Mechanical Properties and Swelling Behavior of Cross-Linked Natural Rubber/Chitosan Blends

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Abstract: This article discusses properties such as surface hardness, solvent uptake, cross-link density, diffusion coefficient, and tensile properties of vulcanized natural rubber (NR)/chitosan (CS) blends. Dicumyl peroxide was selected as a cross-linking agent. In the case of tensile properties, peroxide vulcanized blends show higher tensile strength and hardness (Shore A) than the unvulcanized blend. The effect of thermal aging on mechanical properties of vulcanized NR/CS blends was also examined. The solvent-resistance properties of these vulcanized blends were investigated by the equilibrium swelling method using benzene as solvent. The impact of weight fraction of chitosan on the transport properties of vulcanized blend was also analyzed. The improved solvent resistance for peroxide vulcanized blends proved the formation of cross-links in the rubber phase. The blends showed reduced swelling rate due to the tortuosity of the path and the reduced transport area in blended samples.

Keywords: Blending; Chitosan; Cross-link density; Natural rubber; Polymer

INTRODUCTION

The aim of polymer blending is to develop products with unique properties that cannot be attained from individual constituents. The performance of a polymer blend is determined by various factors, including the nature of the individual components, type of vulcanizing

agent, processing parameters, and, to a certain extent, the application for which it is intended.[1–3] Natural rubber has excellent mechanical properties and heat resistance but poor solvent resistance.[4] Uncured rubber is sticky, can easily deform when warm, and is brittle when cold. In this state, it cannot be used to make articles with a good level of elasticity. Thus, chemical modification of natural rubber has been carried out to improve these properties.

Keeping all these factors in view we have prepared blends of chitosan and natural rubber latex. Chitosan is a biodegradable and semicrys-talline polysaccharide obtained from N-deacetylation of chitin, which is harvested from the exoskeleton of marine crustaceans.[5–8] It was found that the blend is immiscible, but shows good adhesion between natural rubber and chitosan phases.[9,10] Water absorption can also be minimized by vulcanizing the blends.[11] The water absorption of vulcanized samples in boiling water was also studied. The percentage of water absorption in the vulcanized sample is negligible. Therefore it can be used for the production of steam lines. But swelling study shows that the blends have poor solvent resistance.[11] Therefore solvent resistance of the blend is improved by dynamic vulcanization of the elastomeric phase using dicumyl peroxide (DCP). The polymer-polymer interactions in a blend can strongly influence its solvent sorption and transport characteristics.[12–14] The examination of solution and diffusion processes can be an extremely powerful tool for the characterization of blends of different polymers. The presence of DCP in the blends produces reactive radicals upon decomposition at elevated temperature via an exothermic reaction that is beneficial in a rubber compound. It is generally agreed that during the peroxide vulcanization, cross-links or chain scission may occur simultaneously.[15] This article examines the effect of dynamic vulcanization with DCP on the tensile strength, elongation at break, modulus, surface hardness, and solvent uptake in the blend.

EXPERIMENTAL SECTION

Materials

Purified chitin was purchased from HiMedia Laboratories Pvt. Ltd. (Mumbai, India). Its viscosity-average molecular weight was 400000 g/mol. The natural rubber latex was used directly as extracted from the tree (*Hevea brasiliensis*), cultivated around the forest belt of Western Ghats, Karnataka, India. The latex was stabilized by adding ammonium hydroxide solution. The dry rubber content was determined by drying the emulsion in an oven at 110°C for 12 h and is found to be 40%. Dicumyl peroxide (DCP) was also purchased from HiMedia Laboratories Pvt. Ltd. (Mumbai, India).

Preparation and Processing

Chitin was dispersed in 50% (w/w) NaOH solution and heated at 100°C for 2 h. Then the mixture was cooled to room temperature, filtered, and washed with water several times until the filtrate was neutral. The chitosan sample obtained was dried in an oven at 60°C for 48 h. The chitosan solution was prepared by dissolving chitosan in distilled water containing 2% (v/v) of acetic acid. The blends were prepared by mixing chitosan and natural rubber latex to get a homogeneous solution. Chitosan cross-linked rubber blend was prepared by adding dicumyl peroxide to the blend solution. Then the mixture was cast on a petri dish at 45°C. Specimens for testing were compression molded using an electrically heated hydraulic press at 140°C for 10 min. The film thickness was 2 to 2.5 mm.

Mechanical Tests

Tensile tests were carried out according to ASTM D 412 standard on a Shimadzu AGI universal testing machine. The specimen was tested at a constant rate of 500 mm/min at 25°C. Stress-strain curves were plotted for vulcanized and unvulcanized blends. These tests provided ultimate tensile strength (UTS), strain at break, and elastic modulus. Hardness (Shore A) was measured according to ASTM D 2240 method using a hardness tester (Shore A durometer). All the values reported in Table I were obtained by taking the average of four test results.

Aging Studies

The aging of samples was carried out by keeping the samples in a hot air oven for 10 days at 55°C. After that the mechanical properties of the samples were studied using a universal testing machine (UTM).

Swelling Studies

Circular specimens of 20 mm diameter were used for swelling studies. Specimens of known weight were immersed in benzene as the solvent in diffusion test bottles and kept at room temperature. Samples were removed from the bottles at regular intervals, the wet surfaces were quickly dried using tissue paper, and weight of the specimens after swelling was determined until no further increase in solvent

Table I. Tensile results and hardness values of vulcanized and unvulcanized NR/CS blends

Sample code	UTS (MPa)				EAB (%)				Modulus at 100% elongation (MPa)		Hardness (Shore A)	
	Unvulcanized		Vulcanized (3 p.p.h.r)		Unvulcanized		Vulcanized (3 p.p.h.r)					
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unvulcanized	Vulcanized (3 p.p.h.r)	Vulcanized (3 p.p.h.r)	Unvulcanized
0/100 CS/NR	0.46	1.61	2.28	0.58	597	1113	582	376	0.28	0.41	42	20
5/95 CS/NR	1.13	1.56	2.12	0.52	478	379	477	295	0.5	0.73	46	23
10/90 CS/NR	0.98	1.82	3.47	0.91	456	479	546	239	0.57	0.87	52	36
15/85 CS/NR	1.93	2.18	3.27	1.73	438	415	458	181	0.78	1.26	71	51
20/80 CS/NR	1.78	2.17	2.04	2.45	278	331	124	93	1.17	1.84	76	58
35/65 CS/NR	3.25	3.37	2.01	1.62	245	122	27	33	2.46	–	80	68
50/50 CS/NR	0.96	2.33	2.39	2.21	23	48	33	33	0.034	–	83	82

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uptake was detected. The solvent uptake ($Q_t(\%)$) of the samples was
calculated using the equation:

$$Q_t(\%) = \frac{m_t - m_0}{m_0} \times 100 \tag{1}$$

where m_0 and m_t are the weights of samples before and after time t of
immersion.

RESULTS AND DISCUSSION

Mechanical Properties

The effect of dynamic vulcanization on mechanical properties has been
studied in different blend systems, namely, 100/0, 95/5, 90/10, 85/15,
80/20, 65/35, and 50/50 natural rubber/chitosan (NR/CS) blends.
Figure 1 shows the stress-strain behavior of DCP vulcanized NR/CS
blends and pure $NR_{85}CS_{15}$ blend. Table I shows a comparison of
tensile strength between unvulcanized and vulcanized blends for various
NR/CS blend compositions. It is observed that the tensile strength
of unvulcanized blends is maximum for the blend $NR_{65}CS_{35}$. This is
because natural rubber interacts more effectively with chitosan phase
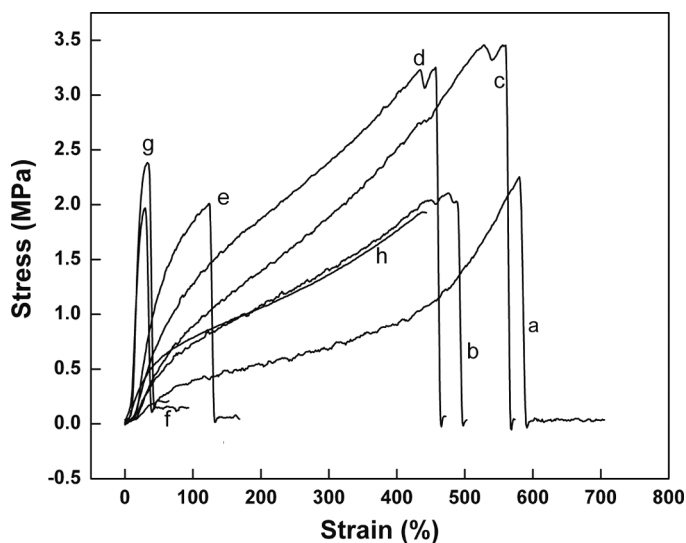
Figure 1. Stress-strain plots of vulcanized (with 3 p.p.h.r DCP) (a) natural
rubber, (b) $NR_{95}CS_5$, (c) $NR_{90}CS_{10}$, (d) $NR_{85}CS_{15}$, (e) $NR_{80}CS_{20}$, (f) $NR_{65}CS_{35}$,
and (g) $NR_{50}CS_{50}$ blends and (h) unvulcanized $NR_{85}CS_{15}$ blend.

in this blend than in other blend ratios. The effect of weight fraction of chitosan on the mechanical properties of natural rubber has already been published by us.[9] Results of thermally aged samples are also given in Table I along with the unaged vulcanized and unvulcanized blend samples. Improved tensile property for the unvulcanized blend by thermal aging may be due to thermal cross-linking within the elastomeric phase.[16]

On dynamic vulcanization with DCP, the tensile strength of blends increases due to formation of cross-links. According to Coran[17] and Dluzneski,[18] the formation of cross-links by DCP in unsaturated polymers such as rubber can be explained by the free radical addition reaction between the DCP and the unsaturated carbon present in NR. The effect of dynamic vulcanization on the tensile strength is shown in Figure 2. Tensile strength of blends vulcanized with DCP is higher than that of the unvulcanized blends except for the blend $NR_{65}CS_{35}$. The tensile strength for vulcanized blends shows a maximum at the blend ratio $NR_{90}CS_{10}$, and an increase of 254% is observed compared to the unvulcanized blend. Vulcanized $NR_{65}CS_{35}$ blend shows a 62% decrease in tensile strength compared to the unvulcanized blend, which may be due to the phase separation in the vulcanized natural rubber phase by the incorporation of CS phase. As percentage of CS increases, the interfacial adhesion between NR and CS increases and consequently
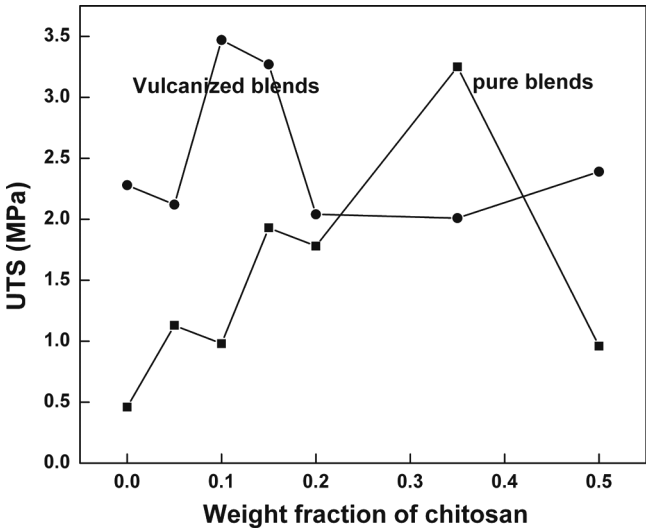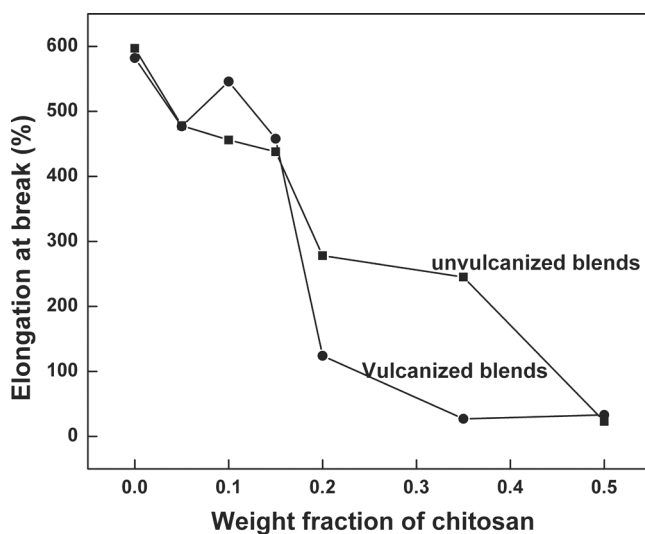

Figure 2. Effect of vulcanization on ultimate tensile strength with the weight fraction of chitosan.

strength increases. However, upon vulcanization NR cross-links with DCP and forms a separate phase, and the extent of interaction between NR and CS decreases. This may be the reason why a decrease in tensile strength is observed for $NR_{65}CS_{35}$.

For the pure vulcanized NR sample, the elongation at break decreased to a small amount because the cross-links restrict the free motion of molecules. The vulcanized $NR_{90}CS_{10}$ blend shows a 20% increase in elongation at break compared to the unvulcanized blend and is shown in Figure 3. Above 15% weight fraction of chitosan, the elongation at break continuously decreased. Lower value of elongation at break for the blends can be explained on the basis of poor adhesion between the two phases in the blend. The values of modulus at 100% elongation are given in Table I. It can be seen that as the weight fraction of chitosan increases, the modulus value also increases. In the case of vulcanized blends, the modulus at 100% elongation increased compared to the unvulcanized blends. This is clear evidence for the significant enhancement of plasticity in NR/CS blend by peroxide vulcanization.

Resistance of the rubber vulcanizate against thermal aging is considered an essential requirement for long service life products. Unvulcanized aged blends have better tensile strength than vulcanized aged blends. The degree of thermal cross-linking may be higher in unvulcanized blends than in vulcanized samples. The decrease in tensile strength as a result of aging at 55°C for 10 days is presented in Table I.

Figure 3.   Variation in elongation at break with the weight fraction of chitosan for vulcanized and unvulcanized blends.
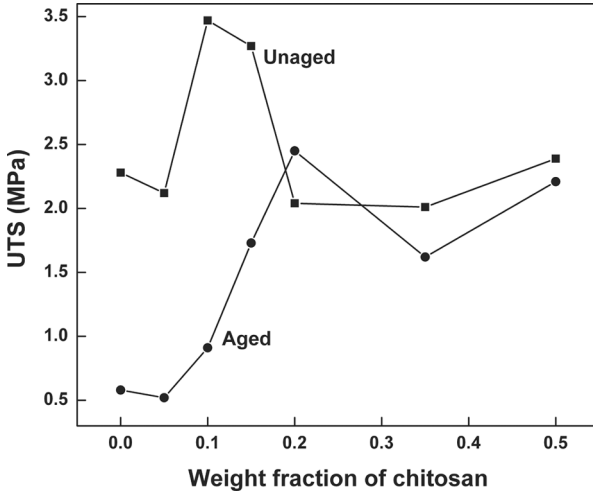
Figure 4. Effect of thermal aging on ultimate tensile strength with the weight fraction of chitosan.

The vulcanized $NR_{80}CS_{20}$ blend is the only one where the ultimate tensile strength increased by thermal aging, as shown in Figure 4. The elongation at break of the vulcanized blend samples decreased by thermal aging, as shown in Figure 5. The reduction of elongation at
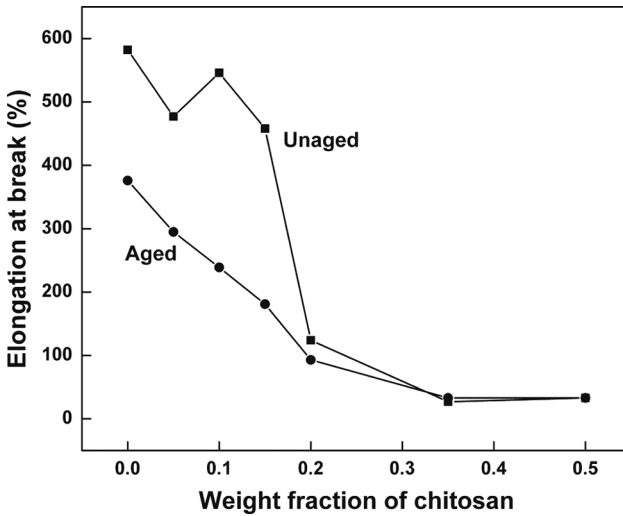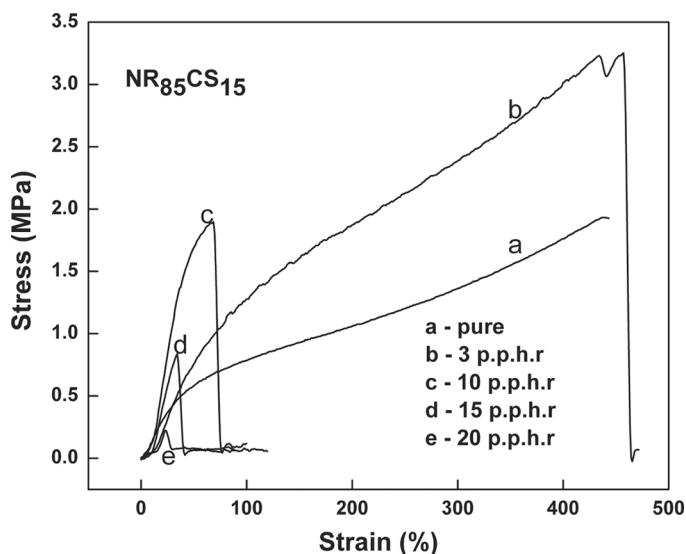

Figure 5. Effect of thermal aging on elongation at break with the weight fraction of chitosan.

Figure 6. Stress-strain plots showing the effect of different DCP concentrations on $NR_{85}CS_{15}$ blend.

break is caused by the chain scission reaction in natural rubber phase in the presence of DCP.[19]

The stress-strain plots of $NR_{85}CS_{15}$ blend system with different DCP concentrations are shown in Figure 6. Table II shows the tensile properties of $NR_{85}CS_{15}$ blend at different DCP concentrations (up to 20 p.p.h.r). With increasing concentrations of DCP, the tensile strength of blends increases first and reaches a maximum at 3 p.p.h.r DCP and then decreases. In binary systems, generally the major component forms

Table II. Tensile test results of vulcanized $NR_{85}CS_{15}$ blend with various amounts of DCP

| Amount of DCP added (p.p.h.r)	UTS (MPa)		EAB (%)		Modulus at 100% elongation	Hardness (Shore A)
	Unaged	Aged	Unaged	Aged		
0	1.93	2.18	438	415	0.78	51
3	3.27	1.73	458	181	1.26	71
10	1.94	1.7	68	31	–	71
15	0.88	1.15	35	32	0.07	70
20	0.27	1.6	24	54	–	70
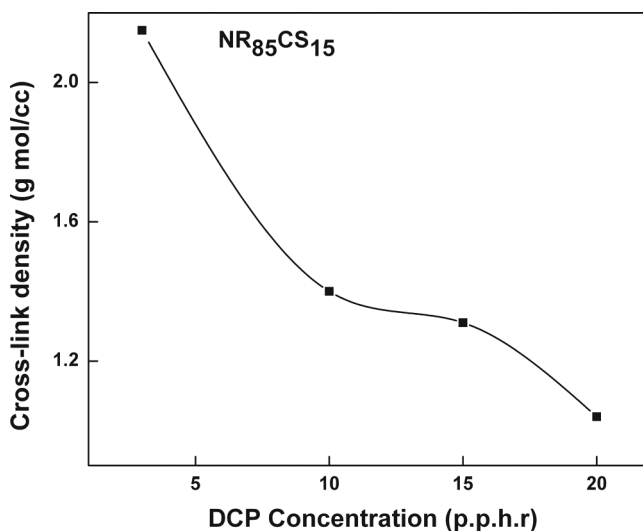
Figure 7. Effect of cross-link density on the $NR_{85}CS_{15}$ blend with different DCP concentrations.

the matrix phase, and the minor component forms a drop-like dispersed phase. However, in the case of dynamic vulcanization, a co-continuous phase may exist before the addition of a cross-linking agent. Immediately after the start of the selective cross-linking process, the viscosity of the rubber becomes very high, and with this, the stresses in the material increase very strongly, leading to the breakup of the co-continuous rubber phase into small dispersed particles. Also, with increase in DCP concentration, the cross-link density decreases (Figure 7). This may be the reason why tensile strength of blends shows a negative deviation at higher DCP concentrations. However, 20 p.p.h.r DCP added blend sample shows a 481% increase in ultimate tensile strength against thermal aging at 55°C for 10 days (Figure 8). Figure 9 shows the elongation at break for the various DCP concentrations (0–20 p.p.h.r) in $NR_{85}CS_{15}$ blend. The elongation at break decreases with the addition of DCP in the blend, and there is comparatively less elongation at break than for the unaged samples.

The variations of hardness as a function of blend ratio for the 3 p.p.h.r DCP vulcanized blends are given in Table I. A significant improvement in surface hardness values was noticed with increase in the volume fraction of chitosan, falling in the range 42–83 Shore A. Perhaps the particle size reduction and accompanying packing densification contributes to the enhanced hardness. The hardness values of the blend $NR_{85}CS_{15}$ for different DCP concentrations are given in Table II.
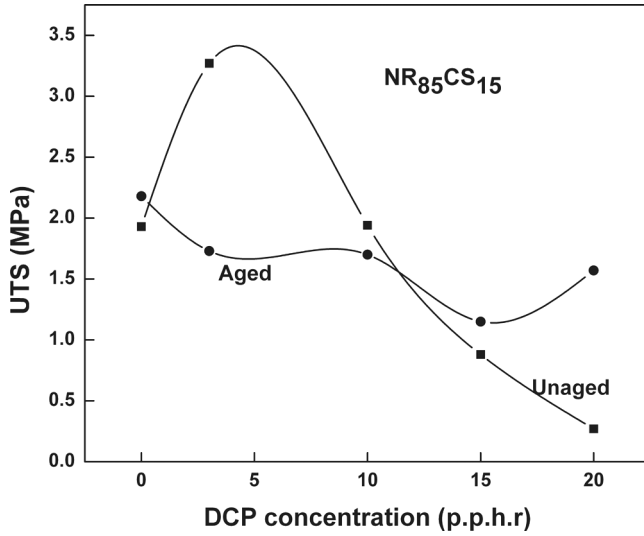
Figure 8. Effect of thermal aging on ultimate tensile strength with the concentration of DCP for $NR_{85}CS_{15}$ blend.
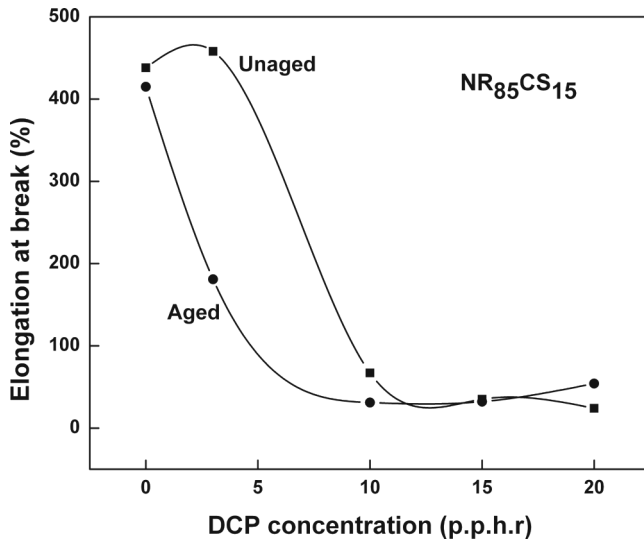

Figure 9. Effect of thermal aging on elongation at break with the concentration of DCP for $NR_{85}CS_{15}$ blend.

Swelling Behavior

The variation in solvent uptake with increase in weight fraction of chitosan in the 3 p.p.h.r DCP vulcanized blend was analyzed using benzene as the solvent. The curves were plotted as the functional uptake of penetrant against $t^{1/2}$. Figure 10 shows change in solvent uptake against time interval for the different blends. Chitosan-blended samples show a reduced solvent absorption compared to pristine polymer. The blends having higher chitosan content show the lowest solvent uptake (Figure 11). This may be due to the tortuosity of the path and the reduced transport area in the blend. This reduced area of the blend restricts the solvent intake, which enhances the solvent resistivity. The equilibrium mole percentage of benzene in the blend decreases with increase in the weight fraction of chitosan. The reduction of equilibrium uptake upon the addition of chitosan in NR is due to the enhanced NR/CS interaction, which prevents the transport of solvent molecules. The swelling experiments were difficult to conduct for unvulcanized blends because the sample could dissolve in benzene.

The diffusion coefficient of benzene in the vulcanized blend has been computed by using Equation (2). Diffusion is a kinetic phenomenon related to penetrant size and polymer segment mobility. The diffusion
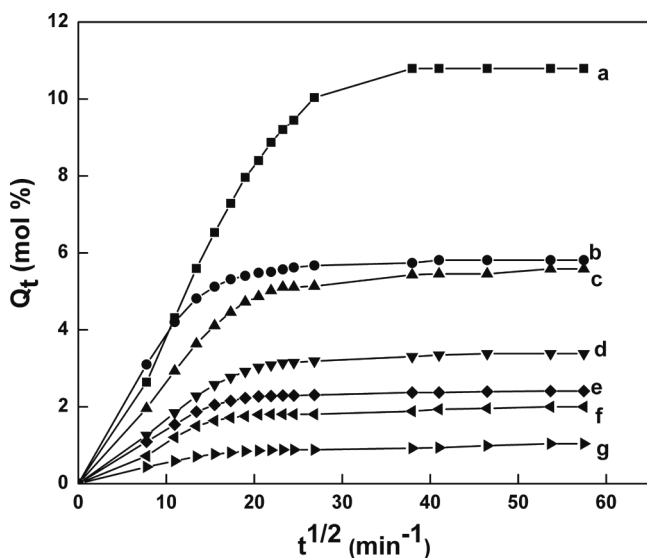
Figure 10. Variation of mol % uptake of solvent with $t^{1/2}$ for 3 p.p.h.r vulcanized (a) natural rubber, (b) $NR_{95}CS_5$, (c) $NR_{90}CS_{10}$, (d) $NR_{85}CS_{15}$, (e) $NR_{80}CS_{20}$, (f) $NR_{65}CS_{35}$, and (g) $NR_{50}CS_{50}$ blends.
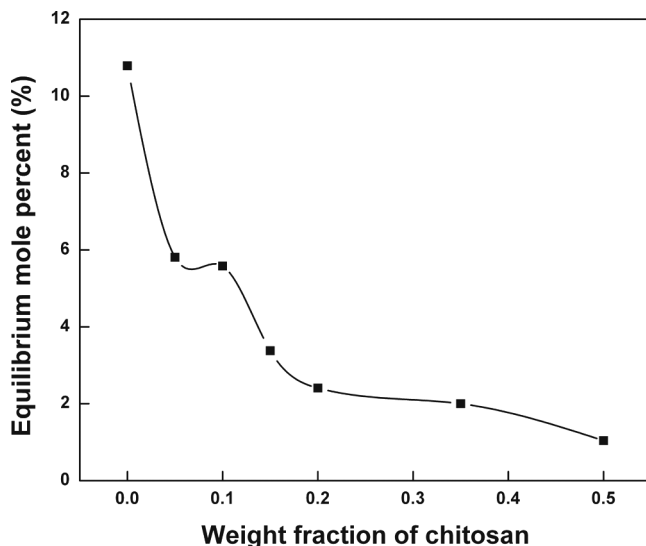
Figure 11. Variation of equilibrium mole percentage on the weight fraction of chitosan for 3 p.p.h.r DCP vulcanized blends.

coefficient of a vulcanized natural rubber/chitosan blend sample immersed in an infinite amount of solvent can be calculated by[20]:

$$\frac{Q_t}{Q_\infty} = 1 - \left(\frac{8}{\pi^2}\right) \sum_{n=0}^{n=\infty} \left[\frac{1}{(2n+1)^2} \exp\left[-D(2n+1)^2 \pi^2 \frac{t}{h^2} \right] \right] \qquad (2)$$

where t is the time, h is the initial thickness of the sample, D is the diffusion coefficient, n is an integer, Q_t is the solvent uptake of the sample at a time t, and Q_∞ is the equilibrium mole percentage uptake. From this equation, it is understood that a plot of Q_t versus $t^{1/2}$ is linear for a short time and D can be calculated from the initial slope. The equation for short time is

$$\frac{Q_t}{Q_\infty} = \frac{4}{h}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2} \qquad (3)$$

By rearranging this equation, the diffusion coefficient can be calculated using

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2 \qquad (4)$$

where θ is the slope of the initial portion of plot of Q_t versus $t^{1/2}$ and Q_∞ is the equilibrium mole percentage uptake. Figure 12 shows the variation in diffusion coefficient of benzene as a function of chitosan weight
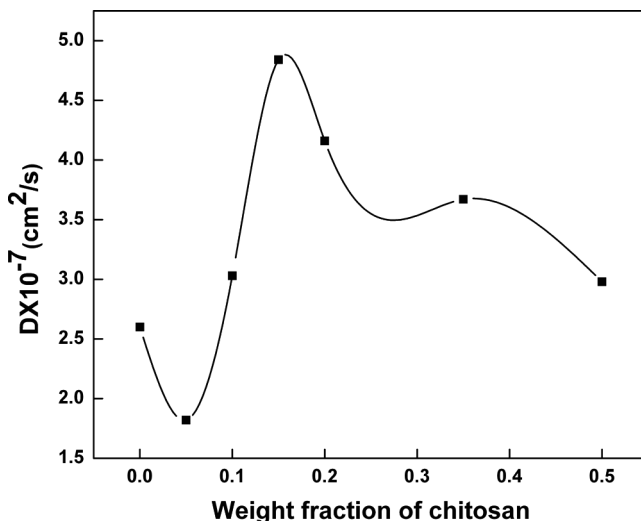
Figure 12. Effect of diffusion coefficient on the weight fraction of chitosan for 3 p.p.h.r DCP vulcanized blends.

fraction. Addition of chitosan to natural rubber latex first decreases benzene diffusivity, followed by an increase up to 0.15 weight fraction of chitosan. Above 0.15 weight fraction, the diffusivity of benzene in the DCP vulcanized blend decreases. The $NR_{85}CS_{15}$ blend system exhibits a higher diffusion coefficient due to the weak interaction between the two components, whereas the blend $NR_{95}CS_5$ shows a lower diffusion coefficient due to the strong interaction between the two components.

Transport Mechanism

Transport properties of polymers can be monitored by using the empirical equation[21]:

$$\log\left(\frac{Q_t}{Q_\infty}\right) = \log k + n \log t \qquad (5)$$

The slope of the plot $\log\left(\frac{Q_t}{Q_\infty}\right)$ versus $\log t$ gives the value of n, indicating the mechanism of transport, and y-intercept is the value of k, which depends upon the structural significance of polymer as well as its interaction with the solvent. According to the n values obtained from the above equation, three basic modes of transport are distinguished. If $n = 1/2$ the diffusion mechanism is Fickian,[22] and the rate of diffusion of permanent molecules is much less than the polymer segment

Table III. Values of n and k of 3 p.p.h.r vulcanized NR and its blends with chitosan for the transport of benzene

Sample	Benzene	
	n	k
$NR_{100}CS_0$	0.31	-0.98
$NR_{95}CS_5$	0.12	-0.36
$NR_{90}CS_{10}$	0.58	0.008
$NR_{85}CS_{15}$	0.61	0.005
$NR_{80}CS_{20}$	0.78	8.9×10^{-5}
$NR_{65}CS_{35}$	0.64	0.005
$NR_{50}CS_{50}$	0.72	0.028

mobility. If $n = 1$, the mechanism is non-Fickian;[22] and this may be considered in systems in which permanent diffusion rates are much faster than polymer relaxation process. If $1/2 < n < 1$, the diffusion mechanism is anomalous,[22] which occurs when the permanent mobility and polymer segment relaxation rates are similar. The value of $n < 1/2$ is due to irregular-shaped particles, and it decreases systematically with increasing cross-linking.[23]

The n and k values of NR and its vulcanized blends (3 p.p.h.r DCP) in benzene are given in Table III. The values of n lie above 0.5, which suggests that the mechanism of diffusion is non-Fickian, anomalous behavior. Increasing the cross-link density of the samples caused a substantial decrease in the n value. The k values of all the blended samples are higher than that of vulcanized rubber, showing higher interaction of the system with the solvent.

Cross-Link Density Measurements

The cross-link density of a rubber vulcanizate can be estimated from swelling measurement, using the Flory-Rehner equation.[24] The samples were allowed to swell in benzene, and the equilibrium uptake was noted. The molecular weight of polymer between cross-links M_c is calculated using the following equation:

$$\frac{1}{2M_c} = \left[\frac{-\rho_r V_s (V_r)^{1/3}}{\ln(1 - V_r) + V_r + \chi^2 V_r^2} \right] \quad (6)$$

where M_c = molecular weight of polymer between two cross-links, ρ_r = density of polymer, V_s = molar volume of solvent, and V_r = volume

fraction of polymer in swollen mass, calculated by the method of Ellis and Welding[25]:

$$V_r = \frac{(d - f_w)\rho_r^{-1}}{(d - f_w)\rho_r^{-1} + A_s\rho_s^{-1}} \quad (7)$$

where A_s is the amount of solvent absorbed, ρ_r and ρ_s are the densities of rubber and solvent respectively, d is the de-swollen weight of the sample, and f_w is the weight of the insoluble components in the sample. The interaction parameter χ is given by the Hildebrand equation[26]:

$$\chi = \beta + \frac{V_s}{RT}(\delta_s - \delta_p)^2 \quad (8)$$

where β is the lattice constant, V_s is the molar volume, R is the universal gas constant, T is the absolute temperature, δ_s is the solubility parameter of the solvent, and δ_p is the solubility parameter of the polymer.

The cross-link density v was calculated from molecular weight between cross-links M_c using the following equation[27]:

$$v = \frac{1}{2M_c} \quad (9)$$

Figure 13 is the plot of cross-link density values for different NR/CS blend ratios. It can be seen that the cross-link density is maximum in
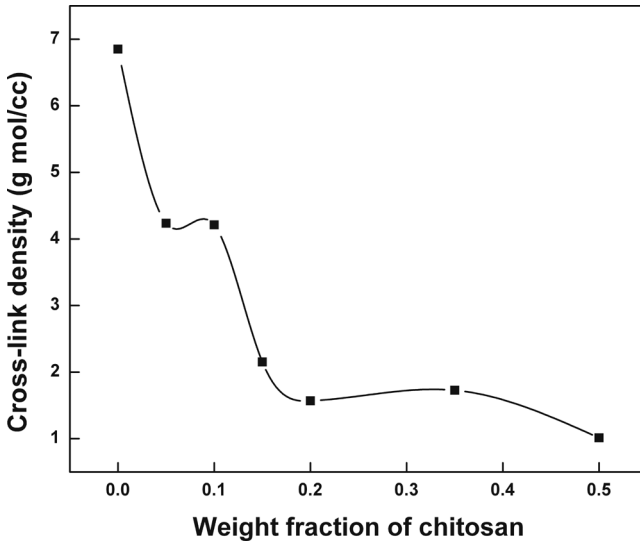
Figure 13. Effect of cross-link density on the weight fraction of chitosan for 3 p.p.h.r DCP vulcanized blends.
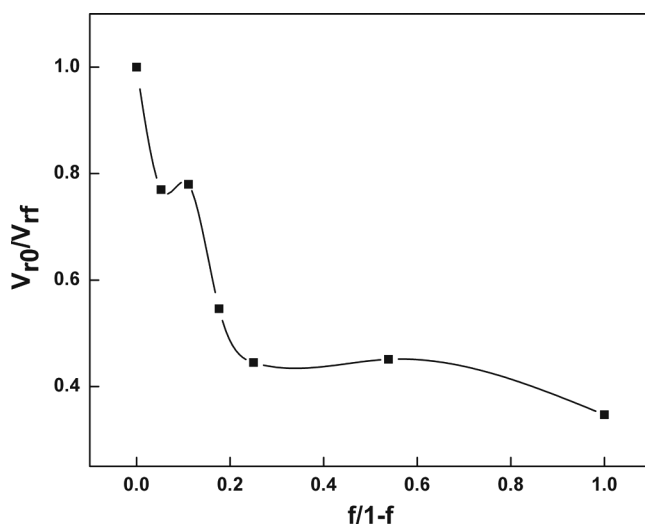
Figure 14. Kraus plot of vulcanized NR/CS system for different blend ratios.

pure natural rubber with 3 p.p.h.r DCP. As the percentage of chitosan increases, the cross-link density value decreases. The decrease in cross-link density with the addition of chitosan is due to the decrease in the amount of rubber and the presence of un-cross-linked phase of chitosan in the blend.

If Equation (6) is applied to rubber-containing reinforcing fillers, the V_{rf} of the rubber phase in the swollen gel is always much higher than that of the pure rubber's V_{r0}. So the ratio $\frac{V_{r0}}{V_{rf}}$ decreases with increase of filler loading. This ratio represents the degree of restriction of the swelling of the rubber matrix due to the presence of filler. It is found that the ratio $\frac{V_{r0}}{V_{rf}}$ of DCP vulcanized samples decreased upon the addition of chitosan to the natural rubber, as shown in Figure 14.

CONCLUSIONS

The mechanical properties of cross-linked NR/CS blends were studied using a UTM. NR/CS blends vulcanized with DCP exhibit higher tensile strength and hardness but lower elongation at break compared to un-cross-linked blends. A maximum increase of tensile strength was observed for the vulcanized $NR_{90}CS_{10}$ blend. The effect of thermal aging on mechanical properties was studied. Upon thermal aging, the vulcanized $NR_{80}CS_{20}$ blend shows an increase in tensile strength, and a decrease is seen for other vulcanized blends. Diffusion and transport

through cross-linked NR/CS blends were studied using benzene as the penetrant at room temperature. Vulcanized blends have shown better resistance to solvent transport. The blends having higher chitosan content show least solvent uptake. Among the calculated values of the diffusion coefficient, the minimum is seen for the vulcanized $NR_{95}CS_5$ blend. The cross-link density value is found to decrease with the addition of chitosan in the vulcanized blends. Thus, vulcanized NR (3 p.p.h.r DCP) blends with chitosan (<20%) were found to be better in terms of tensile and transport properties.

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