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Melt rheological behaviour of natural rubber/poly(methyl methacrylate)/natural rubber-g-poly(methyl methacrylate) blends

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Melt rheological behaviour of natural rubber (NR) and poly(methyl methacrylate) (PMMA) blends has been studied with reference to the effect of blend ratio, processing conditions and graft copolymer concentration as a function of shear stress and temperature. The viscosity of the blend increases as the amount of NR increases. The observed values of viscosity are found to be higher than that calculated from additivity rule. In the case of solution cast samples the melt viscosity increases as the percentage of graft copolymer increases and the blend becomes more sensitive to temperature in the presence of graft copolymers. The influence of dynamic vulcanization of the rubber phase on the flow behaviour of the blends has been analysed. The die swell of the NR/PMMA blends was also evaluated in the presence and absence of graft copolymers. The morphology of extrudates has been analysed as a function of composition, graft copolymer concentration and shear stress conditions. Addition of compatibilizer reduces the domain size of the dispersed phase and stabilizes the morphology. It is also noted that state of dispersion are affected by conditions of blend preparation and extrusion. A shear rate–temperature super position master curve is constructed to predict the melt viscosities of the system as a function of temperature. The rheograms of 50/50 NR/PMMA with varying graft copolymer concentrations are found to coalesce into a master curve using modified viscosity and shear rate functions. © 1997 Elsevier Science Ltd.

(Keywords: rheology; compatibilization; morphology)

INTRODUCTION

Polymer blends are gaining increasing industrial importance as a means of improving the mechanical properties and processability. It is possible to improve properties such as modulus, yield stress, impact strength and tensile strength by appropriate combination of polymer components. Though blending looks very attractive, most of the polymer blends are immiscible and incompatible. Incompatibility leads to poor interfacial adhesion and mechanical properties. Even though most of the polymer blends are immiscible, many may be made compatible by several methods. One such method is to add a third component called compatibilizer which increases the interaction between immiscible phases. The third component can be block, graft or a homopolymer which can interact with both the phases. The interfacial activity of block or graft copolymer has been reviewed by Paul[1]. The compatibilization of immiscible blends by the addition of a copolymer is analogous to the role of a surfactant in oil–water emulsion. Molau[2] observed the emulsifying effect of copolymers in immiscible polymer pairs and found an increase in the stability of dispersion upon the addition of copolymers. Demixing or phase separation occurs at a slow rate in the presence of graft or block copolymers. Several workers later reported on the interfacial modification of polymer blends by the addition of graft or block copolymer or by the reactive route[3–9].

In our earlier publications we have reported[10,11] on the interfacial activity of natural rubber-graft-poly(methyl methacrylate) copolymer in heterogeneous natural rubber/poly(methyl methacrylate) blends. The mechanical properties of blends of NR and PMMA are very poor as they are incompatible and the same can be improved by the addition of graft copolymer which makes the blend more compatible. It has been shown that the above-mentioned blends exhibit tremendous improvement in mechanical properties by the addition of graft copolymer and the properties levelled off at a particular concentration of graft copolymer. A study of the flow behaviour of NR/PMMA/NR-g-PMMA is important to standardize the processing conditions as they can be used for making a large number of automobile and other moulded parts.

Rheological behaviour of polymer blends has been studied by several workers. During processing of polymer blends several factors have to be optimized. Akhtar *et al.*[12] studied the rheological behaviour of blends of high density polyethylene and natural rubber (NR) as a function of blend ratio, dynamic crosslinking

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of rubber phase and carbon black filler. The shear viscosity of these blends was found to be influenced more by shear rate than by temperature. Morphology was found to depend on the blend ratio and shear rate. Willis and Favis[13] have shown that addition of ionomer to an immiscible blend increases the viscosity as a function of ionomer concentration. This indicates that the blends become more viscous when ionomer is added during compounding. Gupta *et al.*[14] examined the melt rheological properties of binary blends of PP and ABS terpolymer and ternary of polypropylene (PP), acrylonitrile styrene butadiene (ABS) and low density polyethylene. Pseudoplasticity increased with increasing ABS content for binary blends and showed insignificant variation in ternary blends. Danesi and Porter[15] studied the rheological behaviour of polypropylene and ethylene propylene rubber. They explained how the state of dispersion is affected by conditions of blend preparation and extrusion. Utracki and Sammut[16] studied the flow properties of various blends based on polystyrene. Kuriakose and De[17] and Thomas *et al.*[18] studied the flow behaviour of various thermoplastic elastomer blends. Recently Varughese[19] studied the rheological behaviour of poly(vinylchloride)/epoxidized natural rubber blends. All these studies indicated that the dispersed phase in an immiscible blend is deformable and may give rise to a wide range of sizes and shapes during processing.

Rheological behaviour of compatibilized blends has been carried out by several people. Germain *et al.*[20] investigated the influence of a block copolymer on the rheological behaviour of polypropylene/polyamide blends. They described rheological behaviour by a dual region flow curve—a low and high shear rate region. At low shear rate region the viscosity is higher than the matrix and the morphology is spherical whereas at high shear rate region the blend becomes less viscous than the matrix phase and possesses a lamellar structure. Lee and Park[21] attempted a new theoretical approach to consider the influence of morphology in determining the rheological properties. The equation constituted by them agrees with the experimental effect of shear flow on the morphology of polystyrene/linear low density polyethylene blends.

In this paper we report on the results of the rheological studies of NR/PMMA blends with and without graft copolymer, by capillary rheometry. The effects of blend composition, shear stress, temperature and concentration of graft copolymer on melt viscosity, flow behaviour index and die swell have been investigated. In addition, the morphology of the extrudate has been examined to understand the influence of blend morphology on flow characteristics. The influence of dynamic vulcanization of the elastomer phase using sulfur and peroxide system on the flow behaviour of blends has been analysed. Shift factor is calculated from the flow curves of different temperatures which in turn is used to predict the viscosity as a function of temperature. Master curves have been generated using modified viscosity and shear rate function that contain melt flow index as a parameter.

EXPERIMENTAL

Materials

Natural rubber used for the experiment was ISNR 5 grade and was supplied by the Rubber Research Institute of India, Kottayam. Poly(methyl methacrylate) was the product of Gujarat State Fertilizer Corporation. The characteristics of the materials used are given in *Table 1*. Graft copolymer of NR and PMMA was prepared in our laboratory by polymerizing methyl methacrylate in the presence of natural rubber latex using a redox initiator[22]. The NR-g-PMMA copolymer was characterized by i.r. spectroscopy, ^{1}H n.m.r. spectroscopy and gravimetric methods[23]. Gravimetric determination as reported earlier[10,23] showed that grafting efficiency and PMMA grafted were 60% and 26% respectively.

Table 1 Characteristics of the materials

Materials	Density ($\mathrm{g\,cm^{-3}}$)	Solubility parameter ($(\mathrm{cal\,cm^{-3}})^{1/2}$)	Intrinsic viscosity ($\mathrm{dl\,g^{-1}}$)	Mol. wt ($\bar{M}_w$)
NR	0.90	7.75	4.35	8.05×10^5
PMMA	1.18	11.80	0.42	2.09×10^5
NR-g-PMMA	1.04	–	3.20	8.76×10^5

Blend preparation

Binary blends of NR and PMMA with and without graft copolymer were prepared by solution mixing and melt mixing techniques. The polymer components were dissolved in toluene at a total concentration of 5% and stirred for about 16 h using a magnetic stirrer at ambient temperature. The polymer solution was cast into films and dried at about 110°C for several weeks in a vacuum oven to eliminate the solvent. The solution cast NR/PMMA blends with 0, 30, 50, 60, 70 and 100% NR are denoted by N_0, N_{30}, N_{50}, N_{60}, N_{70} and N_{100} respectively. 50/50 NR/PMMA blends with 0, 5, 10 and 15% graft copolymer are denoted by $0N_{50}$, $5N_{50}$, $10N_{50}$ and $15N_{50}$ respectively.

Samples were also prepared by melt mixing the components. Melt mixing was carried out using a Brabender Plasticorder-PLE 651 at a temperature of 160°C and at a rotor speed of 80 rpm. PMMA was melted for 2 min and blended with NR for another 2 min. Finally compatibilizer was added and blended for another 4 min. The molten mixture was removed from the Brabender mixing boul, sheeted on a mill and compression moulded into thin sheets of 2 mm thickness. NR/PMMA melt blends with 0, 50, 70 and 100% of NR are denoted by N'_0, N'_{50}, N'_{70} and N'_{100} respectively. The dynamically vulcanized blends using DCP and sulfur are denoted by D_1. The dosage of the crosslinking agent was based on the rubber content (DCP = 0.625 phr, S = 2.5 phr). The 50/50 NR/PMMA melt blends with 0, 5 and 10% graft copolymer are denoted by $0N'_{50}$, $5N'_{50}$ and $10N'_{50}$ respectively.

Rheological measurements

The rheological studies were carried out using a capillary rheometer attached to a Zwick Universal Testing machine model 1474. The capillary used was made of tungsten carbide and has a l/d ratio of 40 and an angle of entry of 180°. The sample for testing was placed inside the barrel of the extrusion assembly and forced down to the capillary with a plunger attached to the moving cross head. The studies were carried out in the shear range of 1.6–833 $\mathrm{s^{-1}}$. The temperature controller provided the facility to increase the temperature gradually across the length of the barrel. With a single charge of the material the machine was operated to give nine different plunger speeds. A warm up period or 3 min was given to the sample before starting the experiment. The melt was extruded through the capillary at preselected speeds of the cross head. The forces corresponding to specific plunger speeds were recorded using a strip chart assembly. The force and the cross-head speed were converted into shear stress (τ_w) and shear rate ($\dot{\gamma}_w$) at wall respectively using the following equations involving the geometry of the capillary and the plunger.

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

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

where F is the force applied at a particular shear rate, A_p is the cross sectional area of the plunger (mm^2), l_c is the length of the capillary (mm), d_c is the diameter of the capillary (mm), and Q is the volume flow rate (mm^3 s^{-1}).

Q is calculated from the velocity of the cross-head and the diameter of the plunger. The flow behaviour index n^1 is defined by

$$n^1 = \frac{d(\log \tau_w)}{d(\log \dot{\gamma}_{wa})} \tag{3}$$

and was determined by regression analysis of the values of τ_w and $\dot{\gamma}_{wa}$ obtained from the experimental data. The apparent wall shear rate ($\dot{\gamma}_{wa}$) was calculated as $32Q/\pi d_c^3$. The shear viscosity η was calculated using the equation

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} \tag{4}$$

Rheological measurements were carried out at temperatures of 130, 140 and 150°C.

Extrudate swell

The extrudates were collected from the capillary die and care was taken to avoid any deformation. The diameter of the extrudate was measured after 24 h of extrusion using a travelling microscope. The ratios of the diameter of the extrudate to that of the capillary was calculated as the die swell (d_e/d_c). The distortion of the extrudate was studied by taking the photograph of the extrudate at different shear rates. The extrudates were fractured under liquid nitrogen and the morphology of extrudate cross section was examined with the help of an SEM.

Melt flow indices

The melt flow indices (MFI) were determined using a Ceast melt flow indexer model 6542 using 49.05 N load as per ASTM D 1238-73. The measurements were made at 200, 210, 220 and 230°C for NR/PMMA blends having 50/50 composition with and without the addition of graft copolymer.

Morphology of the extrudate

Morphological characterization of the extrudate from the barrel of the melt flow indexer was performed using an SEM. The blends with 0, 10 and 15% of graft copolymer was fractured under liquid nitrogen and examined under an SEM. The blends with 0 and 10% graft copolymer were annealed by keeping it inside the barrel of the MFI apparatus for 1 h at 220°C and then extruded. The extrudates before and after annealing were fractured under liquid nitrogen and the morphology was examined by an SEM.

RESULTS AND DISCUSSION

Effect of blend ratio and shear stress on viscosity

The effects of blend ratio and shear stress on the shear viscosity of uncompatibilized NR/PMMA blends N_0, N_{30}, N_{50}, N_{60}, N_{70} and N_{100} prepared by solution mixing at an extrusion temperature of 130°C are shown in *Figure 1*. It can be seen that the viscosity of all the blends decreased with increase in shear stress, indicating pseudoplastic nature of the blends. The pseudoplasticity is due to the random orientation and highly entangled state of the molecules which under high shear get disentangled and become oriented resulting in a reduction of viscosity. The decrease in viscosity at higher shear rate may also be due to the shearing away of the dispersed phase of the incompatible blend (either NR or PMMA depending on the composition). NR exhibits higher viscosity than PMMA. The differences are more prominent at low and intermediate shear rate region. In the shear rate region between 8.3 and 833 s^{-1} the viscosities of the blends are higher than those of the components. From *Figure 2* it is evident that the viscosity of the blends are nonadditive functions of the viscosities of the component polymers. As the per cent of NR increases, viscosity increases up to 60% NR followed by a decrease. Up to 60% NR, PMMA forms the dispersed phase and a strong interaction among the domains can be expected. This can lead to a reversible structural build up leading to an increase of viscosity. As the shear rate increases difference in viscosity between different blends narrow down. The bulk viscosity becomes greater than that of the constituent components especially at lower shear rates. As the level of shear rate increases the structure breaks down and the chances of interaction between the PMMA domains are reduced. This accounts for the absence of positive deviation at high shear rate

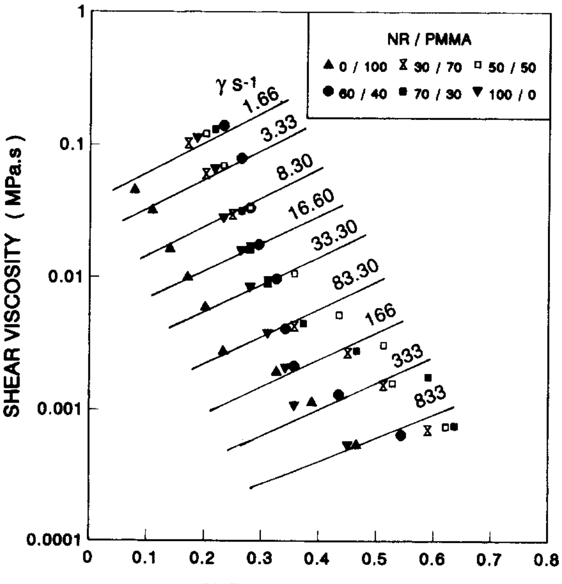


Figure 1 Variation of shear viscosity with shear stress of 0/100, 30/70, 50/50, 60/40, 70/30 and 100/0 NR/PMMA solution cast blends

region. The reduction in viscosity at higher shear rate is also due to the decrease in particle size. During extrusion the dispersed domains are elongated at the entrance of the capillary under the action of shear force resulting in the deformation and consequent break down of the particles. As suggested by Munstedt[24] in the case of rubber modified plastics, at low shear rate, the dispersed phase form a wall structure around the NR matrix. When the shear stress is above a critical value called yield stress the structure breaks down and the viscosity decreases. The maximum viscosity of 60/40 NR/PMMA might be due to the fact that in this composition the domains are well packed together and form a wall structure. A speculative model indicating the structure build up at low and high shear rate is shown in *Figure 3*. Ablanova[25] reported similar behaviour for polyoxymethylene/copolyamide blends. In this case the viscosity vs. composition curve of polyoxymethylene/copolyamide goes through a maximum at low shear stress levels and through a minimum at high shear stress levels.

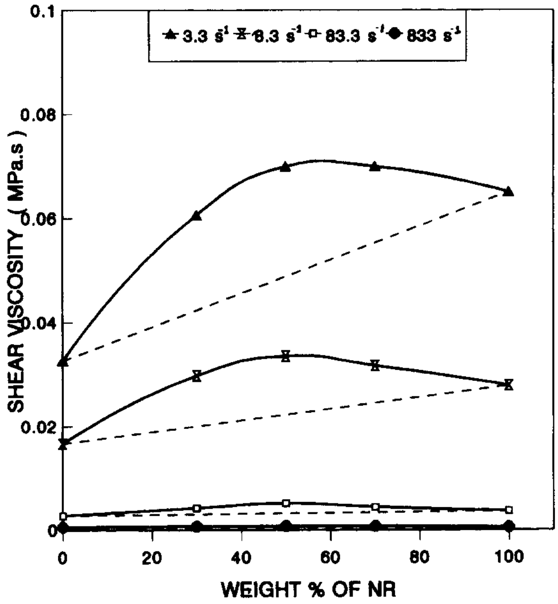
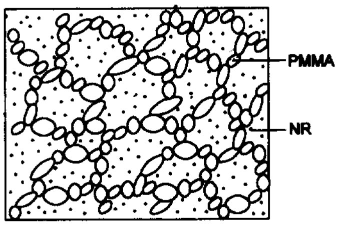
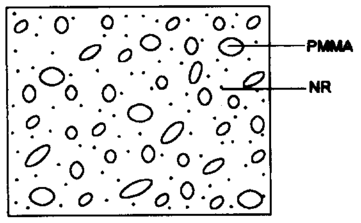


Figure 2 Variation of shear viscosity with wt% of NR in NR/PMMA solution cast blends at different shear rates



(a) At low shear rate 33.3 s^{-1}



(b) At high shear rate 833.3 s^{-1}

Figure 3 Speculative model illustrating the structure development of PMMA domains

Utracki and Sammut[16] showed that positive or negative deviation of measured viscosity from that calculated from the log additivity rule is an indication of strong or weak interactions between the phases of the blend. According to them

$$\ln(\eta_{\mathrm{app}})_{\mathrm{blend}} = \sum_i w_i \ln(\eta_{\mathrm{app}})_i \qquad (5)$$

where w_i is the weight fraction of the ith component of the blend. They indicated that immiscible blends show negative deviation due to heterogeneous nature of the components whereas positive deviation is expected for blends due to high solubility and homogeneous nature of the components[16]. The following models have been used to calculate the viscosity of the blend.

$$\eta = \eta_1\phi_1 + \eta_2\phi_2 \quad \text{(Model 1)} \qquad (6)$$

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

Viscosity can also be calculated using Hashin's upper and lower limit models

$$\eta_{\mathrm{mix}} = \eta_2 + \frac{\phi_1}{1/(\eta_1 - \eta_2) + \phi_2/2\eta_2} \quad \text{(Model 2)} \qquad (7)$$

$$\eta_{\mathrm{mix}} = \eta_1 + \frac{\phi_2}{1/(\eta_2 - \eta_1) + \phi_1/2\eta_1} \quad \text{(Model 3)} \qquad (8)$$

η_1, η_2, ϕ_1 and ϕ_2 have the same significance as before. An altered free volume state model developed by Mashelkar and coworkers[26] was also applied to our system. According to this model,

$$\ln \eta_{\mathrm{mix}} = \frac{\phi_1(\alpha - 1 - \gamma\phi_2)\ln\eta_1 + \alpha\phi_2(\alpha - 1 + \gamma\phi_1)\ln\eta_2}{\phi_1(\alpha - 1 - \gamma\phi_2) + \alpha\phi_2(\alpha - 1 + \gamma\phi_1)} \quad \text{(Model 4)} \qquad (9)$$

η_1, η_2, ϕ_1, ϕ_2, etc. have the same significance as above. α and γ are calculated as explained in the literature[26]. The experimentally observed viscosity values at a shear rate of 333 s^{-1} are found to be higher than those calculated by different models as shown in *Figure 4*.

Effect of compatibilizer and shear stress on viscosity of 50/50 NR/PMMA blends

The effects of compatibilizer loading and shear stress on the melt viscosities of 50/50 NR/PMMA prepared by solution mixing is shown in *Figure 5*. Shear viscosity is plotted against shear stress for different shear rates. In all the cases viscosity decreased with increasing shear stress indicating pseudoplastic nature. As explained earlier the applied force disturbed the long chain polymer from its equilibrium position and the molecules got disentangled in the direction of the force and this caused a reduction in viscosity. It can be seen that the viscosity increases upon the addition of graft copolymer and the viscosity differences narrow down at higher shear rate. Shear viscosity is plotted as a function of graft copolymer concentration for the 50/50 NR/PMMA blend in *Figure 6*. Viscosity increases by the addition of graft copolymer and levels off beyond 10% of the graft copolymer concentration. This is because the compatibilizer decreases the interfacial tension and hence the interaction between NR

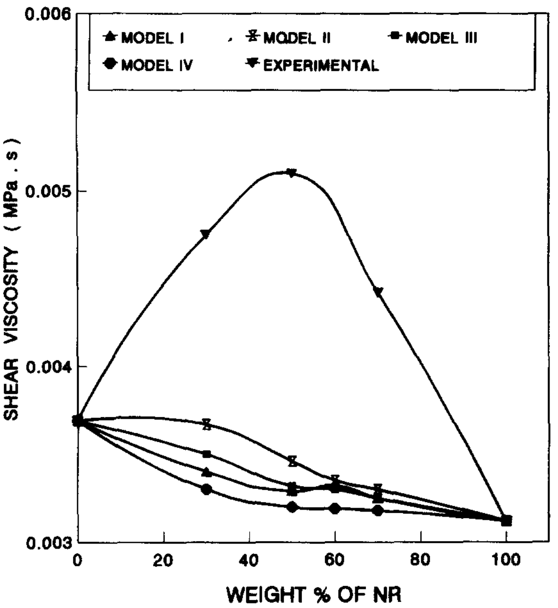


Figure 4 Experiment and theoretical values of shear viscosity as a function of wt% of NR at a shear rate of $333\,s^{-1}$

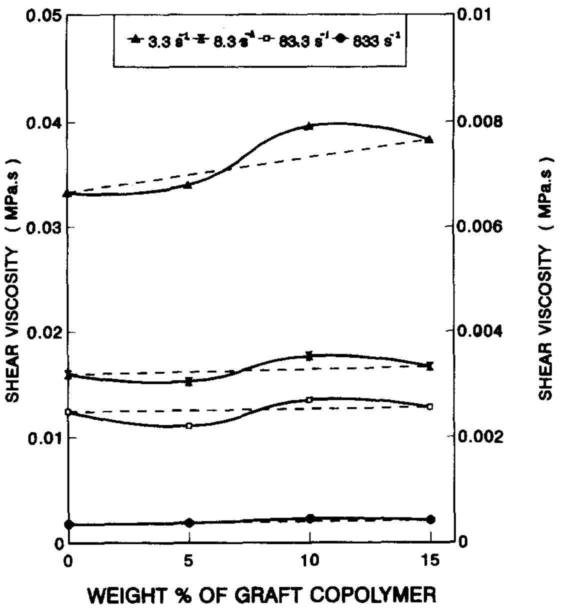


Figure 6 Variation of shear viscosity as a function of graft copolymer concentration of 50/50 NR/PMMA solution cast blends at different shear rates

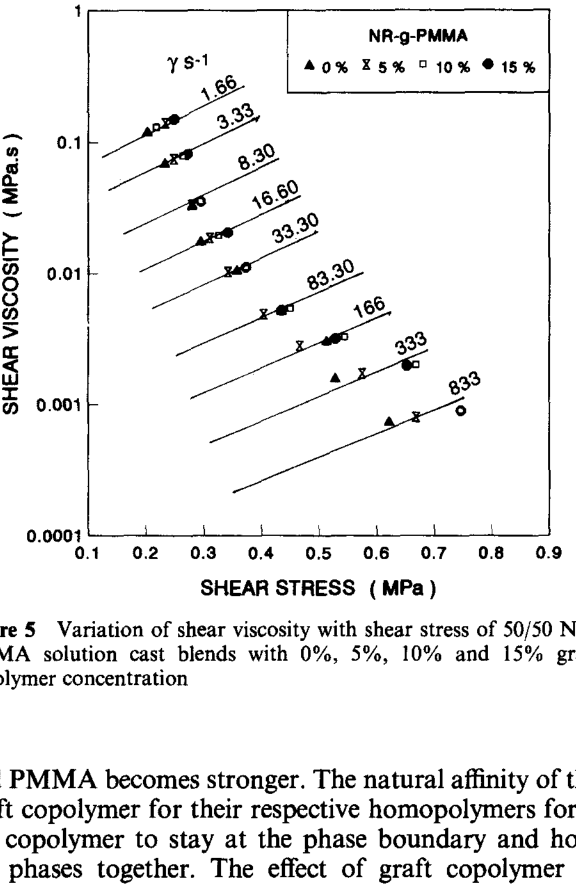


Figure 5 Variation of shear viscosity with shear stress of 50/50 NR/PMMA solution cast blends with 0%, 5%, 10% and 15% graft copolymer concentration

and PMMA becomes stronger. The natural affinity of the graft copolymer for their respective homopolymers force the copolymer to stay at the phase boundary and hold the phases together. The effect of graft copolymer in increasing the viscosity of NR/PMMA blend system is more pronounced in the low shear rate region. But at high shear rate region the viscosity is unaffected by the graft copolymer addition. The increase in viscosity of binary polymer blends upon the addition of compatibilizer has been reported by Willis and Favis[13]. Incompatible blends are characterized by a sharp interface and poor interaction between the two phases. This leads to interlayer slip between phases. The increase in viscosity indicates that there is less slippage at the interface as a result of the addition of compatibilizer.

The SEM photograph of the extrudate cross section of 50/50 NR/PMMA blends with increasing concentration of graft copolymer is given in *Figures 7a–c*. In the absence of graft copolymer, the interface adhesion is very poor. This is evident from the debonded or detached domains of PMMA in the NR matrix (*Figure 7a*). Addition of graft copolymer increases the interface adhesion of the PMMA domains with the natural rubber matrix. No more debonded domains could be observed in the presence of graft copolymer. The domain size of the dispersed PMMA phase is found to be decreasing with copolymer and levels off at higher concentration. Our earlier studies showed that addition of compatibilizer reduces the domain size of the dispersed phase[10,11]. Average domain size in each type of blend was calculated by measuring about 100 domains and is plotted against the percentage compatibilizer loading as shown in *Figure 8*. The domain size decreases sharply by the addition of 10% copolymer followed by a levelling off at higher concentration. The interparticle distance also reduced with increasing concentration of the graft copolymer and reached a critical value (*Figure 9*). One can estimate the optimum amount of compatibilizer required to saturate unit volume of the blend interface (called the critical micelle concentration) from those curves. The CMC values are estimated from the intersection of the straight line obtained at low concentration and the levelling off line at higher concentration and is found to be 11.5% for 50/50 NR/PMMA blend system. The estimation of CMC from the domain size has already been reported[11]. The particle size at CMC was 0.28 μm. In fact the critical micelle concentration is the optimum concentration of graft copolymer required to saturate the interface. Further addition of graft copolymer makes no difference in the domain size and hence the interfacial tension. At the saturation point, the viscosity also shows a levelling off. The relationship between domain size of the dispersed phase and viscosity of NR/PMMA blends as a function of graft copolymer concentration is illustrated in *Figure 10*. Viscosity increases with graft copolymer whereas domain size of dispersed phase decreases with

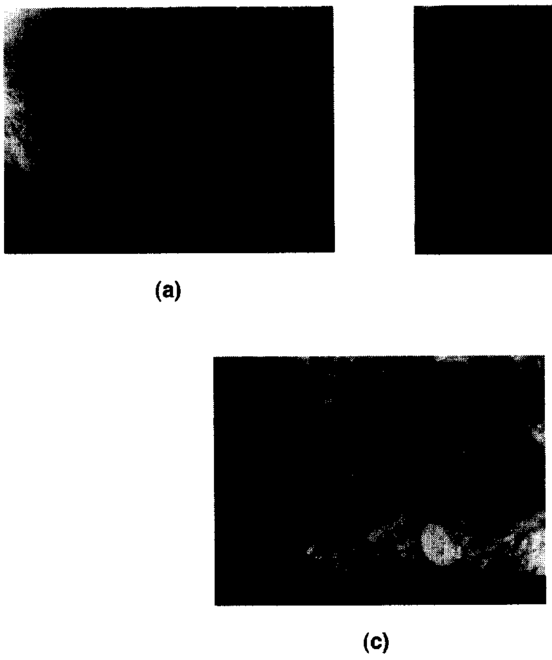


Figure 7 Extrudate morphology as a function of graft copolymer concentration of 50/50 NR/PMMA solution cast blends: (a) 0%, (b) 5% and (c) 10% graft copolymer

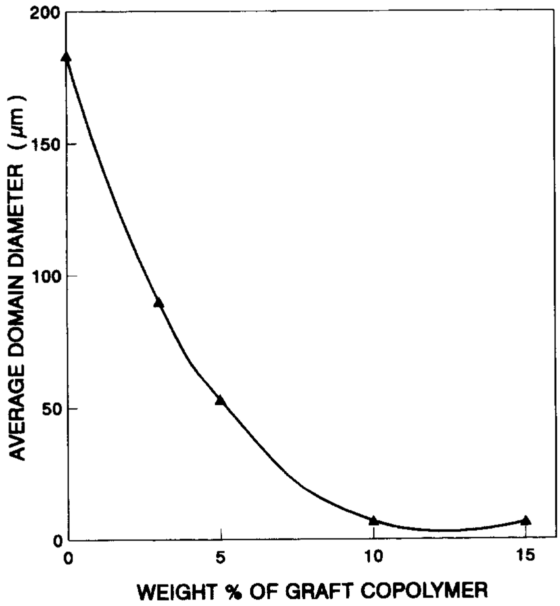


Figure 8 Variation of average domain size as a function of graft copolymer concentration in 50/50 NR/PMMA solution cast blends

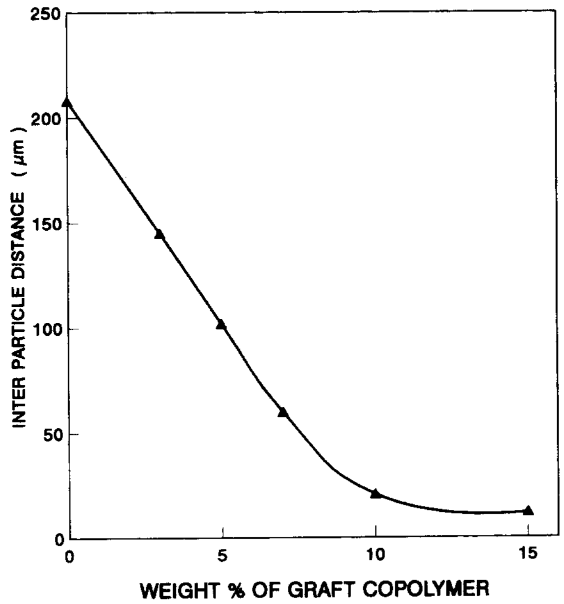


Figure 9 Variation of interparticle distance as a function of graft copolymer concentration in 50/50 NR/PMMA solution cast blends

the graft copolymer concentration and finally both the curves reach a levelling off.

Comparison between melt and solution mixed blends

Unlike solution cast blends the melt mixed blends showed an entirely different pattern of viscosity change with blend composition (*Figures 1* and *11*). In this case PMMA showed higher viscosity than NR and the differences are more prominent at high shear rate region. The observed high viscosity of PMMA as compared to NR can be explained as follows. NR is highly susceptible to degradation by mechanical, thermal and chemical actions. High shearing action (80 rpm) and temperature (160°C) employed during the preparation of the blend by melt mixing technique might have caused severe degradation of NR compared to PMMA resulting in a substantial reduction in the viscosities of NR. Molecular weight determination of NR after melt mixing process supports the degradation of NR during melt mixing. The molecular weight of NR ($\bar{M}_w$) after melt mixing was found to be 3.49×10^5. The initial molecular weight of natural rubber was 7.02×10^5. This high molecular weight accounts for the high viscosity of the solution cast samples. The influence of wt% of NR on the viscosity of melt blended samples at different rates are shown in *Figure 12*. Unlike solution cast blends, it can be seen that the system shows negative deviation from additivity. This is associated with the lack of interaction between the two phases. Unlike solution

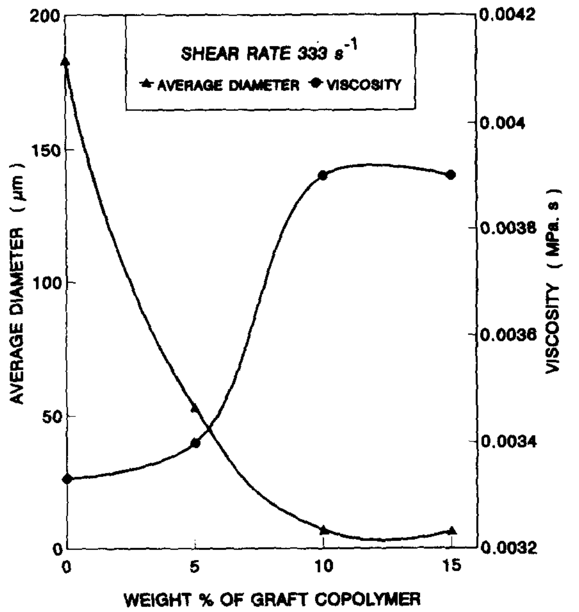


Figure 10 Relationship between average diameters and shear viscosity as a function of graft copolymer concentration at a shear rate of $333 s^{-1}$

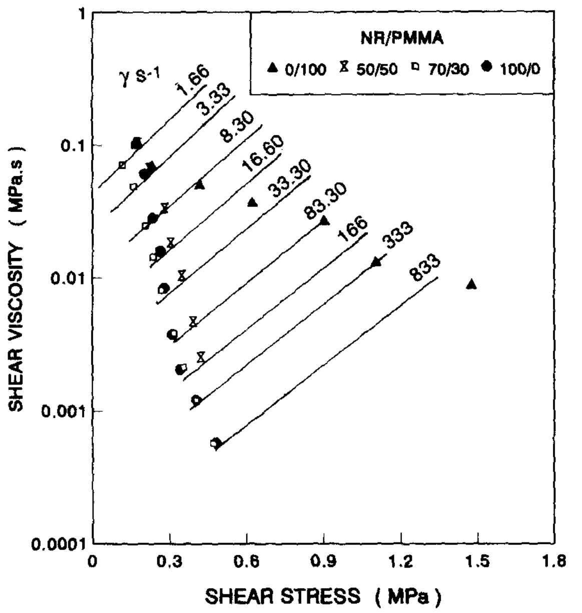


Figure 11 Variation of shear viscosity with shear stress of 0/100, 50/50, 70/30 and 100/0 NR/PMMA melt mixed blends

mixing, molecular level mixing cannot be achieved during melt mixing.

The flow behaviour of the melt mixed blends in the presence of compatibilizer is also quite different from that of the solution mixed blend. This is evident from the graph (*Figure 13*) which shows the effect of compatibilizer and shear stress on melt viscosities of the 50/50 NR/PMMA melt mixed blend with and without the addition of graft copolymer. Viscosities of the blend decreased with increasing shear stress indicating pseudoplastic nature. But contrary to the increase in viscosity observed in the case of solution mixed blends, the viscosity decreased with the addition of graft copolymer as a compatibilizer. As discussed earlier incompatible blends, characterized by a sharp interface and having no interaction between the two phases, usually exhibits interlayer slip. The interlayer slippage will be made easier

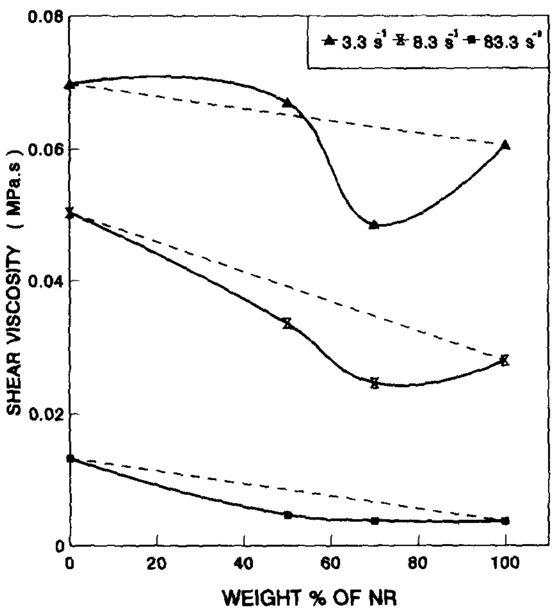


Figure 12 Variation of shear viscosity with weight percentage of NR in NR/PMMA melt mixed blends at different shear rates

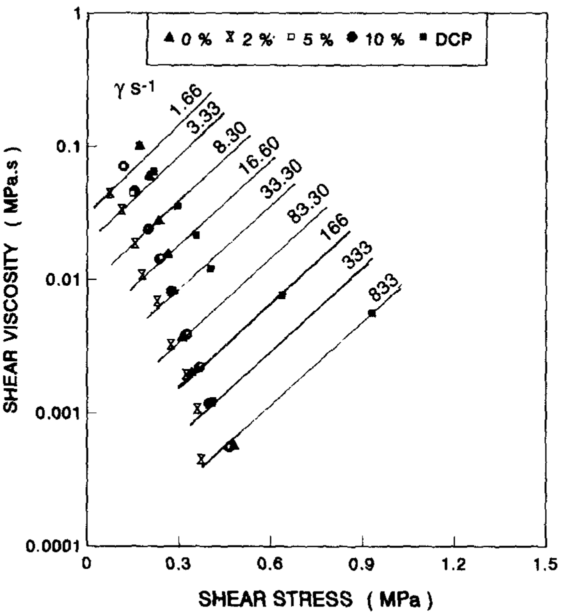


Figure 13 Variation of shear viscosity with shear stress of 50/50 NR/PMMA melt mixed blends with 0, 2, 5 and 10% graft copolymer and dicumyl peroxide vulcanized systems

if one of the components has a lower molecular weight. In the case of melt mixed blends degradation of NR phase that occurred during its preparation, might have produced lower molecular weight fractions. Moreover, molecular level mixing cannot be achieved during melt mixing. Therefore, the copolymer may not be able to diffuse into the interface completely. Considering these factors, it is reasonable to believe that the ineffective mixing and molecular weight breakdown of natural rubber contribute to the decrease of viscosity with increasing copolymer concentration. The influence of dynamic crosslinking of the NR phase using DCP and sulfur can be understood from *Figure 13*. It can be seen that dynamic crosslinking substantially increases the viscosity of the blends. The effect is more pronounced at high shear stress region. Upon dynamic crosslinking, the rubber phase is crosslinked and finally transformed into fine particles which are dispersed in the continuous PMMA matrix. This morphology is highly stable as the crosslinked particles are highly resistant to agglomeration. Since crosslinked particles are less deformable the system shows high viscosity[17]. It is important to mention that dynamic crosslinking is also a novel route for compatibilization of polymer blends.

Effect of temperature on melt viscosity

The temperature dependence of the melt viscosity obtained from capillary rheometer data for 50/50 NR/PMMA melt mixed blend as a function of graft copolymer concentration at a shear rate of $16.6\,s^{-1}$ has been studied. The viscosity of all the blends decreased with increasing temperature. The change in viscosity with temperature is less for uncompatibilized blends compared to compatibilized systems. As the percentage of graft copolymer in the blend is increased, the extent of decrease becomes more pronounced. More information about the influence of temperature on viscosities of compatibilized blends is obtained from Arrhenius plots. In *Figure 14* logarithms of the viscosities are plotted as a function of reciprocal of temperature in absolute value. The activation energies calculated from the plots are given in the *Table 2*. It is seen that the activation energies increased by the addition of graft copolymer. This shows that the blend with compatibilizer is more sensitive to temperature than the blend with no graft copolymer. The higher the activation energy the less temperature sensitive the material will be. This could be useful in choosing the temperature to be used during extrusion, calendering or injection moulding.

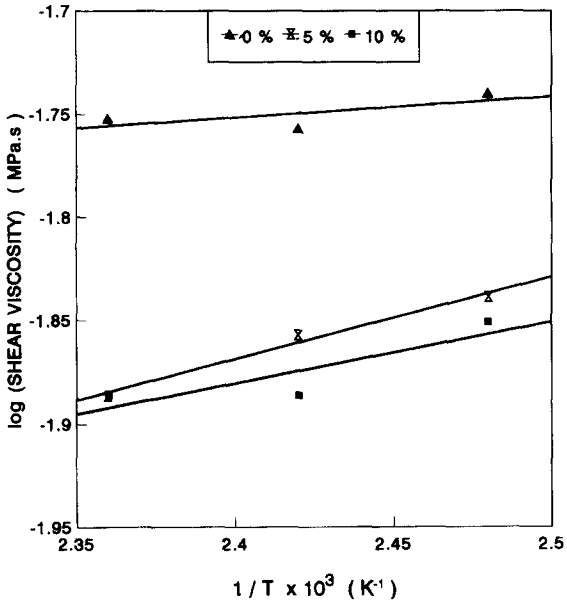


Figure 14 Arrhenius plots for NR/PMMA melt mixed blends with 0, 5 and 10% graft copolymer concentration

Table 2 Activation energy for 50/50 NR/PMMA melt mixed blends

50/50 NR/PMMA with % of graft	E (cal mol^{-1})
0%	201
5%	791
10%	593

Shear rate temperature superposition curve

Anand[27] and Mendelson[28,29] have reported the shear rate–temperature superposition method to determine the shift factor and has used the method to predict the viscosities as a function of temperature. This method has also been successfully applied in our system where flow curves of shear stress vs. log shear rate of 50/50 NR/PMMA are constructed at 130, 140 and 150°C (*Figure 15*). Choosing 140°C as the reference temperature, the average values of the shift factor (a_T) are obtained by considering a shear stress in the flow curve of the reference temperature and shifting the point to coincide with the flow curve of other temperatures at constant shear rate and the a_T is calculated using the equation

$$a_T = \frac{\tau_w(\text{ref})}{\tau_w(T)} \quad \text{(at constant shear rate)} \qquad (13)$$

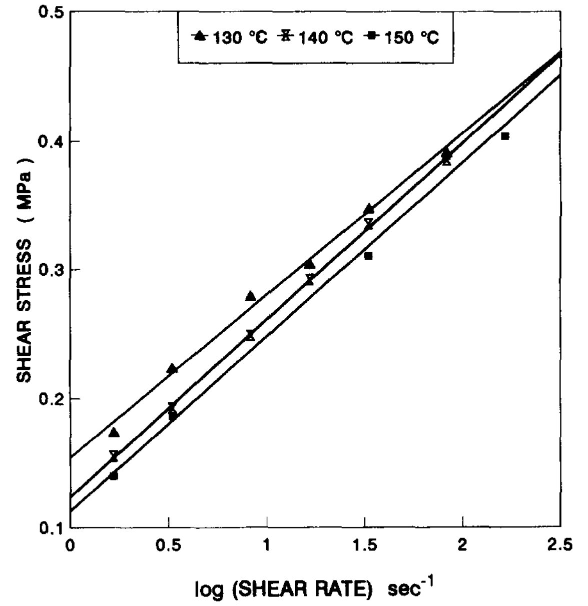


Figure 15 Flow curve of shear stress vs. log shear rate at 130, 140 and 150°C

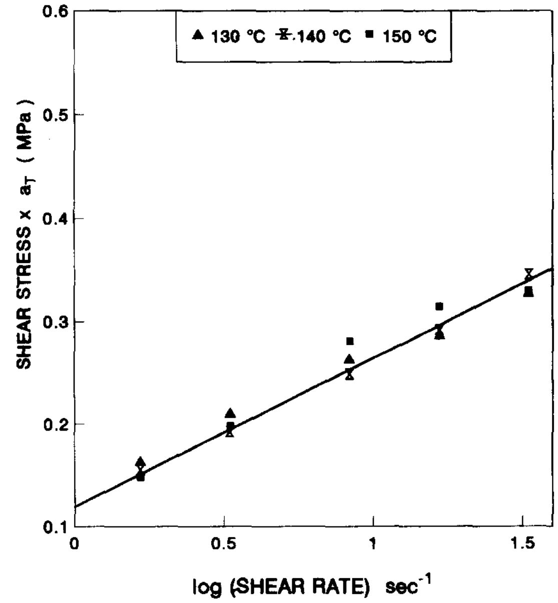


Figure 16 Master curve of modified shear stress vs. log shear rate as a function of temperature

Table 3 Effect of % on NR on flow behaviour index at 130°C

	NR/PMMA (n')					
Type of mixing	100/0	70/30	60/40	50/50	30/70	0/100
Solution blending	0.1286	0.1984	0.1193	0.1848	0.1836	0.2803
Melt blending	0.1545	0.2974	0.2094	0.2104	0.2271	0.4775

Table 4 Flow behaviour index and die swell of 50/50 NR/PMMA blend as a function of copolymer loading

		Flow behaviour index, *n*		
50/50 graft	NR/PMMA with % of copolymer	130°C	140°C	Die swell
Melt blending	0	0.1848	0.2104	1.50
	5	0.2180	0.2494	1.49
	10	0.2130	0.2319	1.44
Solution blending	0	0.1848	0.1652	1.95
	5	0.1730	0.1596	1.70
	10	0.1997	0.1995	1.59

In this equation τ_w(ref) is the shear stress at reference temperature. $\tau_w(T)$ is the shear stress at given temperature. The average values of a_T are obtained by choosing three different shear rates and averages of these values are taken to minimize the error. A master curve is constructed by plotting modified shear stress ($\tau_w \times a_T$) vs. log shear rate ($\log \dot{\gamma}_w$) (*Figure 16*). It is clear that the points at different temperatures fall on the reference temperature curve.

Flow behaviour index

The effect of blend ratio, compatibilizer and temperature on the flow behaviour indices of NR/PMMA blend both in solution and melt mixed state are given in *Tables 3* and *4*. The n' values are less than one indicating pseudoplastic behaviour. The flow behaviour index of PMMA is greater than that of NR. The melt blended samples show high flow behaviour index due to the degradation of the sample during melt mixing. It is observed that 60/40 NR/PMMA blend exhibits the lowest flow behaviour index and is more pseudoplastic than other compositions in both cases. The n' value increases by the addition of graft copolymer and also with the rise in temperature. However the values do not show a regular change with blend ratio, compatibilizer and temperature.

Deformation of the extrudate

Extrudate of the blends N_0, N_{30}, N_{50}, N_{70}, N_{100} and $0N_{50}$, $5N_{50}$, $10N_{50}$ and $15N_{50}$ were examined by taking the optical photograph of the extrudate (*Figure 17*). At low shear rate most of the extrudates have smooth surfaces. However at higher shear rate extrudate surfaces exhibit roughness. They have no uniform diameter due to distortion. The surface irregularities arise from the extensive stretching of the extrudate surface. Surface irregularities are extreme in homopolymers and are reduced in the case of blends. The 50/50 NR/PMMA blend exhibits comparatively low roughness indicating high resistance compared to the other blends. According to Brydson[30] irregularly shaped extrudate known as melt fracture is due to the variations in processing temperature, molecular weight or due to the absence of filler. Smooth extrudate is obtained at a low shear rate and above a critical shear rate the extrudate becomes uneven. The form of distortion varies widely. In some cases extrudate is screwed thread or rod like in nature due to secondary effects. In the case of NR/PMMA blends melt fracture takes place at a shear rate of 333 s^{-1}. It is also clear that the presence of compatibilizer reduces the extrudate distortion even at high shear rate. The compatibilizer makes the blend rigid and hence exhibit low degree of distortion. The uncompatibilized blends

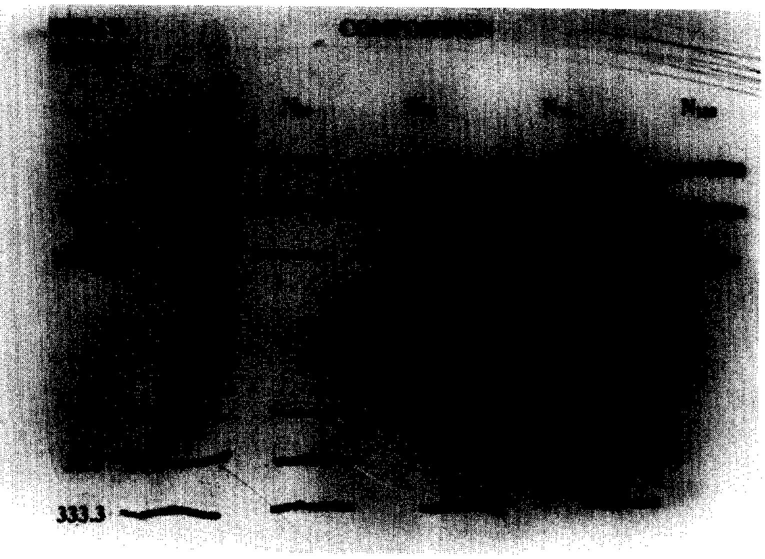


Figure 17 Extrudate deformation at different shear rates of NR/PMMA blends as a function of blend ratio and compatibilizer loading

exhibit surface irregularities even at low shear rate and the distortion enhances at higher shear rate.

Die swell

The swelling of an extrudate on emerging from a capillary is typical of non-Newtonian viscoelastic fluids and is related to their elastic properties. When the molten polymer flows through the capillary, shear tends to maintain molecular orientation of polymer chains. When the melt emerges from the die, reorientation of molecules occurs leading to the phenomenon of die swell. Die swell values of 50/50 NR/PMMA blends with and without addition of graft copolymer extruded at a shear rate of 333 s^{-1} and at a temperature of 130°C are also given in *Table 4*. Compatibilizer increases the rigidity of the blend and thus imparts less elastic recovery of the macromolecular chains under the influence of the applied shear stress. Therefore the elastic recovery and consequently the die swell of the compatibilized blend is less than the uncompatibilized blend. The effect of compatibilizer in reducing the die swell was less prominent in the melt mixed blends. Between melt mixed and solution mixed blends, the latter always showed higher die swell due to high molecular weight of the NR phase in this type of blend.

Melt flow indices

Melt flow index and rheometer data. Melt flow index values of NR/PMMA solution cast blends are given in *Table 5*. It is seen that MFI values are high for 50/50 NR/PMMA with no graft copolymer. MFI values decrease by the addition of graft copolymer and also as the percentage of NR in the system increases. The results are in agreement with the capillary rheometer data.

Melt flow index provides information about flow behaviour. The values agree with the flow behaviour of the compatibilized blends. As the blends get compatibilized by the addition of graft copolymers, the system will become more rigid and the viscosity increases as indicated by the MFI values. Shenoy *et al.*[31,32] have demonstrated the unifying approach to coalesce rheograms of resin grades with different shearing history in terms of a modified viscosity function ($\eta \times$ MFI) and a modified shear rate ($\dot{\gamma}$/MFI). The master curve so generated can be used for estimating the rheograms of polymer waste any required temperature merely from the knowledge of the MFI of the polymer. Bhagawan *et al.*[33] also obtained a master curve in the case of filled 1,2-polybutadiene. In this study the systems with calcined clay, china clay and HAF black coalesce very smoothly into a single curve. *Figure 18* is a plot of modified shear viscosity function $\eta \times \mathrm{MFI}/\rho$ vs. modified shear rate function $\log \gamma\rho/\mathrm{MFI}$ for 50/50 NR/PMMA systems. It is found that the systems with 0, 5 and 10% graft copolymer coalesce smoothly into a single curve. From the master curve it is possible to construct rheograms of any system with different loading of the compatibilizer simply by knowing the MFI of the sample.

Table 5 MFI values of NR/PMMA solution cast blends

Sample NR/PMMA compositions	Graft copolymer %	MFI values (in g 10 min^{-1})			
		200°C	210°C	220°C	230°C
50/50	0	1.2030	0.7135	1.3687	5.3039
	5	0.4373	0.5439	1.0566	3.4105
	10	0.5711	0.3086	0.7145	2.7970

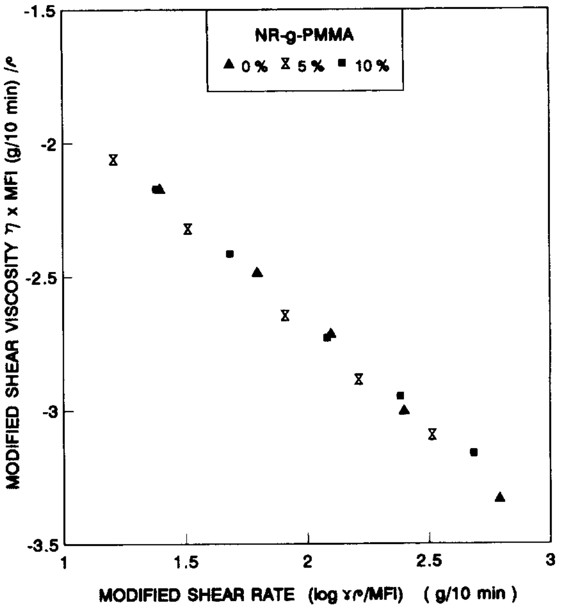


Figure 18 Master curve of modified shear viscosity *versus* modified shear rates as a function of graft copolymer concentration at 130°C

Influence of processing history on morphology and stability of the blend

The influence of processing history on morphological variation has been studied by Danesi and Porter[15] on a blend of ethylene–propylene rubber/polypropylene system. It has been demonstrated that the change in morphology is due to the extrusion alone or due to the combined effect of extrusion and annealing. Morphological variation due to processing has been studied with 50/50 NR/PMMA blend with and without graft copolymer. *Figure 19a* gives the SEM photograph of the extrudate of 50/50 NR/PMMA with no graft copolymer. The PMMA phase exists as domains in the continuous NR matrix and has an average domain size of 15 μm. The dispersed nature is due to the higher viscosity of PMMA phase. *Figure 19b* shows the morphology of the same sample extruded after annealing for 1 h in the extrusion barrel. It is interesting to note that the domains are irregular and larger in size (28 μm). *Figures 19c* and *d* give the extrudate morphology of 50/50 NR/PMMA with 10% graft copolymer before and after annealing. It can be seen that morphology of the compatibilized system is unaffected by annealing. This indicates the role of the compatibilizer towards stabilizing of blend morphology.

CONCLUSION

The rheological properties of NR/PMMA blend system with and without the addition of compatibilizer have been studied. The viscosity of the blends decreased with increase in shear stress indicating pseudoplastic nature of the system. The viscosity of NR/PMMA system varies with composition of NR and 60/40 NR/PMMA system exhibits maximum viscosity. The calculated η values using different models are found to be lower than the experimental value. The positive deviation is not only due to interphase interaction but also due to the viscosity

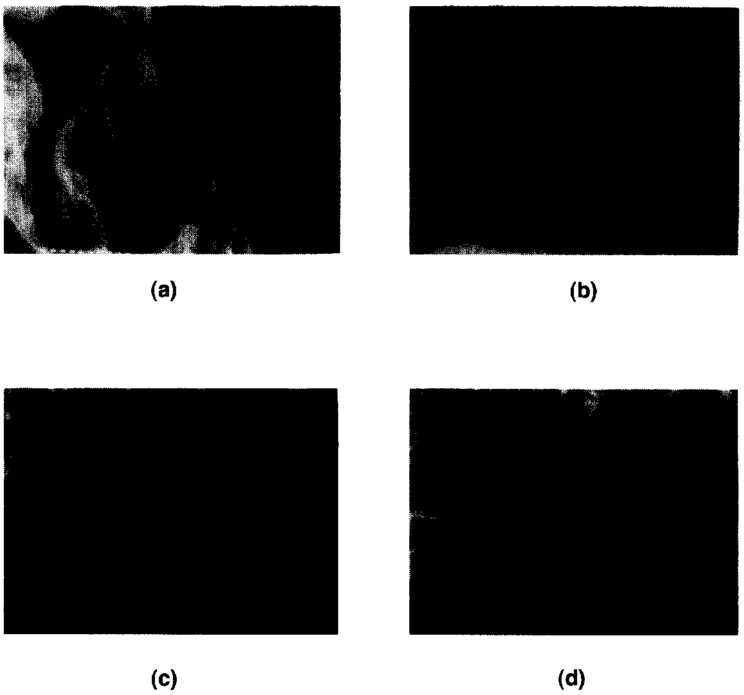


Figure 19 SEM photograph of extrudate of 50/50 NR/PMMA blends: (a) 0% graft copolymer before annealing; (b) 0% graft copolymer after annealing; (c) 10% graft copolymer before annealing; (d) 10% graft copolymer after annealing

difference of the matrix and dispersed phase. The lower values of the flow behaviour index also support the pseudoplastic nature. Melt viscosity increases with the addition of graft copolymer indicating high interfacial interaction. The compatibilizer increases the adhesion between the phases. The domain size is found to decrease by the addition of copolymer followed by a levelling off at higher concentration. The levelling off point can be considered as the so-called critical micelle concentration. The viscosity is found to increase with the addition of the compatibilizer and reaches a levelling off at the critical concentration of the copolymer. The dynamic crosslinking of the natural rubber phase increased the viscosity of the system. The temperature dependence of viscosity was studied by using the Arrhenius equation. The activation energy for flow decreases with temperature, and its values also reveal that compatibilized NR/PMMA systems are more sensitive to temperature compared to the incompatible systems. The shear rate–temperature superposition method was used to determine the shift factor. These values are helpful in predicting the viscosity of the system at any desired temperature. Addition of compatibilizer was found to reduce the die swell of the blend.

Master curves obtained from MFI and rheometer data could be used to construct rheograms of the NR/PMMA blend systems. Finally the influence of processing conditions on the morphology and stabilities of the blends has been examined. The compatibilized blends are found to be much more stable than the uncompatibilized systems.

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