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Interaction of crosslinked natural rubber with chlorinated hydrocarbons

G. Unnikrishnan[a] **and Sabu Thomas**[b,*]
[a] *School of Technology and Applied Sciences, M.G. University, Kottayam, 686 561 Kerala, India*
[b] *School of Chemical Sciences, M.G. University, Kottayam-686 560 Kerala, India*
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The transport characteristics and the subsequent reduction in mechanical strength of natural rubber vulcanizates have been investigated using chlorinated hydrocarbons as probe molecules. The transport process has been examined by a sorption–desorption–resorption–redesorption technique. The mode of transport was found to change from the anomalous nature to the regular Fickian trend after a sorption–desorption cycle. The modulus of rubber samples decreased considerably under swollen conditions. The marching trend of stress–strain curves vanished after solvent saturation which has been explained on the basis of the absence of strain-induced crystallisation in swollen specimens. The modulus of solvent-saturated samples was found to be a function of rubber–solvent interaction which has been explained in terms of the differences in the contribution of physical entanglements to the total crosslink density. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The transport of small organic molecules through macromolecular networks is a complex process with a variety of technological applications. Polymer films are widely employed in such diverse areas of technology as controlled release of drugs and pesticides, clinical haemoperfusion, pervaporation, ultrafiltration, electrodialysis, microelectronics, etc.[1-5]. The selection or development of polymeric materials for use in all these applications, with stringent specifications relating to their solution and transport behaviour, requires knowledge and understanding of the many factors which affect those phenomena.

One of the major factors controlling the transport characteristics of polymers is their glass transition temperature (T_g). Below T_g, a polymer is hard and may be brittle, these properties being intimately related to restricted polymer chain mobility. Polymers of this type are very dense structures, with very little internal void space. Hence it is not surprising that penetrant diffusivity through such a structure is low. On the other hand, polymers in the rubbery state, well above their T_g, typically are tough and flexible, with such properties associated with free chain motions. Understandably, a larger amount of free volume is then available through which transport may take place[6].

In our earlier works, we investigated the solvent transport behaviour of different rubbers with special reference to the effects of vulcanising systems, fillers, cure time temperature etc.[7-14]. The present paper presents the sorption and diffusion results of three chlorinated hydrocarbons through natural rubber (NR), one of the most widely used elastomers.

The swelling behaviour, as a result of liquid sorption and diffusion, has been extensively used for the characterisation of polymer networks[15,16]. It has also been used to critically evaluate various theories of network elasticity[17,18]. Dogadkin *et al.*[19] examined the effect of swelling on the strength of vulcanizates. They showed that swelling decreases the strength of rubber in different ways depending on the type of rubber, type of liquid and the nature of interaction between rubber and liquid. Rennar and Oppermann[20] studied the swelling behaviour and mechanical properties of endlinked poly(dimethyl siloxane) (PDMS) networks and randomly crosslinked polyisoprene networks. They concluded that the measurements of the small strain modulus and the determination of the equilibrium degrees of swelling of PDMS and polyisoprene networks both demonstrate the importance of permanent entanglements or other topological interactions giving rise to an enhancement of network density. Venkatraman *et al.*[21] examined the deformation behaviour of PDMS networks by equilibrium swelling and demonstrated the use of a modified form of the Flory–Rehner equation to predict equilibrium swelling ratios. All these works highlight the need for carefully examining the relationship between swelling behaviour and deformation characteristics of macromelecular networks. Therefore, attempts have also been made in this paper to investigate the reduction in the mechanical strength of NR vulcanizates with solvent imbibition.

EXPERIMENTAL

The NR used in this work was a technically specified form of rubber, obtained from the Rubber Research Institute of India, Kottayam, India. This rubber satisfied the Bureau of Indian Standards' specifications for ISNR-5 grade NR. The solvents, dichloromethane, chloroform and carbon tetrachloride (S.D. Fine Chem. Ltd., Bombay, India) were of reagent grade and were double distilled before use. All other chemicals were of laboratory-reagent grade.

The NR was vulcanised by four vulcanising systems, viz., dicumyl peroxide (DCP), conventional (CV), efficient (EV)

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[*] To whom the correspondence should be addressed

Table 1 Formulation of the mixes (phr)

Ingredients	Mixes			
	DCP	EV	Mixed	CV
Natural rubber	100	100	100	100
Stearic acid	—	1.5	1.5	1.5
Zinc oxide	—	5	5	5
MOR	—	—	0.6	0.6
TMTD	—	1	—	—
CBS	—	1.5	—	—
Dicumyl peroxide	4	—	1.5	—
Sulphur	—	0.6	1.5	2

phr, parts per 100 rubber; MOR, morpholine benzothiazyl sulphenamide; TMTD, tetramethyl thiuram disulphide; CBS, *N*-cyclohexyl-2-benzothiazyl sulphenamide

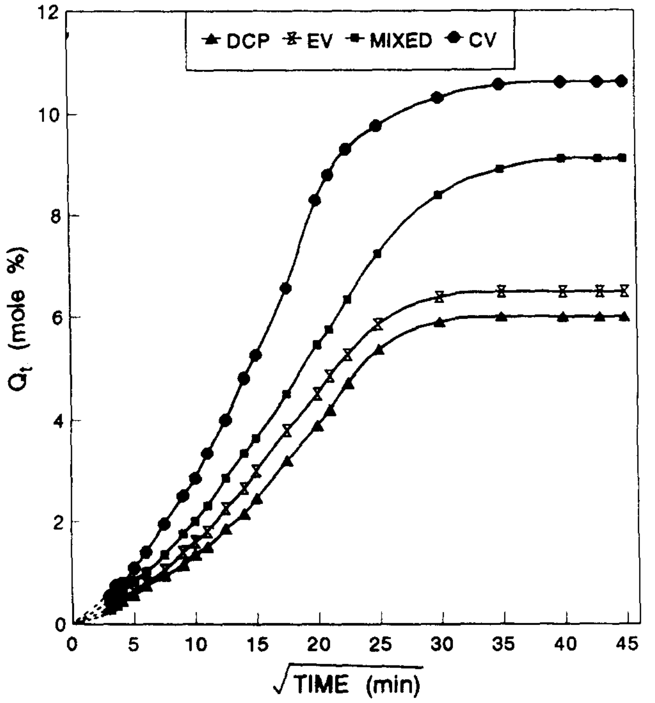

Figure 1 CCl_4 uptake (mol%) of NR vulcanized by different systems. The samples were cured to a common torque of 33.8 dN M

and a mixture of sulphur and peroxide (Mixed). The basic formulation of the mixes is given in *Table 1*. In order to examine the effect of mode of crosslinking on rubber–solvent interaction the rubber samples were cured in such a way that all of them develop the same rheometric torque. This was to minimise the differences in the magnitude and distribution of crosslinks in the macromolecular structure of NR. The curing of the sample was done at 160°C, in a hydraulic press having electrically heated platens, under a pressure of 30 tonnes.

Circular samples of diameter 1.9 cm were punched out from the vulcanised rubber samples using a sharp steel die and were used in sorption experiments that monitored liquid sorption gravimetrically. The thickness of the samples was measured at several points with an accuracy of ± 0.001 cm by using a micrometer screw gauge. An average of several values was taken as the initial sample thickness. The samples (0.5500–0.6250 g) were then immersed in 20 ml of solvents contained in stoppered glass bottles kept in an air oven. At regular intervals the test samples were removed from the solvent and the surfaces were dried between filter papers. The drying of the samples was done within 5–10 s and was just to remove the residual solvent from their surfaces. They were then weighed immediately using an electronic balance that measured reproducibly within ± 0.0001 *g*. The samples were reimmersed in test bottles to permit the continuation of the kinetic sorption until saturation in excess liquid was established. After attaining equilibrium in the liquids, the NR samples were desorbed fully, keeping them in a thermostatically controlled oven at 28°C. The decrease in weight of the samples was also noted at regular intervals. The desorbed samples were exposed to solvents for resorption followed by redesorption. Thus a sorption (S)–desorption (D)–resorption (RS)–redesorption (RD) experiment has been used for studying the transport phenomenon. This technique has been successfully

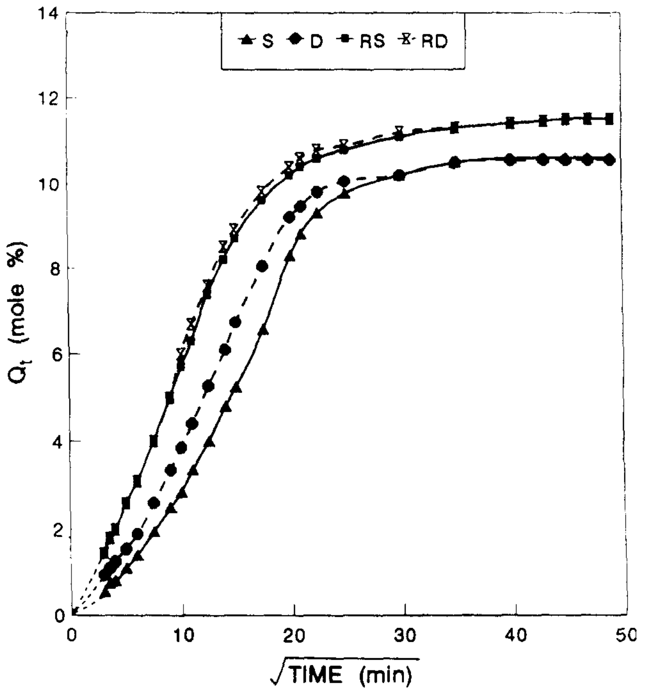

Figure 2 S–D–RS–RD curves of CV system

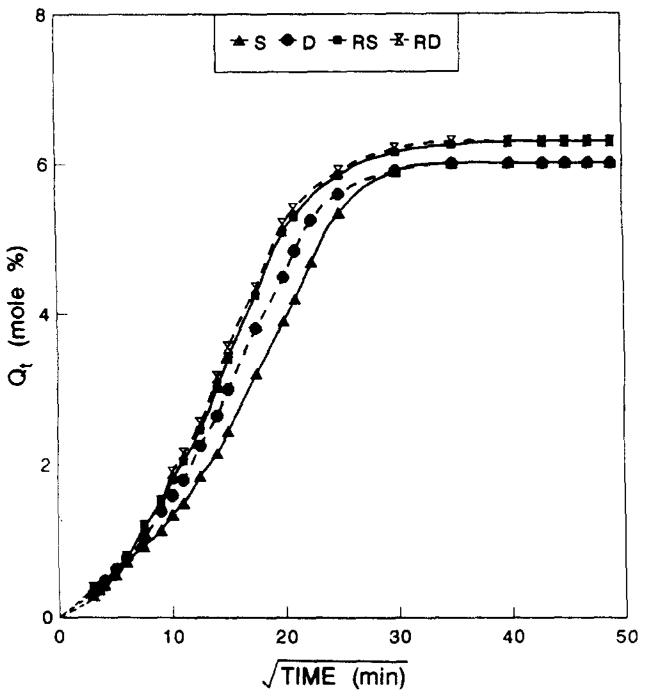

Figure 3 S–D–RS–RD curves of DCP system

Table 2 Values of *n* and *k*

System	n						$k \times 10^2$ (min^{-n})					
	Sorption			Resorption			Sorption			Resorption		
	CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4	CH_2Cl_2	$CHCl_3$	CCl_4
DCP	0.61	0.62	0.64	0.52	0.52	0.54	4.31	4.60	5.12	4.82	5.01	5.36
EV	0.62	0.63	0.65	0.53	0.52	0.54	3.83	4.39	4.83	4.21	4.76	5.09
Mixed	0.64	0.64	0.65	0.53	0.53	0.55	3.11	3.48	3.96	3.84	3.81	4.46
CV	0.64	0.65	0.66	0.54	0.54	0.56	2.64	2.94	3.13	3.07	3.43	3.82

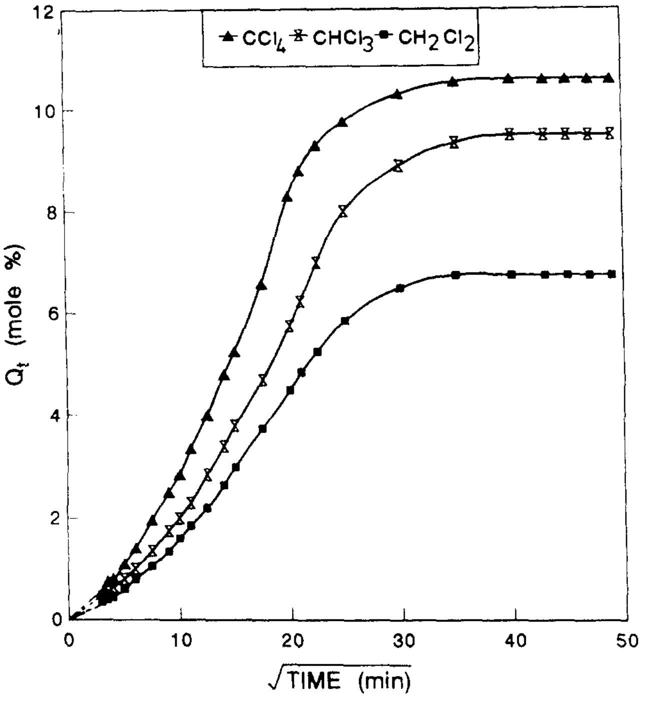

Figure 4 Solvent uptake (mol%) of DCP system

employed by Aminabhavi and Phayde[22] for investigating the solvent transport into Santoprene thermoplastic rubber samples exposed to *n*-alkanes. The results of the experiments have been expressed in terms of the number of moles of the liquid sorbed or desorbed by 100 g of the sample, Q_t.

The tensile strength of the rubber samples under pre-swollen, swollen and de-swollen conditions was determined using a Zwick Universal Testing machine model 147 A according to ASTM test method D 412-51 T.

RESULTS AND DISCUSSION.

Figure 1 represents the liquid sorption behaviour of NR samples vulcanised by the four modes viz., DCP, CV, EV and Mixed. The solvent used was CCl_4. It is clear from the figure that the maximum liquid sorption decreases in the order CV > Mixed > EV > DCP. This observation is in qualitative agreement with our experiments using aromatic and aliphatic hydrocarbons[7,8]. The difference in the sorption behaviour of the four rubber samples has been attributed to the differences in the nature and distribution of crosslinks between the macromolecular chains of NR.

The plots of S–D–RS–RD experiments with CCl_4 as the solvent, for CV and DCP samples are given in *Figures 2 and 3*, respectively. It is seen that the sorption and desorption curves do not exhibit identical patterns. This clearly indicates the deviation of transport mode from the regular Fickian trend. However, the resorption and redesorption curves exhibit identical patterns. The resorption curves show that the equilibrium uptake values and the time to attain equilibrium are higher, compared to the first sorption process. In a sorption–desorption cycle the available free volume of the rubber might increase due to the rearrangement of rubber chains, and the subsequent sorption process is different from that of the original. These effects have been successfully described by the network relaxation in terms of the times required for the molecular rearrangements of the chains and that of the solvent diffusion into the polymer[23]. However, segmental mobility of the polymer might be increased due to solvent ingression and this depends upon the ability of the solvent molecules to penetrate and thereby weaken the intermolecular forces of the polymer network structure.

The influence of nature of the penetrant on the liquid transport through NR is presented in *Figure 4*. Higher Q_t values are observed for NR–CCl_4 system compared to the other two systems, viz., NR–$CHCl_3$ and NR–CH_2Cl_2. This is, in fact, due to the difference in polarity of the probe molecules. The non-polar NR matrix has more affinity towards the non-polar CCl_4 molecules with zero dipole moment values. The liquid sorption decreases with increase in the polarity of the solvent molecules.

The mechanism of transport in the systems under investigation was followed by using the equation[24,25].

$$\log \frac{Q_t}{Q_\infty} = \log k + n \log t \qquad (1)$$

where Q_t and Q_∞ are the mol% increase in sorption at time t and at equilibrium respectively; k is a constant depending on the structural characteristics of the polymer in addition to its interaction with the solvent. The magnitude of n denotes the transport mode. For normal Fickian mode of transport (usually described as Case I), where the rate of polymer chain relaxation is higher compared to the diffusion rate of the penetrant, the value of n is 0.5. When $n = 1$, the transport process is said to be Case II (relaxation-controlled) where chain relaxation is slower than the liquid diffusion. If the value of n is between 0.5 and 1, the mode of transport is classified as anomalous. The estimated values of the constants n and k are compiled in *Table 2*. The n values are accurate to ± 0.01 units. The values of n for sorption experiments suggest that the observed diffusion mechanism can be classified as anomalous. However, for resorption experiments the n values are close to 0.5, suggesting Fickian-type transport where the rate of polymer chain relaxation is higher compared to the concurrent solvent diffusion. The change of transport mode from the anomalous nature to the Fickian trend after a sorption–desorption cycle can probably be due to the leaching out of extra network materials (ENM)[26]. The ENM represents all the unreacted materials left behind in the rubber matrix after

Table 3 Values of intrinsic diffusion coefficient ($\bar{D}$) × 10^9 (m^2/s)

System	Penetrant		
	CH_2Cl_2	$CHCl_3$	CCl_4
DCP	4.01	5.11	5.51
EV	4.58	5.63	6.06
Mixed	5.17	6.86	7.41
CV	6.81	8.34	9.60

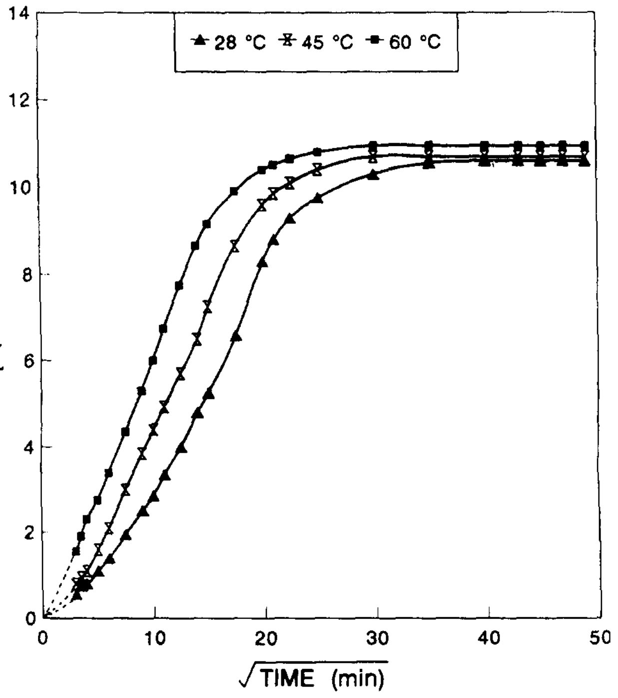

Figure 5 Temperature dependence of mol% CCl_4 uptake of CV system

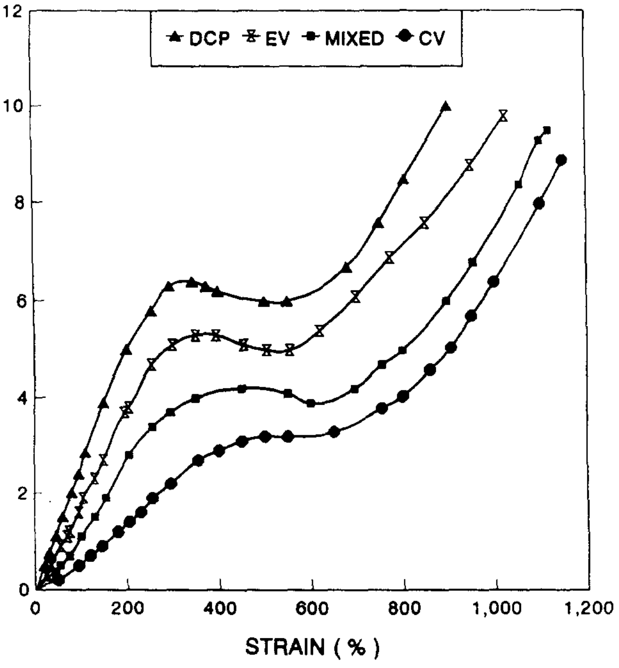

Figure 6 Stress–strain curves of NR samples before swelling

vulcanisation. The presence of these materials can reduce segmental as well as the overall rubber chain mobility causing the deviation of transport mode from the regular Fickian trend.

The kinetic parameter, diffusion coefficient D for the different systems under investigation was determined by using the equation[27,28].

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

where h is the sample thickness, θ the slope of the initial linear portion of the sorption curve and Q_∞ has the same meaning as in equation (1). Since significant swelling of the samples was observed during the experiments in all solvents, correction to diffusion coefficients in the swollen conditions were essential. This was done by calculating the intrinsic diffusion coefficient $\bar{D}$, from the volume fraction ϕ of rubber in the swollen sample using the relation[29].

$$\bar{D} = \frac{D}{\phi^{7/3}} \qquad (3)$$

The values of $\bar{D}$ are given in *Table 3*. The $\bar{D}$ values increase regularly from DCP to CV system in a given penetrant. It is also seen that these values decrease with increase in the polarity of the penetrant. These observations parallel the equilibrium sorption values.

The temperature susceptibility of NR samples in CCl_4 was investigated by conducting the sorption experiments at 45 and 60°C. However, in the case of other solvents, the influence of temperature could not be studied due to their low boiling points. *Figure 5* shows the increase in the rate and equilibrium sorption of CV sample, in CCl_4, with temperature.

One of the most informative mechanical experiments for any polymeric material is the determination of its stress–strain curves in tension. From the stress–strain curves it is possible to determine the differences in the deformation characteristics of rubber samples under an applied load. These curves vary depending upon the nature and distribution of crosslinks in the rubber network. *Figure 6* shows the stress–strain curves of NR crosslinked by the four techniques, viz., DCP, CV, EV and Mixed. These curves are typical of crosslinked elastomers. The marching trend of the curves in *Figure 6* is associated with the strain-induced crystallisation behaviour of NR[30]. From the figure it follows that, for a particular strain, the value of stress is maximum for the sample crosslinked by DCP. The same trend is observed at all strain values. It is also clear from the figure that the slope of the initial portion of the curves is maximum for the DCP sample, indicating its higher modulus. This is definitely associated with the higher degree of crosslinking of DCP samples. The modulus is found to decrease in the order DCP > EV > Mixed > CV. This is in good agreement with the equilibrium sorption values of the rubber samples in different solvents.

Figure 7 shows the stress–strain curves of NR samples after reaching equilibrium saturation in CCl_4. The modulus is found to decrease very significantly under swollen conditions for all the samples; the reduction being predominant for CV sample. The strain at break is found to be reduced to about 25% of the deformation of the corresponding unswollen samples. A comparison of *Figures 6 and 7* gives a very interesting observation that the marching trend of the rubber samples, in the unswollen stage, disappears after they attain equilibrium saturation in a solvent. This can be explained by the absence of strain-induced crystallisation in the solvent-saturated rubber samples. The crystallisation behaviour is due to the stereoregularity in the macromolecular structure of NR, which is *cis*-1,4-poly(isoprene). Under an applied load,

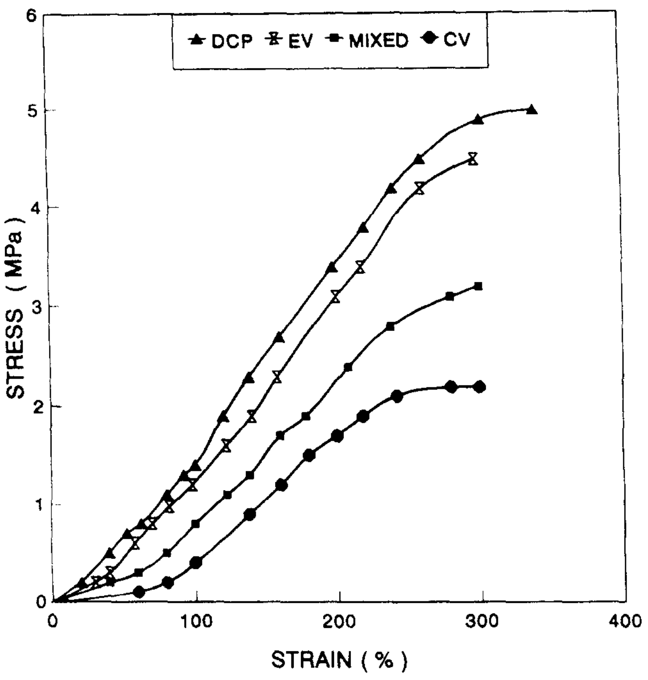

Figure 7 Stress–strain curves of NR samples after establishing equilibrium in CCl_4

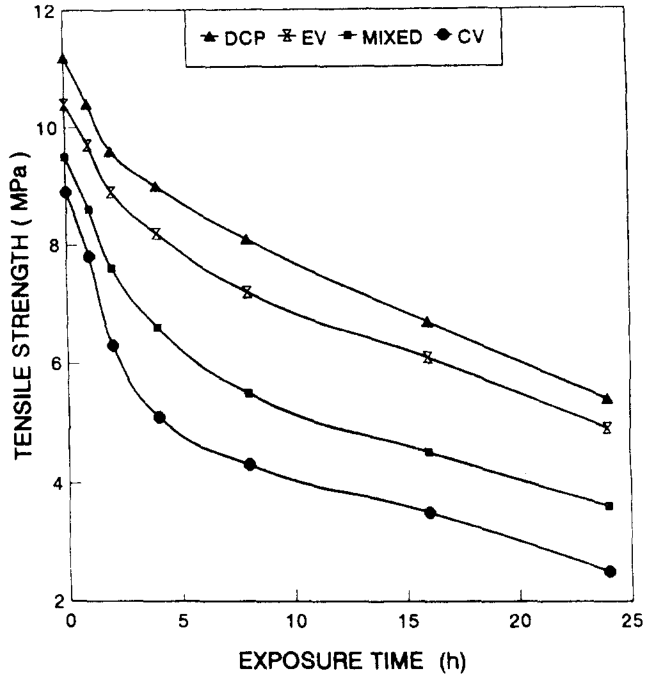

Figure 9 Variation of tensile strength of NR samples with exposure time, in CCl_4

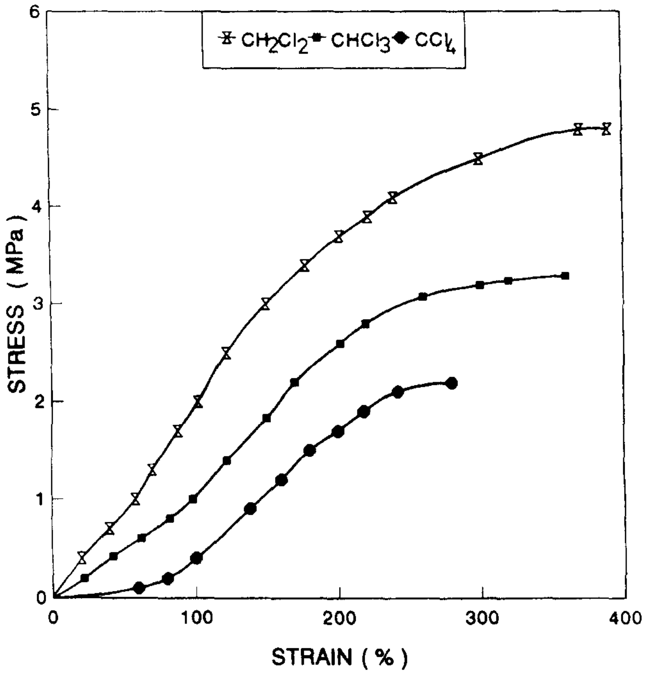

Figure 8 Stress–strain curves of CV sample in different solvents

long-range order (lro) is developed in the rubber due to the stereoregular structure which accounts for its crystallisation tendency. The random distribution of solvent molecules in the swollen specimens effectively opposes the alignment of rubber segments under the applied load, thereby preventing strain-induced crystallisation.

Figure 8 shows the stress–strain behaviour of CV samples after reaching equilibrium in CH_2Cl_2, $CHCl_3$ and CCl_4. The stress values are found to be higher for the sample swollen in CH_2Cl_2, for all strain values. The mechanical properties of swollen specimens are governed by different types of relaxation mechanisms which involve the intramolecular motions of segments and the molecular motions involving conformation changes in chain entanglements. The physical entanglements of the rubber chains contribute significantly to the deformation characteristics of the networks in addition to the contribution of chemically discrete crosslinks. Since the physical entanglements vary depending on the interaction of the rubber segments with the solvents[9,31–33], it is reasonable to think that the stress–strain behaviour of the same rubber sample in different solvents will be different. Of the three solvents in this work, CCl_4 exhibits higher rubber–solvent interaction as can be seen from the equilibrium sorption values. Therefore, the rubber sample exposed to CCl_4 has only minimum contribution of physical crosslinks (due to lesser entanglements) to the total crosslink density. In other words, the minimum modulus and tensile strength of the NR sample swollen in CCl_4 compared to other rubber–solvent systems is associated with the lower degree of physical entanglements in it.

Figure 9 shows the variation of tensile strength of different NR samples as a function of the exposure time in the solvent CCl_4, for the first 24 h. It is seen that the tensile strength values of all the samples decrease regularly as the time of exposure to liquid medium increases. This is in quantitative agreement with the expectation that increase in liquid imbibition weakens the attractive forces between the macromolecular chains of NR. It is interesting to see that almost half of the total reduction in tensile strength of all the samples occurs during the first 6 h of exposure to the solvent medium.. The rate of decrease declines with increase in exposure time.

Figure 10 represents the stress–strain curves of NR samples after a sorption–desorption cycle. Evidently, the curves follow the behaviour of those of the unswollen samples (*Figure 6*). However, the stress values are found to be a little lower for all strain values compared to the curves of unswollen samples. This reduction may probably be due to the removal of ENM during a cycle of sorption and desorption.

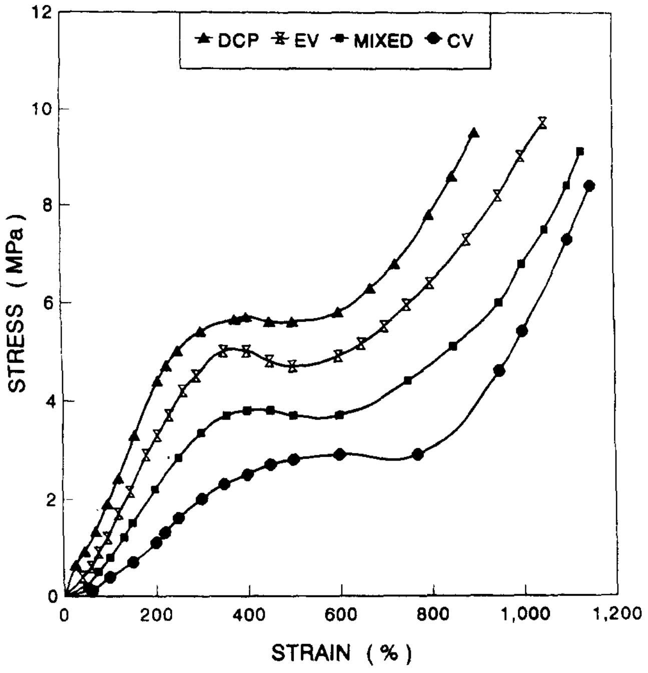

Figure 10 Stress–strain curves of NR samples after a sorption–desorption cycle

CONCLUSIONS

The interaction of NR with chlorinated hydrocarbons has been followed by a sorption (S)–desorption (D)–resorption (RS)–redesorption (RD) technique. The mechanism of diffusion was found to be anomalous for sorption. However, the resorption mechanism followed the regular Fickian trend. This has been attributed to the leaching out of extra network materials after a sorption–desorption cycle. The mechanical strength of the rubber samples was found to decrease significantly after establishing equilibrium in solvents. The stress–strain curves clearly indicated the absence of strain-induced crystallisation in the swollen specimens. This observation has been accounted for by the prevention of the long-range order, due to the stereoregular structure of NR, by the randomly distributed solvent molecules in the rubber matrix. The modulus of a given sample was found to be different in different solvents. This has been explained in terms of the differences in the contribution of physical entanglements to the total crosslink density. Research in this field is going on and these results will be reported in subsequent papers.

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