

Studies on Double Networks in Natural Rubber Vulcanizates

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ABSTRACT: The concept of double networks is a rather new idea, by which one imparts chain orientation in elastomers. Double networks were made in natural rubber vulcanizates cured with a single and a new binary accelerator system. Double networks with different extensions were prepared and their effects on tensile properties were analyzed. The influence of extent of initial cure on double-network formation was examined. Thermal stability of the double network formed was analyzed by ageing of the double networks and was found to improve with residual extension. Crosslink density of the networks formed was determined by swelling methods and stress–strain analysis.

It was found that crosslink density increased with double-network formation and residual extension. The stress–strain behavior and moduli were analyzed to study the effect of these properties on double-network formation. Double networks were hardly affected by the binary accelerator system. Based on the studies it was found that residual extension was the major factor determining the final properties. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1068–1076, 2004

Key words: rubber; networks; binary accelerator; mechanical properties; crosslinking

INTRODUCTION

The modulus and strength of materials containing flexible chain polymers can be increased by orientation and crystallization of polymer chains. In plastics and fibers, molecular chain orientation is maintained after processing as the chains are frozen by glassy state or crystallization. On the other hand, in rubbers, orientation produced during simple processing will decay after processing. When the rubber is cured away from elastic equilibrium, configurations prevailing during crosslinking will shift the subsequent equilibrium state away from zero strain.^{1,2} However, when a crosslinking reaction occurs in a deformed state, an anisotropic crosslink network can be produced.³ The network formed when a rubber is crosslinked will have an equilibrium set of chain configurations. These configurations are usually associated with a macroscopic state of zero strain because this corresponds to a condition of zero stress.⁴

Double-network rubber refers to an elastomer that has been crosslinked twice, the second time while in a deformed state. The deformation employed is simple tension, resulting in a rubber whose final length exceeds the length after the initial, isotropic crosslinking.

The ratio of these two lengths, referred to as residual strain, does not uniquely define a double-network elastomer. A given residual strain can be achieved with different combinations of strain and crosslinking proportions, between the two networks.⁵

Double-network rubbers offer a route to obtaining superior mechanical properties, in that they may allow circumvention of the usual compromise between stiffness and strength. Roland and coworkers^{4,5} showed that gum natural rubber double network crystallizes at lower strain and can have enhanced tensile strength and fatigue life compared to that of conventional single networks. Rubber vulcanizates with permanent chain orientation can be produced by preparing double networks or composite networks. They can be viewed as interpenetrating networks in which the same chain segments belong to both networks and, more important, the component networks are oriented. It is this orientation that gives rise to enhancement and anisotropy in properties.^{6,7} The expectation, confirmed by experiment, is that the modulus of a double-network rubber will differ from the modulus of the corresponding isotropic elastomer. The equilibrium modulus is high at higher residual strains. Mechanical and optical behaviors of double-network rubbers have been studied by Mott et al.⁸ The properties of an elastomeric network depend not only on the density of junctions but also on the distribution and orientation of the chains when the junctions are formed. Double networks can also arise spontane-

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TABLE I
Formulation of the Mixes

Ingredient	C0	C1
NR (g)	100	100
ZnO (phr)	5	5
Stearic acid (phr)	2	2
Sulfur (phr)	0.5	0.5
DTB (phr)	0	0.5
MBS (phr)	1.5	1.5

ously by chain scission⁹ by strain-induced crystallization¹⁰ or in the presence of reinforcing fillers.^{11,12}

Because double-network formation results in increased modulus and crosslinking in rubber, studies with different accelerator systems are of interest. In the present work attempts were made to characterize double networks of natural rubber vulcanizates cured with a new binary accelerator system. The effect of the newly developed binary accelerator system based on 1-phenyl-2,4-dithiobiuret (DTB) and 2,4-morpholino thiobenzothiazole (MBS) was studied. Samples were subjected to different extensions. Physical properties such as stress-strain behavior and modulus, for example, were investigated. The influence of thermal ageing on the strength and modulus was also studied. Swelling studies were also conducted to investigate the crosslink density of the samples.

EXPERIMENTAL

Materials

Natural rubber (ISNR-5), obtained from the Rubber Research Institute (Kottayam, Kerala, India), was mixed with ingredients in a two-roll mill with a friction ratio 1 : 1.4 according to ASTM specifications. The formulation of the mixes is given in Table I. The accelerator MBS was obtained from Bayer AG (Leverkusen, Germany). All other ingredients, except DTB, were obtained from Ranbaxy (Bombay, India). DTB was synthesized according to our previously reported work.¹³ Optimum cure time of the mixes was obtained using an oscillating disc rheometer R-100 (Monsanto, USA).

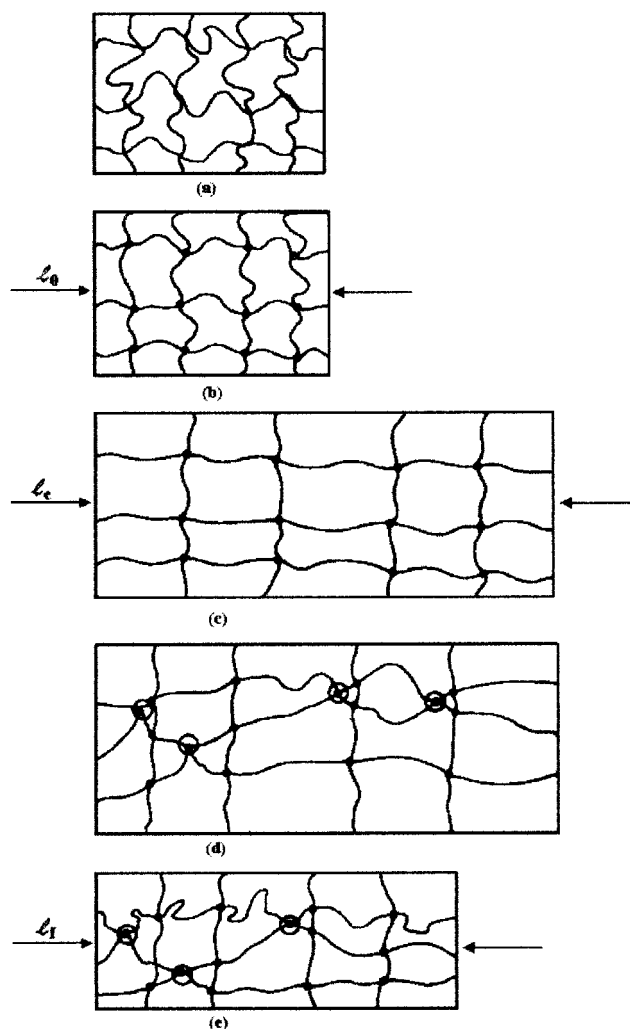
Double-network formation

The schematic representation of the double-network formation is given in **Scheme 1**. The cure characteristics of the mixes were found using a Monsanto R-100 rheometer (Monsanto, St. Louis, MO). Curing of the compounds was done in two steps. In the first step the rubber compound was cured for T_{50} (50% of the optimum cure time) at 120°C in a hydraulic press at a pressure of 150 kg/cm². In the second step, partially crosslinked rubber (T_{50}) was extended uniaxially to

various desired lengths using a metal holder. The experiment was also conducted by preparing initially cured sheets at T_{70} (70% of the optimum cure time). The experimental setup is shown in Figure 1. The extended rubber, placed in between the metallic holder, was kept in an air oven at 100°C to complete the cure. Lower temperature was used for completing the cure, to minimize the degradation during curing under tension. Polysulfidic crosslinks should be avoided in the initial cure to prevent network rearrangement during the second curing. Keeping this in mind, we selected only the efficiently vulcanized mixes for the present study.

Mechanical properties

The tensile properties of various double-networked rubber vulcanizates were determined using a universal tensile tester (TNE series 500) at a constant cross-



Scheme 1 (a) Uncrosslinked network; (b) initial crosslinked network; (c) extended network; (d) secondary crosslinks; (e) relaxed state after double-network formation.

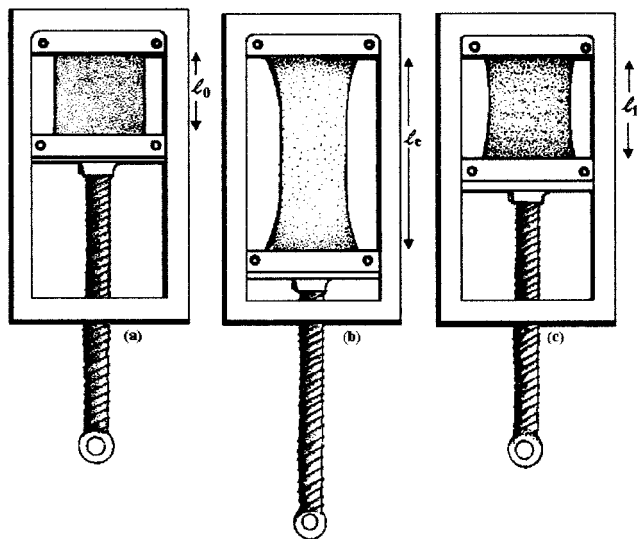


Figure 1 Experimental setup for preparing double networks: (a) rubber specimen kept within holders; (b) extended rubber, placed in between the metallic holder; (c) extended sample released after double-network formation (l_0 , initial unstretched length; l_e , stretched length; l_f , final length).

head speed of 500 mm/min at room temperature. The ageing of the samples were done in an ageing oven at 70°C for 24 h according to ASTM D572-99 and the tensile properties were examined after ageing.

Swelling studies

A circular test piece weighing about 0.2g was cut from the double-networked rubber. The sample was immersed in pure toluene at room temperature to allow the swelling to reach diffusion equilibrium.¹⁴ At the end of this period the test piece was taken out and the adhered liquid was rapidly removed by blotting with filter paper and the swollen weight was immediately measured. The samples were dried in vacuum to constant weight and the desorbed weight was taken. The swelling ratio is defined as

$$R = (W_1 - W_0) / W_0 \quad (1)$$

where W_0 is the weight of the test piece before swelling and W_1 is the weight of the swollen test piece after time t of immersion. The swelling ratio is a direct measurement of the degree of crosslinking; the smaller the ratio, the higher the degree of crosslinking. The concentration of the crosslinks was determined using the equilibrium swelling data.¹⁵ The volume fraction of rubber (V_r) in the swollen network was then calculated by the method reported by Ellis and Welding¹⁶ using the following equation:

$$V_r = \frac{D\rho_p^{-1}}{D\rho_p^{-1} + A_0\rho_s^{-1}} \quad (2)$$

where D is the deswollen weight of the test specimen, A_0 is the weight of the solvent absorbed, ρ_p and ρ_s are the density of the polymer and solvent, respectively. The crosslink density was determined using the Flory–Rehner equation.¹⁷:

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

where V_s is the molar volume of the solvent and χ is the interaction parameter, which is given by the equation proposed by Hildebrand¹⁸:

$$\chi = \beta + (V_s/RT)(\delta_s - \delta_p)^2 \quad (4)$$

where β is the lattice constant, which was taken as 0.38; R is the universal gas constant; T is the absolute temperature; and δ_s and δ_p are the solubility parameters of the solvent and polymer, respectively. The χ value was found to be 0.42 for the NR–toluene system.

Stress–strain measurements

The load–displacement curves were used to calculate the physically effective crosslink density. The physically effective crosslink density, which is obtained by stress–strain analysis, contains a contribution attributed to the chain entanglements and loose chain ends acting as crosslinks in rubber. The physically effective crosslink density was measured using the Mooney–Rivlin equation,²⁰ expressed as follows:

$$\nu = \frac{F}{2A_0\rho RT(\alpha - \alpha^{-2})} \quad (5)$$

where ν is the physically effective crosslink density, F is the force, A_0 is the area of cross section, R is the universal gas constant, T is the absolute temperature, and α is the extension ratio of the sample. In this method the crosslink density is related to the extension ratio of the samples subjected to tension.

RESULTS AND DISCUSSION

Formulations of the mixes are given in Table I. Samples were initially cured for two different times. In the first case the sample was cured for T_{50} (50% of the optimum cure) and T_{70} (70% of the optimum cure). The T_{50} and T_{70} cured samples were treated separately. The stretching ratio and the residual extension ratio of various doubly networked rubbers along with their mechanical properties for the T_{50} are given in Table II and, for the T_{70} samples, are given in Table III.

TABLE II
Stretching Ratio (α_e), Residual Extension Ratio (α_r), and Mechanical Properties of Rubber Vulcanizates (T_{50})

Sample	T_{50} cured				
	α_e	α_r	Tensile strength (MPa)	Modulus at 300% elongation (MPa)	Elongation at break (%)
C0	1	1	17.6	3.1	1104
	2.18	1.22	15.69	4.6	809
	3	1.3	20.4	4.8	876
	4	1.63	21.6	5.18	818
	6	2.66	24	5.34	772
C1	1	1	18.5	3.5	1203
	1.54	1.31	16.5	3.61	1264
	2	1.36	19.74	4.2	921
	2.18	1.5	21	4.5	1244
	3	1.64	22.5	4.1	957
	4	1.83	24.0	5.9	863

The amount of stretching is expressed as α_e , which is defined as the ratio of uniaxially stretched length (l_e) to that of the first cured unstretched length (l_0). Similarly, the residual strain α_r is defined as the ratio of the final length (l_f) of the double-networked rubber at the state of ease to that of the first cured unstretched sheet (l_0).

$$\alpha_e = l_e/l_0 \quad (6)$$

$$\alpha_r = l_f/l_0 \quad (7)$$

As the residual extension ratio is increased, tensile strength is initially decreased and then increased. The decrease in tensile strength for lower residual extension may be attributed to the destruction of the primary formed networks upon strain. After a certain residual extension, resulting from the preserved orientation, strength begins to increase. This is more clearly seen in the case of the T_{70} -cured sample; however, at the same time modulus is increased. This is very much expected, given that double networks maintain the orientation of hydrocarbon chains. In the case of the DTB-cured system, however, no significant decrease in tensile strength was shown with an in-

crease in residual extension ratio α_r . Also there is an appreciable increase in modulus with increase in α_r . The modulus values of DTB-cured samples are higher than those of other cases and this is highly advantageous. This may be a consequence of the improvement in crosslink density of DTB-cured samples.

Stress-strain graphs for T_{50} -cured double networks, cured with MBS alone and with DTB/MBS, are given in Figure 2. It is clear from the graph that modulus of the networks increased with residual extension. It is also clear from the figure that DTB-cured samples show higher modulus, which might be attributable to the increased crosslink density. The graph shown here is a representative one and similar behavior is shown by vulcanizates cured with other binary systems. It was previously observed by researchers¹ that the modulus of a double-network rubber exceeds that of a conventional elastomer having the same total crosslink density. This is an important result because the strength, and other failure properties of conventional elastomers, exhibit maximum values as a function of crosslink density. It is clear from Table III that, for the T_{70} -cured samples, increases in tensile strength are observed with residual extension after an initial

TABLE III
Stretching Ratio (α_e), Residual Extension Ratio (α_r), and Mechanical Properties of Rubber Vulcanizates (T_{70})

Sample	T_{70} cured				
	α_e	α_r	Tensile strength (MPa)	Modulus at 300% elongation (MPa)	Elongation at break (%)
C0	1	1	14.68	3.07	1012
	1.5	1.04	11.67	3.3	846
	2.18	1.16	13.65	3.21	1006
	3.0	1.23	18.25	3.56	843
C1	1.47	1.06	15.27	3.2	997
	2.18	1.2	16.7	3.4	1295
	2.82	1.31	21.2	3.78	1008
	4.0	1.65	23	3.92	942

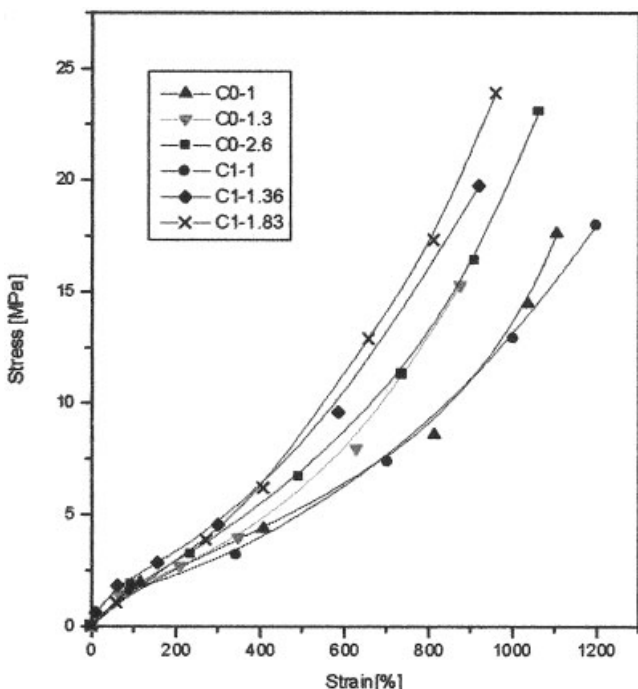


Figure 2 Stress-strain plot of double networks with varying residual extension.

decrease in both samples, with and without DTB. This could be explained as being attributed to the breaking of original networks and by minimization in the changes of the first crosslinked network during the second crosslinking. Such behavior may be attributed to two factors. (1) Because of the orientation of the network structure in the direction of stretching and a higher probability of strain-induced crystallization during tensile measurements, and (2) the decreasing effect of the modulus resulting from disentanglement of some weak mechanical interlocks during the second crosslinking step. At relatively low residual extensions, the decreasing process predominates. However, this effect is cancelled by the increasing effect, above a certain level of residual extension.

Between the T_{70} - and T_{50} -cured samples it is seen that the basic criterion for better modulus is the residual extension. A minor contribution is provided by the amount of stretching. It is noted that, for the same residual extension, the modulus values are comparable. It might be noted that, in all cases, DTB-cured vulcanizates show increased modulus and strength. This is most probably attributable to the increased crosslink density. The enhanced crosslink density shown by DTB is clear from our previous studies.^{19,20}

Swelling studies

The extent of swelling of the single- and double-network samples was investigated. It may be clearly seen

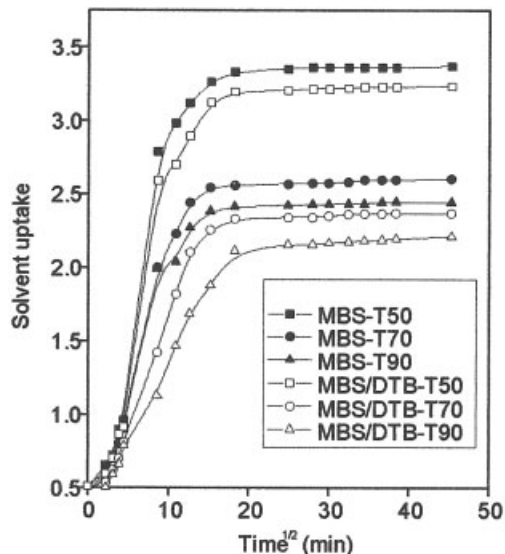


Figure 3 Extent of solvent (toluene) uptake in samples with varying of extent of cure.

from Figure 3 that solvent uptake depends on the extent of crosslinking. It may also be seen that DTB-cured vulcanizates show less uptake than that cured with MBS alone. It is also to be noted that the difference in uptake between samples C0 and C1 is lower in T_{50} -cured samples. Swelling of the samples shows maximum uptake for T_{50} -cured samples, attributed to fewer crosslinks in the T_{50} -cured samples. It is also important to note that samples cured with the new binary system DTB/MBS show better resistance to solvent uptake, because of having higher crosslink density, which is clear from our previous studies.²⁰

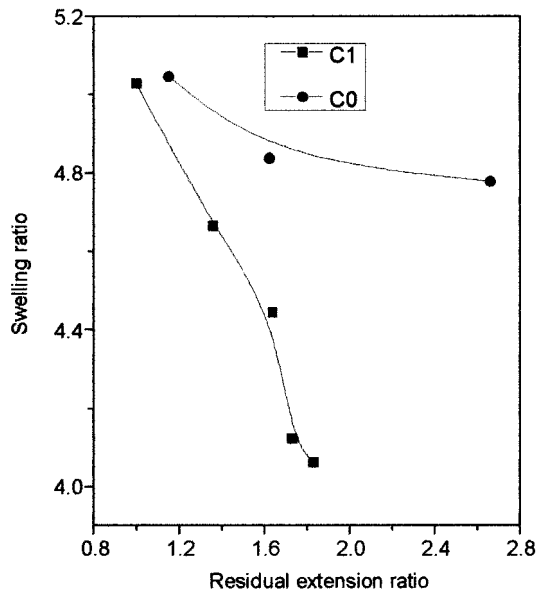


Figure 4 Variation of swelling ratio with residual extension ratio.

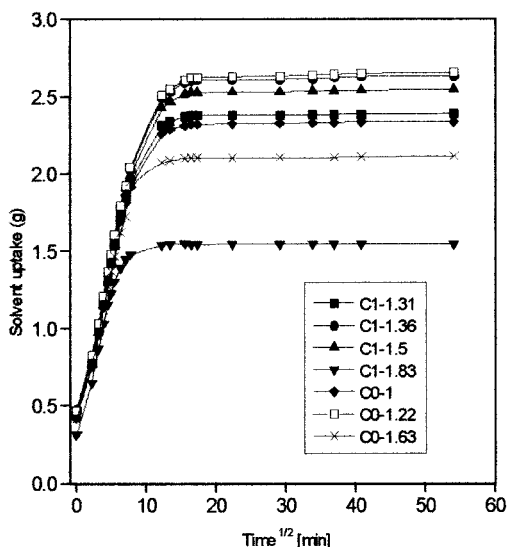


Figure 5 Extent of solvent (toluene) uptake with residual extension ratio of rubber cured with and without DTB.

Figure 4 depicts the effect of swelling ratio on residual extension ratio of DTB/MBS (T_{50})-cured and MBS-cured samples. It is clear from the figure that swelling ratio decreases with residual extension ratio of the samples. Swelling ratio is an indirect measure of the crosslink density.

Detailed swelling measurements were carried out to determine the nature of uptake through samples with different residual extension ratios. As may be seen from Figures 5 and 6, the residual extension ratio resists the uptake of solvent through the rubber. Higher residual extension means that increasingly more crosslinks are present between the hydrocarbon chains, which resist the solvent uptake. From Figure 5, it may be noted that the DTB/MBS-cured system shows better solvent resistance, compared to that cured with MBS alone, which is attributed to the increased residual extension resulting from the increased crosslink density. The initial uptake of solvent through rubber with varying residual extension ratios is shown in Figure 6. It may be seen that the lowest initial uptake is by the sample with the highest residual extension. The ability of double-network formation thus helps to resist the solvent uptake, which results from the orientation of the rubber chains.

Crosslink density

Crosslink density analysis was done by swelling and the values are given in Table IV. It may be seen that crosslink density increases upon residual extension ratio (λ_r). We are interested in the trend shown on the apparent crosslink density with residual extension. It may be seen that, as the residual extension (λ_r) is increased, the apparent crosslink density is found to

increase. This may be explained as follows. As the residual extension increases the hydrocarbon chains are maintained in a more elongated fashion compared to those with lower residual extension ratio. Higher residual extension is achieved by means of the additional crosslinks formed because of the closer alignment of the chains. The chains are said to be aligned in a less-relaxed way, which resists the uptake of solvent. It may be noted that, as the samples were cured in an air oven, the calculated crosslink density is only apparent. With respect to comparison of crosslink density, curing in an extended manner is much more effective in the sense that the closer the hydrocarbon chains are the easier is crosslink formation. Samples cured with DTB show increased crosslink density, as shown in the case of a single-network vulcanizate. No adverse results are shown by double-networked DTB-cured vulcanizate. Swelling ratio measurements also confirmed that crosslink density increases with λ_r .

Physically effective crosslink density was measured from the stress-strain analysis and is also given in Table IV. Because the extension ratio of a sample depends on the chemical crosslinks and physical entanglements, a higher value for crosslink density is obtained by this method. At the same time the trend in crosslink density shown is similar to that of the swelling method. This confirms the increase in apparent crosslinking with residual extension. It may be seen that, for double networks, the crosslink density calculated is higher and increases with residual extension.

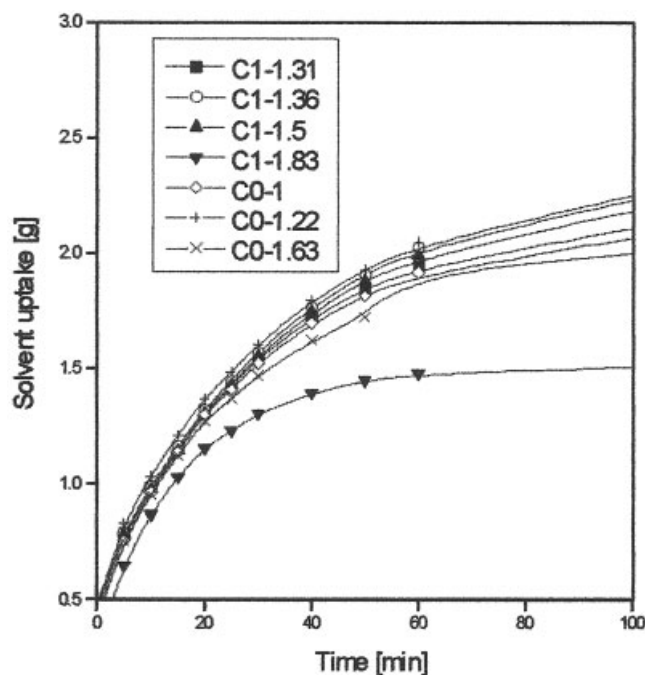


Figure 6 Variation in initial solvent uptake in double networks.

TABLE IV
Network Analysis of Double Networks

Sample	Residual extension ratio	Crosslink density from swelling, ($\nu \times 10^6$) (mol/g)	Crosslink density from stress-strain analysis, ($\nu \times 10^6$) (mol/g)	Swelling ratio
C0 (T_{50})	1	5.92	112.9	7.16
	1.22	6.18	125.4	6.01
	1.3	6.52	179.6	5.82
	1.66	6.75	172.8	5.26
	2.63	8.5	181.2	4.31
C1 (T_{50})	1	6.59	124.3	5.02
	1.31	7.83	108.8	4.65
	1.36	8.01	158.9	4.67
	1.5	8.45	131.2	4.71
	1.64	9.53	175.8	4.44
	1.72	12.48	186.7	3.21

Ageing studies

The influence of thermal ageing on doubly networked samples was studied in an air oven at 70°C for 24 h. Figure 7 corresponds to the samples cured with MBS accelerator and Figure 8 corresponds to samples cured with the MBS/DTB system. It is clear from Figures 7 and 8 that tensile strength of the double-network samples was found to increase with ageing. This may be attributable to the further crosslinking of the T_{90} -cured samples. With lower residual extension, an initial decrease in tensile strength was observed. The ageing behavior is similar in both systems, which proves no alteration has occurred for the ageing mechanism of the double networks with the new accelerator. For this study we selected an efficient vulcanization system for which the majority of crosslinks were monosulfidic

and disulfidic: mono- and disulfidic linkages are thermally stable compared to polysulfidic linkages. The secondary networks are formed on extended hydrocarbon chains. The extension of the chains causes the chains to come closer. This in turn favors the formation of mono- and disulfidic linkages. This may be the reason for the enhanced thermal stability of the networks. This figure also indicates the stability of double networks toward ageing. The thermal stability increases with residual extension. This is industrially highly advantageous with respect to ageing resistance of natural rubber. This could be used as an effective way to improve the resistance of natural rubber to air, ozone, and heat. This method could be used to eliminate the use of toxic antioxidants, which are harmful to human body.

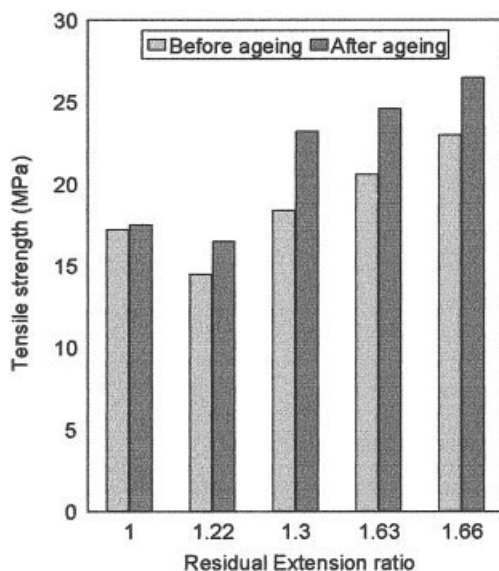


Figure 7 Effect of ageing on double networks prepared with MBS accelerator system.

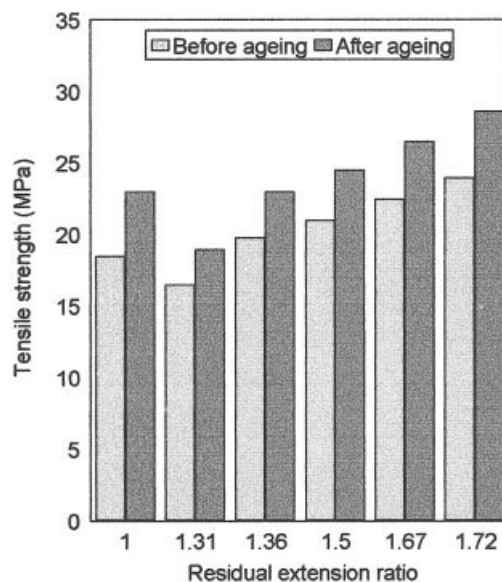


Figure 8 Influence of ageing on tensile strength with residual extension ratio.

Dynamic mechanical properties

It is observed from the mechanical properties that the introduction of double networks changes the modulus of the rubber. Keeping this in mind, studies were aimed at the dynamic mechanical behavior of double networks. The storage modulus values are plotted against temperature for mixes with and without the binary accelerator (Fig. 9). In this case we selected only samples with different residual extension. The graphs can be divided into three distinct regions: the glassy region, the transition (leathery) region, and the rubbery region. The plateau modulus in the rubbery region is higher for double-networked samples with higher residual extension. This may be associated with the increased entanglement density attributed both to secondary crosslinks and to the greater orientation of networks. It may be seen that mixes with DTB show higher modulus than those without DTB. The increase in crosslink density is clear from Table IV. From Figure 9, it may be seen that in the rubbery region of the double network, the modulus of the networks with higher residual extension ratio is higher than that of networks with lower residual extension ratio. As expected, at low temperature the modulus is unaffected as a result of the introduction of double networks because of the glassy state of the polymer chains. The moduli also increase with residual extension.

Crosslinking raises the glass-transition temperature T_g of a polymer by introducing restrictions in the molecular motions of the chain. The plot of $\tan \delta$ as a function of temperature is given in Figure 10. The peak of the curve is taken as the T_g . The T_g values show a slight increase with increase in crosslink den-

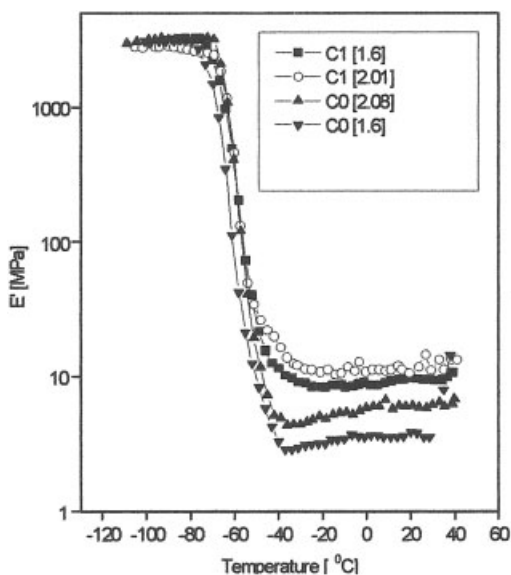


Figure 9 Variation of storage modulus with temperature of double-networked rubber with different residual extension ratios.

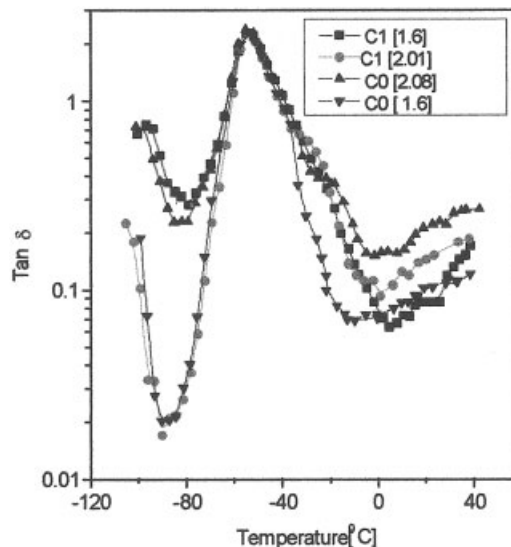


Figure 10 Variation of loss tangent with temperature on residual extension of double-networked rubber.

sity. The peak width at half height or the peak area is a measure of the damping shown by the compounds. It is directly related to the service performance of the products. A slight decrease in damping is shown with an increase in residual extension. This may be attributable to the increased crosslink density with residual extension.

CONCLUSIONS

Double networks were prepared in natural rubber cured with single and binary accelerator systems. The effect, of different degrees of initial cure, on mechanical properties of the double networks prepared was examined. It was found that the lower the initial cure, the higher will be the amount of double networks formed and as a result the higher will be the residual extension. Double networks with different residual extensions were prepared and mechanical properties such as tensile strength and modulus were measured. It was found that modulus increased with residual extension even if tensile strength shows an initial slight decrease and then an increase with increase in residual extension. Crosslink density also registered an increase with residual extension. DTB-aided vulcanization showed improvements in modulus and crosslink density. Double-network samples showed stability toward thermal ageing. Thermal resistance of natural rubber was found to improve with double-network formation, which indicates formation of more mono- and disulfidic linkages. It is noted that the new binary accelerator DTB imparted an improvement in mechanical properties of double-networked natural rubber compared with those cured without DTB. Dynamic storage modulus showed an increase with re-

residual extension and crosslinking. Glass-transition temperature slightly increased with residual extension of the double networks.

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