

Rheological behaviour of thermoplastic elastomers from polypropylene/acrylonitrile–butadiene rubber blends: effect of blend ratio, reactive compatibilization and dynamic vulcanization

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Abstract

The rheological behaviour of polypropylene (PP)/acrylonitrile–butadiene rubber (NBR) blends has been investigated with special reference to the effect of blend ratio, compatibilization and dynamic vulcanization. The morphology of the extrudates and the size and distribution of domains were examined. PP/NBR blends show pseudoplastic behaviour, which is evidenced by the decrease in viscosity with increasing shear rate. The melt viscosity of these blends increased with increasing nitrile rubber concentration and shows negative deviation from the theoretically predicted values. Compatibilization of the blends with phenolic-modified polypropylene (Ph-PP) increases the melt viscosity at low concentrations of Ph-PP. The rheological behaviour of PP/BR blends was correlated with the blend morphology. Dynamic vulcanization has a decreasing effect on die swell values. The effect of temperature on the melt viscosity of the blends was examined and attempts have been made to construct a shear rate–temperature superposition master curve. The melt-flow index values for these blends were measured and have been correlated with rheometer data to develop a master curve for different blend compositions. The morphological analysis indicates that compatibilization of the blends prevents the coalescence of dispersed NBR domains during annealing. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

During the last few decades the commercial importance of polymer blends has increased, owing to the possibility of attaining a wide range of properties by simple blending. Immiscible blends are preferable over miscible blends since in immiscible blends a combination of properties of the individual components is obtained, while in miscible blends an average of the individual properties is obtained [1]. However, very often many of the immiscible blends exhibit poor mechanical properties because of a lack of physical and chemical interactions across the phase boundaries and poor interfacial adhesion. The interfacial adhesion and physical properties of these blends can be improved by the addition of compatibilizers or interfacial agents [2].

As the commercial importance of polymer blends is increasing, it is necessary to optimize the processing

conditions required for each blend. Generally, in the case of homopolymers, the flow behaviour depends on the flow geometry and processing conditions such as the temperature, shear rate, time of flow, etc. In the case of polymer blends, the flow behaviour becomes more complex and is influenced by additional factors like the miscibility of the system, the morphology, interfacial adhesion and interfacial thickness. Generally the melt viscosity of polymer blends shows three types of behaviour: (1) positive deviation behaviour (PDB) where the blend viscosities show a synergistic behaviour, i.e., blend viscosity is higher than the log additivity value; (2) negative deviation behaviour (NDB) where the blend viscosity shows a negative deviation from log additivity values; and (3) positive–negative deviation behaviour (PNDB). In this case the same blend exhibits both positive and negative deviation behaviour depending on the composition, morphology and processing conditions [3].

The complex rheological behaviour of polymer blends has been investigated by several researchers [3–14]. The

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Table 1
Formulation of dynamic vulcanized PP/NBR blends

Ingredients	Sulfur system (PS)	DCP system (PC)	Mixed system (PM)
PP	70	70	70
NBR	30	30	30
ZnO	5	—	5
Stearic acid	2	—	2
CBS ^a	2	—	2
TMTD ^b	2.5	—	2.5
Sulfur	0.2	—	0.1
DCP ^c	—	2	1.0

^a *N*-cyclohexyl benzothiazyl sulfenamide.

^b Tetramethyl thiuram disulfide.

^c Dicumyl peroxide.

miscibility of polymer components has a significant effect on the flow behaviour of polymer blends. Kim and co-workers [4] investigated the effect of miscibility on rheological behaviour by studying the miscible and immiscible blends of poly(methyl methacrylate) (PMMA)/acrylonitrile–butadiene–styrene copolymer (ABS) with ABS having different acrylonitrile contents. The rheological study of these blends indicated that miscible blends showed viscosities lower than the additive values due to a dilution effect and immiscible blends with ABS-rich phase showed a positive deviation. Recently, in this laboratory, the flow behaviours of various thermoplastic elastomer blends have been investigated by Thomas et al. [5,6]. They found that in natural rubber (NR)/poly(ethylene-*co*-vinyl acetate) (EVA) blends, at low concentration of EVA, the system showed positive deviation, which has been explained by the strong interactions among EVA domains, while at higher concentration of EVA negative deviation was observed. The viscosity of the blend was found to increase with NR concentration. Such an increase in viscosity upon the incorporation of rubber in a

plastic phase has been reported in systems such as plasticized poly(vinyl chloride) (PVC)/epoxidized natural rubber (ENR), polypropylene (PP)/NR, high-density polyethylene (HDPE)/NR and PP/ethylene–propylene–diene rubber (EPDM) [7–12]. In PVC/ENR, for miscible blends, the observed negative deviation is attributed to the composition-dependent plasticizing effect of ENR [7,8].

The addition of compatibilizers to polymer blends affects their flow behaviour [15–19]. Chemical reactions occurring between the components of a blend upon compatibilization generally increase the viscosity of the system. The viscosity of PP/polyamide (PA) blend was found to increase on compatibilization with maleic-anhydride-grafted styrene(ethylene-*co*-butylene)–styrene copolymer (SEBS-*g*-MA), as a consequence of the chemical reactions taking place between amine and anhydride groups [15]. Germain et al. [16] reported the effect of a block copolymer on the

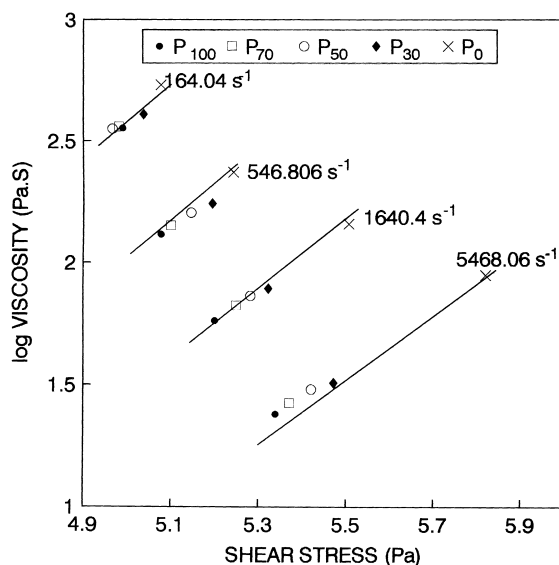


Fig. 1. Effect of shear stress on the melt viscosity of PP/NBR blends.

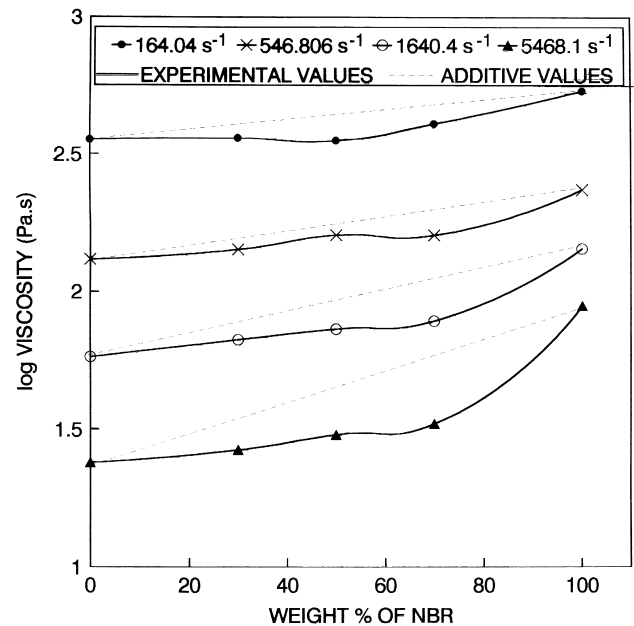


Fig. 2. Variation of the melt viscosity of PP/NBR blends with NBR concentration.

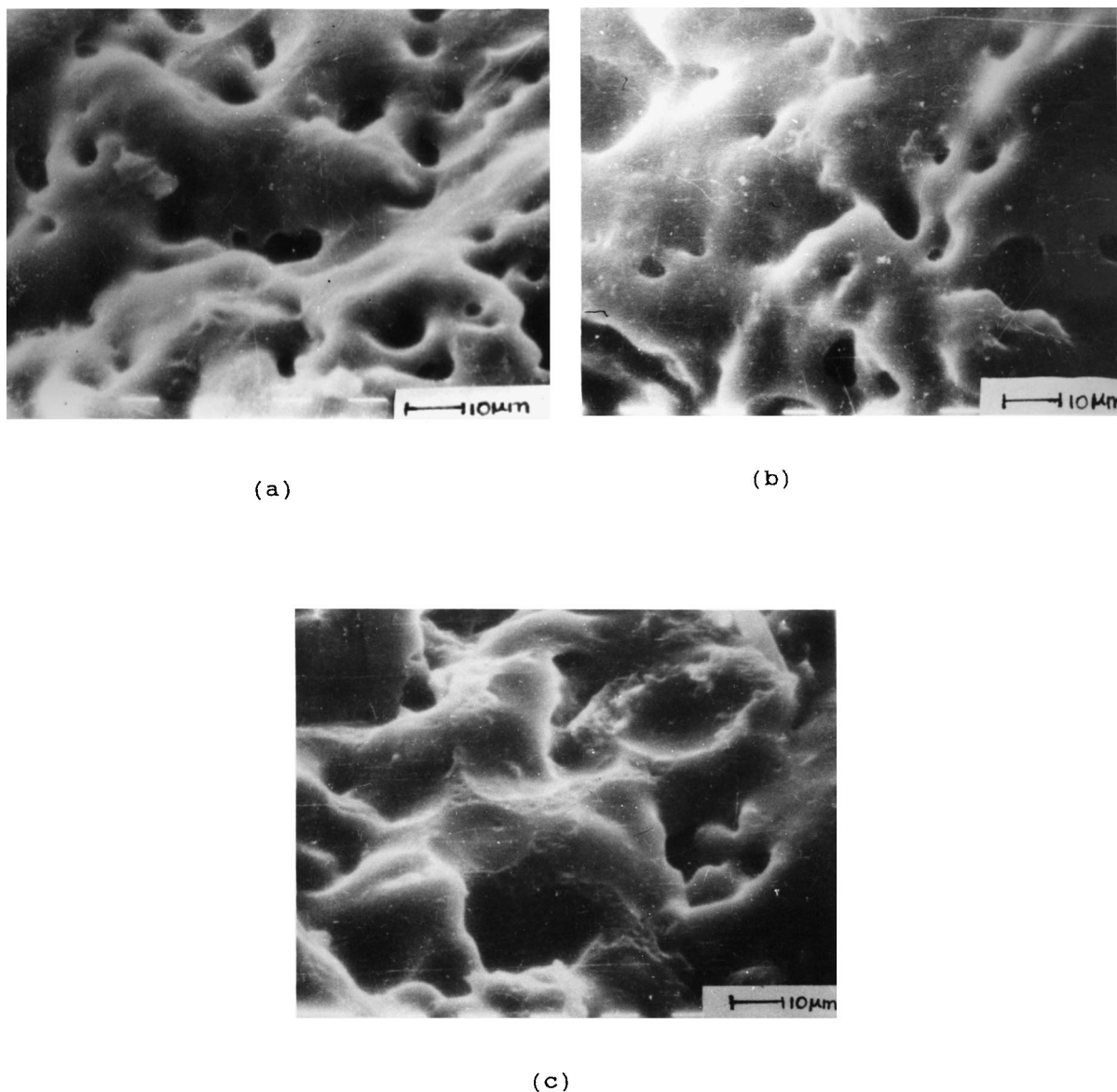


Fig. 3. Extrudate morphology of the (a) P_{70} , (b) P_{50} and (c) P_{30} blends.

rheological behaviour of PP/PA blends. A dual flow behaviour was observed in these blends: at low shear rates the blend viscosity is higher than that of the matrix and at high shear rates, the viscosity is lower than that of the matrix. They have correlated this behaviour with the morphology of the system and have used an emulsion model to predict the behaviour at the low-shear-rate region. Very recently, in this laboratory, the flow behaviour of PMMA/NR blends compatibilized with poly(methyl methacrylate)-grafted natural rubber (PMMA-*g*-NR) copolymer was investigated [19]. The binary blends show positive deviation at low shear rates. On compatibilization the viscosity of the blend increases due to the high interfacial interaction.

Recently Okoroafor et al. [20] analysed the viscosity of immiscible polymer blends using different rheological models for the flow behaviour. In these models, the

viscosity of the polymer blend has contributions from the viscosities of the pure components and also from the viscosity of the interface. According to the authors, in the absence of an interphase in mechanically mixed polymer blends without any chemical reaction, the positive and negative deviation behaviours (PDB and NDB) depend on the viscosity ratio, η_d/η_m . In the case of blends with an interface, the synergism is related to the viscoelastic properties of the interphase and to its volume fraction ϕ_1 in the blend.

The effect of dynamic vulcanization on the rheological behaviour of various rubber–plastic blends has been investigated by several researchers [9,21–24]. It has been reported that the viscosity of the blends increased with increasing curative concentration [21]. Kuriakose et al. investigated the effect of various vulcanizing agents on

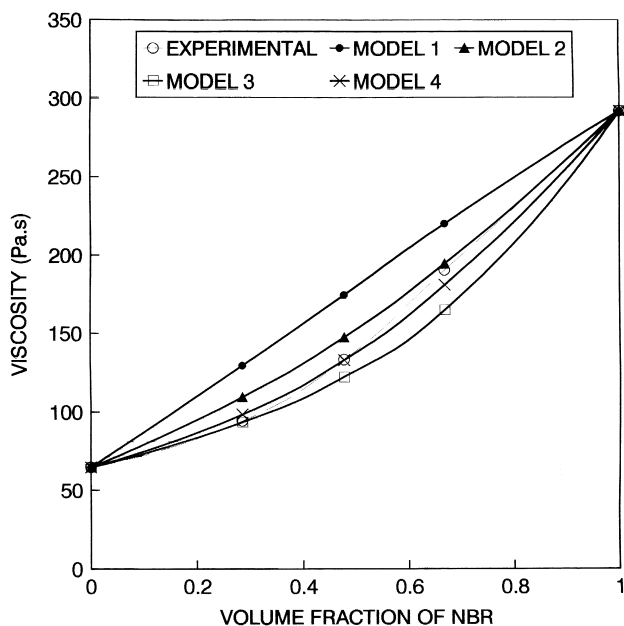


Fig. 4. Theoretical and experimental viscosity values of PP/NBR blends.

the rheological behaviour of PP/NR and HDPE/NR blends [9,22].

Blends of isotactic polypropylene and nitrile rubber have raised a lot of interest because of their oil-resistant characteristics. Recently we reported the morphology, mechanical and dynamic mechanical properties of these blends [25,26]. To our knowledge, no serious attempts have been made to study the rheological behaviour of these blends. In this paper, we have investigated the rheological properties of

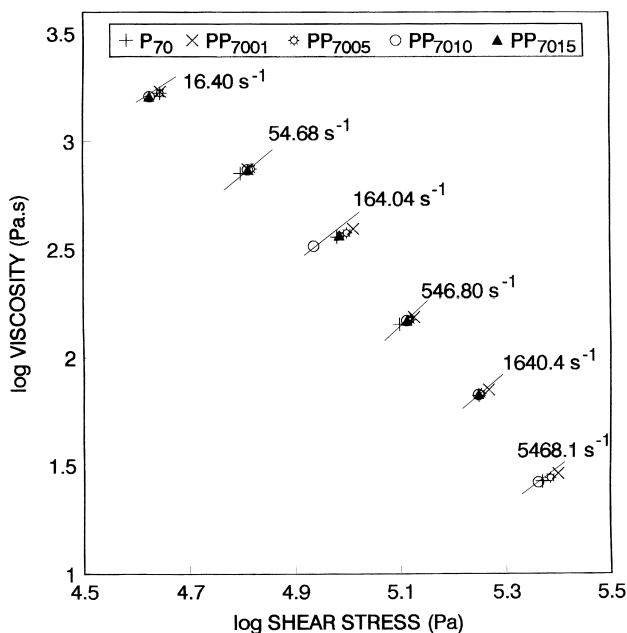


Fig. 5. Effect of shear stress on the melt viscosity of Ph-PP compatibilized 70/30 PP/NBR blends.

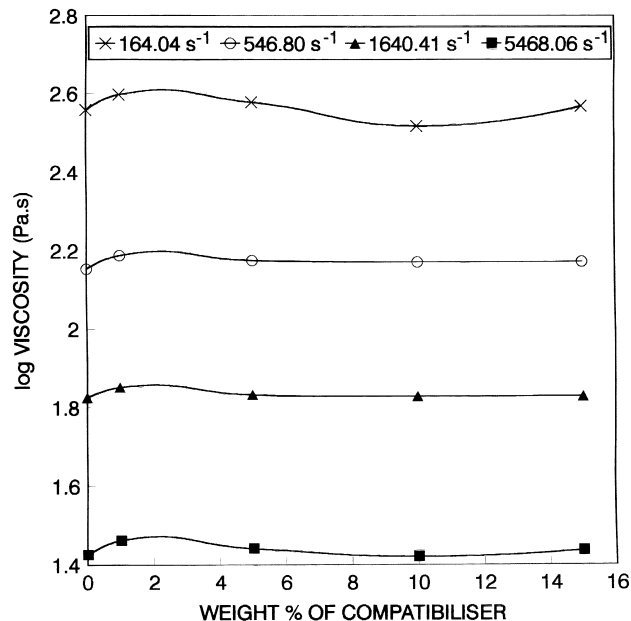


Fig. 6. Variation of viscosity with compatibilizer concentration.

PP/NBR blends. The effects of blend ratio, compatibilization and dynamic vulcanization on the flow characteristics have been studied. The morphology of the extrudates was also examined and correlated with the flow properties.

2. Experimental

Isotactic polypropylene (PP) having a melt-flow index (MFI) of 3 g/10 min was supplied by IPCL, Baroda. Acrylonitrile–butadiene rubber (NBR) having an acrylonitrile content of 34% was obtained from Synthetics and Chemicals, Bareilly, U.P. The compatibilizer, phenolic-modified polypropylene (Ph-PP), was prepared by melt-mixing polypropylene (100 parts) with dimethylol phenolic resin (SP-1045, 4 parts) and stannous chloride (0.8 parts) at 180°C [25].

Blends were prepared in a Brabender plasticorder PLE-330 by melt-mixing the components at a temperature of 180°C and rotor speed of 60 rev min⁻¹ for 6 min. The binary blends are denoted as P₁₀₀, P₇₀, P₅₀, P₃₀ and P₀, where the subscripts denote the weight percentage of PP in the blend. The compatibilized 70/30 PP/NBR blends with 1, 5, 10 and 15 wt% Ph-PP are denoted as P₇₀₀₁, P₇₀₀₅, P₇₀₁₀ and P₇₀₁₅, respectively. The dynamically vulcanized blends were prepared from the formulations shown in Table 1.

2.1. Rheological measurements

The rheological measurements were done in an Instron capillary rheometer (model 3211) at different plunger speeds. The plunger speed was varied from 0.06 to 20 cm min⁻¹. The melt was extruded through the capillary at predetermined plunger speeds after a warm-up period of

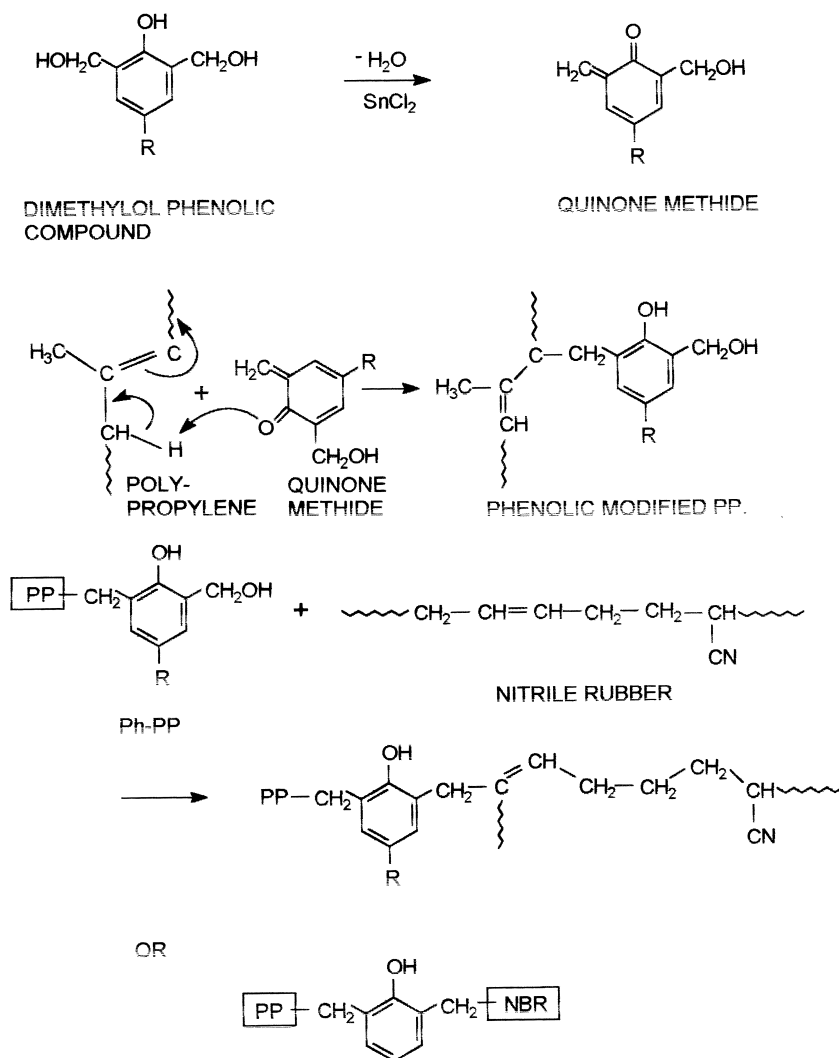


Fig. 7. Mechanism of the compatibilization reaction of PP/NBR blends.

5 min. The measurements were done at a temperature of 200°C . For studying the effect of temperature, the samples P_{100} , P_{70} , PP_{7010} and P_0 were analysed at 190, 200 and 210°C .

The true shear rate, $\dot{\gamma}_w$, was calculated from the apparent shear rate, $\dot{\gamma}_{wa}$, by means of the following equation, assuming that the blend behaves as a power-law fluid:

$$\dot{\gamma}_w = \left(\frac{3n' + 1}{4n'} \right) \dot{\gamma}_{wa} \quad (1)$$

n' , the flow behaviour index, is defined as:

$$n' = \frac{d(\log \tau_w)}{d(\log \dot{\gamma}_{wa})} \quad (2)$$

where τ_w is the shear stress and was determined by regression analysis.

The shear viscosity, η , was calculated with the equation:

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \quad (3)$$

2.2. Extrudate swell

The extrudates were carefully collected as they emerged out from the capillary die, taking care to avoid any deformation. The diameter of the extrudate was measured after 24 h. The die swell is calculated from d_e/d_c , where d_e is the diameter of the extrudate and d_c the diameter of the capillary.

2.3. Extrudate morphology

The morphology of the extrudates was analysed by scanning electron microscopy (SEM). The samples for morphology measurement were prepared by cryogenically fracturing them in liquid nitrogen. The NBR phase was extracted preferentially from these samples with chloroform.

2.4. Determination of crosslink density

The crosslink density of dynamic vulcanized samples was measured by the equilibrium swelling method and use of the

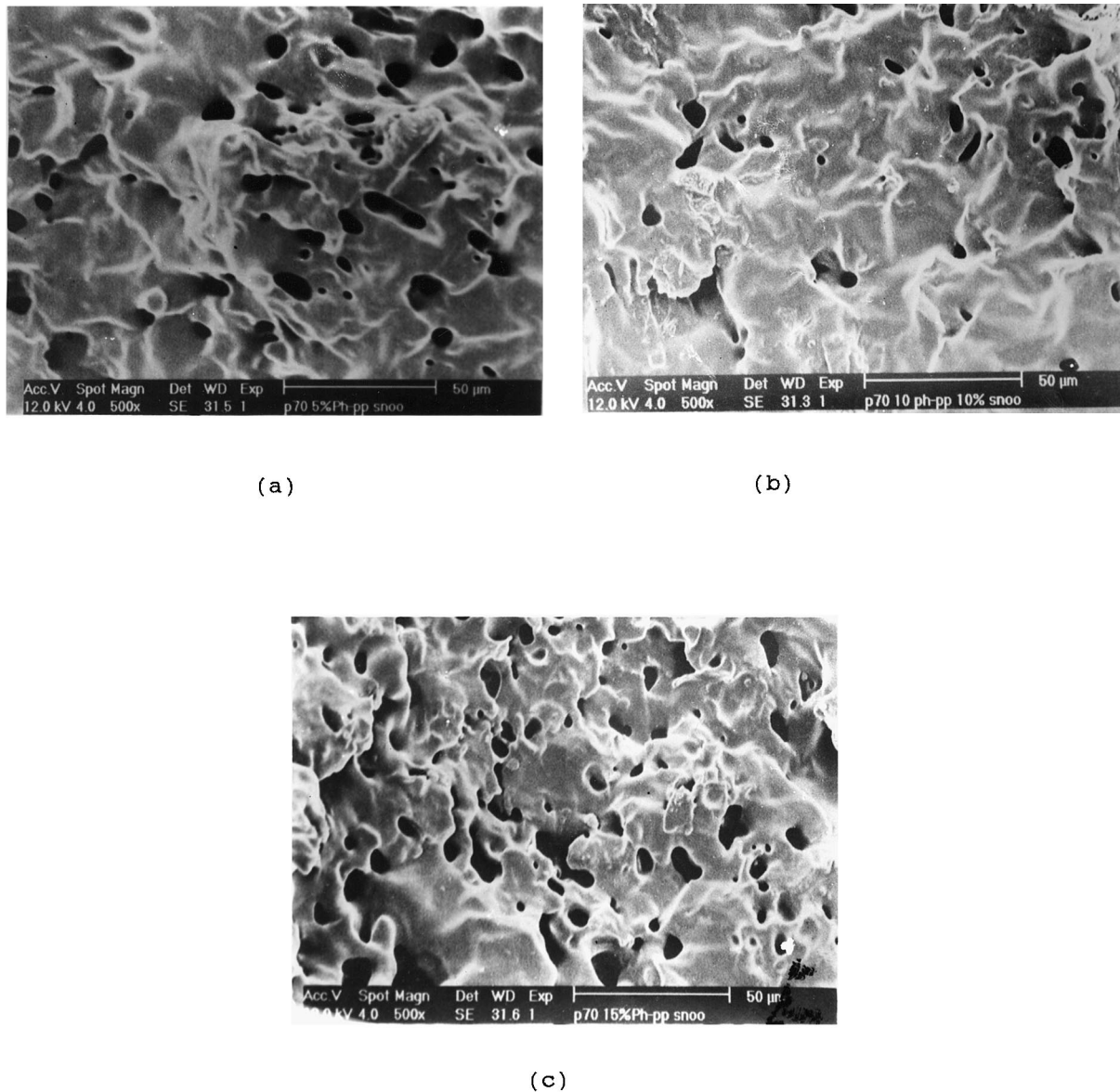


Fig. 8. Effect of Ph-PP addition on the extrudate morphology of 70/30 PP/NBR blend: (a) 5 wt%, (b) 10 wt% and (c) 15 wt% Ph-PP.

equation [27]

$$M_c = \frac{-\rho_p V_s \phi^{1/3}}{[\ln(1 - \phi) + \phi + \chi \phi^2]} \quad (4)$$

where ρ_p is the density of the polymer, V_s is the molar volume of the solvent and ϕ is the volume fraction of

Table 2
Average diameter of NBR domains in Ph-PP compatibilized P₇₀ blends

Sample	\bar{D}_n (μm)	\bar{D}_w (μm)	PDI (\bar{D}_w/\bar{D}_n)	\bar{D}_{vs} (μm)
P ₇₀	8.168	11.59	1.418	15.001
P ₇₀₀₁	5.322	7.516	1.412	9.3073
P ₇₀₀₅	4.9918	7.34	1.472	9.264
P ₇₀₁₀	5.06	6.17	1.219	10.219
P ₇₀₁₅	6.19	7.72	1.24	9.028

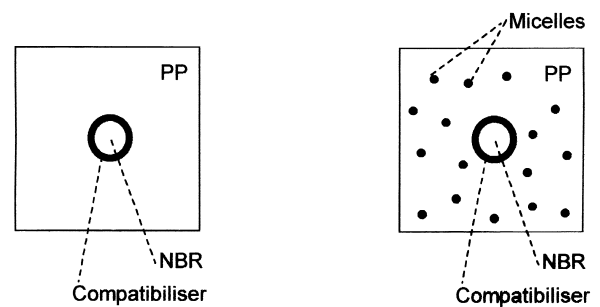


Fig. 9. Schematic representation of the formation of micelles in PP/NBR blend above the critical micelle concentration.

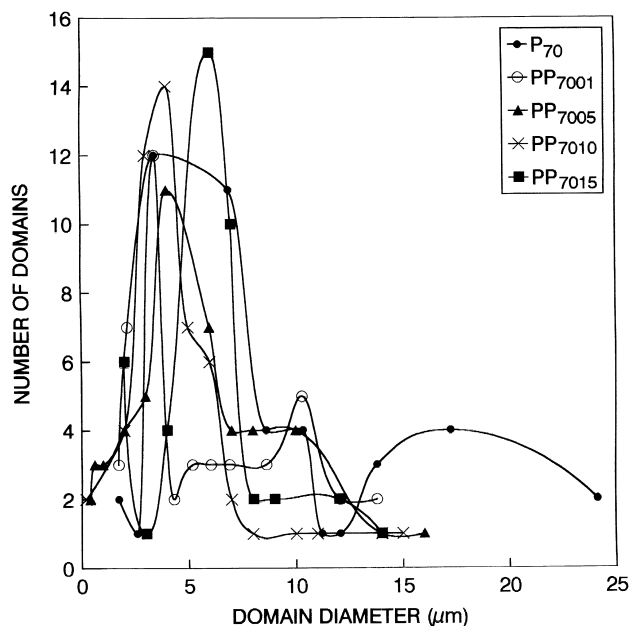


Fig. 10. Domain size distribution curves of Ph-PP compatibilized P₇₀ blends.

swollen rubber. The latter is given by:

$$\phi = \frac{(d - fw)\rho_p^{-1}}{(d - fw)\rho_p^{-1} + A^s \rho_s^{-1}} \quad (5)$$

where d is the deswollen weight of the sample, f the volume fraction of filler, w the initial weight of the sample, ρ_s the density of the solvent and A^s the amount of solvent

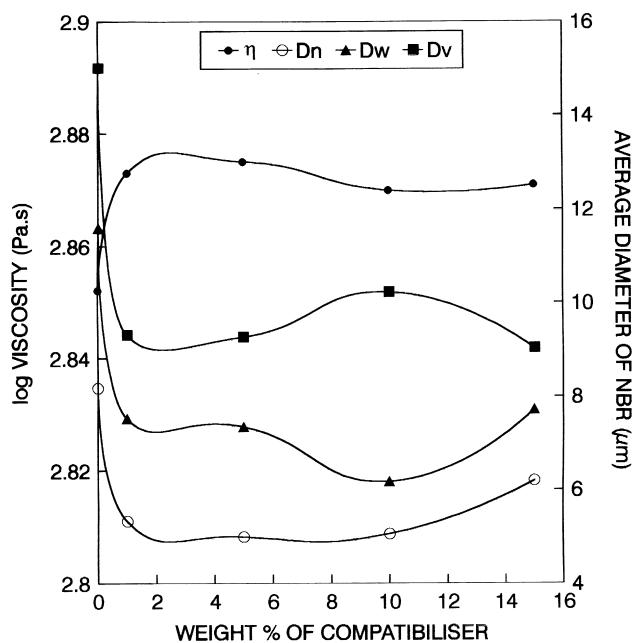


Fig. 11. Variation of NBR domain size and viscosity with compatibilizer concentration.

absorbed. The interaction parameter χ is given by:

$$\chi = \beta + (V_s/RT)(\delta_s - \delta_p)^2 \quad (6)$$

where β is the lattice constant (0.34), R is the gas constant and T is temperature, with δ_s and δ_p being the solubility parameters of the solvent and polymer, respectively.

3. Results and discussion

3.1. Effects of blend ratio and shear stress on viscosity

The effect of shear stress on the viscosity of polypropylene, nitrile rubber and their binary blends is shown in Fig. 1. The viscosities of pure components and their blends decrease with increasing shear stress, indicating pseudoplastic flow behaviour. The pseudoplastic nature of polymers arises from the randomly oriented and entangled nature of the polymer chains which, on application of high shear rates, become oriented and disentangled [28]. The viscosity of NBR decreases with shear rate at a lower rate than for polypropylene and the blends. At low shear rates PP shows a higher viscosity than P₇₀ and P₅₀, and at high shear rates the viscosity of the blends lies in between those of the homopolymers. Fig. 2 shows the viscosity variation with blend composition at different shear rates. As the rubber content in the blend increases, the blend viscosity is increased. Such an increase in viscosity on incorporation of rubber phase has been reported for several systems [7–11]. In polymer blends, the viscosity depends on interfacial thickness and interface adhesion in addition to the characteristics of the component polymers. This is because, in polymer blends, there is interlayer slip along with orientation and disentanglement on the application of shear stress. From Fig. 2 it is seen that the viscosity of the PP/NBR blend shows negative deviation and this indicates the incompatibility of the system. When a shear stress is applied to a blend it undergoes an elongational flow. When the interface is strong, deformation of the dispersed phase would be effectively transferred to the continuous phase. However, in the case of weak interphases interlayer slip occurs and, as a result, the viscosity of the system decreases. The extent of negative deviation is more prominent at the high-shear-rate region than at the low-shear-rate region. It can be seen that viscosity increases marginally up to 50% NBR content, followed by a sharp increase at higher NBR content. This behaviour can be explained in terms of the morphology of the system. SEM micrographs of cross-sections of the extrudates of PP/NBR blends are shown in Fig. 3. In P₇₀ and P₅₀ NBR is dispersed as spherical domains with \bar{D}_n equal to 8.16 and 11.59 μm , respectively, in the continuous PP matrix; in P₃₀, NBR also forms a continuous phase resulting in a co-continuous morphology. The co-continuous nature of PP and NBR in P₃₀ is responsible for the sharp increase in viscosity in this blend.

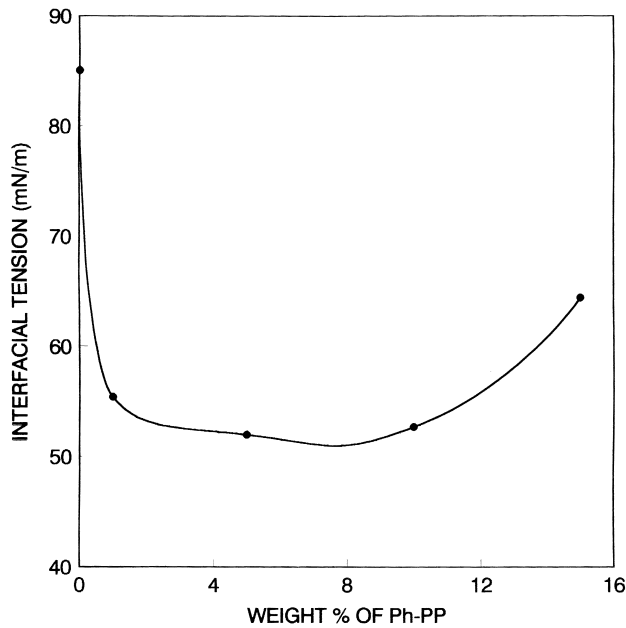


Fig. 12. Variation of the interfacial tension of 70/30 PP/NBR blends with compatibilizer concentration.

3.2. Comparison with theoretical predictions

The viscosity of these blends has been correlated with various theoretical models. The following models have been used to calculate the viscosity.

$$\eta = \eta_1 \phi_1 + \eta_2 \phi_2 \quad (\text{Model 1}) \quad (7)$$

where η_1 and η_2 are the viscosities of the components and ϕ_1 and ϕ_2 their volume fractions.

According to Hashin's upper- and lower-limit models [29]:

$$\eta_{\text{mix}} = \eta_2 + \frac{\phi_1}{1/(\eta_1 - \eta_2) + \phi_2/2\eta_2} \quad (\text{Model 2}) \quad (8)$$

$$\eta_{\text{mix}} = \eta_1 + \frac{\phi_2}{1/(\eta_2 - \eta_1) + \phi_1/2\eta_1} \quad (\text{Model 3}) \quad (9)$$

where η_1, η_2, ϕ_1 and ϕ_2 have the same meanings as before.

An altered free volume model developed by Mashelkar and co-workers [30] was also used to calculate the viscosity.

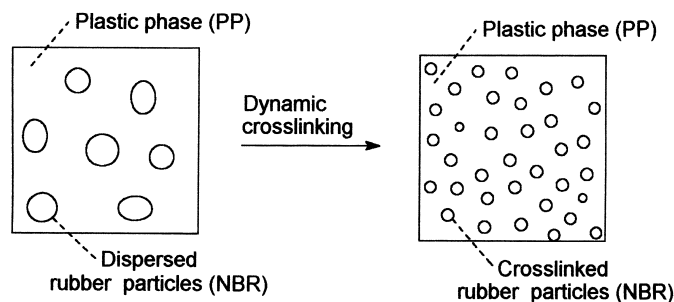


Fig. 13. Schematic representation of the morphology formed during dynamic vulcanization of polymer blends.

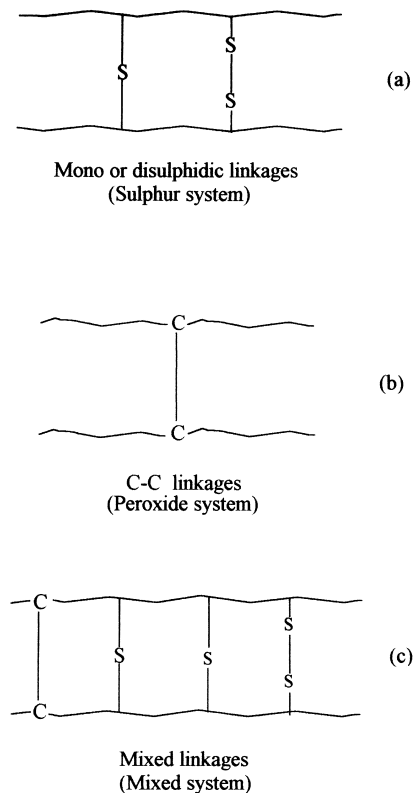


Fig. 14. Schematic representation of various crosslinks formed during vulcanization using (a) sulfur, (b) peroxide and (c) the mixed system.

According to this equation:

$$\ln \eta_{\text{mix}} = \frac{\phi_1(\alpha - 1 - \gamma\phi_2) \ln \eta_1 + \alpha\phi_2(\alpha - 1 + \gamma\phi_1) \ln \eta_2}{\phi_1(\alpha - 1 - \gamma\phi_2) + \alpha\phi_2(\alpha - 1 + \gamma\phi_1)} \quad (\text{Model 4}) \quad (10)$$

where

$$\alpha = \frac{f_2}{f_1} \quad (11)$$

and

$$\gamma = \frac{\beta}{f_1} \quad (12)$$

f_1 and f_2 are free volume fractions of components I and II,

Table 3
Crosslink density values of dynamic vulcanized P₇₀ blends

Sample	Crosslink density ($\times 10^5 \text{ mol cm}^{-3}$)
PS-70	2.06
PC-70	2.33
PM-70	2.04

respectively, and β is an interaction parameter.

$$f = f_g + \alpha(T - T_g) \quad (13)$$

where $f_g = 0.025$.

$$\alpha_f = \frac{B}{2.303C_1C_2} \quad (14)$$

where $B = 0.9 \pm 0.3 \approx 1$, $C_1 = 17.44$ and $C_2 = 51.6 \text{ K}$.

For the calculations, the value of γ was varied to obtain best-fit values with the experimental results. Fig. 4 presents viscosity values from the theoretical models and also from the experiments. It is seen from the figure that the viscosity of the blend shows negative deviation and the experimental curve lies between those of Hashin's upper- and lower-limit models. The viscosity values can be better explained using Mashelkar model with $\gamma = -0.04$. This value of γ corresponds to an interaction parameter $\beta = -4.376 \times 10^{-3}$ according to Eq. (12).

3.3. Effect of compatibilization

The addition of block or graft copolymers or modified

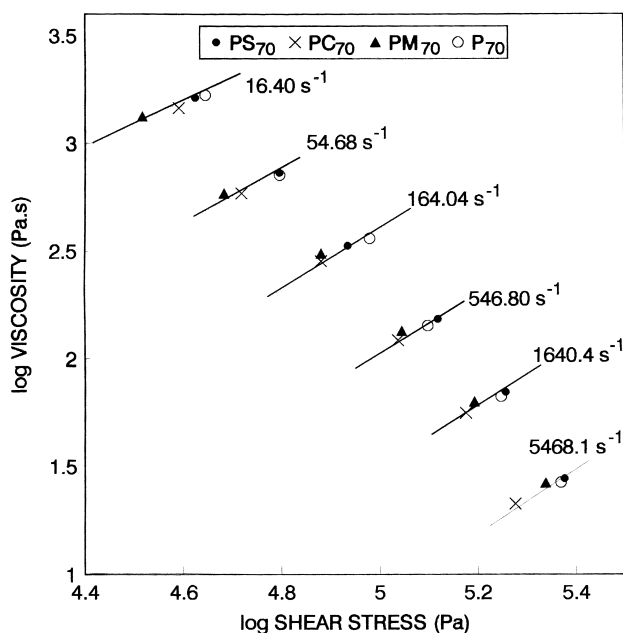


Fig. 15. Effect of shear stress on the melt viscosity of dynamic vulcanized PP/NBR blends.

polymers to immiscible blends is found to improve their physical and mechanical properties [31,32]. A suitably selected compatibilizer will locate at the interface between the two phases, leading to a reduction in interfacial tension and an improvement in interfacial adhesion [2]. In this laboratory, we have successfully used phenolic-modified polypropylene (Ph-PP) and maleic-anhydride-modified polypropylene as compatibilizers in PP/NBR blends [25,26]. These compatibilizers are found to modify the morphology of the blends and also improve the viscoelastic and mechanical properties.

The effect of shear stress on the viscosity of 70/30 PP/NBR blend containing phenolic-modified polypropylene is shown in Fig. 5. It is seen from the figure that, at lower shear rates, the viscosity of the compatibilized system is higher than that of the uncompatibilized system. At high shear rates the viscosity seems to be unaffected by compatibilization. Fig. 6 depicts the variation of viscosity as a function of compatibilizer concentration. With the increase in compatibilizer loading the viscosity initially increases, followed by a levelling-off at higher loading. The variation in viscosity is more pronounced at lower shear rates. Such increase in viscosity on compatibilization of immiscible polymer blends has been reported by several researchers [15–19]. We have already discussed in the Introduction that the viscosity of a polymer blend has a contribution from the interphase. Upon compatibilization of an immiscible blend, the compatibilizer will generally locate at the interface between the dispersed phase and the matrix. This will lead to an increase in interfacial thickness. According to Okoroafar et al. [20], the viscosity of the compatibilized blend is given by:

$$\frac{1}{\eta_{\text{blend}}} = \frac{\phi_m'}{\eta_m} + \frac{\phi_d'}{\eta_d} + \frac{\phi_i'}{\eta_i} - \left(\frac{1}{\eta_m} - \frac{1}{\eta_d} \right) \phi_m' \phi_d' + \left(\frac{\phi_m'}{\eta_m} - \frac{\phi_d'}{\eta_d} \right) \phi_i' + \frac{\phi_i'}{\eta_m} (\phi_d' - \phi_m') \quad (15)$$

where ϕ is the volume fraction, η the viscosity, and the subscripts m, d and i denote matrix, dispersed phase and interphase, respectively. Hence the viscosity of these blends depends on the interface volume fraction and also on the viscosity of the interface. In the case of PP/NBR blends compatibilized with Ph-PP, the Ph-PP reacts with NBR to form a copolymer as shown in Fig. 7 [25]. As a result of the addition of Ph-PP the interface thickness increases; this leads to effective stress transfer between the dispersed phase and the continuous phase and an increase in interfacial adhesion. This contributes to the reduction in interlayer slip and therefore to an increase in viscosity. The levelling-off in the viscosity–compatibilizer loading curve at higher concentrations of Ph-PP can be understood from the morphology of the system. SEM micrographs of extrudates of the 70/30 blend compatibilized with Ph-PP are shown in Fig. 8. As the concentration of Ph-PP increases, the size of

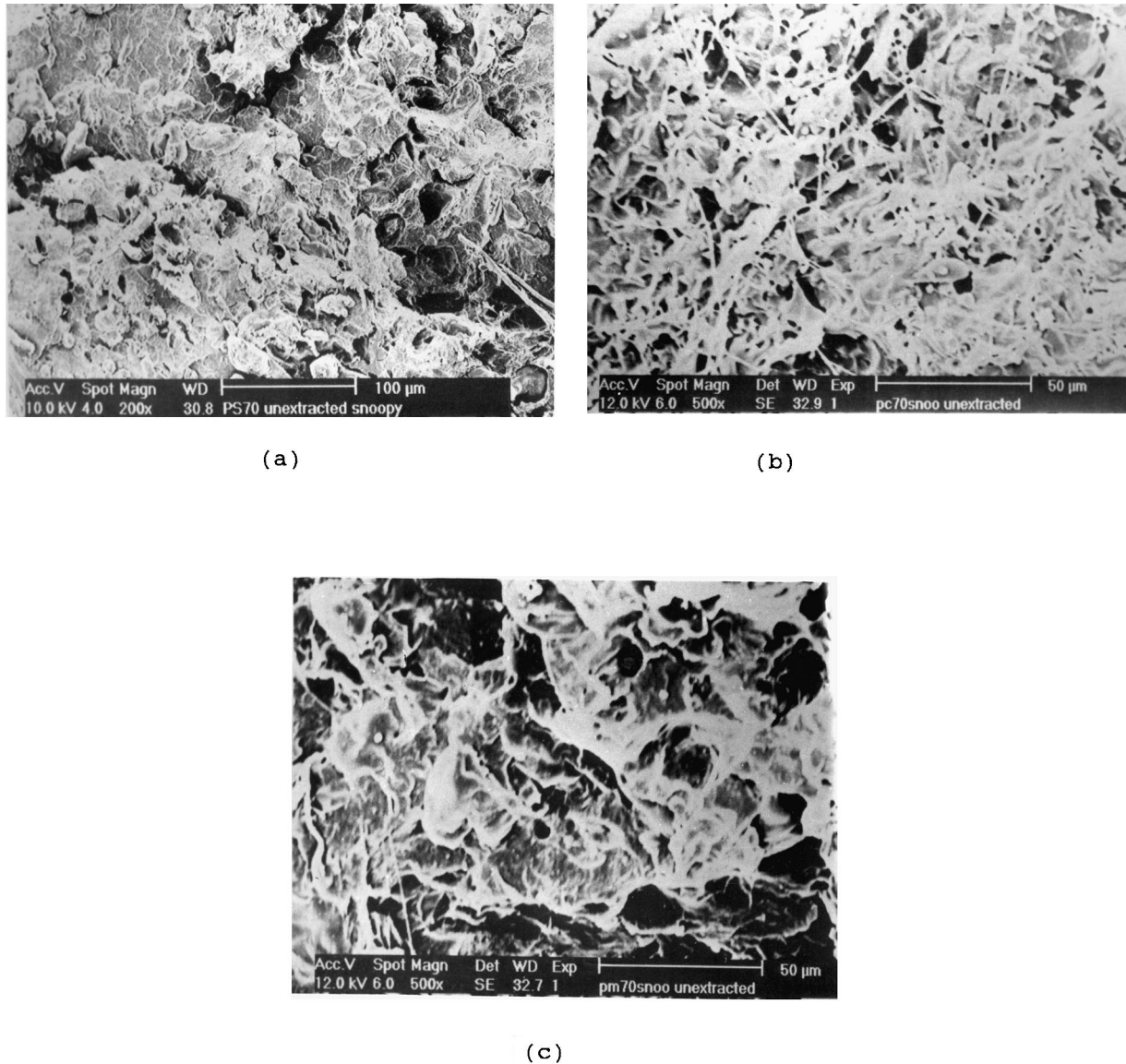


Fig. 16. Extrudate morphology of dynamic vulcanized 70/30 PP/NBR blends: (a) PS-70, (b) PC-70 and (c) PM-70.

the dispersed NBR phase decreases. The size of the NBR domains measured from the SEM micrographs may be expressed in different ways, such as:

$$\bar{D}_n = \frac{\sum N_i D_i}{\sum N_i} \quad (16)$$

$$\bar{D}_w = \frac{\sum N_i D_i^2}{\sum N_i D_i} \quad (17)$$

and

$$\bar{D}_{vs} = \frac{\sum D_i^3}{\sum D_i^2} \quad (18)$$

where N_i is the number of domains having diameter D_i , \bar{D}_n is the number-average diameter, \bar{D}_w the weight-average diameter and \bar{D}_{vs} the surface-area-average diameter. The

polydispersity index, which is a measure of domain size distribution, was also calculated from:

$$PDI = \frac{\bar{D}_w}{\bar{D}_n} \quad (19)$$

A large number of domains (> 100) from different micrographs was considered for determination of the domain diameter. Table 2 shows the results of these measurements. It is seen from the table that the domain diameter decreases with increase in compatibilizer loading up to 5% and thereafter shows a slight increase. The increase in domain size at high concentrations is due to the formation of micelles in the continuous polypropylene matrix, which is shown schematically in Fig. 9. The polydispersity index values decrease with increasing compatibilizer loading. The domain size distribution curves of the P₇₀

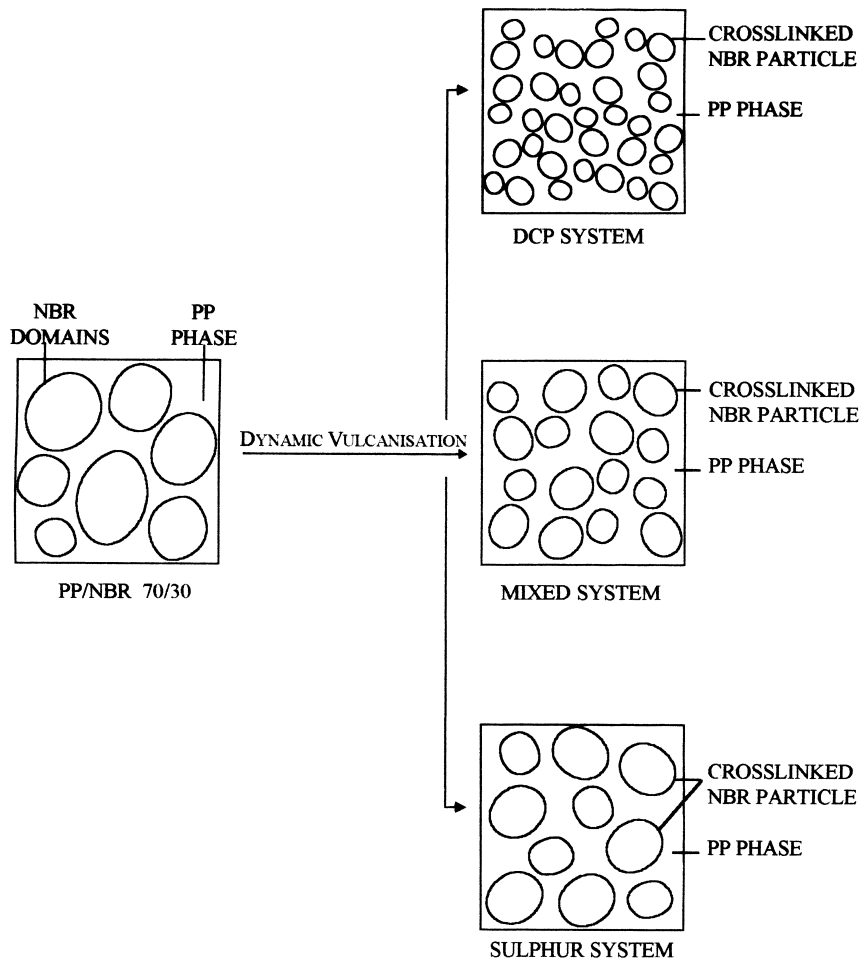


Fig. 17. Schematic representation of the morphology of PP/NBR blends vulcanized with sulfur, peroxide and the mixed system.

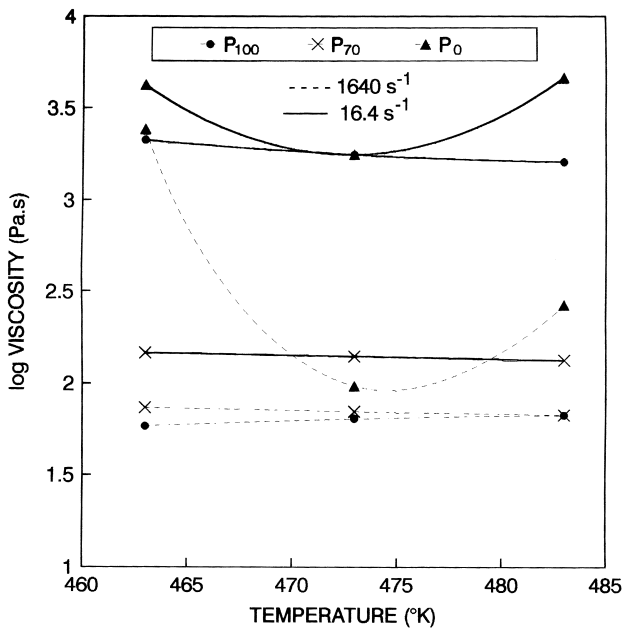
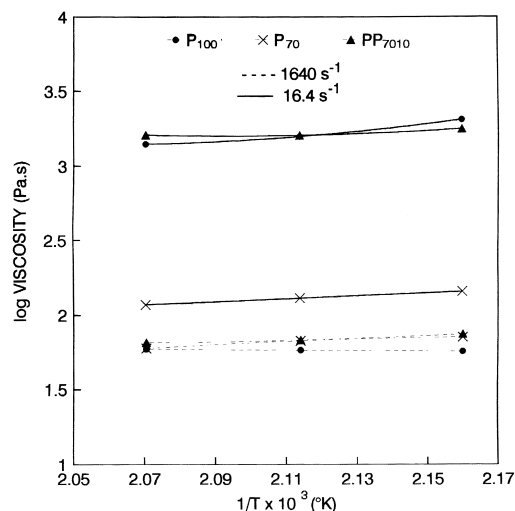


Fig. 18. Effect of temperature on the melt viscosity of polypropylene, nitrile rubber and the 70/30 PP/NBR blend.

blend compatibilized with different Ph-PP loadings are shown in Fig. 10. The uncompatibilized blend shows a broader distribution curve, showing the non-uniform nature of the distribution of NBR domains. As the compatibilizer loading increases the distribution curve becomes narrow and the size of the NBR domains also decreases.

Fig. 11 depicts the variation of NBR domain size and viscosity of the 70/30 PP/NBR blend as a function of compatibilizer concentration. As the Ph-PP concentration increases the size of the NBR domains decreases and viscosity increases, followed by a levelling-off at higher concentrations. The decrease in domain size upon the addition of Ph-PP to PP/NBR blends indicates that the interfacial interaction between PP and NBR phases increases and the interfacial tension decreases. The levelling-off at higher concentration for both domain size and viscosity is due to interfacial saturation, above which the compatibilizers form micelles in the continuous PP phase (Fig. 9). Such an interfacial saturation on the addition of compatibilizers has been reported by several authors [32–34]. The influence of interfacial energy and viscosity ratio on the particle size of the dispersed phase is given by the relationship proposed

Fig. 19. Arrhenius plots for P₁₀₀, P₇₀ and P₇₀₁₀ blends.

by Wu [35]:

$$G\eta_m a_n / \dot{\gamma} = 4(\eta_d / \eta_m)^{0.84} \quad \text{for } p > 1 \quad (20)$$

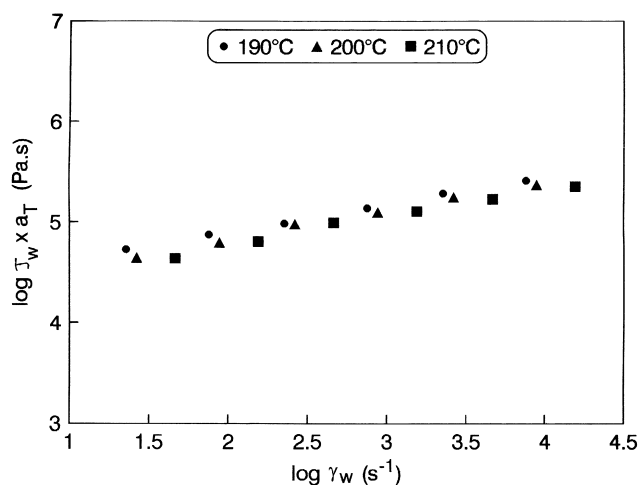
where $p = \eta_d / \eta_m$, G is the shear rate, a_n is the number-average diameter of the domains, $\dot{\gamma}$ is the interfacial tension, and η_d and η_m are the viscosities of the dispersed phase and matrix, respectively. It is seen from this equation that, at constant shear rate and viscosity ratio, the reduction in particle size is due to the reduction in interfacial tension. Hence the interfacial tension of uncompatibilized and compatibilized blends was calculated with Eq. (20). The calculation of interfacial tension by use of Eq. (20) gives higher values than the literature values. However, we are interested in the trend in the variation of interfacial tension with compatibilizer concentration and the results show that the interfacial tension decreases with the incorporation of Ph-PP as compatibilizer (Fig. 12).

3.4. Effect of dynamic vulcanization

Vulcanization of the rubber phase during mixing has been used as a way to improve the physical properties of thermoplastic elastomers [36–38]. This process, which is commonly known as dynamic vulcanization, leads to a stable morphology with a fine and uniform dispersion of rubber particles in the continuous plastic matrix, as shown schematically in Fig. 13. Here we have used three different types of vulcanizing agent: sulfur, peroxide and a mixed system composed of sulfur and peroxide. A schematic

Table 4
Activation energies of PP/NBR blends

Sample	E (kJ mol ⁻¹)
P ₁₀₀	46.62
P ₇₀	18.39
P ₇₀₁₀	44.35

Fig. 20. Shear rate–temperature superposition master curve of P₁₀₀.

representation of the crosslinks formed in these three cases is shown in Fig. 14. In the sulfur-cured system S–S linkages are formed, while on peroxide curing more stable C–C linkages are formed. In the mixed cured system both S–S and C–C linkages are present. The crosslink density values of these samples are given in Table 3. Among the three different vulcanizing systems used, the DCP-crosslinked system showed the highest crosslink density. The sulfur-cured and mixed cure system show almost the same crosslink density values.

The effect of dynamic vulcanization on the viscosity of the 70/30 PP/NBR blend with the sulfur, peroxide and mixed system is shown in Fig. 15 as a function of shear stress. Here also the viscosity decreases with increasing shear stress, which indicates pseudoplastic behaviour. Among the three vulcanizing systems used, the sulfur-cured system shows the highest viscosity compared with the unvulcanized blend. At low shear rates the peroxide-cured system shows slightly higher viscosity than the

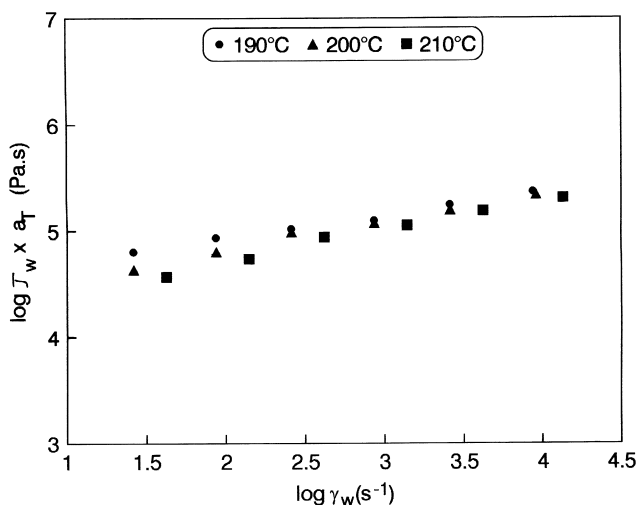
Fig. 21. Shear rate–temperature superposition master curve of P₇₀.

Table 5
Shift factor (a_T) values of P₁₀₀ and P₇₀

Temperature (°C)	P ₁₀₀	P ₇₀
190	0.842	0.834
200	1	1
210	1.535	1.629

mixed system and at high shear rates the trend is reversed. In mixed and peroxide-cured systems, during shearing at high temperature, the peroxide degrades the polypropylene phase and, as a result, the viscosity decreases. In these systems (peroxide and mixed systems) the degradation of PP overshadows the effect of crosslinking of the NBR phase. In the case of the sulfur-cured system the NBR phase is crosslinked and no degradation of PP takes place.

The morphology of extrudates of PP/NBR blends vulcanized with sulfur, DCP and the mixed system is shown in Fig. 16. From the figures it is seen that, in the sulfur-cured system, the size of the dispersed NBR domains is larger than those in peroxide and mixed cured systems. In the peroxide-cured system, the distribution is fine and uniform and the crosslinking is also more effective in DCP system. However, this effect of crosslinking is not so predominant on the properties of the peroxide-vulcanized system due to degradation of the PP phase in the presence of DCP. The morphologies of differently crosslinked samples are schematically shown in Fig. 17. The PP/NBR blend vulcanized with the sulfur system has the highest domain size while the blend vulcanized with DCP has the lowest. The blend vulcanized with the mixed system has a domain size between those of the DCP- and sulfur-cured systems.

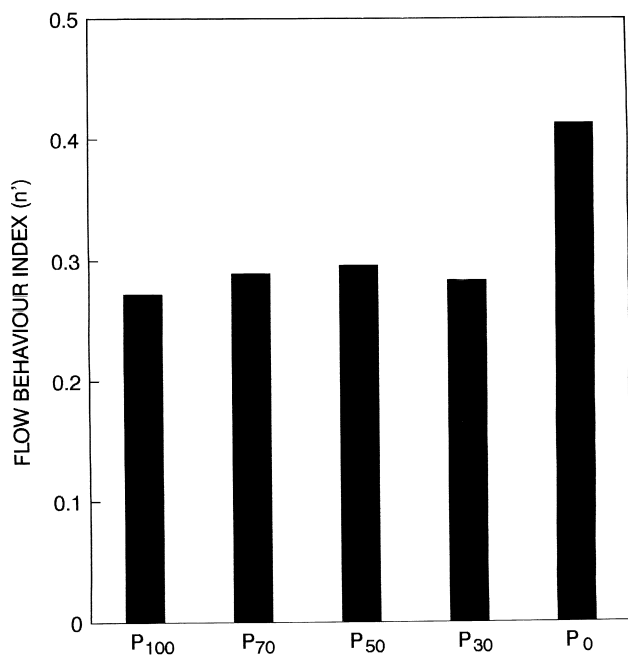


Fig. 22. Effect of blend ratio on the flow behaviour index n' .

Table 6
Flow behaviour index, n' , and die swell value, d_e/d_c , of compatibilized and dynamic vulcanized samples

Sample	n'	d_e/d_c
P ₇₀	0.289	1.44
P ₇₀₀₁	0.298	1.43
P ₇₀₁₀	0.294	1.42
PS	0.303	1.286
PC	0.281	1.162
PM	0.329	1.136

3.5. Effect of temperature

The effect of temperature on the melt viscosity of PP, NBR and the 70/30 PP/NBR blend is shown in Fig. 18. In the case of polypropylene, the viscosity decreases with increasing temperature, while in nitrile rubber the viscosity decreases initially and then increases at high temperature. This increase in viscosity of NBR at high temperatures is due to crosslinking. In the case of the 70/30 PP/NBR blend, the viscosity reduction upon increase in temperature from 200 to 210°C is lower compared with that in pure polypropylene. This may be due to crosslinking of the NBR phase in the blend. In fact, two reactions take place in the blend at high temperature: crosslinking of the NBR phase and degradation of the PP phase. The activation energy was calculated from the plot of $\log \eta$ versus $1/T$ for polypropylene, the 70/30 PP/NBR blend and the compatibilized blend. The plots of $\log \eta$ versus $1/T$ for these blends are shown in Fig. 19. The results are given in Table 4. It is seen from the table that the activation energy decreases on blending PP with NBR, while compatibilization increases the activation energy. Generally, the higher the activation energy, the more temperature-sensitive the material will be. Hence, upon compatibilization, the temperature sensitivity of the material increases. This effect of increase in activation energy on compatibilization was reported earlier [19]. It is important to add that the activation energy values are useful in choosing the temperature to be used during processing routes such as injection moulding, calendaring and extrusion.

The shear rate–temperature superposition analysis has been used to predict the melt viscosity of polymers [39]. The superposition shift factors were obtained from the equation

$$a_T = \frac{\tau_{\text{ref}}}{\tau_{(T)\text{constant}} \dot{\gamma}} \quad (21)$$

The shear rate–temperature superposition master curves

Table 7
Average diameter of NBR domains in PP/NBR blends

Sample	\bar{D}_n (μm)	\bar{D}_w (μm)	PDI (\bar{D}_w/\bar{D}_n)	\bar{D}_{vs} (μm)
P ₇₀	8.168	11.59	1.418	15.00
P ₅₀	11.89	15.68	1.318	18.65

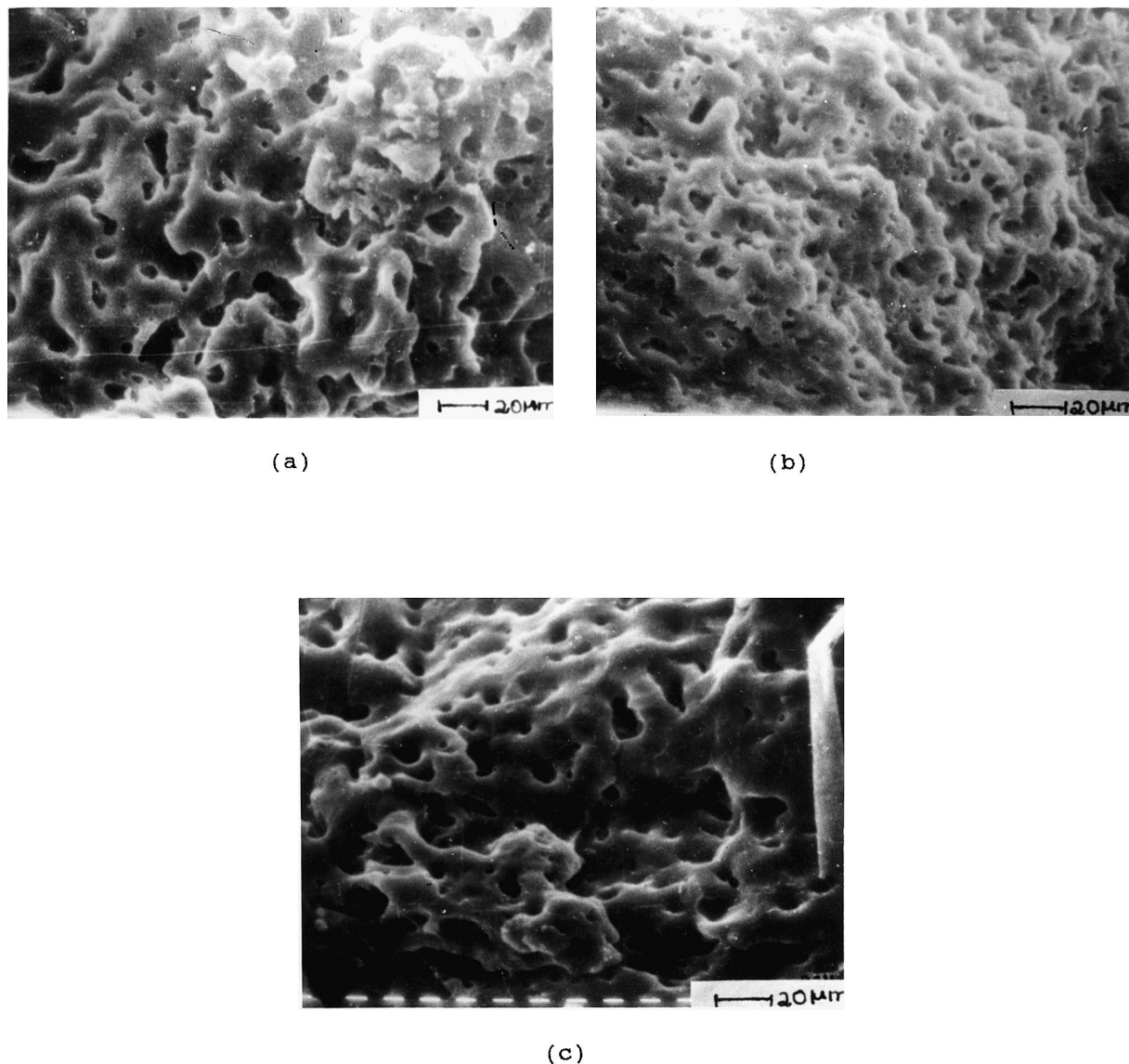


Fig. 23. Effect of shear rate on the extrudate morphology of 70/30 PP/NBR blends: (a) 16.40 s^{-1} , (b) 164.04 s^{-1} and (c) 1640.4 s^{-1} .

of the PP/NBR 70/30 blend and P_{100} have been constructed by plotting the modified shear stress ($\tau \times a_T$) against $\dot{\gamma}$ at a reference temperature of 200°C . In the case of polypropylene and the P_{70} blend, superposition of the data was obtained in the temperature range and shear rate studied (Figs. 20 and 21). The values of a_T for different temperatures of P_{100} and P_{70} are shown in Table 5. Hence it is possible to develop the rheograms at different temperatures from the rheogram at any temperature by knowing the shift factor (a_T) values.

3.6. Flow behaviour index

The flow behaviour index gives an idea about the nature of flow, i.e., whether it is Newtonian or non-Newtonian. Most polymers show pseudoplastic behaviour with flow behaviour index n' less than 1. For Newtonian liquids, n'

is 1. The effect of blend ratio on the flow behaviour index is shown in Fig. 22. The low values of n' for PP, NBR and their blends indicate pseudoplastic behaviour. The incorporation of NBR increases the flow behaviour index slightly; i.e., the incorporation of NBR does not change the flow behaviour of polypropylene very much. The effect of compatibilization and dynamic vulcanization on the flow behaviour index is given in Table 6. It is clear from the table that compatibilization and dynamic vulcanization using the sulfur and mixed systems increase the n' values, indicating an increased Newtonian behaviour. However, the DCP-vulcanized system shows lower n' value.

3.7. Extrudate morphology

The extrudate morphology of the blends depends on the viscosity of the individual components, the composition,

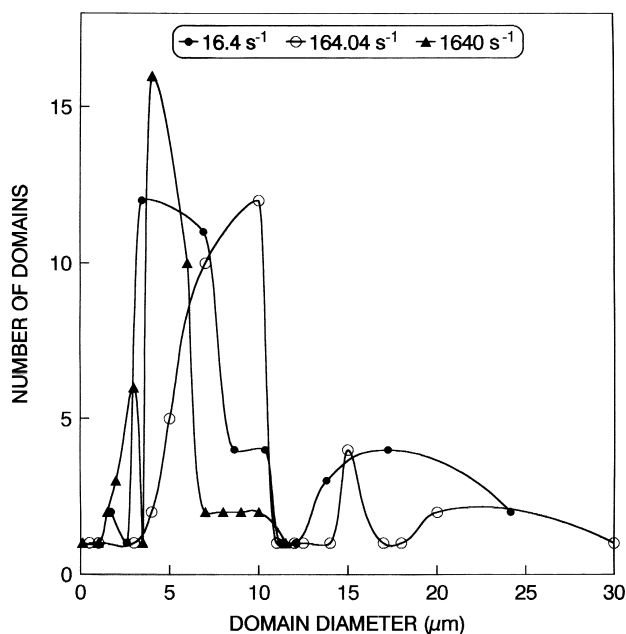


Fig. 24. Domain size distribution curves of P₇₀ extruded at different shear rates.

interfacial tension and shear rate. According to Danesi and Porter [40], when the polymers have similar melt viscosities, the minor component will be finely and uniformly distributed in the major component. When the two polymers have different melt viscosities, the morphology of the blend depends on whether the minor component has lower or higher melt viscosity than the major one. Generally, the least viscous component forms the continuous phase, irrespective of composition [41]. In PP/NBR blends, we have already seen that polypropylene has lower viscosity than nitrile rubber. Thus in P₇₀, in which NBR is minor phase, NBR forms dispersed phase; i.e., NBR is dispersed as a spherical domains in the continuous PP matrix as expected. In P₅₀, for the intermediate composition also NBR forms the dispersed phase and in this case the size of the dispersed NBR domains increases due to coalescence of the rubber domains during shearing. The domain size of P₇₀ and P₅₀ blends is shown in Table 7. In P₃₀, where the minor component PP has a lower viscosity, both NBR and PP form continuous phase, resulting in a co-continuous morphology. This is due to the fact that the low-viscosity phase has a tendency to form continuous phase irrespective of the composition. The effect of shear rate on the extrudate morphology is shown in Fig. 23. As the shear rate increased

the size of the dispersed domains decreases and becomes more uniform. The domain size distribution curves of 70/30 PP/NBR blends extruded at different shear rates is shown in Fig. 24. As the shear rate increases from 16.4 to 1640 s⁻¹, the distribution curve becomes narrow indicating more uniform distribution at high shear rates. The number- and weight-average diameter of NBR domains and the polydispersity index values are given in Table 8. As the shear rate increases the diameter of NBR domains decreases and the distribution of NBR domains becomes more uniform, as shown by the low values of polydispersity index. Under the action of shear, the dispersed phase undergoes elongational deformation and finally the droplet will break up as shown schematically in Fig. 25. The droplet break-up depends on the viscosity ratio, η_d/η_m . The break-up is easier when η_d/η_m is close to unity. Taylor's equation has been developed for the deformation of a Newtonian drop suspended in a Newtonian matrix [42,43]. The equation gives the deformation of a droplet in terms of the critical Weber number. According to Taylor's equation:

$$W_c = G\eta_m a_n / \dot{\gamma} \quad (22)$$

where G is the shear rate, η_m the viscosity of the matrix phase, a_n the average diameter of the dispersed rubber particle and $\dot{\gamma}$ the interfacial tension.

According to Wu's equation (Eq. 20), it is clear that the average size of the particles is small when the shear rate is high, the interfacial tension is low and when the η_d/η_m ratio is small. Thus, as the shear rate increased, in PP/NBR blends the dispersed NBR domains are elongated in the direction of flow and at higher shear rates the elongated NBR phase is broken down into small particles.

3.8. Extrudate swell

The melt elasticity of polymers leads to different phenomena like extrudate swell, melt fracture, shark skin, etc. during flow through a capillary [8]. In the capillary the polymer molecules undergo orientation under the action of shear. On emerging from the die, the oriented molecules have a tendency to recoil. As a result, lateral expansion takes place which leads to extrudate swell. The extrudate deformation characteristics of these blends are shown in Fig. 26(a) and (b)(b). At low shear rate the deformation of the extrudates is less, whereas at high shear rate the deformation is very prominent. This is associated with melt fracture which occurs at high shear forces, where the shear stress exceeds the strength of the melt. As the concentration of rubber increases, the surface of the blend exhibits more roughness and the extrudates have a non-uniform diameter since the elastic response increases with increase in concentration of the rubber phase. It is clear from the figure that compatibilization and dynamic vulcanization reduce the extrudate deformation. In unvulcanized blends during extrusion, the rubber particles undergo a large extent of deformation in the die or are broken down into small particles at high

Table 8
Average domain diameter of NBR in P₇₀ extruded at different shear rates

Shear rate (s ⁻¹)	\bar{D}_n (μm)	\bar{D}_w (μm)	PDI
16.4	9.57	13.962	1.459
164.04	8.168	11.59	1.418
1640.4	4.398	5.915	1.345

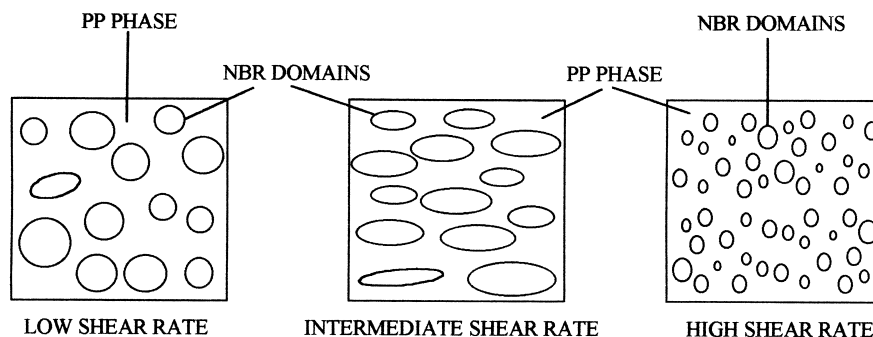
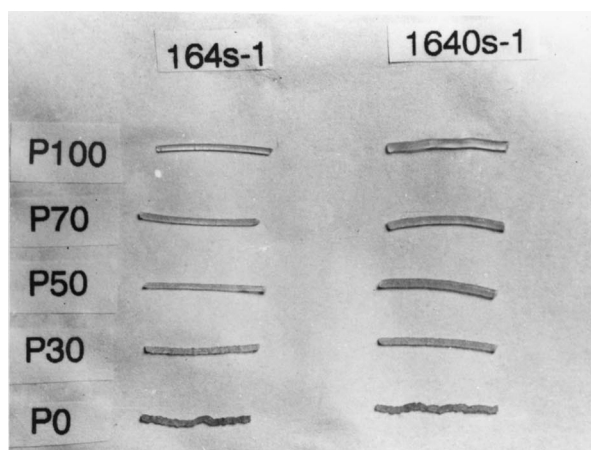
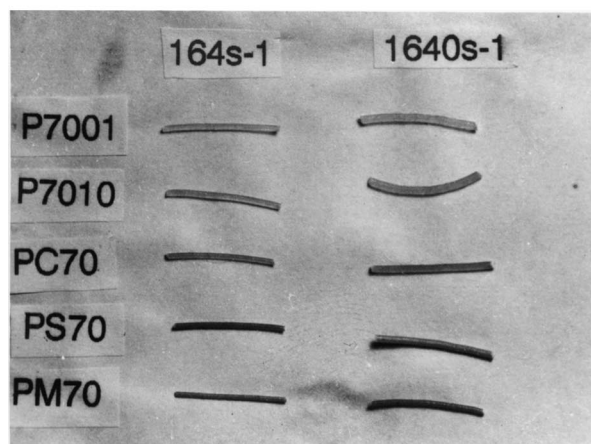


Fig. 25. Schematic representation of the droplet break-up during shearing.



(a)



(b)

Fig. 26. Photographs of the extrudates of (a) PP/NBR binary blends and (b) dynamic vulcanized and compatibilized blends at shear rates of 164 and 1640 s^{-1} .

shear rates, and after extrusion they show a deformed morphology. However, in dynamic vulcanized blends, the rubber particles undergo less deformation during extrusion through the die and retain their morphology after extrusion. The change in morphology of a dynamic vulcanized blend during the extrusion process is shown schematically in Fig. 27. Kuriakose et al. [22] have reported that, upon dynamic vulcanization of PP/NR blends, the extrudate distortion decreases due to the reduced deformation and quick recovery of the crosslinked rubber particles in these blends. The effect of NBR addition on the extrudate swell (d_e/d_c) of PP/NBR blend is shown in Table 9. As the rubber content in the blend increases the extrudate swell decreases. This is due to the elasticity of the rubber phase. The effect of shear rate and temperature on the die swell value of the 70/30 PP/NBR blend is shown in Table 10. As expected, the increase in shear rate increases the die swell values, while the increase in temperature decreases the values. Compatibilization of the blend decreases the die swell marginally. The dynamic vulcanization has a significant effect on die swell values (Table 6) due to the elasticity of the network as a result of dynamic vulcanization. On dynamic vulcanization of PP/NBR blend using sulfur, peroxide and mixed systems, the die swell values decrease and the effect is more pronounced in the case of the mixed cured system. Coran [41] reported that in the case of dynamically vulcanized thermoplastic elastomers, the die swell values are very low or even absent, since the viscosity can approach infinity at zero shear rate in these types of thermoplastic vulcanizate upon emerging from the die.

3.9. Melt-flow index

The MFI values of PP/NBR blends are given in Table 11. The melt-flow index of the blends decreases with increasing concentration of nitrile rubber, which is in agreement with the viscosity data obtained from capillary measurements. The MFI values give an idea about the processing behaviour of polymers. However, usually the actual processing conditions (such as temperature and shear rate) employed in product development differ from those of the conditions used in MFI tests. Several authors have made an attempt

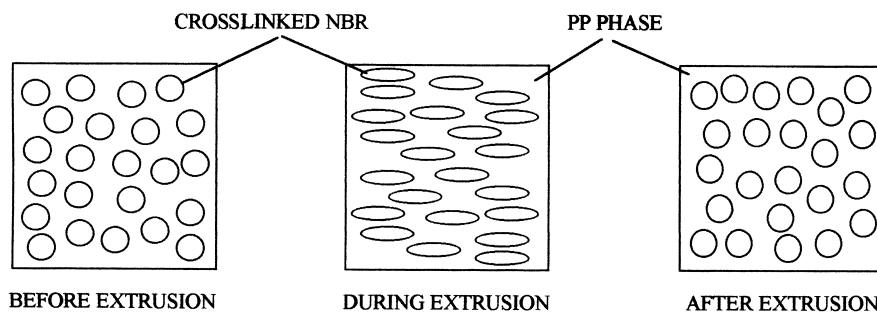


Fig. 27. Schematic representation of morphology changes during extrusion of dynamic vulcanized blends.

to correlate the MFI values with rheograms and to develop master curves [44,45]. Recently, in this laboratory, Oommen et al. [19], George et al. [46] and Asaletha et al. [47] combined MFI data and capillary rheometer data to provide master curves.

In PP/NBR blends, a master curve is obtained by combining the MFI values and capillary rheometer data as shown in Fig. 28. For different blend compositions, the plots of $\dot{\gamma} \times \rho/\text{MFI}$ versus $\eta \times \text{MFI}/\rho$ (where ρ is the density for various PP/NBR blends) unified into a single curve. Thus, it is possible to generate the viscosity versus shear rate curves from the master curve by simply knowing the MFI values without the use of sophisticated rheological instruments.

3.10. Effect of annealing

The influence of phase coarsening and coalescence occurring during annealing on the morphology of polymer blends is important, since these materials often undergo annealing during processing and fabrication steps. The phase coarsening and coalescence phenomena in polymer blends have been reported by various researchers [2,39,48–50]. The coalescence of dispersed particles leads to unstable morphology and poor mechanical properties. A schematic model illustrating the coalescence phenomena in the blends is shown in Fig. 29. It has been reported that coalescence in immiscible blends can be prevented by compatibilization. In the case of compatibilized blends, the compatibilizer forms a shell around the dispersed phase and therefore the coalescence is suppressed [51]. SEM micrographs of the annealed P₇₀ and P_{70/10} blends are shown in Fig. 30. The samples were annealed by keeping the samples in the barrel for 1 h before extrusion at 200°C. It is seen from the figure that, during annealing, the size of the dispersed NBR particles increases in P₇₀. However, in the presence of compatibilizer, the

domain size is unaffected on annealing. The increase in domain size during annealing is due to coalescence of the dispersed NBR particles. On compatibilization with Ph-PP, it forms a shell around the NBR particles that prevents the rubber particles from coalescing and leads to a stable morphology. Hence, in compatibilized blends, the size of the dispersed phase is unaffected by annealing. The dispersed phase size of the P₇₀ and P_{70/10} blends before and after extrusion is shown in Table 12. Oommen et al. [19] reported that compatibilization of the PMMA/NR blend with PMMA-*g*-NR prevents the coalescence of dispersed domains. Danesi and Porter reported that, in PP/EP blends, the PP particles coalesce into larger domains during annealing and have indicated the high instability of the morphological species with annealing above the melting point of polypropylene [39].

4. Conclusion

The melt rheological behaviour of polypropylene/nitrile rubber blends has been investigated. The blends showed pseudoplastic behaviour which is indicated by a decrease

Table 9
Die swell ratio of PP/NBR blends

Sample	d_e/d_c
P ₁₀₀	1.48
P ₇₀	1.44
P ₅₀	1.43

Table 10
Die swell ratio of 70/30 PP/NBR blends

Shear rate (s ⁻¹)	Temperature (°C)		
	190	200	210
16.4	1.33	1.34	1.34
164.04	1.49	1.44	1.38
1640.4	2.07	1.88	1.71

Table 11
MFI values of PP/NBR blends

Sample	MFI (g/10 min)	Viscosity (Pa s)
P ₁₀₀	2.014	4 169.1
P ₇₀	0.68	11 282.1
P ₅₀	0.487	19 194.2
P ₃₀	0.239	47 675.8

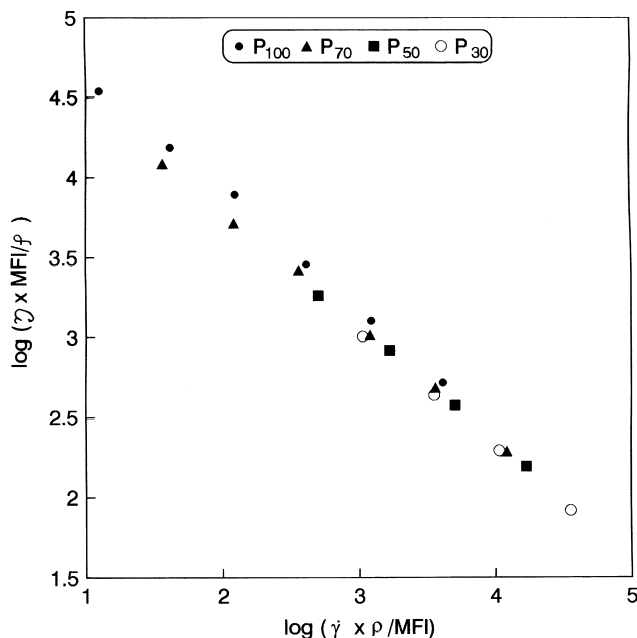


Fig. 28. Master curve of modified shear viscosity versus modified shear rates as a function of blend ratio at 200°C.

in viscosity with shear rate. The viscosity of these blends increased with increasing NBR concentration and showed a sharp change after 50 wt% NBR. The variation in viscosity was correlated with the phase change of NBR from a dispersed phase to a continuous phase. The blends showed negative deviation, which indicated a lack of interaction between the polar nitrile rubber and the non-polar polypropylene. Various theoretical models have been used to predict the experimental viscosity values. The viscosity values fit well with those calculated using an altered free volume model. The compatibilization of these blends with phenolic-modified polypropylene was found to increase the viscosity of the system, indicating an increase in interfacial interaction. The variation in viscosity was correlated with the morphology. As the compatibilizer concentration increases the domain size decreases and shows a leveling-off at high concentration. The dynamic vulcanization of PP/NBR blends leads to a fine and uniform distribution of NBR particles, the size of the dispersed NBR particles varying in the order DCP < mixed < sulfur-cured system.

Among the dynamic vulcanized blends, the sulfur-cured system has the highest viscosity and the DCP-cured system has the lowest viscosity. In peroxide and mixed cured systems PP was degraded in the presence of DCP. The die swell values of the blends are decreased on dynamic vulcanization. The temperature dependence of viscosity was studied by use of the Arrhenius equation. The compatibilized system showed higher values of activation energy compared with uncompatibilized one. A shear rate–temperature superposition master curve has also been developed for polypropylene and 70/30 PP/NBR blends. The melt-flow index of PP/NBR blends decreased with increasing rubber concentration and correlated the MFI values obtained from capillary rheometer data, so that a master curve was obtained for different blend compositions. The effect of annealing on the morphology of uncompatibilized and compatibilized blends has been investigated. The domain size of NBR particles increased in the uncompatibilized system upon annealing the samples for 1 h. Interestingly, the morphology of the compatibilized system was really stable.

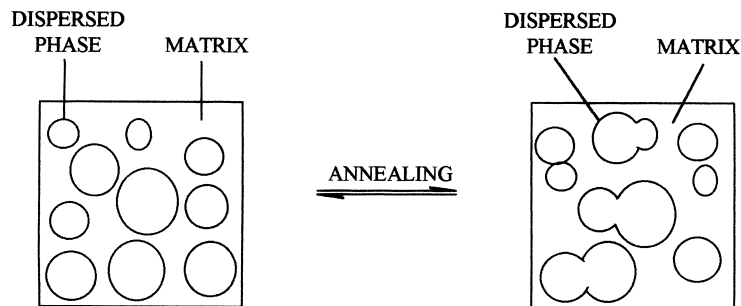
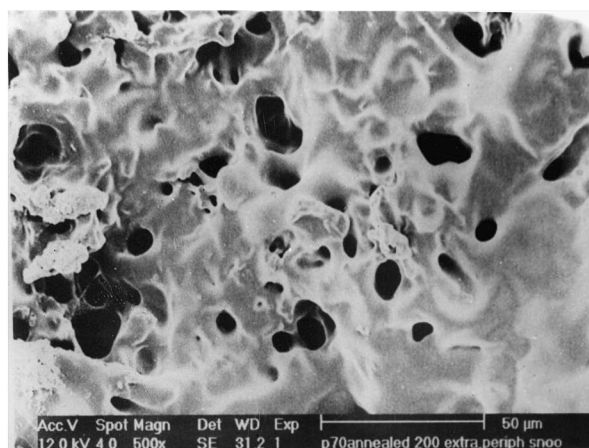
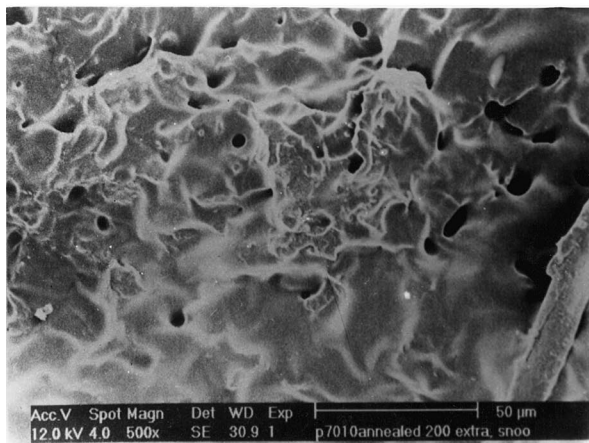


Fig. 29. Schematic representation of coalescence phenomena in PP/NBR blends.



(a)



(b)

Fig. 30. SEM micrographs of (a) P₇₀ and (b) P₇₀₁₀ annealed for 1 h at 200°C.Table 12
Average diameter of NBR domains in annealed samples

Sample	\bar{D}_n (μm)	\bar{D}_w (μm)	PDI
P ₇₀	8.168	11.59	1.418
P ₇₀ annealed	9.711	13.438	1.283
P ₇₀₁₀	5.06	6.17	1.219
P ₇₀₁₀ annealed	5.0	6.673	1.37

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