Natural Rubber–Styrene Butadiene Rubber Latex Blends: Time-Dependent Rheological Behavior and Film Formation

JYOTHI T. VARKEY,[1] PRABHA R. CHATTERJI,[2] S. SOMESWARA RAO,[3] SABU THOMAS[1]

[1] School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam-686 560, Kerala, India

[2] Organic Coatings and Polymer Division, Indian Institute of Chemical Technology, Hyderabad-500 007, India

[3] Propellant Engineering Division, Vikram Sarabhai Space Centre, Thiruvananthapuram-695 022, Kerala, India

ABSTRACT: This article focuses mainly on the effect of maturation time on the rheological behavior of unvulcanized natural rubber (NR)–styrene butadiene rubber (SBR) latex blends. Viscosity shows a composition-dependent behavior with maturation time. It was found that there is a marginal decrease in viscosity for all the systems with maturation time except for the 70/30 NR–SBR blend. In this blend, there is a sharp decrease in viscosity with maturation time. This is associated with the exchange of stabilizers with one another until an equilibrium is reached; that is, all the particles of the blend are stabilized with random mixture of stabilizers. The structural build up observed in 70/30 NR–SBR blend was found to be diminished as the maturation time increases. At equilibrium, there is no further exchange of stabilizers. The behavior of this blend has been explained with the help of a schematic model. The effects of blend ratio and surface active agents on the viscosity were also studied. In addition, the time-dependent flow behavior of prevulcanized latex blends was evaluated as a function of vulcanizing systems and prevulcanization time. There is a regular increase in viscosity with prevulcanization time. However, after 3 h, the viscosity of almost all blends levels off, indicating that the curing reaction is complete within this time. Finally, the morphological changes occurred during film formation of the blends were studied using scanning electron microscopy. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1473–1483, 1998

Key words: natural rubber; styrene butadiene rubber; latex blends; viscosity; film formation

INTRODUCTION

Blending of various latices has become a common practice to improve the processing as well as the ultimate properties. Blending of different types of latices[1–3] can present difficulties unless their polymer–water interfacial systems are similar. If the interfacial systems are dissimilar, thickening usually occurs on mixing of the latices.[4] This thickening can be pronounced and, although it is generally only temporary, several hours may elapse before the viscosity of the latex blend is low enough for subsequent compounding. By adding a suitable stabilizer before blending, the thickening can be substantially reduced. There are number of reports regarding the blending of different kinds of latices.[5–11]

The time-dependence of viscosity of latices is of great importance, although the latex user may evaluate them only in a qualitative manner. Blackley and Charnock[12–14] reported on the changes that occur after blending natural rubber (NR) and styrene butadiene rubber (SBR) latices. They also reported on the effect of added soap on

the viscosity of this system. Viscosity of mixtures of natural and chloroprene rubber latices was studied by Belyaev et al.[8] Initial high viscosity of the blend decreases as this storage time increases. In addition to that the effect of temperature on the viscosity of blends was studied. Angove[15,16] reported on the effect of order of mixing on the viscosity of latices. Recently, in this laboratory, we have reported[17,18] on the effect of shear rate, various surface active agents, and temperature on the rheological behaviour of NR–SBR and NR–epoxidised natural rubber (ENR) latex blends. In addition to that, we have investigated the effect of surface active agents and temperature on the rheological behavior of natural and synthetic rubber latices.[19] Krieger and Elrod[20] and Maron and coworkers[21–24] have done exhaustive work on the rheology of GR-S and other uncompounded latex systems. Most practical uses of latices in processing and in various coating applications require some control of viscosity. The viscosity of NR latex is particularly dependent on concentration. The concentration dependence of rubber latices are extensively reported.[25,26] Therefore, knowledge of the factors that can be used to alter the rheological behavior of the latex system is of considerable value.

An important characteristic of a latex is its film-forming behavior. Latex dispersions are commonly used in paints, paper, adhesive, and coating industries, where the properties of the film are of great importance. When dried, some latices produce continuous and strong films if the application temperature is above the minimum film formation temperature (MFT), while others form powdery layers. The mechanism of film formation during drying is of theoretical and practical interest since film properties affect the performance of the resultant material. Numerous models and mechanisms have been proposed to describe the formation of films from latex dispersion.[27–36] In some reports, the mechanism of film formation is known as interdiffusion of polymers, followed by healing at the particle–particle interface. The interdiffusion at the polymer–polymer interface of miscible pairs during latex film formation has been extensively studied.[37–41] However, little is known about the interdiffusion between immiscible and partially miscible polymers, where the limited interdiffusion near the phase separation temperature is thermodynamically controlled. A number of studies have been made on the factors controlling the drying and formation of films from polymer latices. According to Van der Hoff,[42] the main stages for the process of drying of a polymer latex are as follows.

1. At the initial stage, evaporation of water occurs at the interface of latex film. In this process, the loss of water is linear and is same as that of evaporation of water itself. During this stage, the particles are forced into irreversible contact.
2. At the intermediate stage, the evaporation rate decreases rapidly. The aqueous phase now occupies the interstices between the particles, which coalesce under the combined interfacial tensions of the water, air, and water–polymer surfaces.
3. At the final stage, the complete coalescence of the particles takes place, and the removal of residual water and a complete homogeneous film is formed.

The nacent film is normally weak in its mechanical properties, such as tensile and tear strength, which improve gradually, and it often requires days or weeks to reach the final properties.[43] It is commonly believed that the enhancement of tensile strength is a consequence of polymer diffusion across the particle–particle interface in the film.[44–48] Important factors responsible for the interdiffusion capability of polymers in latices are the molecular weight of the polymer, the temperature at which the film is formed, the spatial distribution of chain ends near the interface, and the steric[49] and electrostatic stabilization of the latex.

The aim of this article is to specifically discuss the effect of maturation time on the rheological behaviour of NR–SBR latex blends. The effects of blend ratio, surface active agents (casein), and temperature on the viscosity of the blends have been evaluated. Moreover, the time-dependent flow behaviour of prevulcanized latex blends is analyzed. Finally, the time-dependent morphological changes of the films of NR–SBR latex blends has been investigated in detail.

EXPERIMENTAL

Rheological Measurements

NR latex was supplied by Padinjarekara Agencies, Kottayam, India, and SBR latex was supplied by Synthetics and Chemicals, Chennai, India. Other chemicals are of laboratory reagent grade.

Table I   Formulation of Mixes for CV (phr)

Ingredients	N_0	N_{50}	N_{60}	N_{70}	N_{100}
60% NR latex	0	50	60	70	100
38% SBR latex	100	50	40	30	0
10% KOH solution	1	1	1	1	1
50% Sulphur dispersion	2.5	2.5	2.5	2.5	2.5
50% ZDC[a] dispersion	1	1	1	1	1
50% ZMBT[b] dispersion	1	1	1	1	1
50% ZnO dispersion	3	3	3	3	3

[a] ZDC is zinc diethyl dithiocarbamate.
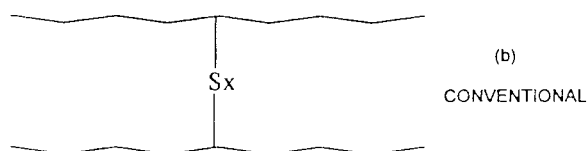[b] ZMBT is zinc mercaptobenzothiazole.

NR and SBR latices were blended together to have compositions ranging from 0, 50, 60, 70, and 100% of NR. The blends are designated as N_0, N_{50}, N_{60}, N_{70}, and N_{100} where the subscripts indicate the weight percent of NR in the blend. The weights were calculated according to dry rubber content (DRC). Extra ammonia was added to each system for stabilization purpose. A 5% aqueous solution of the surface active agent (casein) was prepared. Dosage of surface active agent was fixed to be 0.5 phr (parts per hundred rubber). Rheological measurements were carried out using a Haake viscometer. A coaxial cylinder sensor system consisting of an MV-I cup was used for all the measurements. Rheological measurements of blends with and without casein were analyzed after 0, 1, 2, 3, and 4 h. The experiments were conducted at 40°C.

Formulations for the prevulcanization of blends are given in Tables I and II. In a conventional system (CV), more concentration sulphur is used than accelerator, and an efficient system (EV) utilizes more dosage of accelerators than sulphur. In a conventional system, there are more polysulphidic linkages, that is, a crosslink in which two polymer chains are bridged by a chain of three or more sulphur atoms. In an efficient system, more monosulphidic linkages are formed. This is schematically shown in Figure 1. Compounded latex blends were prepared by adding ball-milled dispersions of all the compounding ingredients to the latex blends and stirred using a mechanical stirrer for half an hour to ensure homogenization of the ingredients. The mix was kept undisturbed for 1 h. Prevulcanization was carried out by heating the latex blends in a beaker immersed in water bath at 60°C. Samples were withdrawn after 0, 1, 2, 3, and 4 h, and flow char-
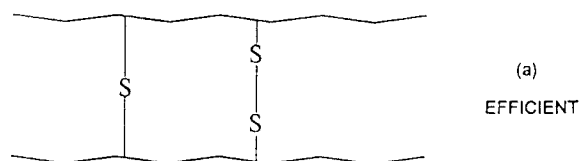
(a) EFFICIENT

Predominantly mono or disulphidic linkages

Table II   Formulation of Mixes for EV (phr)

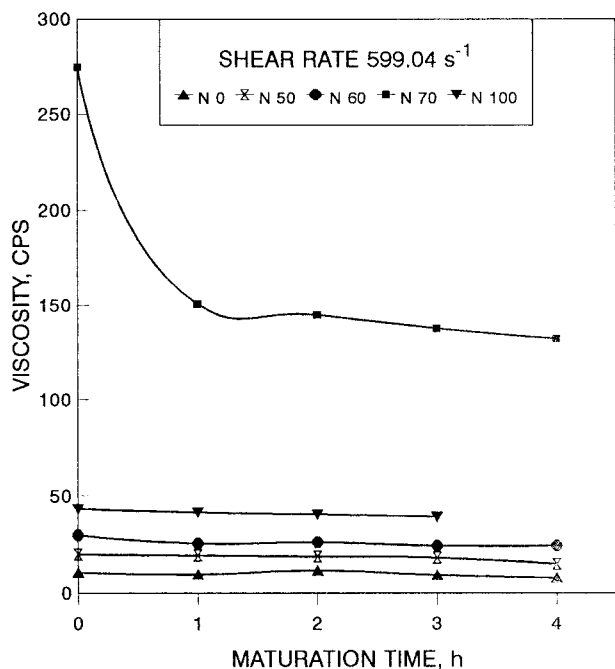| Ingredients	N_{60}	N_{100}
60% NR latex	60	100
38% SBR latex	40	0
10% KOH solution	1	1
50% Sulphur dispersion	1	1
50% ZDC dispersion	1.5	1.5
50% ZMBT dispersion	1	1
50% ZnO dispersion	3	3

(b) CONVENTIONAL

Sx

Predominantly polysulphidic linkages

Figure 1 Schematic representation of types of crosslinks formed during conventional and efficient vulcanization.

Figure 2 Variation of viscosity with maturation time for NR–SBR blends without casein at a low shear rate.

acteristics were measured at room temperature. Here also, NR latex was diluted with extra ammonia due to destabilization problem. The details of the prevulcanization mechanism was reported earlier by our research group.[50]

Film Preparation

The NR latex and blends were directly coated on an aluminium stub at room temperature. The surface morphologies were observed with a Stereoscan-360 automatic scanning electron microscope. The instrument was operated at an accelerating voltage of 20 keV. The coated latex was dried for 4, 9, and 24 h. The surface morphologies were examined at different drying times.

RESULTS AND DISCUSSION

All the results of the rheological measurements were analyzed using the power law equation as reported earlier.[17–19] The effects of maturation time on the viscosity of NR–SBR latex blends at a shear rate of 599.04 s^{-1} is given in Figure 2. It is clear from the graph that in the case of all the blends and homopolymer latices except N_{70}, there is only a marginal decrease in viscosity with maturation time. In the case of N_{70}, the viscosity de-
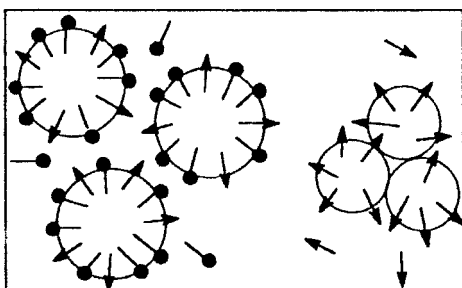
creases sharply during the first h of maturation, followed by a marginal decrease. This can be explained as follows. When two latices like NR and SBR are mixed, there is a tendency for the adsorbed stabilizers to exchange with one another until all the particles of the blend are stabilized with a random mixture of stabilizers. It is not possible that the stabilizers of one latex will desorb and readsorb at the same rate as those of the other. It is believed that the stabilizers of SBR latex are more rapidly desorbed and readsorbed than NR latex; that is, when NR and SBR latices are mixed, a rapid transfer of stabilisers from SBR surface to NR surface takes place, and the resulting blend contains more stabilized NR particles and less stabilized SBR particles. These destabilized SBR domains undergo agglomeration-forming network structure, resulting in a large increase in viscosity. This positive deviation is viscosity and was observed only when SBR content is less than 50%. In other cases, when SBR content is more than 50%, the system contains more SBR stabilizers, and the exchange of stabilisers from SBR to NR is small. Hence, the destabilisation is absent. In fact, the mechanism of the exchange of stabilizers and the consequent structure build up have been illustrated in our earlier publication.[17] As the maturation time increases, the peptidization and redispersion of the SBR network results from the relatively slow transfer of natural rubber stabilizers from NR particles to the SBR particles. This leads to the sharp decrease in viscosity in the case of N_{70} blend. The redispersion is almost complete within 1 h. Figure 3 represents the schematic representation of the network formation and the attainment of equilibrium upon maturation. In all other cases, there is no significant change in viscosity with maturation time. The positive deviation in viscosity in the case of N_{70} blend is not as high as that reported earlier because of the presence of extra ammonia.[17] The ammonia present will reduce the deficiency of stabilisers to some extent. The effect of maturation time on the viscosity of blends can be well understood in Figure 4, where viscosity is plotted against weight percent of NR. The time-dependent drastic change in viscosity of N_{70} blend is more clear in this figure. The decrease in viscosity in the case of N_{70} is more pronounced after 1 h of maturation; after that, there is only slight decrease in viscosity.
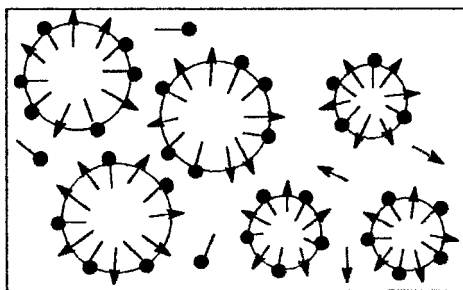
Effect of Surface Active Agent (Casein)

Figure 5 indicate the variation of viscosity with maturation time of NR–SBR blends in the pres-
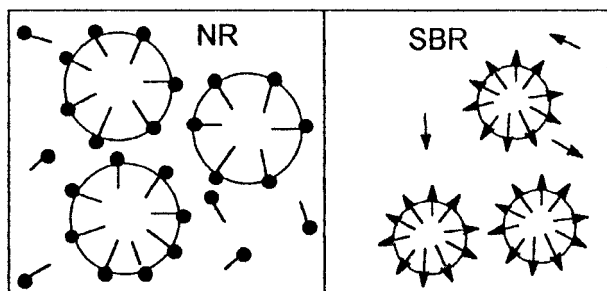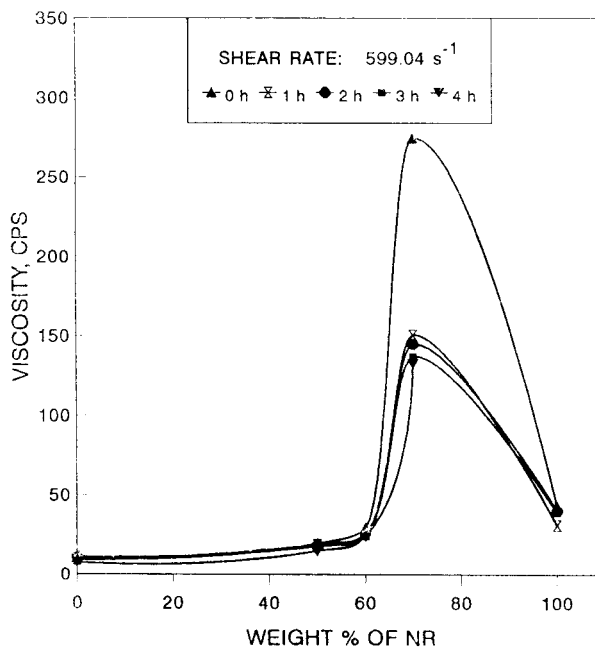
(a)

—● NR Stabilizer
—➤ SBR Stabilizer

Figure 4 Variation of viscosity with composition of the NR–SBR blends without casein.

much higher in the case of 70/30 NR–SBR blend. As discussed earlier, this is due to the fact that, in this blend, the extent of structure build up is maximum due to exchange of stabilizer. This decrease in viscosity with maturation time is made
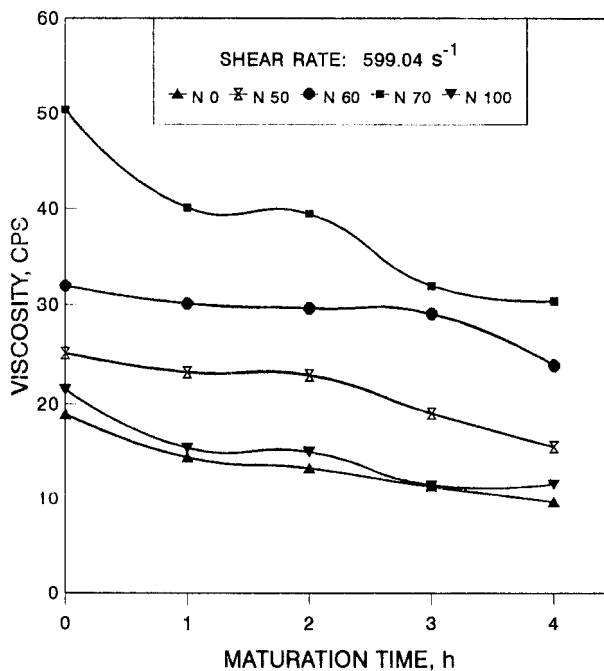

(b)

(c)

Figure 3 Schematic representation of destabilization and attainment of equilibrium of the NR–SBR latex blend: (a) virgin latices; (b) destabilized stage; (c) equilibrium stage.

ence of casein at a shear rate of 599.04 s^{-1}. The viscosity is lowered than the system containing no casein, especially in the case of N$_{70}$ blend. There is a regular decrease in viscosity as maturation time increases. However, the extent of decrease is
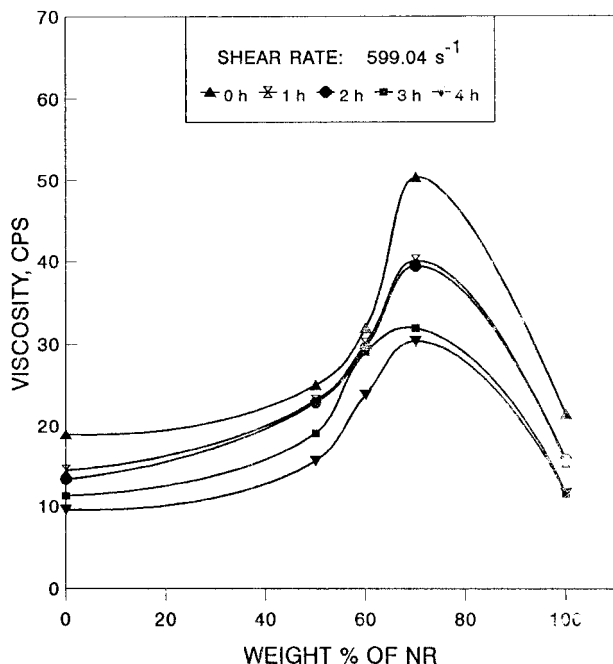

Figure 5 Variation of viscosity with maturation time for the NR–SBR blends with casein at a low shear rate.

Figure 6 Variation of viscosity with composition of the NR–SBR blends with casein.

more clear in Figure 6, where the viscosity is plotted against the weight percent of NR at shear rate of 599.04 s^{-1}. The effect of added casein is to diminish the height of the peak, and it decreases as the time of maturation increases. The extent of microflocculation in this case as is low as compared to the system containing no surface active agent. To some extent, casein reduces the deficiency of stabiliser in this system.
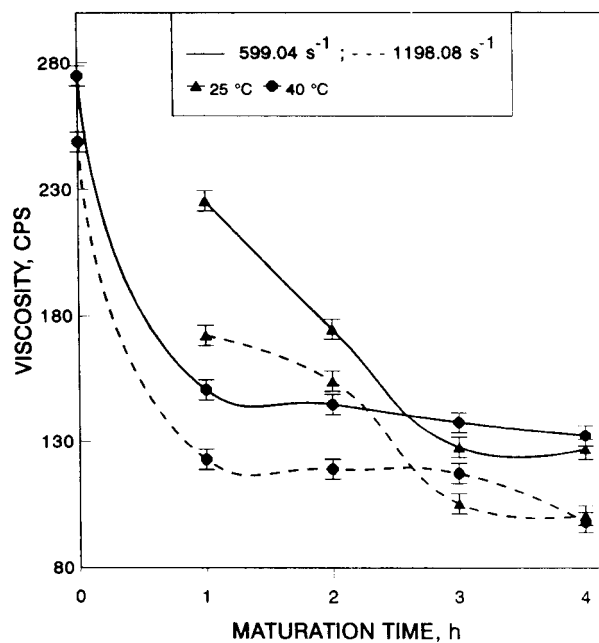
Effect of Temperature

We have selected N_{70} system to study the influence of temperature and maturation time on viscosity. Figure 7 is the plot of maturation time and temperature on the viscosity of N_{70} system. It is found that as the temperature increases, there is a decrease in viscosity. But as the maturation time increases, the differences in viscosity is marginal. In both cases, that is, at 25 and 40°C, there is a decrease in viscosity with maturation time.
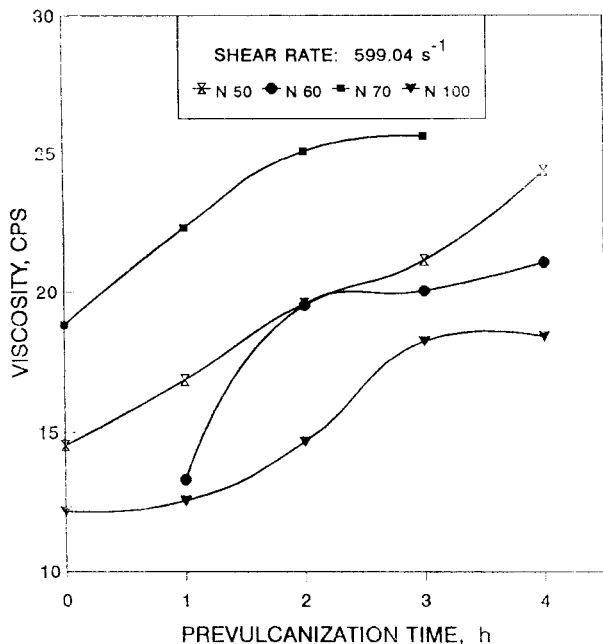
Effect of Prevulcanization

Various theories are proposed to explain mechanism of prevulcanization. The chemistry of the latex prevulcanization process has recently been reported by Porter et al.[51] They explained the occurrence of prevulcanization on the basis that

both the accelerator and sulphur dissolve in the aqueous serum of latex before migrating into the rubber phase. From there, they diffuse into the rubber and crosslink it. When the sulphur and accelerator reach the surface, there are two possibilities, as follows: first, the diffusion of these reactants into the rubber takes place, and then crosslinking. This leads to the formation of homogeneously crosslinked rubber particles. However, it is also possible that crosslinking can take place faster than diffusion. In this case, the core portion will not be crosslinked. This is very important in the formation of films from vulcanized latex. If the particles are preferentially crosslinked near their surface, the reduced mobility of the rubber chains at the surface makes it more difficult for the particles to coalesce, and a highly coherent film would not be expected. In the other case, if the latex compound is homogeneously crosslinked, the particle will coalesce well and form a film with optimum physical properties.

The effect of prevulcanization time on the viscosity of NR–SBR latex blends prevulcanized by CV system is given in Figure 8. We can see that as the prevulcanization time increases, the viscosity increases. But after 3 h, there is a levelling off in viscosity, except in the case of N_{50}. This indicates that the prevulcanization reaction is almost complete within 3 h. In our earlier work,[50] we have reported the increase in viscosity and

Figure 7 Effect of temperature on the viscosity of the NR–SBR 70/30 blend.

Figure 8 Variation of viscosity with prevulcanization time of the NR–SBR blends vulcanized by the CV system.

Figure 9 Variation of viscosity with prevulcanization time of the NR–SBR blends vulcanized by the EV system.
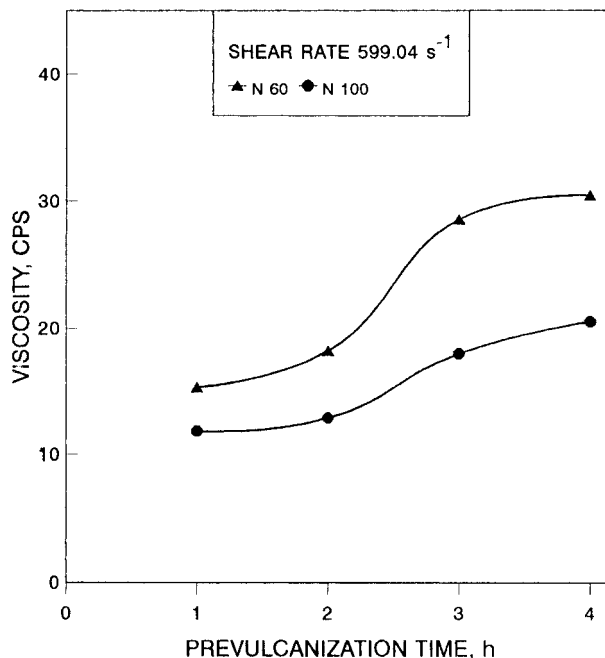
crosslink density with prevulcanization time. Here also, we have estimated the crosslink density values. For this, equilibrium swelling experiments have been conducted to determine the molar mass between crosslinks (M_c) using the Flory–Rehner[52] equation. For a crosslinked polymer network, the molecular weight between two crosslinks is given by

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

where V_s is the molar volume of the solvent, ρ_p is the polymer density, and ϕ_p is the volume fraction of the polymer in the swollen state. The value of ϕ_p is calculated by the following equation[53]:

$$\phi_p = \left[1 + \frac{\rho_p M_a}{\rho_s M_b} - \frac{\rho_p}{\rho_s} \right]^{-1} \qquad (2)$$

where M_a and M_b are the mass of the polymer before and after swelling, ρ_s is the solvent density, and ρ_p is the density of the polymer. The interaction parameter χ is calculated from the following equation[54]:

$$\chi = \beta + V_s / RT (\delta_s - \delta_p)^2 \qquad (3)$$

where V_s is the solubility parameter of the solvent, and β is the lattice constant, which is generally taken to be 0.34 for elastomer–solvent system. The crosslink density is calculated by the equation

$$\nu = 1/2 M_c \qquad (4)$$

Table III   Crosslink Density Values (CV)

System	Crosslink Density Values After (mol/g)	
	1 h	2 h
N_{100}	4.392×10^{-5}	1.062×10^{-4}

Table IV   Crosslink Density Values (EV)

System	Crosslink Density Values After (mol/g)	
	1 h	2 h
N_{100}	7.013×10^{-5}	8.215×10^{-5}

**Table V Pseudoplasticity Values (n)
Without Casein**

System	Maturation Time (h)				
	0	1	2	3	4
N_0	0.894	0.910	0.637	0.887	0.651
N_{50}	1.069	0.993	0.995	0.963	1.320
N_{60}	0.836	1.019	0.643	0.658	0.591
N_{70}	0.856	0.707	0.718	0.770	0.564
N_{100}	0.982	0.978	0.791	0.996	—

The crosslink density value of N_{100} vulcanized by CV at two different prevulcanization times is given in Table III. We can see that as the prevulcanization time increases, crosslink density increases.

Figure 9 indicates the effect of prevulcanization time on the viscosity of NR–SBR blends vulcanized by the efficient system. Here also, the viscosity increases with an increase in prevulcanization time. The crosslink density values of N_{100} vulcanized by the EV system at two different prevulcanization times is given in Table IV. The crosslink density values increase with increase in prevulcanization time.

Pseudoplasticity Values (n)

Pseudoplasticity index values of blends with and without casein are shown in Tables V and VI. Systems having low n values indicate pseudoplastic nature, and systems having high n values indicate dilatant behavior. Viscosity decreases with an increasing rate of shear for pseudoplastics, and viscosity increases with an increasing rate of shear for dilatants. In the case of blends containing casein, the pseudoplastic nature decreases as the maturation time increases; that is,

**Table VI Pseudoplasticity Values (n)
With Casein**

| System	Maturation Time (h)				
	0	1	2	3	4
N_0	0.927	1.277	1.306	1.584	1.674
N_{50}	0.908	0.794	0.801	1.009	1.328
N_{60}	0.901	0.919	0.940	0.966	1.260
N_{70}	0.869	0.993	1.002	1.027	0.921
N_{100}	1.018	1.373	1.356	1.775	1.735
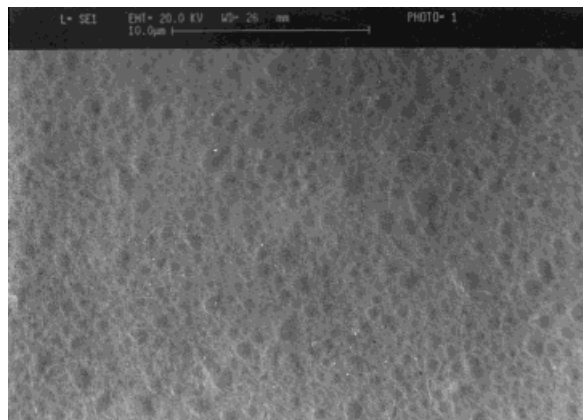
(a)

(b)

Figure 10 Scanning electron photographs of NR latex dried for (a) 9 h ($\times 1000$) and (b) 24 h ($\times 1000$).

the system acquires a more and more dilatant nature.

Film Formation

The scanning electron microscopy (SEM) photo of NR latex dried for 9 h is shown in Figure 10(a). The particles are clearly visible in this figure. The SEM photo after 24 h drying is given in Figure 10(b). Almost complete homogeneous film is obtained after 24 h; that is, the particles are fused. This type of fusion of particle is reported pictorially in the literature.[32,55]
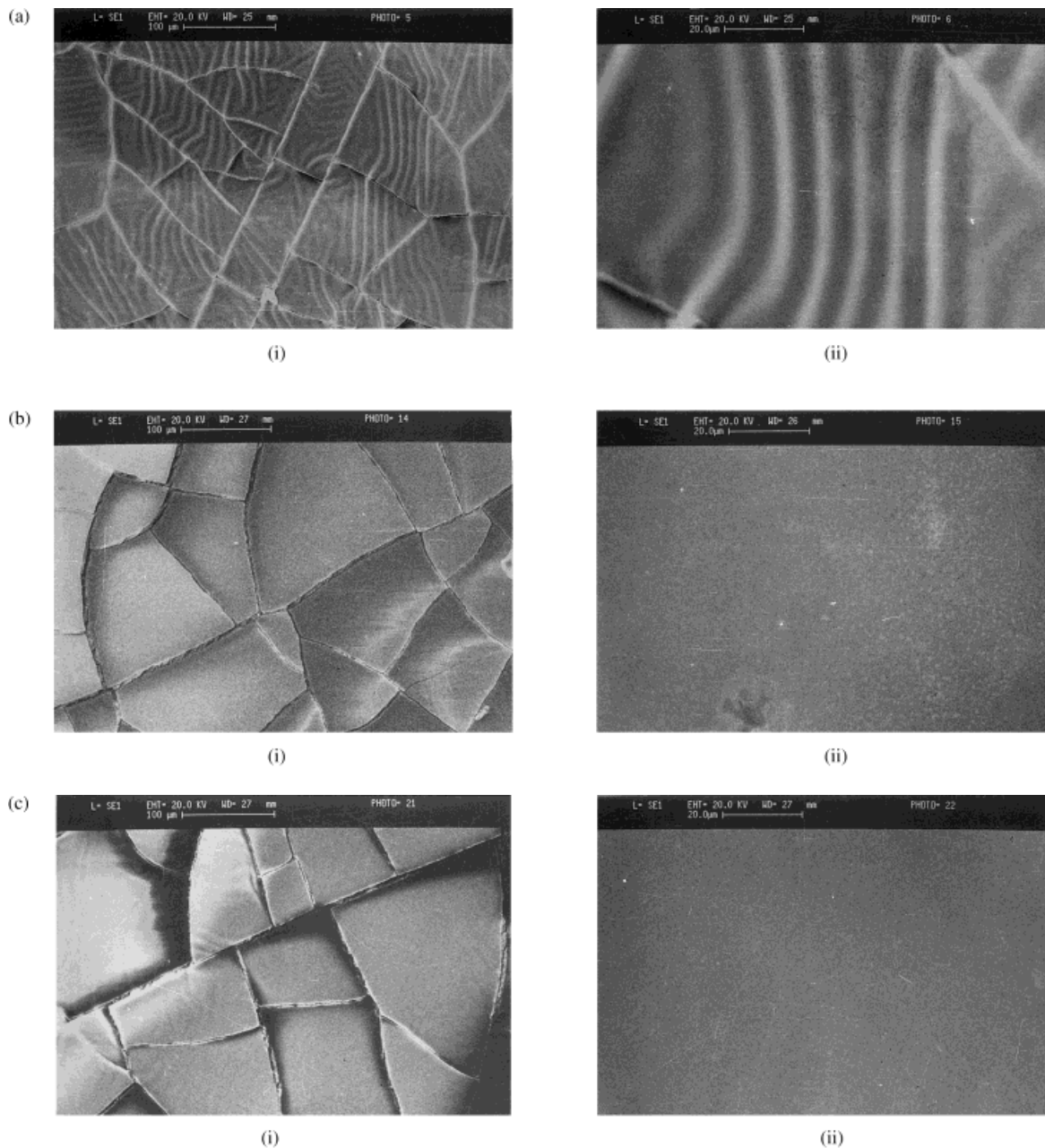
Figure 11   Scanning electron photographs of N_{70} dried for (a) 4 h (i) ($\times$232) and (ii) ($\times$1000), (b) 9 h (i) ($\times$232) and (ii) ($\times$1000), and (c) 24 h (i) ($\times$232) and (ii) ($\times$1000).

For N_{70} system also, as the drying time increases, the wringles are found to decrease [Figures 11(a)–(c)]. In fact, these cracks are formed due to the stresses produced during the drying stage. The stresses are developed due to the difference in thermal expansion coefficient between NR and SBR. Thermal expansion coefficient value for NR is 6.7×10^{-4} and that for SBR is 6.6×10^{-4}. After 24 h of drying, a complete homogeneous film is formed; that is, the complete coalescence of the

particles takes place. However, the cracks are found to remain on the film. Similar results are obtained for $N_{50}N_{80}$ system too.

CONCLUSION

NR and SBR latices were blended, and the viscosity changes were studied after different time intervals. A composition-dependent change in vis-

cosity was observed with maturation time. In the case of the 70/30 NR–SBR (N_{70}) blend, the positive deviation in viscosity was found to decrease as the maturation time increases. This is due to the exchange of stabilizers with one another until the equilibrium is reached, where all the particles of the blend are stabilized with a random mixture of stabilizers. When SBR content is less than 50%, the destabilization of SBR domains takes place, resulting in an agglomerated network structure. As the maturation time increases, the partial collapse of the network structure takes place, and viscosity decreases. In the presence of casein, the extent of positive deviation in N_{70} blend is reduced. Here too, as the maturation time increases, the viscosity decreases. The effect of prevulcanization time on the viscosity of NR–SBR latex blends were also studied. It was found that the viscosity increases with the increase in prevulcanization time due to the increased degree of crosslinking. The crosslink density values are in good agreement with this. But there is a levelling off in viscosity after 3 h in blends vulcanized by both CV and EV systems. The various stages of the film formation of NR latex and NR–SBR blends were studied. At a lower drying time, the particles are clearly visible in NR latex, and as the drying time increases, the coalescence of the particles take place, and a complete homogeneous film is formed. In the blend, the cracks and wrinkles are found to be decreased as the drying time increases. Finally, it is important to mention that the time-dependent rheological behavior and the studies on the film formation from polymer dispersions are highly important for the application of the latices in various fields.

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