Effect of Prevulcanization on the Rheological Behavior of Natural Rubber/Styrene Butadiene Rubber Latex Blends

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SYNOPSIS

The effect of prevulcanization on the rheological behavior of natural rubber (NR), styrene butadiene rubber (SBR) latices, and their blends was studied with special reference to shear rate, blend ratio, vulcanizing systems, prevulcanization time, and accelerator systems. The NR latex showed a sharp increase in viscosity with increase in prevulcanization time due to high extent of crosslinking. However, SBR latex showed marginal effect on viscosity with prevulcanization time due to its low dry rubber content and low degree of unsaturation. Blends showed variations in viscosity according to the change in composition. The use of a single accelerator was found to have marked influence on the viscosity of the blends compared with a combination of accelerators. Swelling experiments were carried out in order to determine the crosslink density of the blends. The viscosity changes have been correlated with the crosslinking density of the latices and their blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Several investigations have been made in the past few years in the field of blending of polymers.[1-4] Blending is used extensively to improve the processing characteristics as well as the properties of the end-products. The influence of blending variations on viscosity of the blends has been studied.[5] Shundo, Imoto, and Minoura[6] found out a relation between the properties of unvulcanized and vulcanized blends of NR and SBR prepared by means of solution blending, latex blending, roll blending, and Banbury mixer blending. Additionally, NR/SBR blends showed a direct relation to their blend ratio, regardless of blending method used. In most cases, latex blending results in a good degree of dispersion, which cannot be achieved by other blending techniques.[7,8] Excellent reports regarding latex blends exist in the literature.[9-14] Matsumoto et al.[10] found that dual-phase electrolytes, those having high ionic conductivity ($>10^{-3}$ S/cm) and good mechanical strength, can be prepared by mixing NBR and SBR latices. Okikura[12] conducted a series of studies on the recent trends in the practical blending of various kinds of latices. The viscosity changes associated with the blends of chloroprene rubber latex and natural rubber latex were studied by Belyaev et al.[13] Colloidal and chemical properties of carboxylated butadiene latex blends were reported.[15] It was found that rheological properties, surface tension, and low temperature resistance of latices are due to the particle interaction and formation of labile loose aggregates. The blends of SBR and NR latices have many potential advantages. For example, blends of 38% solid NR latex and 22% solid SBR latex in the 70/30 ratio have good processability.[16] These blends combine better crack resistance, wet grip, and weather resistance of SBR and the superior strength properties and low temperature characteristics of NR.

Polymer contained in latices and blends can be partially crosslinked in the latex stage without prior coagulation. The product is in effect a latex of vulcanized rubber. Prevulcanized latex is very similar in appearance to vulcanized latex where the original fluidity is retained. The vulcanization takes place in each of the individual latex particles without altering their state of dispersion appreciably. One of the principal advantages of prevulcanized latex is that effective control of the physical properties can

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Table I Formulation of Mixes for CV (phr)

Ingredients	N_{100s}	N_{100c}	N_{70s}	N_{70c}	N_{50s}	N_{50c}	N_{30s}	N_{30c}	N_{0s}	N_{0c}
60% NR latex	100	100	70	70	50	50	30	30	100	100
38% SBR latex	0	0	30	30	50	50	70	70	0	0
10% KOH solution	1	1	1	1	1	1	1	1	1	1
50% Sulfur dispersion	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
50% ZDC dispersion	1	1	1	1	1	1	1	1	1	1
50% ZMBT dispersion	—	1	—	1	—	1	—	1	—	1
50% ZnO dispersion	3	3	3	3	3	3	3	3	3	3

be exercised before articles are manufactured from it. Prevulcanized latex is used nowadays for the development of products, since initial crosslinking of the component is possible during prevulcanization, and the complete vulcanization is achieved by simply drying the final product. Prevulcanized latex is a very convenient form of latex for the manufacture of dipped goods, adhesives, latex foam, and textile combining.

There are different techniques for the prevulcanization of latices.[17-21] The rate of prevulcanization reaction varies with different vulcanizing systems, and the extent of prevulcanization has a profound effect on the final vulcanizate properties. Usually, latex is prevulcanized by heating with dispersions of sulfur and an accelerator, such as zinc diethyl dithiocarbamate, to 50–80°C. The reaction proceeds much more rapidly than the vulcanization of dry rubber at the same temperature with the same vulcanizing ingredients. The speed of the prevulcanization reaction seems to be associated primarily with the presence of water.[22] The effect of various accelerators and other compounding ingredients[23] and various formulations[24] for the crosslinking of NR latex has been reported. It is advantageous to reduce the particle size of the vulcanizing ingredients to that of particles of rubber in the latex for better properties. Effect of particle size of various compounding ingredients on NR latex has been reported.[25] Porter[26] has studied properties of prevulcanized and postvulcanized NR latex films. A de-

tailed study on the technological difference between latices with different preservating systems was carried out by Angove.[5] In addition to that, Angove[27] compared the advantages and disadvantages of the use of vulcanized latex blends in major manufacturing processes.

Viscosity of latex mixes is of great importance in various processes, and so it requires accurate methods of measurements in order to control the processing parameters. For example, in straight dipping, for the manufacture of gloves, the thickness of the film deposited on the former is affected by the viscosity of latex.[28] The viscosity of latices is usually increased very much as we increase the prevulcanization time. It is thus necessary to determine the viscosity of the latex mix over a wide range of shear rate and temperature as a function of prevulcanization time. However, to date no systematic study has been reported on the effect of prevulcanization on the flow behavior of NR/SBR latex blends.

In the present study two different vulcanizing systems have been used to vulcanize NR, SBR, and their latex blends. The main objective of the proposed program is to study the effect of two vulcanizing systems, i.e., conventional (CV), efficient (EV), shear rate, prevulcanization time, and accelerator systems on the rheological properties of latices of NR, SBR, and their blends. The extent of prevulcanization has been analyzed by crosslink density measurements. The viscosity changes have been correlated with the crosslink density of the samples.

Table II Formulation of Mixes for EV (phr)

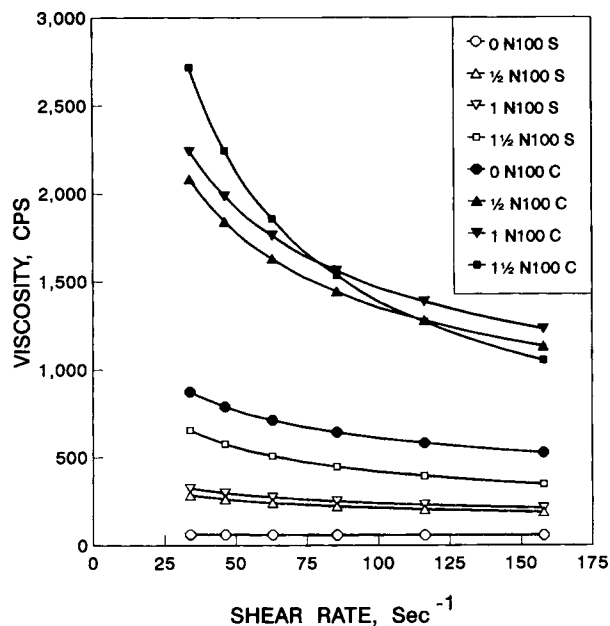| Ingredients	N_{100s}	N_{100c}	N_{70s}	N_{70c}	N_{50s}	N_{50c}	N_{30s}	N_{30c}	N_{0s}	N_{0c}
60% NR latex	100	100	70	70	50	50	30	30	0	0
38% SBR latex	0	0	30	30	50	50	70	70	100	100
10% KOH solution	1	1	1	1	1	1	1	1	1	1
50% Sulfur dispersion	1	1	1	1	1	1	1	1	1	1
50% ZDC dispersion	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
50% ZMBT dispersion	—	1	—	1	—	1	—	1	—	1
50% ZnO dispersion	3	3	3	3	3	3	3	3	3	3

Figure 1 Effect of shear rate on the viscosity of N_{100} prevulcanized by conventional system.

EXPERIMENTAL

Blend Preparation and Compounding

NR latex was supplied by Padinjarekara Agencies, Kottayam, India and SBR latex was given by Synthetics and Chemicals, Madras, India. Other chemicals were of laboratory reagent grade. Natural rubber (NR) and styrene butadiene rubber (SBR) latices were
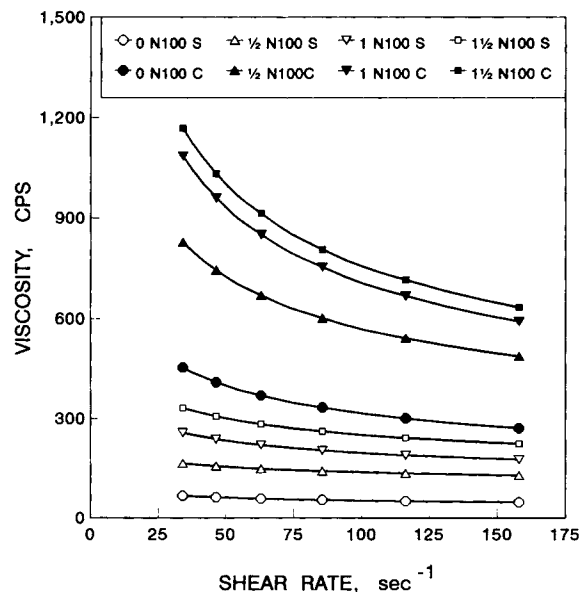

Figure 2 Effect of shear rate on the viscosity of N_{100} prevulcanized by efficient system.

Predominantly mono or disulphidic linkages

Predominantly polysulphidic linkages
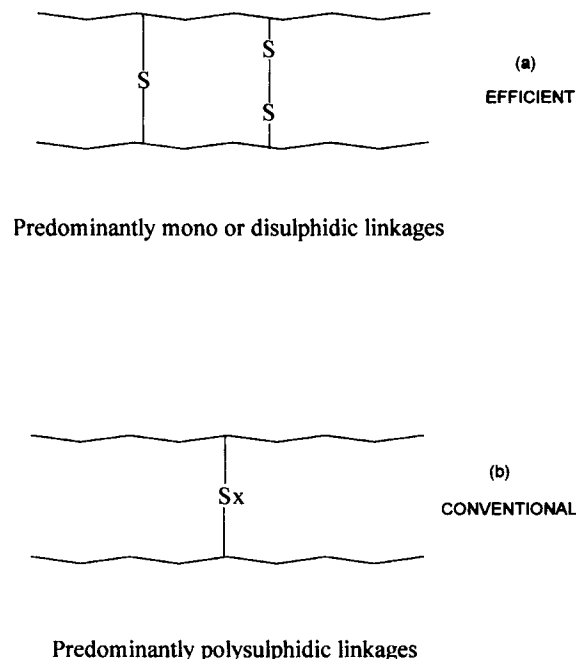
Figure 3 Schematic representation of types of links formed during conventional and efficient vulcanization.

blended in varying compositions starting from 0, 30, 50, 70, and 100 per cent of NR. Weights were calculated according to dry rubber content (DRC). Since there were so many samples with varying parameters, such as composition, vulcanizing systems, accelerator, prevulcanization time, etc., a basic coding system has been adopted throughout this report. For example, in the code $^{CV}0N_{0s}$, CV stands for conventional vulcanization, 0 for a prevulcanization time of 0 h, N_0 indicates the amount of natural rubber as 0, and s indicates the use of a single accelerator system. Similarly, for the code $^{EV}\frac{1}{2}N_{50c}$, EV stands for efficient vulcanization, $\frac{1}{2}$ indicates the prevulcanization time as $\frac{1}{2}$ h, N_{50} indicates the amount of natural rubber as 50, and c indicates the combination of accelerators. Typical formulations used in this work are given in Tables I and II. The CV system is characterized by a low accelerator and high sulfur combination, while the EV system has a high accelerator and low sulfur combination. Compounded

Table III   Crosslink Density Values

| System	Crosslink Density Values (moles/g)
$CV_{1/2N_{100s}}$	6.283×10^{-6}
$CV_{11/2N_{100s}}$	1.595×10^{-4}
$EV_{1/2N_{100s}}$	2.737×10^{-6}
$EV_{11/2N_{100s}}$	1.386×10^{-5}
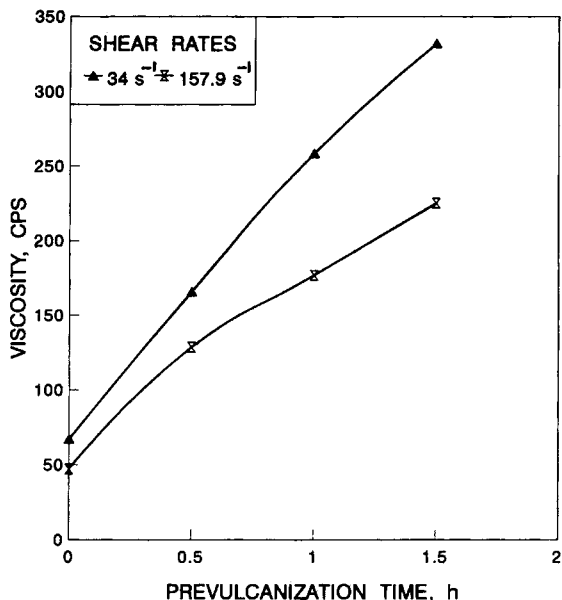
Figure 4 Effect of prevulcanization time on the viscosity of $^{EV}N_{100c}$.

Figure 6 Effect of shear rate on the viscosity of N_0 prevulcanized by conventional system.

latex blends were prepared by standard methods using ball-milled dispersions of zinc oxide, sulfur, zinc diethyl dithiocarbamate (ZDC), and zinc mercaptobenzothiazole (ZMBT). All the ingredients were added to the blend at room temperature and stirred using a mechanical stirrer for half an hour in order to ensure homogenization of the ingredients. Then the mix was kept undisturbed for one hour for maturing. This will impart good technical properties

and will remove the air bubbles introduced into the compound while compounding.

Prevulcanization

Prevulcanization was carried out by heating the compounded latex blend in a beaker immersed in water bath at 55°C. The latex mix was subjected to continuous slow stirring and the beaker was covered
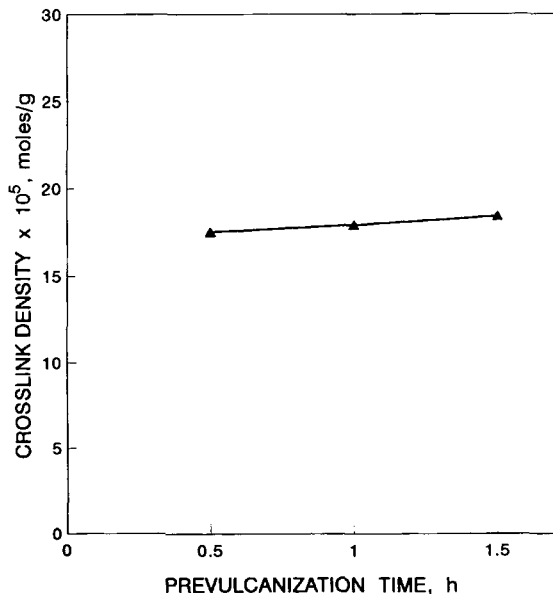

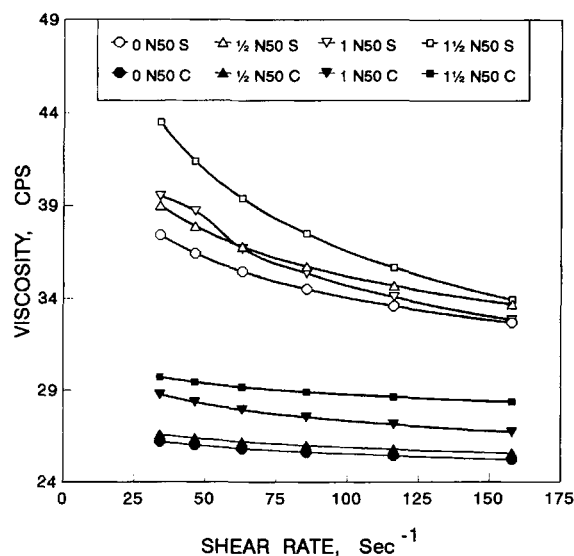**Figure 5** Effect of prevulcanization time on the crosslink density of $^{EV}N_{100c}$.
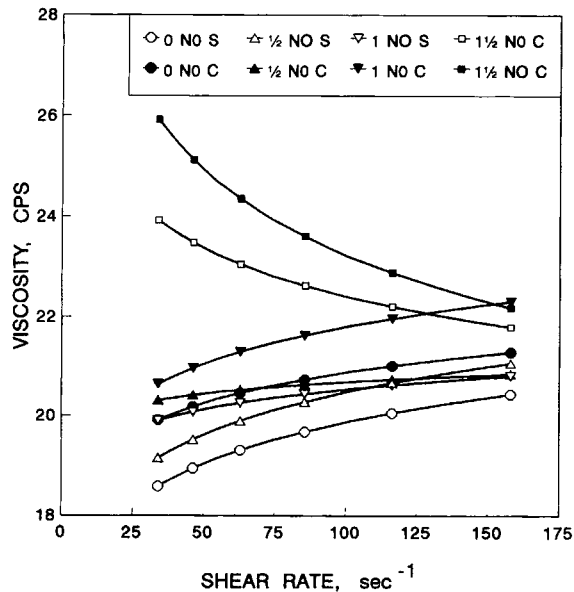
Figure 7 Effect of shear rate on the viscosity of N_0 prevulcanized by efficient system.
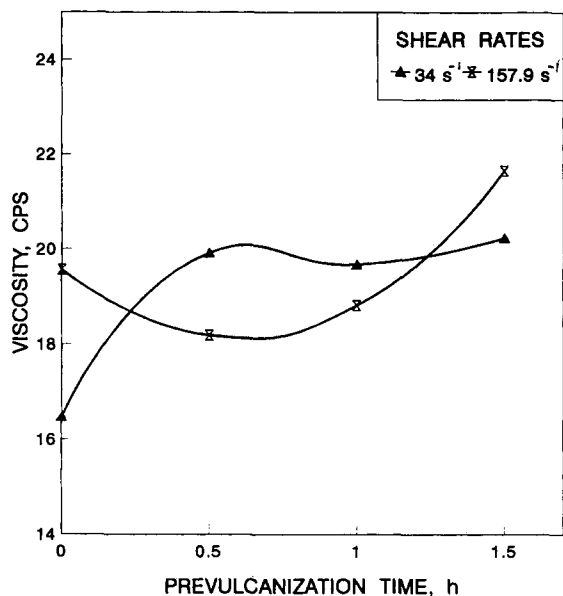
Figure 8 Effect of prevulcanization time on the viscosity of $^{CV}N_{0c}$.

to minimize loss of ammonia. Samples were withdrawn at regular intervals of time 0, $\frac{1}{2}$, 1, and $1\frac{1}{2}$ h. At the end of each heating period the samples were quickly chilled to prevent further vulcanization.

Rheological Measurements

The rheological measurements of all the samples were done at room temperature using a Contraves
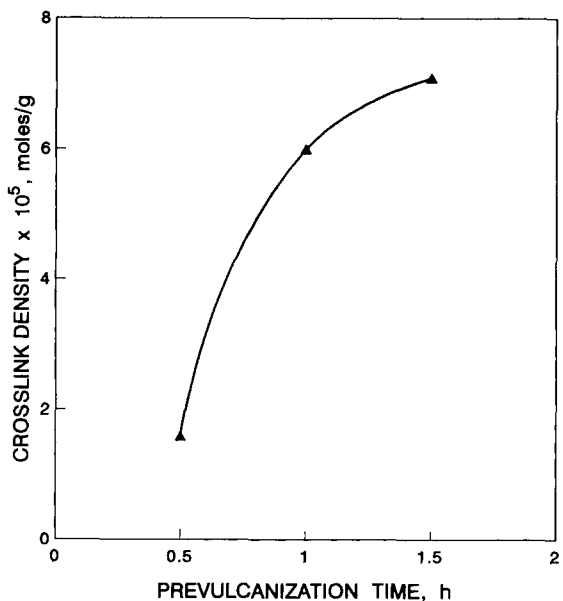
Figure 9 Effect of prevulcanization time on the cross-link density of $^{CV}N_{0c}$.
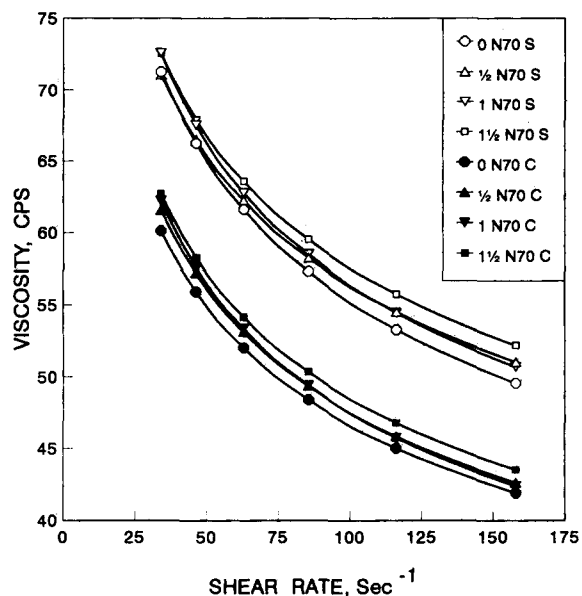
Figure 10 Effect of shear rate on the viscosity of N_{70} prevulcanized by conventional system.

Viscometer Rheomat-30. A concentric cylinder with B cup was used for viscosity measurements.

Equilibrium Volume Swelling Measurements

The latex blends were cast on a glass plate and allowed to dry at room temperature. Circular samples were punched from the sheets and were immersed in toluene at room temperature and allowed to swell for 48 h. At the end of this period, solvent adhering to the surface was removed with filter paper, and
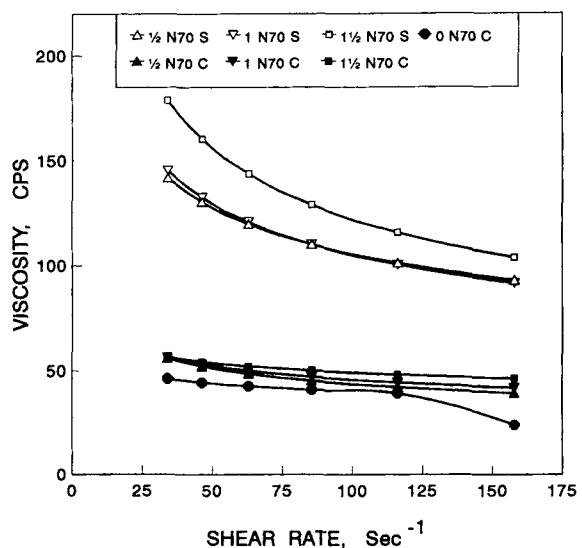
Figure 11 Effect of shear rate on the viscosity of N_{70} prevulcanized by efficient system.
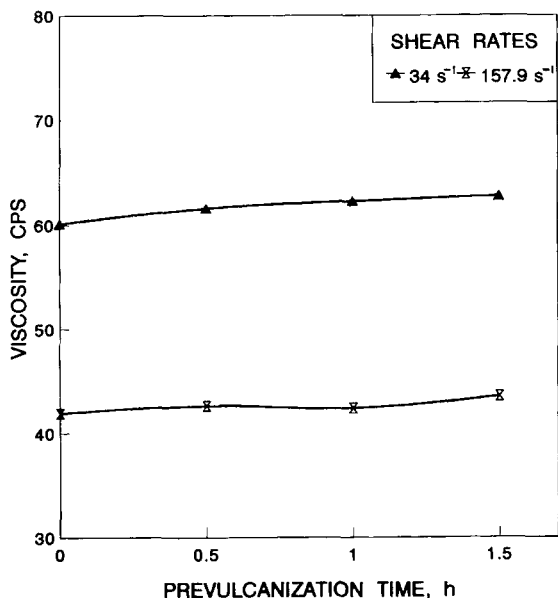
Figure 12 Effect of prevulcanization time on the viscosity of $^{CV}N_{70c}$.

the sample was weighed in a closed weighing bottle. Values of volume of fraction of rubber in the swollen gel were calculated, from which the crosslink density was then estimated.

RESULTS AND DISCUSSION

The results of all the rheological measurements were analyzed using the following Power law equation[29] as reported in our previous studies.[30-32]
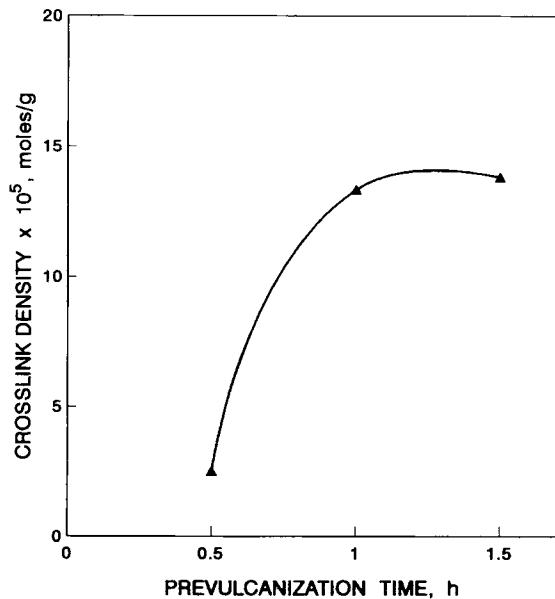

Figure 13 Effect of prevulcanization time on the crosslink density of $^{CV}N_{70c}$.
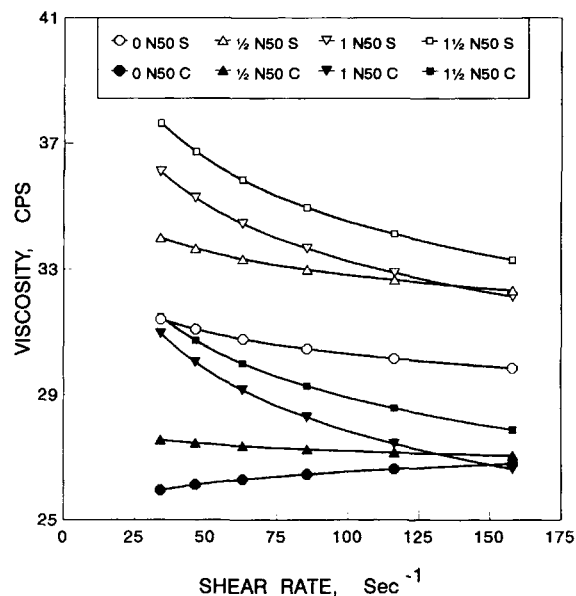
Figure 14 Effect of shear rate on the viscosity of N_{50} prevulcanized by conventional system.

$$\tau = K\dot{\gamma}^n \tag{1}$$

where τ = shear stress (Pa), $\dot{\gamma}$ = shear rate (s^{-1}), n = pseudoplasticity index, and K = viscosity index. Viscosity was calculated using the equation,

$$\eta = K\dot{\gamma}^{n-1} \tag{2}$$

Each rheogram was analyzed for yield stress (τ_o) and pseudoplasticity index (n).

Figure 15 Effect of shear rate on the viscosity of N_{50} prevulcanized by efficient system.
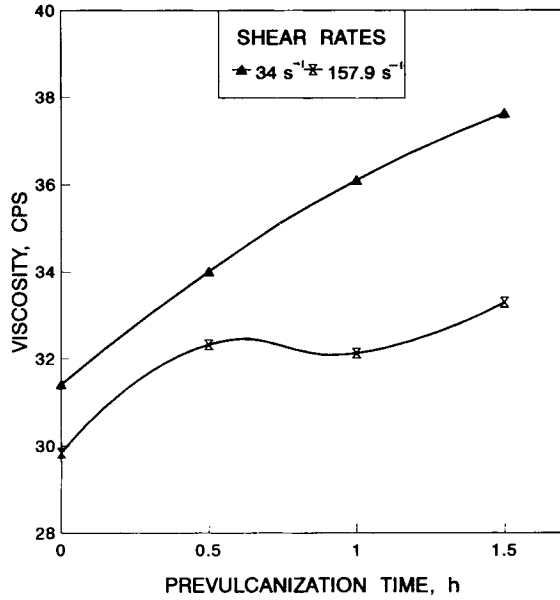
Figure 16 Effect of prevulcanization time on the viscosity of $^{CV}N_{50s}$.

Figure 18 Effect of shear rate on the viscosity of N_{30} prevulcanized by conventional system.

In order to understand the variations of viscosity upon prevulcanization, let us first have a look at the actual mechanism of prevulcanization. In fact, very little is known about the actual mechanism of the prevulcanization reaction. Some studies have been made on the process in order to elucidate the mechanism, but no extensive investigations are reported, and so no entirely satisfactory explanations are available.[33-35] Recently, different theories have been proposed to explain the mechanism of prevulcani-

zation. In some reports[36,37] the authors postulated that the reaction took place as a result of direct contact between particles of reactants and rubber. Another set of commentators[38,39] postulated that the reactants must dissolve in the aqueous phase before diffusing into the rubber particles. It seems most likely that the vulcanizing ingredients are absorbed into the rubber particles from the aqueous phase and not by direct contact between the particles of rubber and the particles of vulcanizing ingredients. These ingredients may be imagined as partitioned
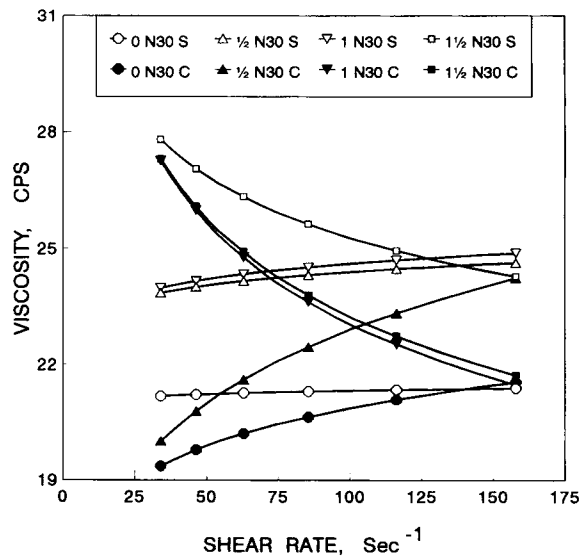

Figure 17 Effect of prevulcanization time on the crosslink density of $^{CV}N_{50s}$.

Figure 19 Effect of shear rate on the viscosity of N_{30} prevulcanized by efficient system.
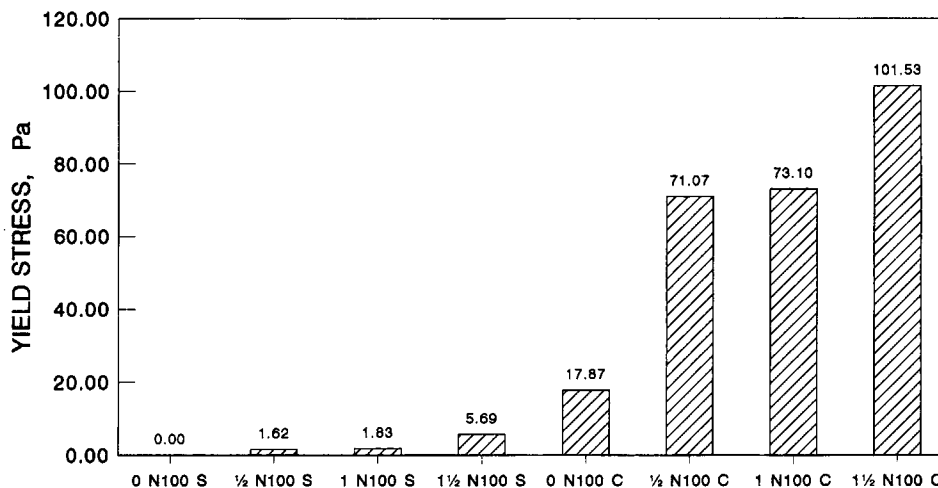
Figure 20   Variation of yield stress with prevulcanization time of N_{100} prevulcanized by conventional system.

between the aqueous phase and the rubber phase. This partitioning will strongly favor the rubber phase, but the aqueous phase will be kept saturated so long as the respective solid phases are present.[40] In support of this view, the interesting fact reported by Humphreys and Wake[41] is that no matter how much sulfur is included in the latex compound, it is not possible to attain more than about 18% combined sulfur with the rubber hydrocarbon.

The chemistry of the latex prevulcanization process has recently been reported by Porter, Rawi, and Rahim.[42] They explained the occurrence of prevulcanization on the basis that both the accelerator and sulfur 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 sulfur and accelerator reach the surface, there are two possibilities, 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.
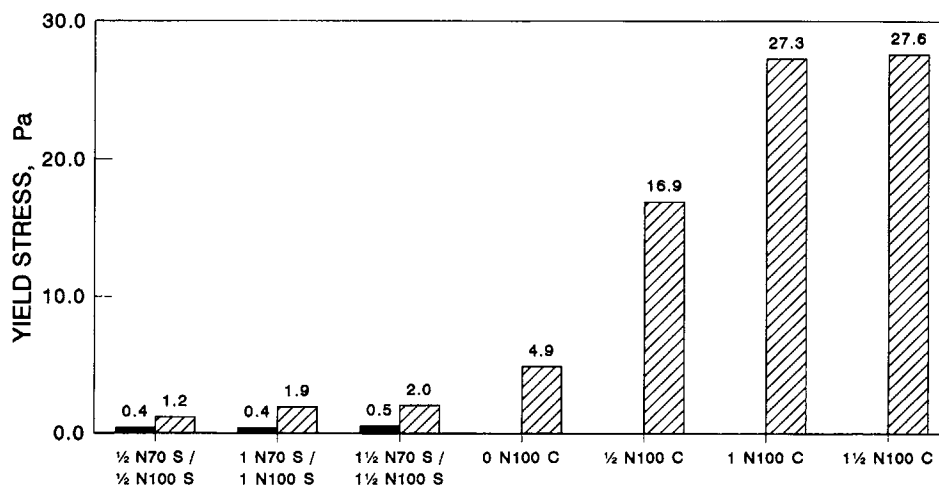

Figure 21   Variation of yield stress with prevulcanization time of NR and NR/SBR blends prevulcanized by efficient system.

Hu and coworkers[43] suggested that the rate of crosslinking is much greater than the rate of diffusion. There is no satisfactory explanation available for this reaction.

Let us now look at the viscosity variations of prevulcanized latices. The variation of viscosity with shear of NR latex in CV and EV systems is shown in Figures 1 and 2, respectively. In both CV and EV systems all the samples having a single accelerator (ZDC alone) show Newtonian behavior at lower prevulcanization time. But as the time of vulcanization increases, the viscosity increases and the system shows a tendency to exhibit pseudoplastic behavior. All the systems having a combination of accelerators (ZDC + ZMBT) show pseudoplastic nature. In addition to that, as the prevulcanization time increases, there is an increase in viscosity, and the maximum is obtained at $1\frac{1}{2}$ h. This increase in viscosity is due to the increase in the degree of crosslinking with vulcanization time. The pseudoplastic nature of the latex upon prevulcanization can be explained as follows. In latex, rubber particles are in a dispersed state. When particles in dispersions or globules in emulsions make contact, links are formed between them. As the prevulcanization time increases, the interparticle links will be increased. Under the influence of shear, these links are stretched, distorted, and oriented. So the interaction among the particles is reduced, leading to a decrease in viscosity.[44] The conventional system shows a higher increase in viscosity compared with the efficient system as the prevulcanization time increases. This is due to the fact that the nature and distribution of crosslink are different in both the cure systems. In the conventional system there are more polysulfidic linkages, i.e., a crosslink in which two polymer chains are bridged by a chain of three or more sulfur atoms. In the efficient system more

Table IV   Pseudoplasticity Index (CV)

| System | Time of Prevulcanization (h) | | | |
	0	$\frac{1}{2}$	1	$1\frac{1}{2}$
N_{100s}	0.9436	0.7270	0.7210	0.5848
N_{100c}	0.6689	0.6036	0.6095	0.3823
N_{70s}	0.7238	0.7845	0.7664	0.7912
N_{70c}	0.7651	0.7664	0.7499	0.7622
N_{50s}	0.9667	0.9670	0.9240	0.9201
N_{50c}	1.0207	0.0880	0.9632	0.9209
N_{30s}	1.0989	1.0367	0.9682	0.9688
N_{30c}	1.0975	1.0939	1.0736	1.9910
N_{0s}	0.8938	0.8938	0.9093	0.9139
N_{0c}	1.2216	1.2153	0.9710	1.2060

Table V   Pseudoplasticity Index (EV)

| System | Time of Prevulcanization (h) | | | |
	0	$\frac{1}{2}$	1	$1\frac{1}{2}$
N_{100s}	0.7726	0.8340	0.7528	0.7471
N_{100c}	0.6665	0.6553	0.6054	0.6095
N_{70s}	—	0.7252	0.6980	0.6345
N_{70c}	0.8660	0.7697	0.8060	0.8721
N_{50s}	0.9127	0.9049	0.8802	0.8388
N_{50c}	0.9759	0.9751	0.9525	0.9702
N_{30s}	1.0065	1.0209	1.0240	0.9117
N_{30c}	1.0697	1.1251	1.8445	0.8508
N_{0s}	1.0619	1.0621	1.0290	0.9395
N_{0c}	1.0438	1.0168	1.0505	0.8985

monosulfidic linkages are formed. The schematic representation of types of bonds formed in EV and CV systems is shown in Figure 3. The CV system has the higher viscosity compared to EV, which can be attributed to the greater extent of crosslinking of the former. This is made more clear from the crosslink density values (Table III). In both CV and EV systems, accelerator combinations are more effective in increasing the viscosity than single accelerator, i.e., a synergistic effect is observed. One can also note that there is not much difference in the viscosity after 1 and $1\frac{1}{2}$ h when accelerator combinations are used (Fig. 1). Greater differences in viscosity are observed between zero and $\frac{1}{2}$ h of prevulcanization. This indicates that the vulcanization reaction is more rapid during the beginning of prevulcanization. There is a difference in viscosity at zero time of vulcanization for ZDC and ZDC + ZMBT systems. This may be due to the difference in vulcanization during maturing time. We have further attempted to correlate the increase in viscosity with the extent of crosslinking. The equilibrium swelling experiments have been conducted to determine the molar mass between crosslinks (M_c) using the Flory-Rehner[45] equation. For a crosslinked polymer network, the molecular weight between two crosslinks is given by

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

where V_s is the molar volume of the solvents, ρ_p the polymer density, and ϕ_p the volume fraction of the polymer in the swollen state. The value of ϕ_p is calculated by the following equation[46]

$$\phi_p = \left[1 + \frac{\rho_p}{\rho_s} \frac{M_a}{M_b} - \frac{\rho_p}{\rho_s} \right]^{-1} \tag{4}$$

where M_a and M_b are the mass of the polymer before and after swelling; ρ_s is solvent density, and ρ_p is the density of the blend. The density of the blends is determined experimentally and the values are in good agreement with the theoretical values. The interaction parameter χ is calculated from the equation,

$$\chi = \beta + V_s/RT(\delta_s - \delta_p)^2 \qquad (5)$$

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 systems. For the determination of solubility parameter of blend (δ_p), the experimental procedure adopted is as follows.[47] Swelling experiments were carried out in a series of solvents. Swelling coefficient (α) is calculated using the equation,

$$\alpha = \frac{(M_a - M_b)}{M_b \rho_s} \qquad (6)$$

where M_a and M_b are weights of the samples after and before swelling, and ρ_s is the density of the solvent. A plot of α versus δ_s is constructed. The maximum value in δ_s is found at $\delta_s = 18.2$, and this gives δ_p. Using this solubility parameter, χ is estimated. The crosslink density (ν) is calculated by the equation,

$$\nu = \tfrac{1}{2}M_c \qquad (7)$$

Crosslink density, prevulcanization time, and viscosity of NR latex are correlated in Figures 4 and 5. In Figure 4, viscosity of $^{EV}N_{100c}$ is plotted against the prevulcanization time, and in Figure 5 crosslink density of $^{EV}N_{100c}$ is plotted against prevulcanization time. It can be seen that as the prevulcanization time increases, viscosity and crosslink density increase.

Figures 6 and 7 indicate the change in viscosity with shear rate of SBR latex using CV and EV systems, respectively. Here the trend is different from that of NR latex. The CV system in the presence of a single accelerator (ZDC), shows pseudoplastic behavior. But when the system contains an accelerator combination (ZDC + ZMBT), dilatancy is observed at zero time and $1\tfrac{1}{2}$ h of prevulcanization. Systems at intermediate times of vulcanization show pseudoplastic behavior. The dilatant behavior of SBR latex is already reported by our research group.[30] The dilatancy is due to the high temperature sensitivity of SBR latex as reported earlier. Utracki[48] reported that the dilatant behavior of synthetic latices is due to the difference in the particle size and

size distribution. As in the case of NR latex, the viscosity increases with prevulcanization time. However, the increase is not as predominant as that of NR. This is because in SBR, the increase in degree of crosslinking upon vulcanization is small as compared to NR. The explanation for this behavior include the low degree of unsaturation and the low DRC of SBR latex.

The EV system shows dilatant behavior at low prevulcanization time, but at higher vulcanization times the system becomes pseudoplastic. There is not much difference in viscosity between CV and EV systems as the prevulcanization time increases. This indicates that there is little difference in degrees of vulcanization between CV and EV systems in SBR. In CV a single accelerator is more efficient in increasing the viscosity than an accelerator combination. But in EV the accelerator combination has much more influence in increasing the viscosity. This is due to the fact that in the EV system ZMBT activates the action of ZDC.

Figures 8 and 9 indicate the correlation of viscosity and crosslink density with prevulcanization time of the $^{CV}N_{0c}$ system. Even though the viscosity of SBR latex is low, there is an increase in viscosity as well as crosslink density as prevulcanization time increases. Corresponding to the viscosity change, there is a change in crosslinking density.

In the case of blends, the effect of prevulcanization on viscosity is different from that of homopolymers. The viscosity variation with prevulcanization time of 70/30 NR/SBR blend is shown in Figures 10 and 11. Here most of the curves show pseudoplastic behavior. There is an increase in viscosity with prevulcanization time. However, the increase is not as predominant as that of pure NR latex. In the binary blend, the vulcanizing ingredients are distributed between the NR and SBR phases. Hence, there will be distribution of crosslinks between the two components of the blend. At zero time of vulcanization the structural buildup as reported earlier[30] is absent in this case. When NR and SBR latices are blended there is destabilization of SBR particles due to the exchange of stabilizers from the SBR phase to NR phase. But in the presence of extra stabilizers like KOH this destabilization can be reduced. Furthermore, the presence of compounding ingredients will impart a dilution effect. This will reduce the deficiency of stabilizer in the system. In both CV and EV systems accelerator ZDC is more effective in increasing the viscosity. The presence of accelerator affects the special structure of the rubber molecules, which in turn determines the physical, chemical, and service properties of the product. Usually, in rubber compounding it is ad-

vantageous to use combinations of two or more accelerators. Vulcanization obtained by the use of a binary accelerator system are usually found to have higher physical and chemical properties,[49] but the combinations do not give satisfactory effects on the viscosity of the NR/SBR blend. The combinations are more effective when (a) the accelerators activate one another, (b) a compound which is readily dissociated into free radicals is formed by redox reaction, or (c) one or more of the accelerators brings about a more rapid activation of sulfur and a more rapid reaction with the polymer.[50] When ZDC alone is present, the EV system shows higher viscosity than CV. The difference in viscosity between CV and EV is due to the variations in crosslink density.

Figures 12 and 13 show the effect of prevulcanization time on the viscosity and crosslink density of the $^{CV}N_{70c}$ system. In the case of the N_{70} system there is only a gradual increase in crosslink density with prevulcanization time. This is in agreement with the variations of viscosity upon prevulcanization.

The behavior of a 50/50 blend is depicted in Figures 14 and 15. The viscosity increases as prevulcanization time increases. Even though the initial viscosity is low there is also a regular increase in viscosity as prevulcanization time increases. For the system $^{CV}N_{50s}$ one can correlate the prevulcanization time with viscosity and crosslink density (Figs. 16 and 17). Figures 18 and 19 indicate the variation of viscosity with prevulcanizing time of a 30/70 blend. Here the trend is similar to that of SBR latex. At low prevulcanization time the system shows dilatant behavior because of higher SBR content.

Yield Stress (τ_o)

NR latex shows yield stress when vulcanized by EV and CV systems (Figs. 20 and 21). The 70/30 blend prevulcanized by the EV system also shows yield stress. All other systems do not show yield stress. The rate of curing reaction in NR latex is more compared to all other systems. This is apparent from the increasing value of yield stress as the time of vulcanization increases. Moreover, NR latex having an accelerator combination shows higher yield stress values than that with a single accelerator. This behavior is observed in NR latex vulcanized by both CV and EV.

Pseudoplasticity Index (n)

Pseudoplasticity index values of the systems are shown in Tables IV and V. In both CV and EV systems, n values of NR latex decrease as the time of prevulcanization time increases. This indicates that the system becomes more and more pseudoplastic as the extent of prevulcanization increases. SBR and SBR rich blends exhibit dilatancy. The low n values of NR-rich blends indicate their more pseudoplastic nature than SBR-rich blends.

CONCLUSION

The effects of various factors like vulcanizing systems, prevulcanization time, accelerator system, and shear rate on the rheological behavior of NR/SBR latex blends have been analyzed. The rate of prevulcanization reaction in homopolymer latices and their blends has been investigated by the variation of viscosity in each time. NR and NR-rich blends show the highest increase in viscosity with prevulcanization time compared with SBR and SBR-rich blends. This is due to the lower unsaturation and low solid content of SBR latex. In most cases pseudoplastic behavior is observed except in the case of SBR and SBR-rich blends. The dilatant behavior of SBR and SBR-rich blends is attributed to the high temperature sensitivity of SBR latex. In most cases swelling experiments indicate that there is a correlation between crosslink density and viscosity. In the case of blends, even though a synergistic effect in viscosity is not observed when a combination of accelerators is used, the crosslink density values indicate that a considerable amount of crosslinking is formed during prevulcanization. The pseudoplasticity index indicates clearly the dilatant nature of SBR and pseudoplastic nature of NR. Yield stress values were found to increase as the prevulcanization time increases. Systems having accelerator combinations show higher yield stress values than systems having a single accelerator in NR latex vulcanized by both CV and EV.

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