J Mater Sci (2010) 45:409–417
DOI 10.1007/s10853-009-3956-z

Transport of methyl methacrylate monomer through natural rubber

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Received: 31 March 2009 / Accepted: 5 October 2009 / Published online: 22 October 2009

Abstract The diffusion and transport of inhibitor-free methyl methacrylate monomer through crosslinked natural rubber (NR) have been studied at different temperatures. NR has been vulcanised by conventional, efficient and peroxide vulcanisation technique. ESR spin probe spectroscopy was used to study the flexibility of NR network chains at different temperatures. The dependence of diffusion coefficient on the nature of crosslinks and temperature has been studied. The intrinsic diffusion coefficient was found to increase with increase of temperature. The interaction parameter, permeability, sorption coefficient and molecular weight between crosslinks have been evaluated using diffusion data. The morphology of the swollen network and thermodynamic parameters has been determined using diffusion data. The efficient and peroxide system showed the least uptake and the conventional system showed the highest uptake. This study also proved that same extent of crosslinking can be achieved for different vulcanising systems by curing the samples to a common rheometric torque. The theoretical modelling shows Fickian mode of diffusion with a slight deviation.

Introduction

The transport phenomenon through polymeric membranes is an important and in certain cases a controlling factor in several applications such as protective coatings and separation process. Recently, great attention has been focussed on separation science and technology, which necessitates the studies of diffusion, sorption and permeation of various penetrants through polymeric membranes. Some of the major factors which play an important role in the transport process are nature of polymer [1], type of crosslinks, crosslink density, size and structure of the penetrants [2, 3] and temperature. The free volume of the polymer and its chain segmental mobility play a vital role in this regard. The polymer chain mobility is decided by extent of unsaturation and crosslinking, degree of crystallinity and the nature of the substituents. Though slight deviations have been reported recently, more or less a satisfactorily explanation of diffusion of liquids through rubbery polymers can be derived from Fick's law of diffusion.

In the study on swelling characteristics of natural rubber (NR) in aromatic solvents, the dependence of transport phenomenon on polymer structure was well studied by Harrogoppad et al. [4]. They found that equilibrium penetrant uptake was influenced by size and shape of the penetrant, polymer morphology and temperature. They also investigated the temperature dependence of the transport

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coefficient to estimate the activation parameters from Arrhenius plots [5]. Poh et al. [6] did elaborative work on the detailed effect of crosslink density on diffusion. They have studied the sorption behaviour of bulk and solution crosslinked NR networks prepared by irradiation with γ-rays. They found that in benzene solutions, crosslinked networks swell more than the corresponding bulk crosslinked network having the same crosslink density. Transport properties of *n*-alkanes through bromobutyl rubber membranes were studied by Aminabhavi and Munnoli [7] using a gravimetric method. Thomas and co-workers have reported on the diffusion and transport of various organic solvents through NR [8], nitrile rubber [9], styrene butadiene rubber [10], epoxidised NR membrane [11] and also through nanocomposites [12].

The sorption and swelling behaviour of NR in various solvents have been of great interest, as NR finds extensive application in various fields. Swelling studies of NR samples in a number of monomers like styrene, acylonitrile, butyl acrylate, etc. are of great research interest, since it constitutes the preliminary step in the preparation of interpenetrating polymer networks (IPNs). The composition, morphology and properties of the IPNs can be well controlled by knowing the swelling rate of the polymer in various monomers.

In this article, the fundamentals of transport phenomenon and the factors affecting the transport of methyl methacrylate through NR are discussed in detail. The NR is vulcanised by three different techniques namely, conventional (CV), efficient (EV) and dicumyl peroxide incorporated (DCP) which was used in the present investigation. For each crosslinked system, samples were vulcanised at different cure times so as to obtain samples of different crosslink densities. The effect of crosslink densities on sorption has been investigated. The temperature dependence of diffusion and NR–methyl methacrylate interaction parameter χ are determined. Efforts are also made to investigate the morphology of the NR network in equilibrium swelling state. Thermodynamic parameters are also computed.

Experimental

Materials

The NR used was of ISNR-5 grade and was supplied by Rubber Research Institute of India (RRII). The methyl methacrylate monomer was made free of inhibitor by washing with 0.1% NaOH and dried using sodium sulphate before it was used for diffusion experiments. The chemicals used in various vulcanising systems were of laboratory reagent grade.

Table 1 Formulations of the mixes

Ingredients (phr)[a]	CV	DCP	EV
Natural rubber	100	100	100
Stearic acid	1.5		1.5
Zinc oxide	5		5
MOR[b]	0.6		
TMTD[c]			1
CBS[d]			1.5
DCP		3	
Sulphur	2		0.6

[a] Parts per hundred rubber by weight

[b] Morpholine benzothiazyl sulphenamide

[c] Tetramethylthiuram disulphide

[d] *N*-Cyclohexyl-2-benzothiazyl sulfenamide

Sample preparation

Natural rubber was vulcanised by conventional (CV), efficient (EV) and peroxide (DCP) techniques. The formulations of the mixes are given in Table 1. The mixing was done in a two roll mixing mill. The rheometric torque is directly proportional to the crosslink density. The mixes were cured at different time intervals: t_{100}, t_{90}, t_{80}. The optimum cure time t_{90} refers to the time for obtaining 90% of the maximum torque.

ESR measurements

The free nitroxide radical 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL) was used as spin probe for ESR measurements. The probe molecules were incorporated into crosslinked rubber samples by swelling these samples in toluene probe solution. The total amount of probe molecules in the samples was 0.15 wt%. ESR measurements were performed on Varian E-109 spectrometer operating at 9.2 GHz, equipped with a Bruker ER 041 XG microwave bridge and a Bruker ER 4111 VT temperature unit. EW (EPRWare) software program was used for data accumulation and manipulation. The number of accumulations varied from 2 to 5 depending on signal-to-noise ratio.

Swelling measurements

Circular samples of radius 1.9 cm were cut from different vulcanised sheets using a sharp steel die. The thickness of the samples was measured by means of a screw gauge. The samples were weighed on an electronic balance and then kept immersed in inhibitor-free methyl methacrylate monomer in test bottles. The test bottles were kept in a thermostatically controlled oven. The samples were taken out of the liquid at specific time intervals, the monomer adhering to the surface rubbed off, and the samples were weighed and replaced in test bottles. The process was continued till equilibrium was reached. Since the weighing was done within 30 s, the error associated with the evaporation of monomer was negligible. The experiments were duplicated or triplicated in most cases and standard deviation was found to range from 0.07 to 0.1. The results of solvent uptake by the polymer were expressed as mole percent of the solvent sorbed by 0.1 kg of the polymer (Q_t). When equilibrium was reached, Q_t was taken as Q_∞, i.e. mole uptake at infinite time.

Results and discussion

Effect of nature of crosslinks and crosslink density

Sorption curves were analysed to obtain conclusions from the diffusion experiments. Figures 1, 2 and 3 show the diffusion curves of NR crosslinked by three vulcanising systems having optimum cure (t_{90}) at three different temperatures 25, 35 and 45 °C. The diffusion curves showed that the monomer uptake is highest in the case of CV and lowest in the case of EV, and DCP takes an intermediate position at room temperature and the difference between DCP and EV decreases as the temperature increases. The diffusion curves were not similar in nature. It was very clear that the rate of swelling was high at the initial stages and starts levelling off at saturation point, i.e. at the equilibrium. The Q_∞ values for the various systems were different which can be attributed to the different types of crosslinking present in the system. The chemical nature of the networks formed during vulcanisation for the three systems are shown in Fig. 4. In the DCP cured samples, there were C–C linkages between the polymer chains that are stable and rigid. They were highly resistant to solvent stress, which restrict the uptake of monomer. Moreover, the branched structure of the methyl methacrylate monomer and presence of bulky groups also influenced the diffusion

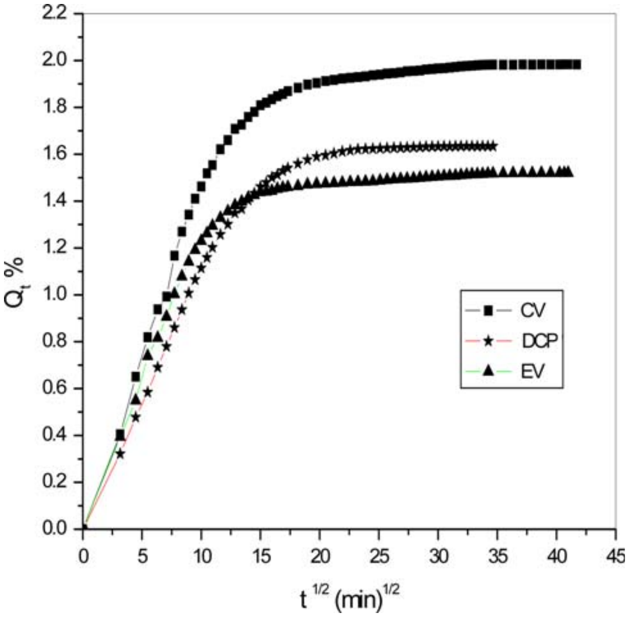

Fig. 1 Sorption curves showing the mole percent uptake of optimum cured CV, DCP and EV at 25 °C

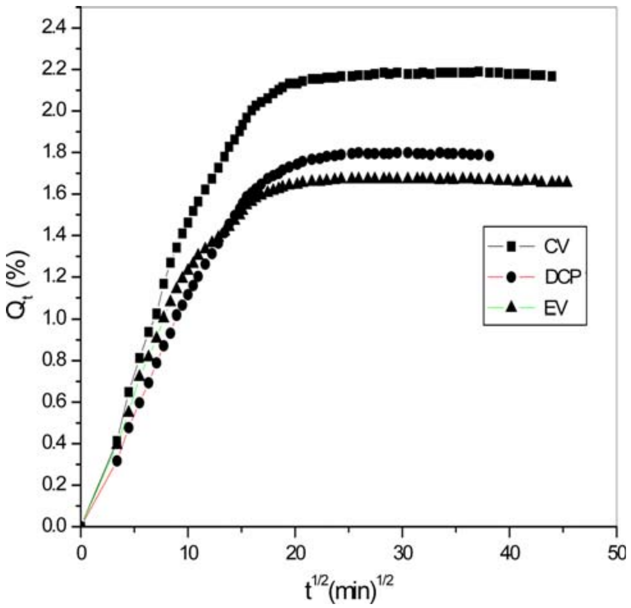

Fig. 2 Sorption curves showing the mole percent uptake of optimum cured CV, DCP and EV samples at 35 °C

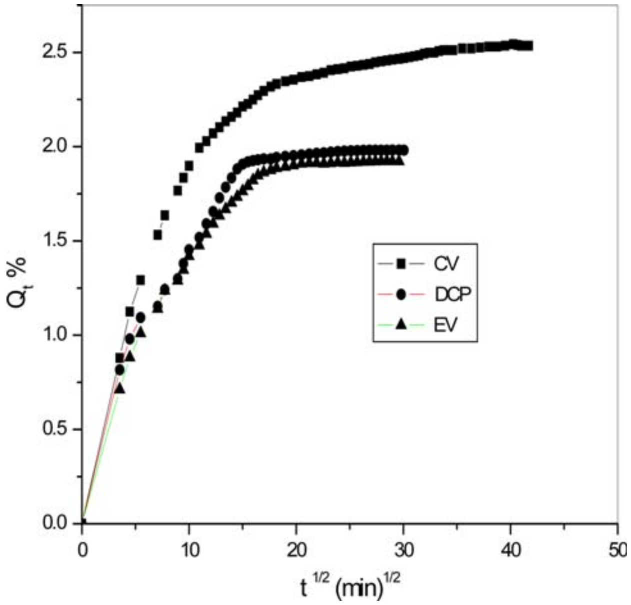

Fig. 3 Sorption curves showing the mole percent uptake of optimum cured CV, DCP and EV samples at 45 °C

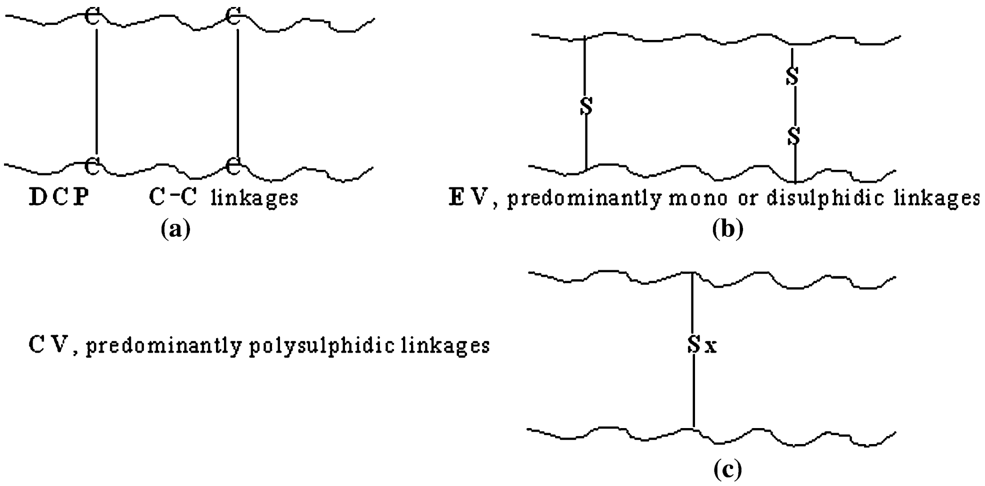

Fig. 4 Schematic representation of the crosslinks formed during curing. **a** DCP, **b** EV and **c** CV

process. Studies revealed that the size and shape of the penetrant molecules influence the transport behaviour of polymers. Permeability generally decreases with increasing permeant size. Many investigators have reported the decrease in diffusivity with increase in size of the penetrant [2, 3]. Mathew et al. [13] studied the diffusion of styrene monomer through NR, and the maximum uptake (Q_∞) they obtained was higher than that of this study. An overall decrease in the monomer (all systems) uptake is shown in this study. CV cured system shows maximum monomer uptake. In CV cured system, the links between the polymer chains were predominantly polysulphide, which were highly flexible when compared to DCP and EV cured system. Thus, CV is comparatively highly susceptible to diffusional stress. So chain flexibility was high in the CV system. As a result, the monomer molecules were more readily accommodated between the rubber chains.

Comparison of the sorption curves at three different temperatures (Figs. 1, 2, 3) reveals as expected, the rate of diffusion as well as Q_∞ values were found to increase with increase of temperature because of increase in free volume and favourable chain conformation during rise in temperature.

The observed sorption behaviour could be explained on the basis of the volume fraction of swollen rubber determined by the relation [12]

$$\phi = \frac{w_1/\rho_1}{w_1/\rho_1 + w_2/\rho_2} \quad (1)$$

where w_1 is the weight of the rubber sample, w_2 is the weight of the methyl methacrylate monomer, ρ_1 is the density of the NR, ρ_2 is the density of the monomer. The ϕ values were a direct measure of crosslink density. The values are given in Table 2. The ϕ values of EV cured samples were found to be higher which show high crosslink density, as a result of which the EV cured samples showed lowest monomer uptake. The values of DCP cured samples also came close to the values of EV, which also showed lesser monomer uptake, i.e. the DCP cured samples also had high crosslink density. When a polymer sample was immersed in a solvent system, the environment around the sample was uniform irrespective of the nature of crosslinks. The approach of solvent molecules into EV and DCP cured samples was not easy because the density of polysulphide and C–C crosslinks per unit volume was high. The transport of solvent molecules was easier in CV system due to the fact that the density of CV linkages was less. The ϕ values of CV system were low as a result of which the monomer uptake was maximum in it. At high temperatures (35 and 45 °C), the same pattern was followed.

Table 2 Values of ϕ for different systems

Temperature (°C)	Cure time	CV	DCP	EV
25	t_{90}	0.32	0.37	0.38
35	t_{90}	0.30	0.34	0.36
45	t_{90}	0.27	0.32	0.33

The effect of nature of crosslinks on the monomer uptake of NR samples was studied by curing the three systems to a common rheometric torque (3 dN m) [14]. These samples were subjected to diffusion experiments. Theoretically, since rheometric torque was directly proportional to crosslink densities, all the samples cured to a common torque were supposed to have same crosslink density. Systems having same crosslink density were supposed to swell equally. The maximum uptake of monomer (Q_∞) by these samples and volume fraction (ϕ) of swollen rubber were computed and are given in the Table 3. The Q_∞ values showed that here also CV sample exhibited highest monomer uptake and EV sample showed the lowest. The Q_∞ values increased in the order EV < DCP < CV.

Table 3 Swelling parameters of NR samples cured to a rheometric torque of 3 dN m

System	Q_∞ (mol%)	ϕ
CV	2.03	0.32
DCP	1.73	0.35
EV	1.53	0.38

Effect of temperature on the flexibility of NR network

ESR spin probe spectra of crosslinked NR (using DCP) at 25 and 45 °C are shown in Fig. 5. Numerous studies have indicated that the rotational correlation times of nitroxide radicals (spin probes) reflect the chain dynamics of the host polymer [15–18]. The spectra showed the characteristics of NR having a sol–gel composition. The spin probe reflected a complex ESR spectra with slow motional component of the composite spectra arose due to the gel phase, especially so-called tight gel, while motionally fast component was attributed to spin probe embedded in sol phase. The spectra revealed motional heterogeneity inside the crosslinked NR matrix. This proves the fact that there were regions inside the matrix that were motionally restricted due to interchain interactions and chain entanglements. This could affect the diffusion process since swelling depends on the flexibility of the polymer network. The spectrum at 45 °C showed the enhanced freedom for nitroxide radicals due to the higher chain mobility and increased free volume inside the network. The contributions from gel regions/motionally restricted regions to the slow component in the spectra were considerably less at higher temperature. This showed that at 45 °C many of the motionally restricted regions in the NR matrix became more flexible and that allowed the NR matrix to hold more monomer at higher temperature. The narrowed spectral lines (45 °C) also indicated the overall flexible nature of the network and the development of larger free volumes within the network.

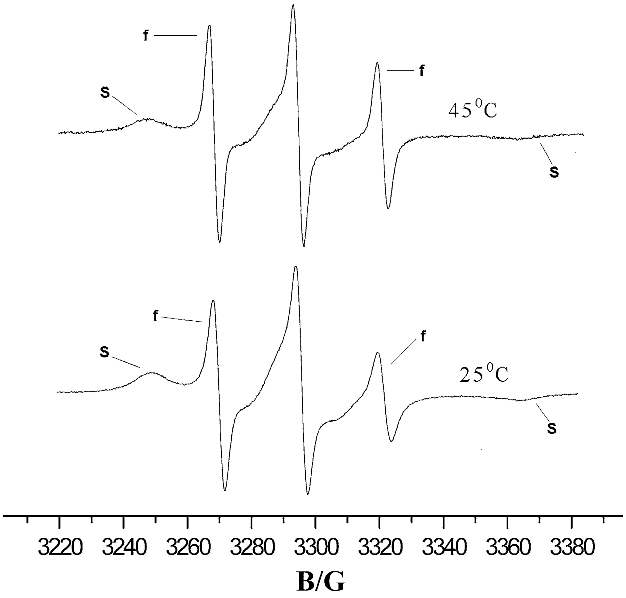

Fig. 5 ESR spectra of crosslinked NR at 25 and 45 °C

Swelling mechanism

In order to investigate the type of transport mechanism, the sorption results were fitted to the following equation:

$$\log(Q_t/Q_\infty) = \log k + n \log t \tag{2}$$

where Q_t and Q_∞ are the mole percent monomer uptake at time t and at equilibrium. k is a constant, which depends both on interaction between monomer and polymer and on the structure of the polymer. The value of n determines the mode of diffusion mechanisms. For the Fickian mode, the value of n is 0.5 and it occurs when the rate of diffusion of permeant molecules is much less than the relaxation rate of polymer chains. Usually rubbery polymers exhibit Fickian diffusion. If $n = 1$, the mode of diffusion is non-Fickian and this arise when the rate of diffusion of permeant molecules is very rapid when compared to polymer chain relaxation process. If $n = 1$ to 0.5, it shows an anomalous mechanism. Plots of log (Q_t/Q_∞) versus log t showed that the values of n were between 0.49 and 0.52 and this suggested that the transport mechanism was close to Fickian with a slight deviation.

Diffusivity and permeability

From the linear portions of the sorption curves, the diffusion coefficient, D, of the polymer solvent systems was calculated using the equation:

$$D = \pi\left(\frac{h\theta}{4Q_\infty}\right)^2 \tag{3}$$

where θ is the slope of the linear portion of the curve, h is the initial thickness of the polymer sample. Since significant swelling of polymer samples was observed during sorption experiments, correction to diffusion coefficients under swollen conditions was essential. This was done by calculating the intrinsic diffusion coefficient D^* from the volume fraction of polymer in swollen samples using the relation:

$$D^* = D/\phi^{7/3}. \tag{4}$$

The modified diffusion coefficient values known as intrinsic diffusion coefficient are given in Table 4. The CV system showed the highest D^* value which showed the easy uptake of MMA monomer when compared to other

Table 4 Values of intrinsic diffusion coefficient ($D^* \times 10^6$ m^2 s^{-1})

Temperature (°C)	CV	DCP	EV
25	4.77	3.51	3.53
35	5.15	3.93	3.92
45	5.85	4.49	4.53

Table 6 Values of permeation coefficient ($P \times 10^6$ m^2 s^{-1})

Temperature (°C)	Cure time	CV	DCP	EV
25	t_{90}	6.65	5.66	5.62
35	t_{90}	6.77	6.14	6.03
45	t_{90}	7.03	6.25	6.58

two systems. Also it was noticeable that in each system, D^* value increased with temperature. The increase of D^* with temperature invariably points out the activation of the diffusion process at high temperatures.

The permeation of a penetrant into a polymer membrane depends on the diffusivity as well as the solubility or sorptivity of the penetrant molecule in the membrane. Hence, sorption coefficient S, which is the maximum saturation sorption value, has been calculated using the equation:

$$S = M_s/M_p \tag{5}$$

where M_s is the mass of the penetrant at equilibrium and M_p is the mass of the polymer sample. The values of S are given in the Table 5.

It was found that the sorption coefficient was maximum for the CV system and minimum for the EV system. DCP systems take intermediate position. The maximum value for the CV system was an indication of the better accommodation of monomer molecules in the highly flexible polymer networks. A higher value of S also implied the tendency of the monomer molecule to dissolve into the polymer. The lowest value for the EV system showed the least capability to accommodate the monomer molecules.

The permeabilities of NR to monomers can be expressed mathematically by the equation:

$$P = D^*S \tag{6}$$

where P is the permeability coefficient, D^* is intrinsic diffusion coefficient, S is sorption coefficient. The values of permeability coefficients are given in Table 6. The CV system showed highest P value indicating high permeability of the system. The diffusion coefficient characterised the ability of the monomer molecule to move among the polymer segments. The sorption coefficient was related to the equilibrium sorption of the penetrant. The permeability coefficient implied the net effect of sorption and diffusion. The temperature activated the permeation too. It was seen from the table that permeation coefficients increased with rise in temperature.

Table 5 Values of sorption coefficient (S)

Temperature (°C)	Cure time	CV	DCP	EV
25	t_{90}	1.98	1.63	1.52
35	t_{90}	2.18	1.79	1.67
45	t_{90}	2.54	1.98	1.92

Interaction parameter

The polymer–monomer interaction parameter χ was calculated from swelling data using the equation:

$$\chi = 0.34 + V_r(\delta_A - \delta_B)^2/RT \tag{7}$$

where V_r is the molar volume of the monomer, R, the universal gas constant, T, the temperature, δ_A and δ_B are the solubility parameters of the polymer and monomer, respectively. The values obtained for the NR–methyl methacrylate system at 25, 35 and 45 °C were 0.677761, 0.581258 and 0.527645, respectively. It was found that interaction parameter decreased with increasing temperature. This suggested a high polymer–solvent interaction at high temperature.

Molecular mass between crosslinks

Knowing that diffusion was influenced by the polymer morphology, in addition to experimental variables, we have estimated the molar mass between crosslinks, M_c. The molecular mass between crosslinks of the network polymer was estimated using the equation developed from Flory–Rehner theory [19].

$$M_c = -\frac{\rho_p V \phi^{1/3}}{\ln(1-\phi) + \phi + \chi\phi^2} \tag{8}$$

where V is the molar volume of solvent, ρ_p is the density of the polymer, ϕ is the volume fraction of the rubber and χ is the interaction parameter of NR–methyl methacrylate monomer system. The values of M_c are given in Table 7. The highest values of M_c were shown by CV cured system which supported the observation of high monomer uptake by it. The values revealed that the CV cured system had

Table 7 Values of M_c (g/mol)

Systems	M_c	M_c (aff)	M_c (ph)
CV	14281.8	14093.8	7046.91
DCP	7697.38	7546.77	3773.89
EV	6245.89	6221.11	3110.56

more space between crosslinks to accommodate the monomer molecules. The EV cured system showed the lowest values for M_c which supported the low monomer uptake by EV cured samples.

Flory and Rehner relations were developed for a network deforming affinely, i.e. the components of each chain vector transform linearly with macroscopic deformation and the junction points were assumed to be embedded in the network without fluctuations. The molecular weight between crosslinks (M_c) for the affine limit of the model [M_c(aff)] was calculated using the formula [20]:

$$M_c(\mathrm{aff}) = \frac{\rho_p V(\phi_{2c})^{2/3}(\phi_{2m})^{1/3}\left[1-\mu/v(\phi_{2m})^{1/3}\right]}{-\left[\ln(1-\phi_{2m})+\phi_{2m}+\chi(\phi_{2m})^2\right]} \tag{9}$$

where μ and V are the number of effective chains and junctions, ϕ_{2m} the polymer volume fraction at swelling equilibrium, ϕ_{2c} the polymer volume fraction during crosslinking.

James and Guth [21] proposed the phantom network model where the chain may move freely through one another. According to the theory, the molecular weight between crosslinks for the phantom limit of the model [M_c(ph)] was calculated by the formula:

$$M_c(\mathrm{ph}) = \frac{(1-2/x)\rho_p V(\phi_{2c})^{2/3}(\phi_{2m})^{1/3}}{-\left[\ln(1-\phi_{2m})+\phi_{2m}+\chi(\phi_{2m})^2\right]} \tag{10}$$

where x is the junction functionality. Both the above models were applied to the optimum cured samples of all the three systems. The values obtained from the above models were compared with the M_c and are shown in Table 7. It was seen that the M_c values were close to M_c(aff). This suggested that in the equilibrium swelling state, the network deforms affinely.

Effect of temperature and thermodynamic functions

Diffusion studies were conducted at 25, 35 and 45 °C. The Q_∞ values were found to increase with increase of temperature because of increase in free volume. But the diffusivity and permeability values decreased with increase of temperature irrespective of the nature of crosslinks. The temperature dependence of transport coefficients (P, D^* and S) can be used for calculating the energy of activation for the process of diffusion and permeation from the Arrhenius relationship.

$$\ln X = \ln X_0 - E_x/RT \tag{11}$$

where X is P, D^* or S and X_0 represents P_0, D^*_0 or S_0, which are constants. E_x is the activation energy, R is the universal gas constant and T is the absolute temperature. Arrhenius plots of ln D^* or ln P versus $1/T$ were constructed and from the slopes of the curves, the values of the activation energy for diffusion E_D, and the activation energy for permeation E_p were estimated by linear regression analysis. The values of E_D and E_p are given in Table 8. The values were given for the t_{90} samples. From the values of E_D and E_P, heat of sorption ΔH_S was calculated. Heat of sorption was given by $E_P - E_D$.

Table 8 Values of activation energy and heat of sorption

Systems	E_D (kJ mol^{-1})	E_P (kJ mol^{-1})	ΔH_S (kJ mol^{-1})
CV	−7.51	2.17	9.69
DCP	−3.62	3.92	7.55
EV	−3.06	6.19	9.25

The activation energy for diffusion and permeation was found to be maximum for EV and minimum for CV system. All the ΔH_S values were found to be positive suggesting that Henry's type sorption predominates.

The molar equilibrium sorption coefficient (K_s) is defined as [22]:

$$K_s = \frac{\text{No. of moles of solvent sorbed at equilibrium}}{\text{Mass of the polymer}}. \tag{12}$$

These values were estimated and are given in Table 9. The trend in K_s value also supported our observation. The CV system showed the highest value and EV the lowest. The values increased with increase in temperature.

From the values of K_s, the enthalpy and entropy of sorption were calculated using the Van't Hoff relation [23, 24]

$$\ln K_s = \Delta S/R - \Delta H_s/RT \tag{13}$$

A typical Van't Hoff plot of ln K_s versus $1/T$ for CV, DCP and EV were constructed and the computed values of ΔH_s and ΔS are given in Table 10. The values of ΔS were negative in all cases, suggesting the retainment of liquid structure in the sorbed state within the polymer matrix. All values of ΔH_s were found to be positive, suggesting an exothermic process. It was interesting to note that these values were in close agreement with those calculated from the difference $E_P - E_D$. It again supported the fact that the molecular transport of methyl methacrylate through crosslinked NR matrix was a net effect of sorption, diffusion and permeation processes.

Table 9 Values of molar equilibrium sorption constant ($K_s \times 10^{-2}$ mol/g)

Temperature (°C)	Cure time	CV	DCP	EV
25	t_{90}	1.98	1.63	1.51
35	t_{90}	2.18	1.79	1.66
45	t_{90}	2.53	1.98	1.92

Table 10 Values of ΔH_s and ΔS

System	Cure time	ΔH_s (kJ mol^{-1})	ΔS (kJ mol^{-1})
CV	t_{90}	9.712	−0.0877
DCP	t_{90}	7.58	−8.779
EV	t_{90}	9.007	−4.64

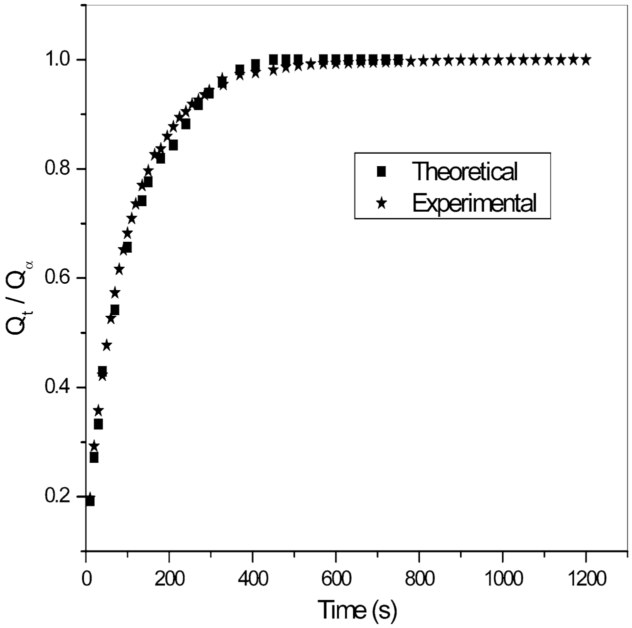

Fig. 6 Theoretical fitting of the experimental curve

Comparison with theory

The theoretical sorption curves were generated using equation [12]:

$$\frac{Q_t}{Q_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\frac{D(2n+1)^2\pi^2 t}{h^2}\right] \qquad (14)$$

Experimentally obtained values of the intrinsic diffusion coefficients were substituted in the equation and the resulting curve was shown in Fig. 6. The theoretical and experimental results were in agreement with only slight deviation. The experimental curve slightly deviated from the theoretical curve which was fully a Fickian mode of diffusion.

Conclusions

From the studies of diffusion of methyl methacrylate monomer through NR, it was clear that the chemical nature of crosslinks have an important role in determining the intrinsic diffusion coefficient D^*. EV and DCP system showed minimum uptake, CV system showed maximum uptake and this can be explained on the basis of difference in flexibility of polymer chains due to different types of crosslinks. ESR spectroscopy showed that the overall flexibility of NR network chains and free volume within the network increased as the temperature is raised to 45 °C. Motionally restricted regions in rubber network became more flexible at higher temperature and this enables the network to hold more monomer at higher temperature (45 °C) than at lower temperature. It was also clear that same extent of crosslinking could be achieved by curing the samples to a common rheometric torque. The value of n suggested a Fickian mode of diffusion with a slight deviation. Theoretical modelling of the experimental results closely fitted with the Fickian mode of diffusion with a slight deviation only. The intrinsic diffusion coefficient (D^*) increased with increase in temperature. The polymer–solvent interaction parameter χ was calculated which suggested a high polymer–solvent interaction at high temperature. Morphology of the swollen network was derived from the diffusion data and found that the network deformed affinely. The thermodynamic parameters were also investigated and it was found to be an exothermic process. The molecular transport of methyl methacrylate through crosslinked NR matrix was a net effect of sorption, diffusion and permeation processes.

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