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Mechanical Properties of Sulphur Prevulcanised and Gamma Radiation Vulcanised Natural Rubber and Carboxylated Styrene Butadiene Rubber Latices and Their Blends

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Blends of natural rubber and carboxylated styrene butadiene rubber latex with varying blend ratio were prepared. The blends were vulcanised by different techniques which include sulphur prevulcanisation, and gamma radiation vulcanisation. Morphology of the blends was investigated from scanning electron micrographs. Mechanical properties such as tensile strength, tear strength, elongation at break and modulus were studied with reference to blend ratio and vulcanisation techniques. The crosslink density of the blends and individual components were determined from the swelling and stress-strain measurements. The sulphur prevulcanisation of latices was carried out at 70ºC for 2 h.The radiation vulcanisation of various systems was carried out using n-butyl acrylate as sensitiser at a dose of 15 kGy/h. The swell ratio of the samples was calculated. The radiation vulcanised systems showed comparable properties as that of sulphur prevulcanised systems. However, the modulus of radiation vulcanised latex films was lower than prevulcanised samples. The gamma radiation vulcanised latices are eco-friendly due to the absence of curing agents. Applicability of various theoretical models were investigated to predict the modulus of the blends.

Key words: latex blends; sulphur prevulcanised; radiation vulcanisation; mechanical properties; radiation vulcanised; carboxylated SBR

Vulcanisation is essential for rubbers to give its characteristic properties such as high elasticity and strength. The commonly used vulcanisation technique for elastomers is sulphur, peroxide, and radiation vulcanisation[1–5]. Among this, sulphur vulcanisation is the conventional method mainly used for the chemical vulcanisation of diene elastomers resulting in cyclic, mono- , di- , and poly-sulphidic linkages at the diene sites in a network structure. Due to the formation of these networks the material become more resistant to solvents, oils, temperature and the like[6]. The peroxide and radiation vulcanisation techniques of elastomers cause C-C linkages through the formation of free radicals.

Polymer latices can be prevulcanised in the latex stage itself. Prevulcanisation of natural rubber latex and other latices are the crosslinking of rubber particles without prior coagulation. The possibility of vulcanising

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the dispersed phase of latex without affecting the colloid stability was first investigated by Schidrowitz[7]. Prevulcanised latex can be widely used for the manufacture of several latex products. The latices are usually prevulcanised by heating with dispersions of sulphur, accelerators, such as zinc diethyl dithiocarbamate to 50ºC – 80ºC[8–12]. The reaction proceeds much more rapidly than the vulcanisation of dry rubber at the same temperature with the vulcanising ingredients. The speed of the prevulcanisation reaction seems to be associated primarily with the presence of water. Varkey *et al.*[13] studied the effect of sulphur prevulcanisation on the rheological properties of natural rubber (NR)/ styrene butadiene rubber (SBR) latex blends. Porter[14] has studied the properties of prevulcanised and post-vulcanised NR latex films. The effect of storage of NR latex concentrate on properties of prevulcanised latex film has been investigated by Clarama and coworkers[15]. Latices can also be prevulcanised by heating with peroxide[3] and by irradiation[16–18]. The radiation-vulcanised latices have definite technical advantages over conventional sulphur cured latex. The advantages are absence of nitrosoamines, low cytotoxicity, low emission of sulphur dioxide and less ash formation, better transparency and softness of dried films. They do not show accelerator-induced allergy. The radiation-vulcanised latices are now used for the manufacture of low modulus products such as toy balloons, medical gloves, endoscopic balloons, condoms *etc*. Usually gamma rays are used for research on radiation vulcanisation of latex[19–26]. The radiation vulcanisation of latices consists of two steps, firstly, mixing of latex with sensitiser. The commonly used sensitiser is n- butyl acrylate and secondly irradiation using Co- 60 gamma rays.

Blending of two polymers can be carried out to get a final product with better performance, reduced cost and for easy processing[29–31]. Latex stage blending of two polymers will result in finer scale of dispersion and there is no contamination by solvents. Thomas *et al.*[32–36] had investigated the mechanical, rheological, viscoelastic, and thermal properties of NR/ SBR and NR/carboxylated styrene butadiene rubber (XSBR) latex blends with reference to various parameters such as blend ratio, shear rate *etc*.

The present study deals with the morphology, mechanical properties, crosslink density and swell ratio of sulphur prevulcanised and radiation vulcanised NR/XSBR latex blends with reference to blend ratio and vulcanisation technique. Colloidal and chemical properties of carboxylated butadiene latex blends have already been reported[37]. The blends of NR and XSBR latices have many potential advantages. NR latex possesses high wet gel strength; it has low cost and has excellent physical properties. XSBR latex has better weather resistance, adhesion properties and less permeable to gases and solvent molecules. Blending of these two polymers will result in new systems with better physical properties. NR is non-polar and XSBR is polar in nature and hence the systems are thermodynamically immiscible.

EXPERIMENTAL

Materials Used

Centrifuged natural rubber latex was procured from Gaico Rubbers Ltd., Kuravilangadu, Kottayam, Kerala, India. XSBR latex was collected from Apar Industries Ltd., Mumbai, Maharashtra, India. The characteristics of materials used are given in *Table 1*.

Film Preparation

Sulphur prevulcanisation. The vulcanisation of the individual latices and their blends were carried out in accordance with the formulation given in *Table 2*. The prevulcanisation of the compounded latex was conducted at 70ºC for 2 h using water bath with constant gentle stirring. Films were prepared by casting on a glass plate and dried at ambient temperature. The samples represented as N_{100sP}, N_{70sP}, N_{50sP}, N_{30sP} and N_{0sP}, where N stands for NR, the subscript numbers represent the weight percentage of NR and sP for sulphur prevulcanisation.

Gamma radiation vulcanisation. The latex samples were irradiated using ^{60}Co radiation source at Rubber Research Institute of India, Kottayam, Kerala, India. The dosage given was 15 kGy/h at room temperature using 5 p.h.r. n-butyl acrylate as sensitiser. The films of the above mentioned vulcanisation methods were prepared by casting on a glass plate and allowed to dry at ambient temperature until it becomes transparent. It was then heated in a hot air oven at 70ºC for 1 h and leached in tap water for 24 h and again dried. The samples are coded as N_{100G}, N_{70G}, N_{50G}, N_{30G} and N_{0G}, where G represents the gamma radiation vulcanisation.

Scanning Electron Microscopic Analysis

The samples were cryogenically fractured and analysed for morphology of blend system using scanning electron microscope, JEOL JSM-840A.

Mechanical Properties

The tensile and tear properties of those samples cut from the film using standard die were determined using Universal Testing Machine in accordance with *ASTM D 412-87*. From the tensile curve the modulus at 300% and elongation at break were analysed.

TABLE 1. CHARACTERISTICS OF MATERIALS USED

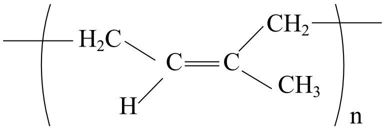
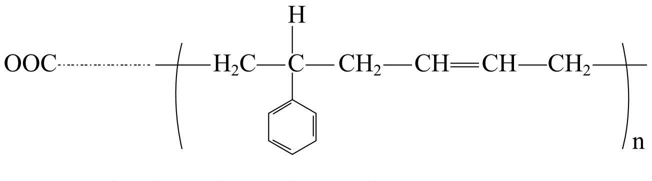
Natural rubber (NR) latex	
Supplier	Gaico Rubbers Ltd., Kuravilangadu, Kottayam
Dry rubber content (DRC) (%)	60
Total solid content (TSC) (%)	61.25
Carboxylated styrene butadiene rubber Latex (PLX-802)®	
Supplier	Apar Industries Ltd., Bombay, India
Dry rubber content (DRC) (%)	47
Total solid content (TSC) (%)	50.66
Styrene content (%)	52

TABLE 2. FORMULATION OF LATEX COMPOUNDING

Item	N_{100sP}	N_{70sP}	N_{50sP}	N_{30sP}	N_{0sP}
60% Centrifuged NR latex	100	70	50	30	–
48% XSBR latex	–	30	50	70	100
10% Potassium hydroxide solution	1.25	1.25	1.25	1.25	1.25
10% Potassium laurate solution	1.25	1.25	1.25	1.25	1.25
50% Sulphur dispersion	1.5	1.5	1.5	1.5	1.5
50% ZDC dispersion	0.75	0.75	0.75	0.75	0.75
50% ZMBT dispersion	0.5	0.5	0.5	0.5	0.5
50% Zinc oxide dispersion	0.2	0.2	0.2	0.2	0.2

ZDC = zinc diethyl dithiocarbamate, ZMBT= zinc mercaptobenzothiazole

Crosslink Density Measurements

The crosslink density (ν) and swelling ratio (Q) of the S-vulcanised and radiation vulcanised samples were determined by keeping a circular piece of weighed samples with particular dimension immersed in toluene until equilibrium was reached and weights at equilibrium swelling were taken. The sample was then taken out and blotted with filter paper and weighed. The crosslink density (ν) was calculated using the equation[38]:

$$\nu = \frac{1}{2M_c} \qquad \ldots 1$$

M_c is the molecular weight of polymer between crosslinks, as shown in *Equation 2*:

$$M_c = \frac{-\rho_r V_s \phi^{1/3}}{\ln[1-\phi] + \phi + \chi\phi^2} \qquad \ldots 2$$

where: ρ_r is the density of polymer
V_s is the molar volume of solvent
ϕ is the volume fraction of rubber in the solvent-swollen sample, and is given by:

$$\phi = \frac{d/\rho_p}{d/\rho_p + A_s/\rho_s} \qquad \ldots 3$$

where: d is the deswollen weight
ρ_p is the density of polymer
A_s is the amount of solvent absorbed.

In *Equation 2*, χ is the interaction parameter and is given by Hildebrand equation:

$$\chi = \beta + \frac{V_s(\delta_s - \delta_p)^2}{RT} \qquad \ldots 4$$

where: β is the lattice constant
R is the universal gas constant
T is the absolute temperature
δ_s is the solubility parameter of solvent
δ_p is the solubility parameter of polymer.

The crosslink density of those samples were also calculated from the stress-strain measurements using the equation[39]:

$$\nu = \frac{F}{2A_oRT\rho\left(\alpha - {}^{1}/_{\alpha^2}\right)} \qquad \ldots 5$$

where: F is the maximum load
A_o is the initial area of cross-section of the tensile specimen
ρ is the density
R is the universal gas constant
T is the absolute temperature
α is the extension ratio (α = Change in length/ Original length).

The swelling ratio (Q) was computed using the equation:

$$Q = \frac{(W_1 - W_o)}{W_o} \qquad \ldots 6$$

where: W_1 is the weight of swollen sample
W_o is the initial weight of sample before swelling.

RESULTS AND DISCUSSION

Morphology of Blends

The morphology of blends was obtained from scanning electron micrographs (SEM) of cryogenically fractured surfaces. In the case of heterogeneous blends the properties depend largely on its morphology. In the present blend system, natural rubber is non-polar and XSBR is polar and are highly immiscible exhibiting independent characteristics. The factors determining the morphology of blends are their ratio of each component, reactive functionalities, the viscosity of two phases and the presence of ingredients. According to Paul and Barlow[40] the morphology developed during mixing depends upon interfacial tension between the phases, the viscosity and the elasticity. Many researchers[41–42] studied the effect of mixing time on the morphology of melt-mixed elastomer blends. Thomas and *et al.*[43–46] extensively investigated the morphology of various polymer blends using SEM.

Figure 1(a) is the SEM of 70/30 NR/XSBR blend. In this figure the dark portion indicate the dispersed XSBR particles in the continuous NR matrix. From *Figure 1(b)* it is clear that the two phases exhibit co-continuous morphology at 50/50 blend ratio, *i.e.*, both the phases are continuous. Morphology of 30/70 NR/XSBR blend system is obtained from *Figure 1(c)*, in which NR is dispersed in the continuous XSBR phase in accordance with blend ratio.

The number average ($\bar{D}_n$) and weight average ($\bar{D}_w$) diameter of dispersed phases is calculated using the relationship,

$$\bar{D}_n = \Sigma n_i D_i \,/\, \Sigma n_i \qquad \ldots 7$$

$$\bar{D}_n = \Sigma n_i D_i^2 \,/\, \Sigma n_i D_i \qquad \ldots 8$$

where n_i is the number of particles with diameter D_i. The values are given in *Table 3*. The domain size of 30/70 NR/XSBR blend is greater than 70/30 system.

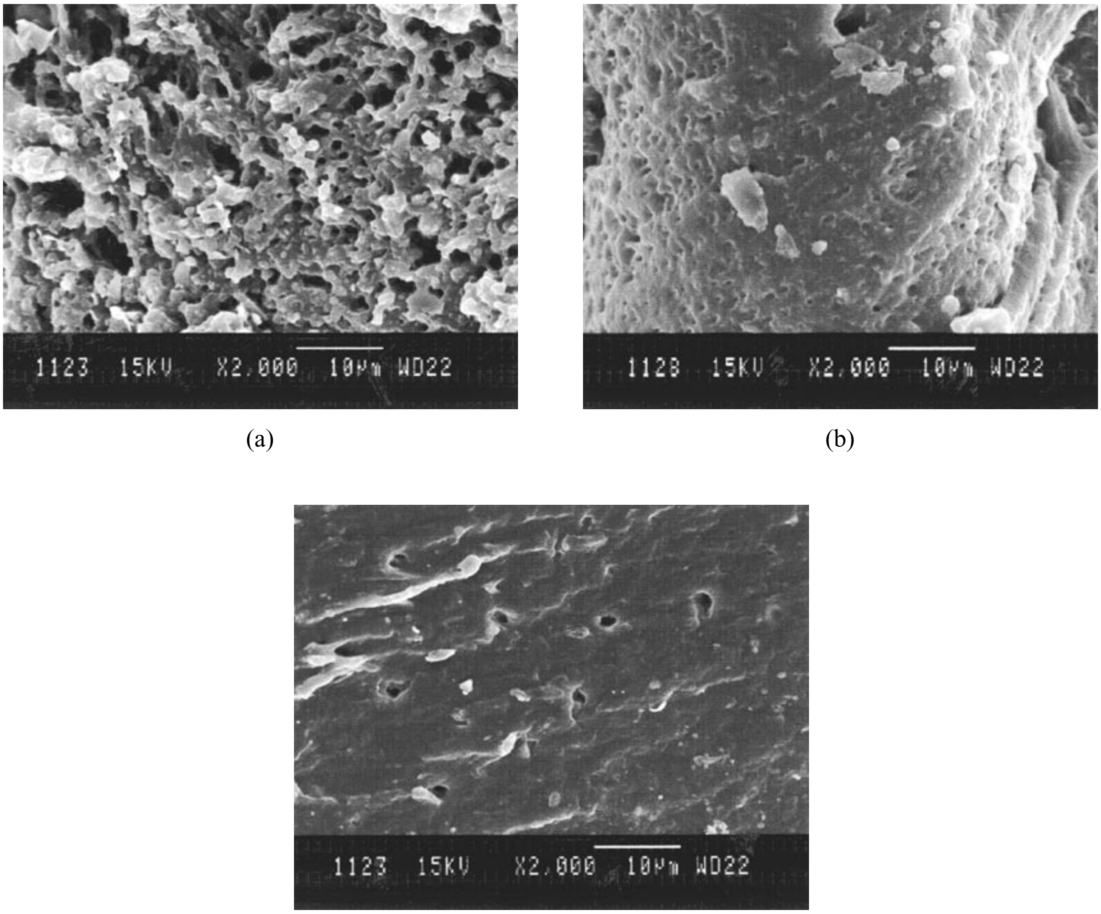
The size of the domains present in N_{70} and N_{30} polymer blends are given in *Table 3*. It depends on the viscosity of the continuous phase. If the matrix is highly viscous the coalescence of dispersed particles decreases and vice versa. The co-continuous nature of N_{50} blend is associated with its comparable viscosity. It is found that the domain size of 30/70 blend are higher than 70/30, it can be attributable in terms of the lower viscosity of the continuous XSBR phase. One can also explain this based on the capillary number:

$$Ca = \frac{\gamma \eta_m D}{2\Gamma} \qquad \ldots 9$$

where, D is the diameter of the droplet, γ is the shear rate , η_m is the matrix viscosity and Γ is the interfacial tension.

Mechanical Properties

Sulphur prevulcanisation of the compounded latices and their blends have been carried out at 70ºC for 2 h using water bath. Different theories have been proposed to explain the mechanism of prevulcanisation. Some of them reported[47–48] that the reaction took place as a result of direct contact between particles of reactants and rubber. In accordance with few scientists the reactants must dissolve in the aqueous phase before diffusing into the rubber



(a) (b)

(c)

Figure 1. Scanning electron micrographs of (a) N_{70}, (b) N_{50} and (c) N_0.

particles. Porter and co-researchers[49] reported the chemistry behind the prevulcanisation of latex. They suggested that the prevulcanisation took place as a result of the dissolution of accelerator and sulphur in the aqueous serum of latex followed by migrating into the rubber phase. It then diffuses into the rubber phase and crosslinks it. There are two possibilities for the prevulcanisation of latex; first one is the reaching of vulcanising agents to the surface, occurrence of diffusion followed by crosslinking. In the other case crosslinking takes place faster than diffusion. Homogeneously crosslinked rubber particles are formed in the former case while in latter only the surface gets crosslinked, the core will not be. If the latex is homogeneously crosslinked, the particles will coalesce well and form a film with good ultimate properties. According to Hu *et al.*[50] the rate of crosslinking is much greater than the rate of diffusion.

Figure 2 is the stress-strain curves of sulphur prevulcanised NR, XSBR and their

TABLE 3. NUMBER AVERAGE ($\bar{D}_n$) AND WEIGHT AVERAGE ($\bar{D}_w$) DOMAIN DIAMETER OF DISPERSED PHASES IN N_{70} AND N_{30} BLENDS

Sample	$\bar{D}_n$(μm)	$\bar{D}_w$(μm)
N_{70}	1.7	2.0
N_{30}	2.4	2.6

TABLE 4. SWELL RATIO VALUES OF OF SULPHUR PREVULCANISED AND RADIATION VULCANISED LATEX BLENDS

Sample	Swell ratio
N_{100sP}	4.74
N_{70sP}	4.91
N_{50sP}	6.39
N_{30sP}	5.06
N_{0sP}	4.21
N_{100G}	6.17
N_{70G}	7.62
N_{50G}	7.12
N_{30G}	6.49
N_{0G}	5.68

blends. The deformation behaviour of various blends under an applied load is obtained from stress-strain measurements. NR shows strain induced crystallisation nature, which is the reason for good mechanical properties than other synthetic rubbers. The strain-induced crystallisation of NR has been extensively studied by X-ray diffraction technique since the 1940s[51–53]. However, the vulcanised synthetic rubbers are considerably weaker than the natural rubber because of the lacking ability to crystallise under stretching at room temperature. Recently, Toki and Hsiao[54–56] found that under high strains (>600%) a very large fraction of unoriented amorphous (~75 wt%) phase still remained in the stretched sample in addition to ~20 wt% strain-induced crystals along with ~5 wt% oriented amorphous chains. According to their investigations, due to the non-homogeneous distribution of crosslinked network only a small fraction of crosslinked chains are responsible for the entire mechanical performance of the natural rubber. The non-homogeneous network topology is due to the presence of chemical reactive center, unsaturated bond, and the average chain length between the two adjacent reactive points. The molecules of small chain length between the densely packed networks can be oriented and form crystallites whereas the molecules of much longer chain lengths would remain in the random coil state under stretching. In conventionally vulcanised rubber the network formed is composed of molecules with a broad distribution of chain lengths between the network points and hence it cannot create a homogeneous network distribution. From *Figure 2* it is clear that the strain-induced crystallisation is predominant in NR and 70/30 NR/XSBR blend, in which XSBR dispersed in the NR continuous matrix as discussed earlier. As the weight percentage of XSBR increases the crystallites formation of rubber under strain reduces.

The variation in tensile and tear strength with blend ratio is shown in *Figure 3*. It shows negative deviation from the additivity line. This is explained to the immiscibility of NR/XSBR blend systems. Therefore it exhibits reduced mechanical properties than its individual components. The 70/30-blend system has higher properties than XSBR due to the nature of continuous NR matrix. It is due to the superior strength of NR continuous phase owing to its strain-induced crystallisation behaviour. However, the tensile strength of blends decreases at lower concentration of NR. This can be further explained to the morphology of blend systems as shown in *Figure 1*. At lower concentration of NR, the NR is dispersed in the continuous XSBR matrix. The higher strength of NR rich blends is also explained by the fact that NR has higher degree of unsaturation than XSBR. As a result the NR phase gets over-cured. The uneven

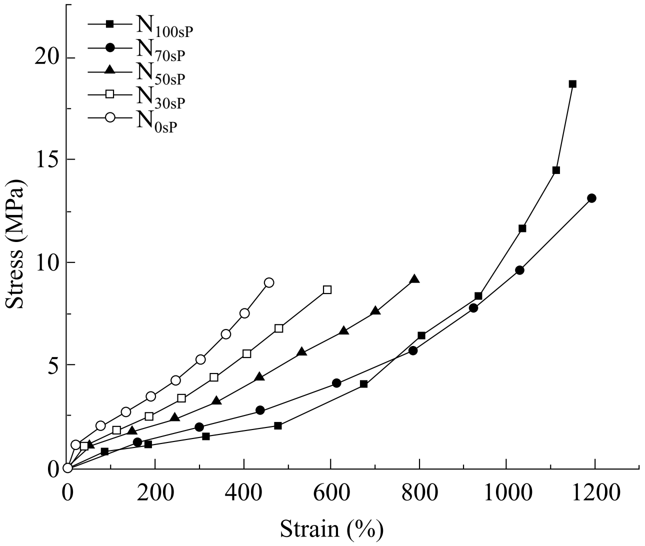


Figure 2. Stress-strain curves of sulphur prevulcanised latices and their blends.

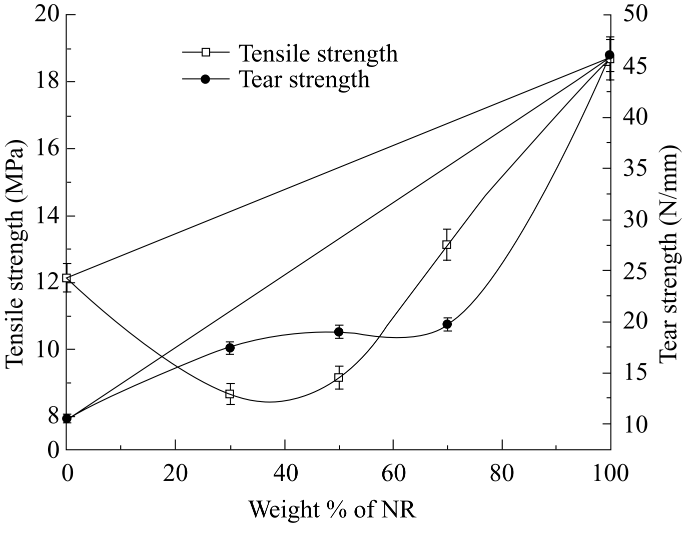


Figure 3. Variation in tensile and tear strength with weight percentage of NR for sulphur prevulcanised latices.

distribution of networks within the phases worsenes the properties. It can be concluded that the reduced strain induced crystallisation with the increasing concentration of XSBR, the uneven distribution of curing agents and poor interfacial adhesion between the polar XSBR and non-polar NR be the reason behind the reduced properties of XSBR rich blends.

During radiation vulcanisation carbon-carbon crosslinks are formed through the formation of free radicals. Radiation vulcanised latex films possesses strength superior to sulphur prevulcanised samples, except modulus. Makuuchi *et al.*[5,20,21,28] found that the presence of various olefinic monomers are the promoters of radiation induced latex prevulcanisation. The effectiveness of olefinic monomers will depend partly upon their ability to become absorbed in the rubber particles when added to the latex and partly upon their inherent efficiency as promoters of gamma radiation induced crosslinking. Another important factor is that the presence of the monomer during irradiation should not affect the colloid stability of latex. From *Figure 4* it is observed that the deformation behaviour is similar to sulphur prevulcanised blends, here also the strain induced crystallisation increases with weight percentage of NR in the blend. Due to the nature of continuous NR matrix the 70/30 NR/XSBR blend shows strain induced crystallisation behaviour. *Figure 5* presented the tensile and tear strength of radiation vulcanised latex blends. The curves exhibit negative deviation for 30/70 and 50/50 blends and positive deviation for 70/30 blends from the additivity line. The sharp increase in the properties of 70/30 blends is associated with the ease of formation of C-C linkages in NR due to the presence of unsaturation in the polymer chain. In this blend XSBR is the dispersed phase. Therefore chemically active centres of NR interact with the reactive groups of XSBR resulting in enhanced properties. The enhancement in properties of 70/30 NR/XSBR is also associated with the high strength of the continuous NR phase due to strain–induced crystallisation behaviour.

Elongation at break and modulus at 300% elongation of sulphur and radiation vulcanised latex blends are displayed in *Figures 6* and *7*, respectively. The strain to failure values of blends are found to be intermediate between the virgin polymers. The modulus of blend systems decreases as a function of weight percentage of NR as compared to XSBR, which is polar in nature. Being XSBR a polar material it has high cohesive interaction than NR. Therefore it can be concluded that the higher modulus of XSBR and its blends is associated with the high cohesive interaction between the polymer chains. It appears that films having tensile strength greater than sulphur prevulcanised samples could be obtained from radiation vulcanised latices and their blends in the presence of n-butyl acrylate as sensitiser. The changes in the mechanical properties of films from the irradiation of latices containing monofunctional monomers are primarily a consequence of physical entanglement of polyacrylate macromolecules with the rubber molecules.

Crosslink Density Measurements

Crosslinking of polymers can be carried out to improve a wide variety of properties including strength, heat resistance and recovery from deformation. Generally in blend systems uneven distribution of crosslinks can be observed due to the difference in affinity towards curatives of the two phases. The migration of vulcanising agents depends on the ratio of two components, degree of chemical reactive center (unsaturation or double bond), polarity *etc*. Even rather small change in relative polarity of the rubbers in a blend will affect the crosslink density distribution[57]. A plot of

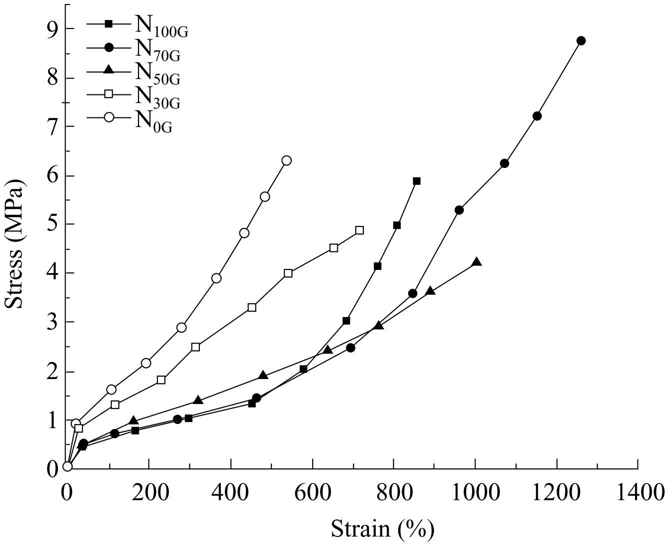


Figure 4. Stress-strain curves of gamma radiation vulcanised latices and their blends.

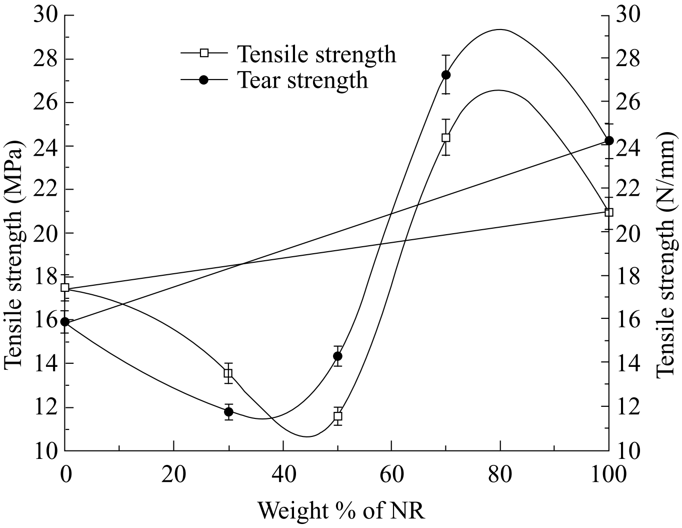


Figure 5. Variation in tensile and tear strength with weight percentage of NR for gamma radiation vulcanised latices.

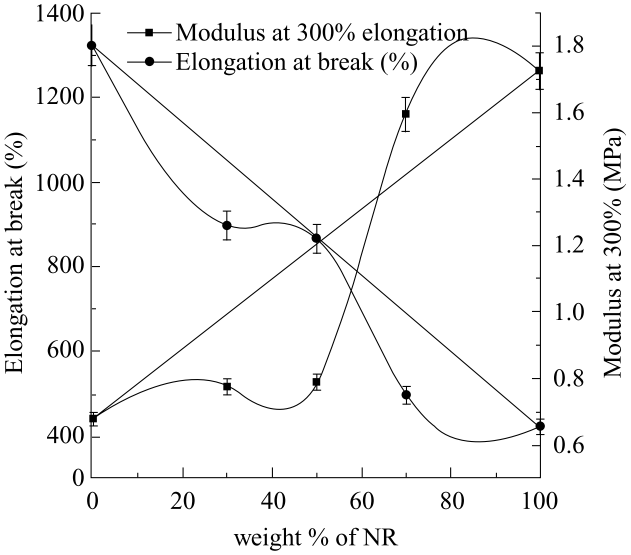


Figure 6. Variation in modulus and elongation at break (%) with weight percentage of NR for sulphur prevulcanised samples.

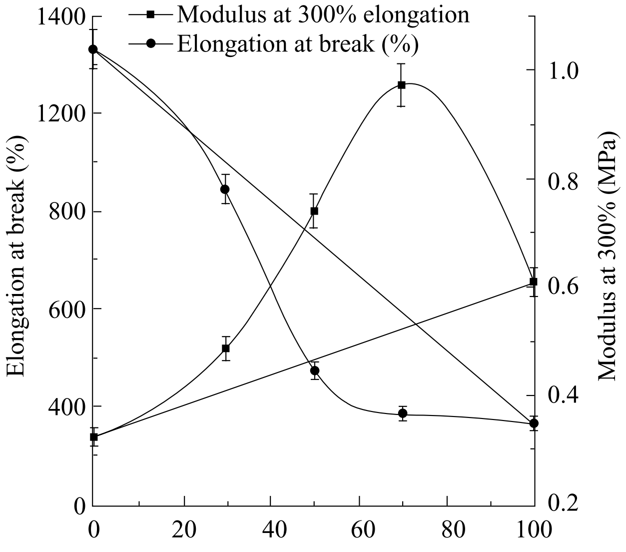


Figure 7. Variation in modulus and elongation at break (%) with weight percentage of NR for gamma radiation vulcanised samples.

crosslink density values of NR/XSBR latex blends obtained from equilibrium swelling method and stress-strain measurements is shown in *Figure 8*. The values obtained from stress-strain measurements are higher since it is the sum of the network chains joined chemically and the network chains formed from entanglements (both trapped and untrapped). However, untrapped entanglements have no contribution whereas the trapped entanglements contribute significantly towards swelling. Therefore, stress-strain method exhibits higher crosslink density than swelling method. XSBR possesses higher crosslink density values than NR due to the self-curing nature and the formation of zinc carboxylate crosslinks of XSBR owing to the presence of polar carboxyl group. The presence of zinc carboxylate crosslinks formed will enhance the modulus of XSBR and its blends. Crosslink density values of blends determined by both methods are lower than virgin polymers. This is associated with the uneven distribution of curing agents and the immiscibility of the two phases resulting in the formation of non-homogeneous networks.

As compared to virgin polymers, the crosslink density values of radiation vulcanised latex blends are lower (*Figure 9*). The modulus of the films is highly sensitive to crosslink density. Therefore, radiation vulcanised systems exhibit lower modulus as compared to sulphur prevulcanised systems. The solvent resistance properties of blends are obtained from the swelling ratio. The values are given in and it is observed that blends are less resistant to solvent due to the immiscibility of two components. As a result, the voids are formed at the interface, which will enhance the swelling process.

Theoretical Modeling of Mechanical Properties

The theoretical correlation of mechanical properties of experimentally determined values is relevant for predicting the nature of the blend systems. Various composite models have been applied to relate the experimental results with theoretical predictions. The structure and properties of the interface can be understood from these models.

Different models have been applied for predicting the mechanical property of NR/XSBR latex blends. These include parallel, series and Kunori. The upper bound parallel model is given by the rule of mixtures[58]:

$$M = M_1\phi_1 + M_2\phi_2 \qquad \ldots 10$$

where M is the mechanical property of blend
M_1 is the mechanical property of component 1
M_2 is the mechanical property of component 2
ϕ_1 is the volume fraction of component 1, and
ϕ_2 is the volume fraction of component 2.

This equation is suitable for models in which the components are connected parallel to each other and the applied stress elongates each component by the same amount. In the lower bound model the components are perpendicular to the applied force. The equation is given by:

$$\frac{1}{M} = \frac{\phi_1}{M_1} + \frac{\phi_2}{M_2} \qquad \ldots 11$$

Nielsen[59] and Kunori and Geil[60] stated that the mechanical property of a blend depends on the interfacial adhesion. According to them, the mechanical property of a blend in the absence of adhesion between components may be written as:

$$\sigma_b = \sigma_m(1 - A_d) \qquad \ldots 12$$

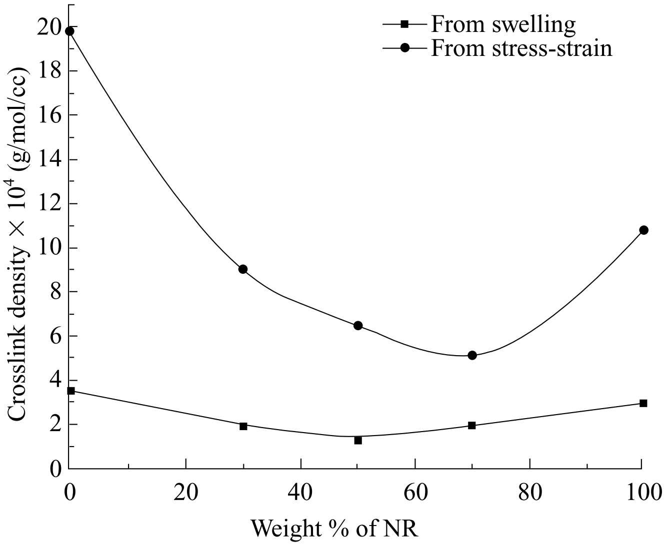


Figure 8. Effect of blend ratio on the crosslink density values of sulphur prevulcanised latex.

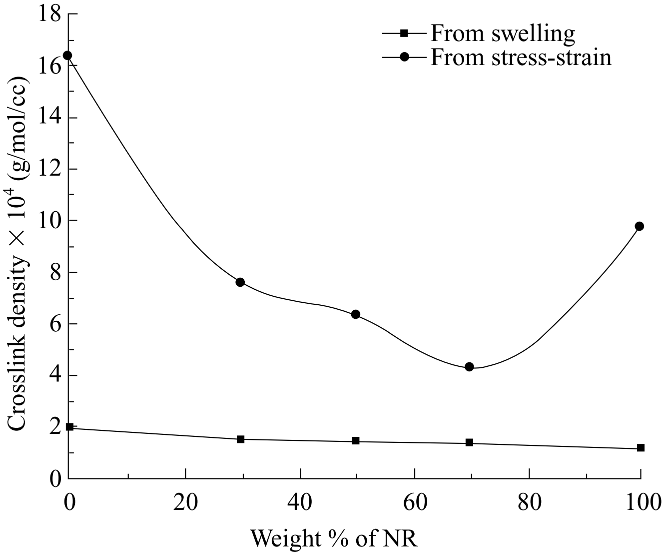


Figure 9. Effect of blend ratio on the crosslink density values of gamma radiation vulcanised latex.

where σ_b is the mechanical property of blend
σ_b is the mechanical property of the matrix, and
A_d represents the area of fraction occupied by the dispersed phase in transverse cross section.

Kunori and Geil[60] assumed that if there is a strong adhesive force between blend components, the dispersed phase would also contribute to the strength of blend. Based on this they modified *Equation 12*, as shown below:

$$\sigma_b = \sigma_m(1-A_d) + \sigma_d A_d \qquad \ldots 13$$

If the fracture propagates mainly through the interface, *Equation 13* becomes:

$$\sigma_b = \sigma_m(1-\phi_d^{2/3}) + \sigma_d \phi_d^{2/3} \qquad \ldots 14$$

If the fracture propagates through the matrix, then *Equation 13* may be written as:

$$\sigma_b = \sigma_m(1-\phi_d) + \sigma_d \phi_d \qquad \ldots 15$$

From *Figure 10* it is clear that sulphur prevulcanised 30/70 blends fits more to parallel and Kunori-2 models indicate that the two phases are immiscible and the fracture propagates through the matrix. The morphology studies disclose that in 30/70 blends NR is dispersed in the continuous XSBR matrix. Due to the co-continuous morphology of 50/50 blend it deviates from all theoretical predictions. The 70/30 NR/XSBR blend agrees well with theoretical values for series model, in which XSBR is dispersed in the continuous NR matrix. The theoretical relation of radiation vulcanised modulus values to experimental results can be obtained from *Figure 11*. Similar to sulphur prevulcanised 30/70-blend radiation vulcanised also shows values closer to Kunori-2 and parallel models, representing the immiscibility of the two phases and the fracture propagates through the matrix. It further indicates the less susceptibility of synthetic latices towards sulphur and radiation vulcanisation as compared to natural rubber latex. Radiation vulcanised 50/50 and 70/30 agrees well with series and Kunori-1 model. This can be explained in terms of the interface reaction between the two latices on irradiation through the formation of active centres. In this case the fracture propagates through the interface.

CONCLUSIONS

Morphology of the blends was analysed from SEM. Due to the immiscibility of two phases heterogeneous blend morphology was observed. In 70/30 NR/XSBR blend system XSBR was dispersed in the continuous NR matrix and in 30/70 NR/XSBR, NR was dispersed in the XSBR phase. The 50/50 blend ratio exhibited co-continuous morphology in which both the phases were continuous and was associated with the lower viscosity difference of the two latex systems. The mechanical properties, crosslink density and swell ratio of NR/XSBR blend systems were studied with special reference to blend ratio and crosslinking techniques. The tensile and tear properties of sulphur prevulcanised blends exhibited negative deviation from the additivity line. This was explained to the immiscibility of the two phases. Gamma radiation vulcanised 70/30 NR/XSBR blend showed higher tensile and tear properties than virgin polymers and other blend systems due to the strain-induced crystallisation behaviour of continuous NR matrix. It was also due to the interaction between chemically active centres of NR and reactive groups in XSBR upon irradiation. The modulus of the blends increased with the increase in XSBR content for all types of vulcanisation due to the cohesive interaction between polymer chains owing to the polar nature of XSBR. The higher modulus in sulphur prevulcanised XSBR and XSBR rich

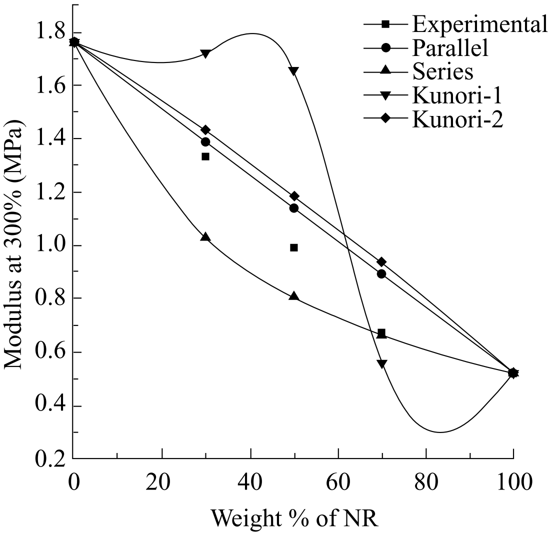


Figure 10. Theoretical correlation of modulus of sulphur prevulcanised latex blends.

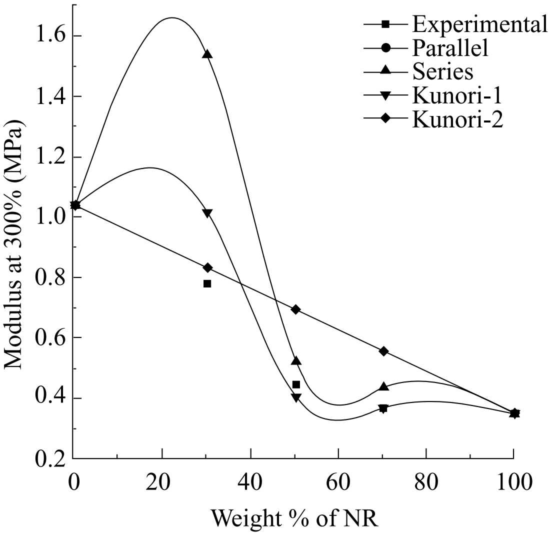


Figure 11. Theoretical comparison of modulus of gamma radiation vulcanised latex blends.

blends than radiation vulcanised samples were explained to the formation of zinc carboxylate crosslinks. Sulphur prevulcanised systems exhibited lower elongation at break except for NR than gamma radiation vulcanised systems.

Crosslink density values were determined by swelling and stress-strain measurements. Due to the difference in unsaturation and polarity of two phases the affinity of these latices towards curing agents are different. Therefore the blends showed reduced crosslink density than individual components. When compared to radiation vulcanised latices and their blends sulphur prevulcanised latex samples showed higher crosslink density. The decreased modulus values of radiation vulcanised latex samples were described in terms of the lower crosslink density values.

Finally, attempts were made to compare experimental result with theoretical predictions. The nature of the interface and the extent of miscibility of the two components can be understood from the theoretical predictions of the mechanical properties. For correlation, various composite models such as parallel, series and Kunori were applied to NR/XSBR system.

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REFERENCES

1. BLACKLEY, D.C. (1997) Types of Latexes. *Polymer Latexes: Science and Technology*, 2^{nd} edn., Vol. 2. London: Chapman and Hall.
2. BLACKLEY, D.C. (1997) Latexes. *Encyclopedia of Polymer Science and Technology*, Vol. 8, 647.
3. PENDLE, T.D. (1993) Recent Advances in Latex Technology, *Novel Prevulcanized Latexes*, 49.
4. GAZELEY, K.F. AND PENDLE, T.D. (1990) *Proc. Int. Symp. Radial Vulc. Nat. Rubb. Latex, JAERI-M-89-228, Tokyo, Japan*, 189.
5. MAKUUCHI, K., YOSHI, F., ISHIGAKI, I., TSUSHIMA, K., MOGI, M. AND SAUTO, T. (1990) *Radiat. Phys. Chem.*, **154**, 35.
6. TRIPATHY, A.R., MORIN, J.E., WILLIAMS, D.E., EYLES, S.J. AND FARRIS, R.J. (2002) *Macromolecules*, **35**, 4616.
7. SCHIDROWITZ, P. AND GOLDBROUGH, H.A. (1915) *Brit. Pat. No.1*, 111.
8. VAN DALFSEN, J.W. (1943) *Rubb. Chem. Technol.*, **16**, 318.
9. HUMPHREYS, N.C.H. AND WAKE, W.C. (1950) *Trans. Inst. Rubb. Ind.*, **25**, 334.
10. SUTTON, S.D. (1951) *Trans. Inst. Rubb. Ind.*, **27**, 93.
11. PANICH, R.M., FODIMAN, N.M. AND VOYUTSKI, S.S. (1959) *Sov. Rubb. Technol.*, **18(2)**, 14.
12. HU, Y.M., CHOU, Y.F. AND CHEN, W.T. (1966) *Kexue Tongbao*, **17(10)**, 451.
13. VARKEY, J. T., RAO, S.S. AND THOMAS, S. (1996) *J. appl. Polym. Sci.*, **62**, 2169.
14. PORTER, M. (1989) *Advances in Rubber Technology*. New Delhi: Tata Mc Graw Hill Pub., Ltd., 268.
15. CLARAMMA, N.M., VARGHESE, L. AND MATHEW, N.M. (1997) *Kautschuk Gummi Kunststoffe*, **50**, 857.
16. GREGSON, T.C., ROGERS, T.H., BANGS, L.B. AND PEABODY, D.W. (1961) *Rubber age*, **89**, 81.
17. MINOURA, Y. AND ASAO, M. (1961) *J. appl. Polym. Sci.*, **5**, 233.
18. KARTOWARDOYO, S. AND SUNDARDI, F. (1977) *J. appl. Polym. Sci.*, **21**, 3077.

19. SEBASTIAN, M.S. (1999) *Rubber Asia*, 76.

20. JAYASURIYA, M.M., MAKUUCHI, K. AND YOSHII, F. (2001) *Euro. Polym. J.*, **37**, 93.

21. VARGHESE, S., KATSUMURA, Y., MAKUUCHI, K. AND YOSHII, F. (1998) *Rubb. Chem. Technol.*, **72**, 308.

22. TANGBORIBOONRAT, P., SUCHIVA, K. AND REISS, G. (1995) *Polymer*, **36(4)**, 781.

23. PEETHANBARAN, N.R. AND KURIAKOSE, A.P. (1989) Kaut. Gimmi Kunst., **42(12)**, 1118.

24. HAQUE, M.E., DAFADER, N.C., AKHTAR, F. AND AHMAD, M.U. (1995) *Radiat. Phys. Chem.*, **46(1)**, 119.

25. SASIDHARAN, K.K., JOSEPH, R., RAJAMMAL, G., VISWANATHA PILLAI, P. AND GOPALAKRISHNAN, K.S. (2001) *J. appl. Polym. Sci.*, **81**,

26. SABHARWAL, S., DAS, T.N., CHAUDHARI, C.V., BHARDWAJ, Y.K AND MAJALI, A.B. (1998) *Radiat. Phys. Chem.*, **51(3)**, 309.

27. RATNAM, C.T., YOSHI, F., MAKUUCHI, K. AND ZAMAN, K. (1999) *J. appl. Polym. Sci.*, **72**, 1421.

28. MAKUUCHI, K., YOSHI, F. AND GUNE WARDENA, J.A.G.S.G. (1995) *Radiat. Phys. Chem.*, **46(4)**, 979.

29. ZANZIG, D.J., MAGNOS, F.L., HSU, W.L., HALASA, A.F. AND TESTA, M.E. (1993) *Rubb. Chem. Technol.*, **66**, 456.

30. HAO, P. T., ISMAIL, H. AND HASHIM, A.S. (2001) *Polymer Testing*, **20**, 539.

31. ISMAIL, H. AND HAIRUNEZAM, H.M. (2001) *Eur. Polym. J.*, **37**, 39.

32. VARKEY, J.T., THOMAS, S. AND RAO, S.S. (1995) *J. Appl. Polym. Sci.*, **56**, 451.

33. VARKEY, J.T., THOMAS, S. AND RAO, S.S. (1996) *Polym. Plast. Technol. Eng.*, **35**, 1.

34. VARKEY, J.T., RAO, S.S. AND THOMAS, S. (1995) *Plast. Rubb. Comp. Proc. Appl.*, **24**, 249.

35. VARKEY, J.T., CHATTERJI, P.R., RAO, S.S. AND THOMAS, S. (1998) *J. appl. Polym. Sci.*, **68**, 1473.

36. STEPHEN, R., NAIR, S.V., RAJU, K.V.S.N., VARGHESE, S., OOMMEN, Z. AND THOMAS, S. (2003) *J. appl. Polym. Sci.*, **88**, 2640.

37. KUZNENTSOV, V.L., RAIMAN, I.R., KRAYUSHKINA, E.I. AND TUTERSKVI, I.A. (1985) *Kauch Rezina*, **2**, 24.

38. FLORY, P.J. AND REHNER, J. (1943) *J. Chem. Phys.*, **11**, 521.

39. CLUFT, E.F., GLADDING, E.F. AND PRAISER, R. (1960) *J. Polym. Sci.*, **45**, 341.

40. PAUL, D.R. AND BARLOW, J.W. (1980) *J. Macromol. Sci. Rev., Macromol. Chem.*, **18**, 109.

41. AVGEROPOULOS, G.N., WEISSERT, F.C., BIDDISON, P.H. AND BOHM, G.G.A. (1976) *Rubb. Chem. Technol.*, **49**, 93.

42. HAMED, G.R. (1982) *Rubb. Chem. Technol.*, **55**, 151.

43. GEORGE,. J., JOSEPH, R., THOMAS, S. AND VARGHESE, K.T. (1995) *J. appl. Polym. Sci.*, **57**, 449.

44. VARGHESE, H., BHAGAWAN, S.S. AND THOMAS, S. (1999) *J. appl. Polym. Sci.*, **71**, 2335.

45. MATHEW, A.P., PACKIRISAMY, S. AND THOMAS, S. (2000) *J. appl. Polym. Sci.*, **78**, 2327.

46. ARAVIND, I., ALBERT, P., RANGANATHAIAH, C., KURIAN, J.V. AND THOMAS, S. (2004) *Polymer*, **45**, 4925.

47. VAN DALFSEN, J.W. (1943) *Rubb. Chem. Technol.*, **16**, 318.

48. VANGILS, G.E. (1977) *Rubb. Chem. Technol.*, **50**,141.

49. PORTER, M., RAWI, R. AND RAHIM, S.A. (1992) *J. nat. Rubb. Res.*, **7(2)**, 85–101.

50. HU, Y.M., CHOU, Y.F. AND CHEN, W.T. (1984) *Proc. Int. Rubb. Conf., Moscow*, A27.

51. GEHMAN, S.D. AND FIELD, J.E. (1939) *J. appl. Phys.*, **10**, 564.

52. BUNN, C.W. (1942) *Proc. R. Soc. London A*, **180**, 40.

53. TOKI, S., FUJIMAKI, T. AND OKUYAMA, M. (2000) *Polymer*, **41**, 5423.

54. TOKI, S., SICS, I., RAN, S., LIU, L., HSIAO, B.S., MURAKAMI, S., SENOO, K. AND KOHJIYA, S. (2002) *Macromolecules*, **35**, 6578.

55. MURAKAMI, S., SENOO, K., TOKI, S. AND KOHJIYA, S. (2002) *Polymer*, **43**, 2117.

56. TOKI, S. AND HSIAO, B.S. (2003) *Macromolecules*, **36**, 5915.

57. KARNIKA, D.S.K.G. AND LEWAN, M.V. (1998) Blends of NR: *Novel Techniques for Blending with Speciality Polymers* (*Tinker, A.J. and Jones, K.P. eds.*). Chap. 6, 68. London: Chapman and Hall.

58. NIELSEN, L.E. (1974) *Mechanical Properties of Polymers and Composites*, Vol. 2. New York: Marcel Dekker.

59. NIELSEN, L.E. (1974) *Rheol. Acta*, **13**, 86.

60. KUNORI, T. AND GEIL, P.H. (1980) *J. Macromol. Sci. phys.*, **B18(1)**, 93.