Studies on the Melt Flow Behavior of Thermoplastic Elastomers from Polypropylene—Natural Rubber Blends

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The melt flow behavior of thermoplastic polypropylene-natural rubber blends has been evaluated with specific reference to the effects of blend ratio, extent of dynamic crosslinking of the rubber phase and temperature, on viscosity, flow behavior index, and deformation of the extrudate. The proportion of rubber in the blend and the extent of dynamic crosslinking of the rubber phase were found to have profound influence on the viscosity of the blends at lower shear stresses. But at higher shear stresses, the effect of blend ratio on viscosity was comparatively less for the uncrosslinked blends than that for the crosslinked blends. At lower shear stress, the viscosity of the blend increased with increase in degree of crosslinking but at higher shear stress, the effect of crosslinking on viscosity was found to vary depending on the ratio of the plastic and rubber components in the blend. The deformation of the extrudates was also very much dependent on both blend ratio and degree of crosslinking.

INTRODUCTION

Thermoplastic elastomers combine the excellent processing characteristics of the thermoplastic materials at higher temperatures and a wide range of physical properties of elastomers at service temperatures (1–4). The materials prepared by melt mixing of a thermoplastic material and an elastomer under high shearing action, have gained considerable attention due to the simpler method of preparation and easy attainment of the desired physical properties (5). It has been further shown that addition of small quantities of crosslinking agent during the mixing operation improves the final properties, mildly affecting the processing behavior (6–12). This process is known as dynamic crosslinking. Since these materials can be processed in the same way as the thermoplastics, melt flow studies of thermoplastic elastomers have become important in optimizing the processing conditions, and in developing new processing equipment and the dies necessary for the production of various types of extruded and injection molded products.

The rheological behavior of polymer blends and that of polymers containing gel and crosslinked particles have been studied by different research groups (13–21). The effects of rubber particles, carbon black and non-black fillers on the flow properties of polymer melts have also been studied (22–25). Various factors affecting the die swell, melt fracture, and deformation of extrudates have been reported by several authors (26–30). Studies on the rheological behavior of thermoplastic block copolymers (31–34), metal sulfonated ethylene propylene terpolymers (35), and those of the blends of a thermoplastic polyolefin and an elastomer (36–38), have become the subject of recent interest due to the growing importance of the thermoplastic elastomers. In this paper, we report on the results of the melt flow studies on dynamically crosslinked thermoplastic elastomers from natural rubber (NR)-polypropylene (PP) blends. The effects of blend ratio, extent of dynamic crosslinking and temperature, on viscosity, flow behavior index, and melt fracture of the extrudate have been studied.

EXPERIMENTAL

Base Materials Used

The NR used for this study was Indian Standard Natural Rubber, ISNR 5 grade, conforming to IS 4588-1977 specifications. PP used in the present study was isotactic polypropylene (Koylene M0030 of Indian Petrochemicals Corporation Ltd.). The characteristics of the above two base materials are given in *Table 1*.

Preparation of the Blends

Formulations of the blends are given in *Table 2*. The blend ratios are denoted by letters B, D, and

Table 1. Characteristics of NR and PP

Property	NR	PP
Molecular Weight $\bar{M}_n$	—	1,06,000
$\bar{M}_w$	7,80,000	5,30,000
Molecular Weight Distribution $\bar{M}_w/\bar{M}_n$	—	5.0
Intrinsic Viscosity (Benzene, 30°C; dl/g) $[\eta]$	4.45	—
Melt Flow Index (230°C and 2.16 kg) MFI	—	10.0
Wallace Plasticity P_o	59.0	—

Table 2. Composition of the NR-PP Blends

Components	B	D	F
Natural Rubber[a]	30	50	70
Polypropylene[b]	70	50	30
Curing systems[c]	U, D, M, S	U, D, M, S	U, D, M, S

[a] Crumb rubber ISNR 5 grade, obtained from the Rubber Research Institute of India, Kottayam, Kerala, 686 009.

[b] Koylene M0030 received from M/s Indian Petrochemical Corporation Ltd., Vadodara, Gujrat.

[c] U Uncrosslinked system.
D Dicumyl peroxide (DCP) cure system (40 percent DCP, 1.0 phr level, based on rubber phase only).
S Sulfur cure system (zinc oxide 5.0, stearic acid 2.0, N-cyclohexyl benzothiazyl sulphenamide (CBS) 2.0, tetra-methyl thiuram disulphide (TMTD) 2.5, and sulfur 0.30 phr, based on rubber phase only).
M Mixed cure system (40 percent DCP 1.0, zinc oxide 5.0, stearic acid 2.0, CBS 1.0, TMTD 1.25, and sulfur 0.15 phr, based on rubber phase only).

F. The suffixes U, D, M, and S denote the blends without any curative, that containing dicumyl peroxide (DCP), mixed and sulfur cure systems, respectively. Thus, the blend B_M means NR:PP as 30:70 with mixed crosslinking system. The blend ratios were selected to represent thermoplastic elastomer ranges of the polyolefin-elastomer blends. Blends of NR and PP were prepared in a Brabender Plasti-corder model PLE 330, using a cam-type mixer with a rotor speed of 80 rpm and the mixer chamber temperature set at 180°C. PP was melted in the mixer for one min. and then NR was added and the blend was allowed to mix for four mins. At the end of five mins., curatives were added and the mixing continued for three more mins. The blend was taken out and sheeted through a laboratory mill at 2.0 mm nip setting. The sheeted material was cut into small pieces and again mixed in the Plasti-corder at 180°C for one min. and then finally sheeted out in the mill so as to get uniform dispersion of the ingredients. Except DCP, all the ingredients were added as masterbatches. For blends containing mixed cure system, DCP was added after four mins. blending of PP and NR and then the mixing continued for one min. Other ingredients were added after this step. Specimens of dimensions 5.0 by 5.0 by 2.5 mm were cut from the sheets and used for the melt flow measurements.

Melt Flow Measurements

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°. 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 five mins. the melt was extruded through the capillary at pre-selected speeds of the crosshead which varied from 0.5 to 500.0 mm per min. 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 wall by using the following equations involving the geometry of the capillary and the plunger:

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

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

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 crosshead and diameter of the plunger. n' is the flow behavior index defined by $n' = d(\log \tau_w)/d(\log \dot{\gamma}_{w \cdot a})$ and was determined by regression analysis of the values of τ_w and $\dot{\gamma}_{w \cdot a}$ obtained from the experimental data. $\dot{\gamma}_{w \cdot a}$ is the apparent wall shear rate calculated as $32Q/\pi d_c^3$. The shear viscosity η was calculated from τ_w and $\dot{\gamma}_w$.

RESULTS AND DISCUSSIONS

Our earlier studies (39, 40) on the physical properties and tensile and tear failure of these blends showed that the physical properties of the blends were improved with increase in degree of crosslinking of the rubber phase. The degree of crosslinking of the rubber phase in the blend was in the order, sulfur cure > mixed cure > DCP cure, as measured by the V_r values (volume fraction of rubber in the solvent swollen sample of rubber vulcanizates containing the same level of curatives), which were 0.07, 0.13, and 0.17 respectively for DCP, mixed and sulfur cured samples.

Effect of Blend Ratio and Shear Stress on Viscosity

Figure 1 shows the effect of blend ratio and shear stress on viscosity of the thermoplastic PP-NR blends. At lower shear stresses, the viscosity of the blend increases with increase in proportion of rubber in the blend. The viscosity decreases with increase in shear stress and at high shear stresses (2×10^7 Pa), the difference between the viscosity of the blends containing various proportions of PP and NR is only marginal. At lower shear stresses, the viscosity of fresh PP pellets is higher than that of 30:70 NR:PP blend (B_U). Thermal degradation and the corresponding decrease in melt viscosity of PP had been reported by White, *et al* (41). Melting and mixing of PP in the Plasti-corder at 180°C for

8 mins. degraded the PP in the blend and reduced its viscosity. This is evident from the lower viscosity of the PP which has been melted and sheared in the Plasti-corder for 8 mins. at 180°C and 80 rpm, compared with that of fresh PP pellets. However, the zero shear viscosity shown by blend B_U at lower shear stress remains unexplained.

Effect of Dynamic Crosslinking and Shear Stress on Viscosity

The effect of shear stress on viscosity of the 30:70 NR:PP blends containing rubber particles having different extents of crosslinking is shown in *Fig. 2*. At lower shear stresses, the viscosity of the blends increases with increase in degree of crosslinking of the rubber phase. At higher shear stresses also, the trend is the same, even though the differences in viscosities of the blends having different extent of crosslinking of the rubber phase is only marginal. Blend B_U shows lower viscosity at lower shear stresses and higher viscosity at higher shear stresses than the blends containing crosslinked rubber particles (B_D, B_M, and B_S). Since the dispersed rubber phase is having higher viscosity than the continuous PP phase (*Fig. 1*), the continuous phase experiences the same deformation in all the blends whereas, the deformation undergone by the dispersed phase depends on its melt viscosity (36). It has been reported that the uncrosslinked rubber particles in polypropylene-elastomer blends are bigger in size and highly deformable (38) and that these particles are broken down into smaller ones under high shear rates (37), as observed in other heterogeneous blends (42). Crosslinking of the elastomer phase increases its viscosity and decreases the deformation of the dispersed particles as indicated by the increase in Brabender mixing torque values (at 180°C, 80 rpm rotor speed) from 5.5 Nm for the uncrosslinked blend (B_U) to 8.0 Nm for the sulfur crosslinked blend (B_S). Considering the above details, the changes in morphology of the blend B containing uncrosslinked and crosslinked rubber particles, under low and high shear stress conditions, may be represented as dipicted in *Fig. 3*. The uncrosslinked rubber particles in the blend are elongated at the entrance of the capillary and are broken down into smaller particles whereas, the crosslinked particles which are less deformable, retain the morphology of the blend even at high shear stresses. Thus, the observed difference in viscosities of the uncrosslinked blend B_U and crosslinked blends B_D, B_M, and B_S at low and high shear stresses is due to the change in morphology of the uncrosslinked blend under high shear stress conditions. The DCP cured 30:70 NR:PP blend (B_D) shows lower viscosity compared with that of blends B_U, B_M, and B_S. It has been reported that DCP degrades PP at elevated temperature and that this effect is more prominent at higher proportions of PP in NR-PP blends, as evidenced by increase in melt flow index values of these blends (7). Thus the lower viscosity of the blend B_D can be attributed to the degradative effect of DCP on PP at high temperature of blending.

In the 50:50 NR:PP blend, there is a sharp increase in viscosity with crosslinking at lower shear stresses and blends D_M and D_S show yield stresses (*Fig. 4*). Münstedt (22) has reported that in rubber

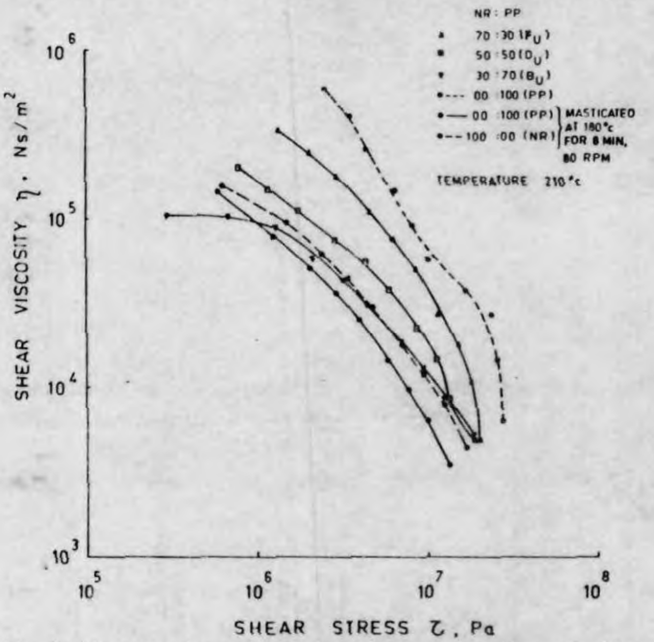

Fig. 1. Viscosity-shear stress plots showing the effect of rubber content, in NR-PP blends at 210°C.

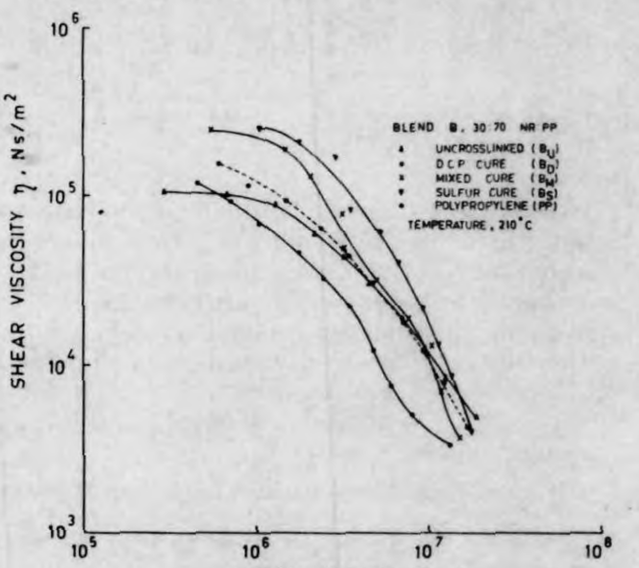

Fig. 2. Viscosity-shear stress plots showing the effect of extent of crosslinking, in 30:70 NR:PP blend at 210°C.

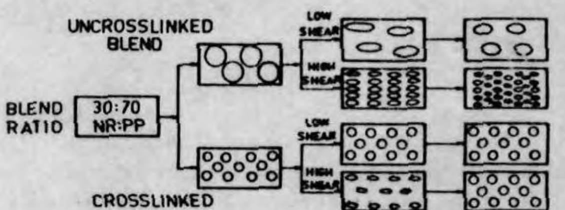

Fig. 3. Representation of possible morphology of 30:70 NR:PP blend, showing the effect of shear stress on uncrosslinked and crosslinked particles during extrusion.

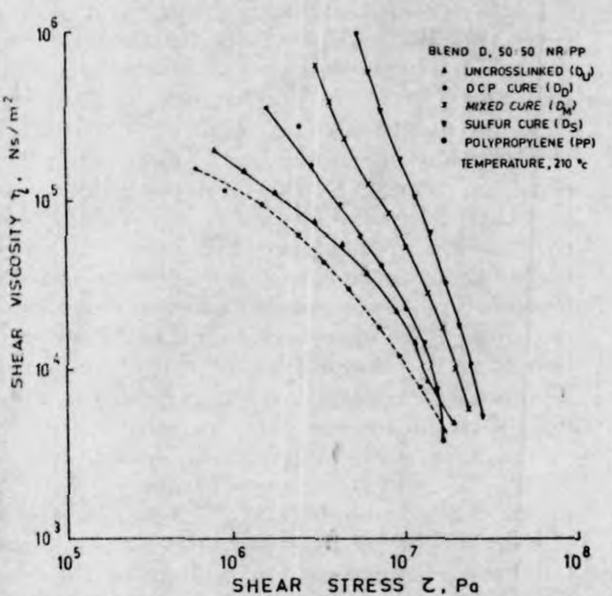

Fig. 4. Viscosity-shear stress plot showing the effect of extent of crosslinking, in 50:50 NR:PP blend at 210°C.

modified styrene-acrylonitrile and poly(vinyl chloride) the viscosity increase in lower shear stresses is due to structure build-up of rubber particles and that the viscosity increase is more pronounced at higher concentration and smaller size of the rubber particles. At higher extents of crosslinking, the smaller size of the mixed and sulfur cured rubber particles in blends D_M and D_S, compared with that of uncrosslinked and slightly crosslinked blends, form some sort of structure build-up inside the system, which leads to yield stress in these blends. The degradative effect of DCP on PP is evident from the lower viscosity of the blend D_D at higher shear stress. In 70:30 NR:PP blends (*Fig. 5*), the observed differences in viscosities of the blends F_U, F_D, F_M, and F_S are proportional to the degree of crosslinking of the rubber phase. The viscosities of the blends F_U and F_D are comparable and the blends F_M and F_S also show the same trend at lower shear stresses, unlike the viscosities of the blends in the D series, which show wide difference (*Fig. 4*). The degradative effect of DCP on PP which has been observed in blends B_D and D_D is not prominent in blend F_D. It is also seen that the effect of extent of crosslinking on viscosity is less pronounced for the blends in F series at higher shear stresses unlike that observed for the blends in D series.

Effect of Temperature and Dynamic Crosslinking on Flow Behavior Index

The effects of temperature and degree of crosslinking of the rubber phase on n' values are presented by histograms in *Fig. 6*. For the 30:70 NR:PP blends, at 210°C the n' values decrease with increase in extent of crosslinking of the rubber phase. At 200°C blend B_S shows slightly higher values for n' than that for B_M. Similarly at 190°C blend B_D shows slightly higher value than blend B_U. Blend B_S shows maximum value for n' at 200°C whereas for blends B_U, B_D, and B_M, n' values are maximum at 210°C. In 50:50 NR:PP blends, the n' values decrease with increase in degree of crosslinking and this trend is shown at all the three temperatures. For these blends, a tendency to form maximum value for n' at 200°C is also observed. In the case of blends in F series, no regular change in n' values with increase in temperature or crosslink density of the rubber phase is observed except for blend F_S which shows gradual decrease in n' value with increase in temperature. Blends F_U and F_M showed minimum values at 200°C.

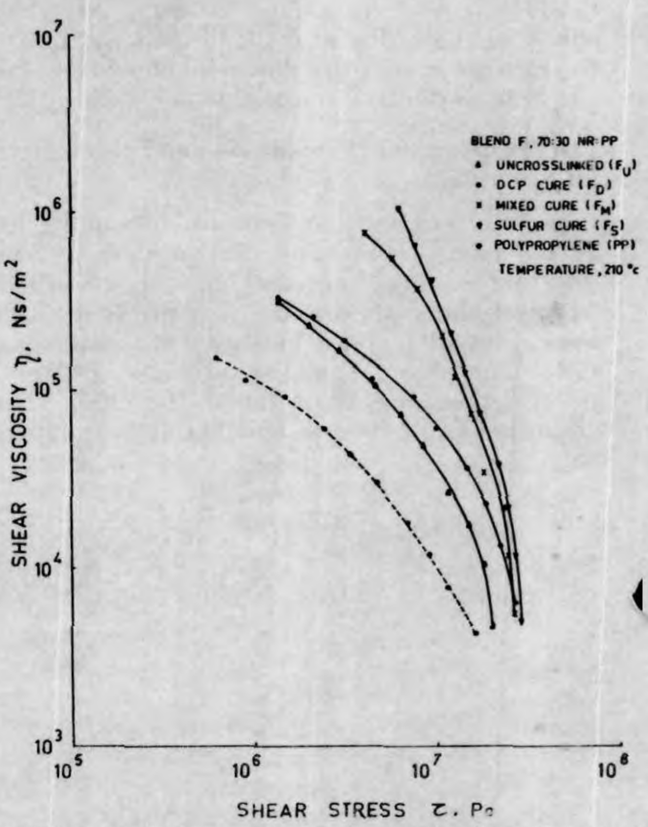

Fig. 5. Viscosity-shear stress plot showing the effect of extent of crosslinking in 70:30 NR:PP blend at 210°C.

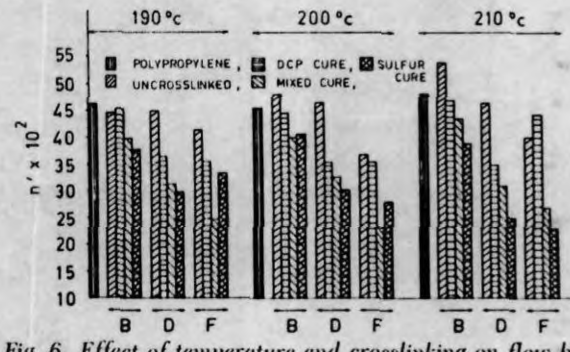

Fig. 6. Effect of temperature and crosslinking on flow behavior index of NR-PP blends.

Effect of Dynamic Crosslinking on Melt Fracture

Figure 7 shows that the deformation of the extrudate is increased with increase in shear rate, both for the uncrosslinked and crosslinked blends. Increasing the rubber content in the blend beyond 30 percent increases the melt fracture of the extrudates as the elastic response increases with increase in proportion of the rubber phase. At higher shear rates the distortion of the extrudates de-

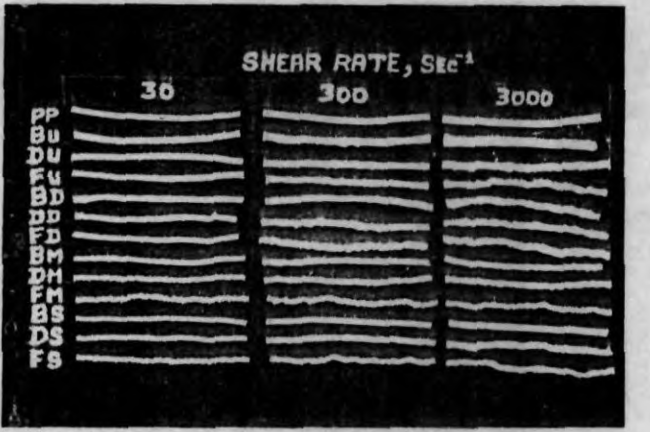

Fig. 7. Effect of extent of crosslinking on distortion of extrudates of NR-PP blends at 210°C.

creases with increase in crosslink density of the rubber phase. DCP cured blends show higher deformation and the sulfur cured blends give least deformation at all blend ratios. This is due to less deformation and quick recovery of the rubber particles containing higher degree of crosslinking.

CONCLUSIONS

The following conclusions can be drawn from the present study:

1. In thermoplastic PP-NR blends, the increase in viscosity with increase in rubber content is predominant only at lower shear stresses.
2. Dynamic vulcanization of the elastomer phase increases the viscosity of the blends, the extent of which depends on the degree of crosslinking of the rubber phase.
3. The effect of dynamic vulcanization on viscosity of the blends depends also on the blend ratio.
4. Crosslinking of the elastomer phase reduces the distortion of the extrudates at higher shear stresses.
5. Dynamically vulcanized thermoplastic PP-NR blends can be processed by extrusion and injection molding techniques as the viscosity at higher shear stresses is low.

NOMENCLATURE

NR = Natural Rubber
ISNR = Indian Standard Natural Rubber
PP = Isotactic polypropylene
DCP = Dicumyl peroxide, 40 percent active ingredient
V_r = Volume fraction of rubber in vulcanizate swollen in benzene at 35°C for 48 h
rpm = Revolutions per minute
phr = Parts per hundred rubber
l_c = Length of capillary (mm)
d_c = Diameter of capillary (mm)
d_e = Diameter of extrudate (mm.)
A_P = Cross-sectional area of the plunger (mm^2)
F = Extrusion force (N)
Q = Volume flow rate
n' = Flow behavior index, defined by $d(\log \tau_w)/d(\log \dot{\gamma}_{w\text{-}a})$
τ_w = Apparent shear stress at wall (Pa)
$\dot{\gamma}_w$ = Shear rate at wall (s^{-1})
$\dot{\gamma}_{w\text{-}a}$ = Apparent shear rate at wall (s^{-1})
η = Shear viscosity (Ns/m^2)

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