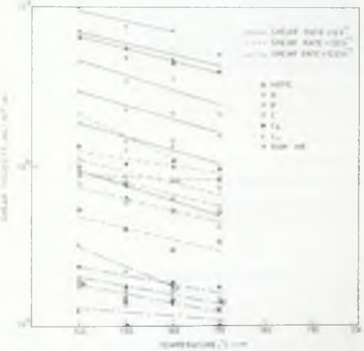

Fig. 4 Shear viscosity versus temperature at different shear rates.

than the unfilled blend. The dynamically crosslinked blend shows the highest viscosity at all temperatures and shear rates.

Table 2 shows the effect of temperature on the flow behaviour index (n') of the blends. Both unvulcanized NR and HDPE individually show a discernible increase in n' with increasing temperature. On the other hand, their blends show only a marginal increase in n' up to 160°C, but at 170°C they register a slightly higher value. The black filled blend shows a gradual and regular increase in n' with temperature. In sharp contrast, the blend containing DCP shows a regular decrease with increasing temperature. This behaviour can be explained in the following way: it has been found in unvulcanized rubber that an increase in gel content leads to an increase in the viscosity.[10] Partial crosslinking of the rubber produces an increase in the gel content and hence the viscosity is higher for the crosslinked blend (Fig. 1). Further, during dynamic vulcanization of blends the gel content increases with increasing temperature because the crosslinking increases, hence the flowability decreases with increasing temperature. In the case of the crosslinked blend, the flow became very erratic at 170°C and the viscosity could not be determined accurately.

Figure 5 shows the variation in extrudate swell with rubber content in NR–HDPE blends at three different shear rates. The extrudate swell is least in the case of 30 NR–70 HDPE blend at all the shear rates examined. The extrudate deformation characteristics are shown in Fig. 6. The 30–70 and 50–50 NR–HDPE blends show a little extrudate deformation at the high shear rate only. The 70–30 NR–HDPE blend shows typical melt fracture at the lowest shear rate. This phenomenon is anticipated since HDPE tends to form a sheath in the extrudate due to its lower viscosity. This will be discussed later in this paper. The thin film gets fractured at the die head as the extrudate leaves the capillary at a slow extrusion rate and appears as flakes on the extrudate surface. The black filled blend also shows a similar phenomenon at the low shear rate, but is comparatively smooth at other shear rates. The most pronounced extrudate deformation is shown by the crosslinked blend at all shear rates: knotty bead like structures appear on the surface of the extrudate and the surface is no longer smooth. This type of extrudate distortion is called random fracture.[11] Shear rate does not have much influence on the extrudate deformation in this blend (C_c).

Table 2. Flow behaviour index n'

Sample	Temperature, °C 140	150	160	170
HDPE	0·63	0·63	0·79	0·71
A	0·51	0·53	0·54	0·62
B	0·41	0·43	0·44	0·49
C	0·31	0·31	0·34	0·42
Raw NR	0·13	0·10	0·27	0·18
C_c	0·28	0·22	0·18	—[a]
C_b	0·29	0·27	0·32	0·34

[a] Due to erratic flow behaviour, the n' of the C_c could not be determined accurately at this temperature.

3.1 Morphology of the blends

Figures 7, 8 and 9 show the extrudate cross-section morphology of the 30 NR–70 HDPE blend at three different shear rates, viz. 12, 122 and 1223 s^{-1} respectively. The holes on the surface correspond to the NR phase which has been extracted by nitric acid treatment. The NR phase appears to be distributed as particles in the continuous and dominant HDPE phase. It can also be seen that the particle size of the rubber phase decreases with increasing shear rate. It is generally accepted that the morphology of polyblends is governed by their rheologi-

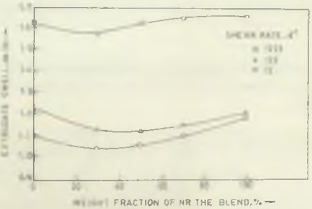

Fig. 5 Extrudate swell versus weight fraction of rubber in the blend at 150°C.

Fig. 6 Extrudate distortion in NR–HDPE blends at 150°C at different shear rates.

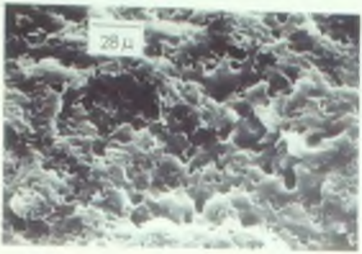

Fig. 7 SEM photomicrograph of blend A (30 NR–70 HDPE) extruded at a shear rate of $12 s^{-1}$

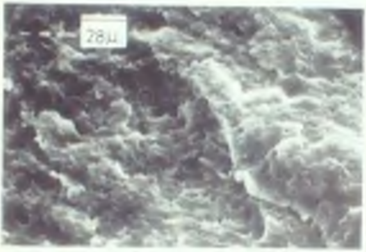

Fig. 8 SEM photomicrograph of blend A (30 NR–70 HDPE) extruded at a shear rate of $122 s^{-1}$

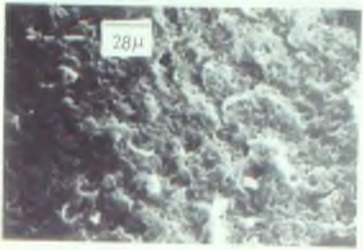

Fig. 9 SEM photomicrograph of blend A (30 NR–70 HDPE) extruded at a shear rate of $1 223 s^{-1}$

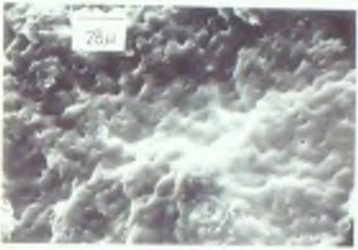

Fig. 10 SEM photomicrograph of blend B (50 NR–50 HDPE) extruded at a shear rate of $12 s^{-1}$

cal characteristics and by the processing history. For the same processing history, the blend ratio and the shear viscosities of the individual components determine the morphology. When two incompatible polymers such as NR and HDPE are mixed, a heterophase system results. Further, when the melt viscosities of the components are very different, the minor phase (which has the higher viscosity) will be coarsely distributed in the major constituent.[illegible]

It can be seen from Fig. 1 that as the extrusion rate is increased, there is a decrease in the shear stress. The morphology also changes accordingly. To begin with, the experimental conditions of extrusion (low shear rates and a long capillary) assure a laminar flow inside the capillary.[3] The decrease in the particle size of the rubber phase with increasing shear rate can be explained in the following way: under the above mentioned conditions, the rubber particles in the blend are elongated at the entrance of the capillary; this structure is unstable and tends to break up into smaller droplets, thus decreasing the domain size and leading to a finer dispersion of the domains.[illegible]

In the case of the 50 NR–50 HDPE blend also, the rubber is dispersed as non-uniform domains in the continuous thermoplastic phase (Fig. 10). As the extrusion rate is increased, the breakdown process of the dispersed domains is accelerated with increasing shear stress (Fig. 11). However, the shape of the domains is not spherical because the minor component is highly viscous and the major component has a relatively low viscosity. Figure 12 is the cross-sectional surface of the 50:50 blend. Figure 13 shows a region (X) of the extrudate (Fig. 12) from the bulk while Fig. 14 shows a region (Y) from the surface of a cavity (resulting from air entrapment inside the extrudate) of the same extrudate. It is apparent that region X is richer in the rubber phase

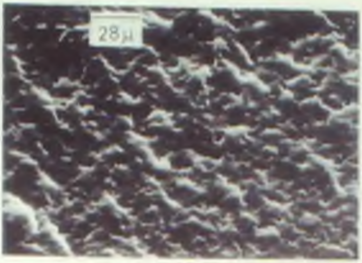

Fig. 11 SEM photomicrograph of blend B (50 NR–50 HDPE) extruded at a shear rate of 1 223 s^{-1}.

Fig. 12 SEM photomicrograph of blend B (50 NR–50 HDPE) extruded at a shear rate of 122 s^{-1}.

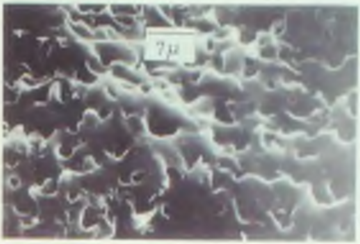

Fig. 13 Enlarged view of region X in Fig. 12.

Fig. 14 Enlarged view of region Y in Fig. 12.

Fig. 15 SEM photomicrograph of blend C (70 NR–30 HDPE) extruded at a shear rate of 12 s^{-1}.

than region Y, giving credence to the theory that the phase with lower viscosity tends to flow towards open surfaces.

Figure 15 shows the morphology of the 70 NR–30 HDPE blend at a low shear rate (12 s^{-1}). Since the NR phase has been extracted, the figure shows a continuous phase which must be the thermoplastic component. This implies that there is no phase inversion even at this blend ratio and in fact both the elastomer and thermoplastic form co-continuous phases. It is generally predicted that if the minor component has a lower viscosity, this component will be finely and uniformly dispersed with domains oriented in the extrusion direction. Although this phenomenon cannot be observed for NR–HDPE blends, the formation of semi-spherical droplet-like domains of the thermoplastic layer (Fig. 15) indicate a tendency towards the formation of separate and distinct spherical domains. These spherical domains have an average 8 μm diameter and are uniformly distributed throughout the whole sample. The smooth round shaped domains denote low adhesion between the matrices.

At a higher shear rate the size of the semi-spherical domains reduces to 2·5 μm (Fig. 16) but there is no further separation of the domains. In blends of thermoplastics and elastomers it is expected that in extrudates there is an increased quantity of the lower melt viscosity polymer at the surface. This phenomenon in the case of 70 NR-30 HDPE blend is shown in Fig. 17, which is a photomicrograph from near the axial surface of the extrudate. It is evident that at the wall the rubber domains are dispersed in a continuous HDPE phase different from Figs 14 and 15 which are from the bulk.

Dynamic crosslinking of the high rubber blend leads to dramatic changes in the morphology (Figs 18 and 19). Crosslinking of the elastomer phase increases its viscosity and reduces n' (Table 2). The crosslinked particles are much less deformable and retain the morphology even at high shear stresses. These features are reflected in the complementary structure of the HDPE phase which can be seen in the figure (after the NR phase has been removed). The coarse and irregular lumps of HDPE form a continuous layer. There is, however, little influence of shear rate on the morphology.

Reinforcement of the elastomer phase by carbon black is reflected in the morphology (Figs 20 and

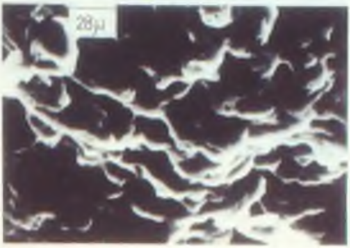

Fig. 18 SEM photomicrograph of blend C (70 NR-30 HDPE-1·0 DCP) extruded at a shear rate of 12 s^{-1}.

Fig. 16 SEM photomicrograph of blend C (70 NR-30 HDPE) extruded at a shear rate of 1223 s^{-1}.

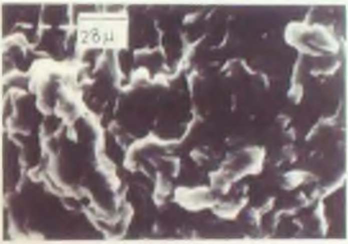

Fig. 19 SEM photomicrograph of blend C (70 NR-30 HDPE-1·0 DCP) extruded at a shear rate of 1223 s^{-1}.

Fig. 17 SEM photomicrograph of blend C (70 NR-30 HDPE) extruded at a shear rate of 122 s^{-1}. Figure shows a region close to the axial surface of the extrudate.

Fig. 20 SEM photomicrograph of blend C (70 NR-30 HDPE-40 HAF) extruded at a shear rate of 12 s^{-1}.

Fig. 21 SEM photomicrograph of blend C_6 (70 NR–30 HDPE–40 HAF) extruded at a shear rate of 1223 s^{-1}

21). The surface shows a continuous HDPE phase in the form of a network with a continuous rubber phase filling in the gaps and a kind of intermesh results. The loose particles correspond to filler aggregates. Shear rate does not have much effect on the morphology.

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