Transport of MMA through SBR for fabrication of IPN based on Cross-linked SBR and PMMA

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Abstract

The diffusion and transport of inhibitor-free Methyl methacrylate (MMA) monomers through cross-linked Styrene Butadiene Rubber (SBR) have been studied at various temperatures and is compared with its transport through Natural Rubber (NR). SBR has been vulcanized by conventional, efficient and peroxide vulcanization techniques. The dependence of diffusion rate on the crosslinking system, cross -link density, size of the penetrant, thickness of the matrix and type of polymer matrices have been studied for the systems. The influence of temperature on the sorption has been evaluated using the diffusion data. The peroxide system showed lowest uptake and the effective system showed highest uptake. Mechanism of transport of MMA through SBR system was also reported in this paper and it follows Fickian mode of transport.

Keywords:

 Cross- linked SBR, NR, diffusion, sorption, Fickian mode of transport

1. Introduction

Transport of liquids through polymeric membranes is a key controlling factor in many of their applications. The transport of organic liquids through polymers is of technological importance in a variety of applications such as pervaporation, reverse osmosis and food packaging.[1] The transport properties of various engineering polymers like polyurethanes, cross-linked polystyrene, natural rubber and various synthetic rubbers have been extensively studied using organic solvents with various polarities and interacting groups and also using aqueous salt solutions of various acids by many researchers. The transport of small molecules through a polymer membrane happens due to random molecular motion of individual molecules.[2]

The diffusion process is a kinetic parameter and it depends on the free volume within the matrix, the nature of the polymer, crosslink density, the nature of fillers, the penetrant size, temperature and the degree of reinforcement.[3] In literature there are numerous studies on the transport properties of solvents through various types of polymers including elastomers[4,5], Interpenetrating Polymeric Networks (IPNs) and blends .[6,7] Unnikrishnan et al. [8] analyzed the role of the nature of crosslinks on the sorption and diffusion of aromatic

hydrocarbons through cross-linked natural rubber. Diffusion of aromatic solvents through SBR vulcanized by different vulcanizing agents and carbon black filled SBR were reported by George et al. [9]

The swelling and sorption behaviors of SBR in various liquids are of great interest[10], as SBR is a well-known polymer having extensive use in everyday life. SBR is a very important general purpose low cost synthetic rubber having wide range of applications in tyre and non-tyre fields. This is a random copolymer whose properties are determined   by the amount of styrene in the copolymer. In the present study, SBR having a styrene content of 25% has been selected for the present study, which shows the best elastomeric properties. The swelling of SBR samples in the presence of monomers like styrene[11], methyl methacrylate, acrylonitrile, butyl acrylate, etc., is of great research interest, since it constitutes the preliminary step in the preparation of interpenetrating polymer networks (IPN).[12, 13]

IPN is a special type of polymer blend. An IPN is an intimate combination of two polymers, where at least one of which is synthesized or cross linked in the immediate presence of the other. Unlike usual polymer blends, by forming networks with chemical bonds or permanent entanglements, IPNs exhibit high interfacial strength between the two polymers and have fewer phase separation problems. [14]

To prepare a rubber-based IPN, the swelling characteristics of the rubber in monomers are to be studied in detail. A clear and accurate knowledge about the swelling rate of the polymer in the monomers helps in controlling the composition, morphology and properties of the resulting IPN. However, no detailed investigation has been made so far on the kinetics of diffusion and sorption of methacrylate monomers through SBR cross linked by different curing systems such as conventional (CV), efficient (EV) and peroxide (DCP) and systems.

In this paper the swelling of SBR in methyl methacrylate monomer has been studied in the temperature range of 30-50°C. This will be the primary step for the development of IPN based on SBR and poly methyl methacrylate (PMMA) having various morphological features and property profiles. The SBR was vulcanized by different techniques, viz. conventional, efficient and peroxide vulcanization systems. The influence of different vulcanizing systems on diffusion properties is analyzed. The effect of crosslink density on sorption has been investigated. Finally the temperature dependence of diffusion is determined.

2. Experimental Details

2.1 Materials

Styrene butadiene rubber (Synaprene 1502) with 25% styrene content was used for this study. The natural rubber (NR) used was of ISNR-5 grade and was supplied by Rubber Research Institute of India (RRII). The MMA monomer (from Sigma Aldrich)is made free of inhibitor by washing with 0.1% NaOH and dried using anhydrous calcium chloride before using for diffusion experiments. All other compounding ingredients were of analytical grade. Important properties of SBR and MMA are summarized in the **Table: 1.**

Table1 Description of Materials used

(A) Description of material used

Material	Molecular weight (g/ mol)	Density (g/cm^3)	Solubility Parameter (Cal cm^{-3})$^{1/2}$	Source
SBR	$M_n = 4 \times 10^5$	0.930	8.1	ISRL
MMA	100.12	0.936	9.3	Sigma Aldrich

(B) Description of solvents used

Material	Molecular weight (g/mol)	Molar volume	Density (g/cm^3)	Boiling point (^{o}C)	Solubility Parameter (Cal cm^{-3})$^{1/2}$
Benzene	78.80	88.70	0.870	96.47	9.2
Toluene	92.14	105.9	0.867	110.6	8.9
Xylene	106.17	123.45	0.860	138.4	8.8

2.2 Preparation of rubber sheet

Mixing of SBR and other ingredients was done in a laboratory scale two roll mixing mill. The formulations of different mixes are given in **Table 2**. Cure properties of the compounded samples were determined using a Moving Die Rheometer at a temperature of 150 ^{o}C. Samples were then moulded by using an electrically heated hydraulic press under a pressure of 150 bar at150 ^{o}C. Only peroxide vulcanized 1phr NR (Natural rubber) sample (100gm.NR+1gm.DCP) is prepared as for the comparison purpose.

Table 2: Formulation of the SBR mixes

Ingredients	Efficient System	Conventional System	Peroxide System (1/2/4 phr)
SBR	100 gm.	100 gm.	100 gm.
Zinc oxide	5 gm.	5 gm.	-
Stearic acid	1.5gm.	1.5 gm.	-
CBS	1 gm.	1.5 gm.	-
TMTD	1.5gm.	-	-
MBTS	1.5gm.	-	-
MBS	-	1.5 gm.	-
Sulphur	0.6gm.	2 gm.	-
DCP	-	-	1/2/4 gm.

*phr -parts per hundred rubber

2.3 Diffusion experiments.

Circular samples were cut from the vulcanized sheets using a sharp-edged steel die. Thickness of the sample was measured at several points using a screw gauge. These circular samples were weighed and then dipped in 30 ml of methacrylate taken in diffusion bottles. Samples were taken out of the bottles at constant time intervals and the adhering solvent was

blotted off from the surface gently and then immediately weighed on a highly sensitive electronic balance. Weighed samples were immediately immersed into the test bottle. The weighing was continued until equilibrium swelling was obtained. In order to avoid the error due to the evaporation of the solvent weighing must be completed within 30 seconds. Transport properties were studied at 3 different temperatures, namely $30^{o}C$, $40^{o}C$, $50^{o}C$ using MMA.

Diffusion of solvent through different rubber samples was determined. Mole% uptake is determined using the formula [15],

$$Q_t \, (mol\%) = \frac{Mass \ of \ solvent \ sorbed \ by \ the \ polymer}{Molecular \ mass \ of \ the \ solvent / initial \ mass \ of \ polymer} \ 100 \tag{1}$$

Diffusion curves are obtained by plotting the mole percentage uptake (%Qt) for the solvent against the square root of time. At equilibrium swelling Q_t becomes Q_α.

3. Results and Discussion

3.1 Effect of nature of crosslinks
The diffusion curves of cross-linked SBR using different vulcanizing systems under a common torque are plotted in Figure1.
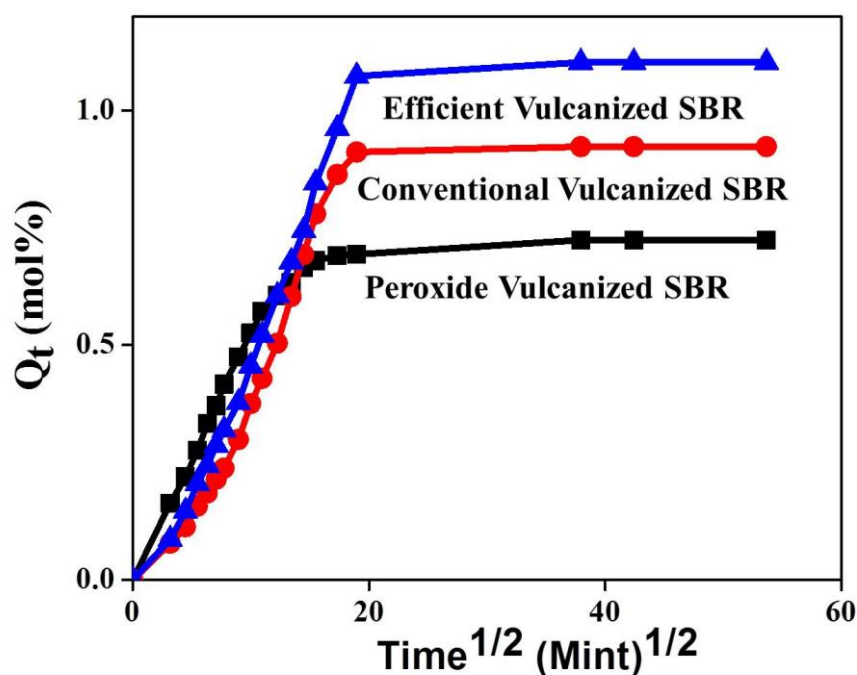

Figure1. Sorption curve showing the mole per cent uptake of optimum cured Efficient Vulcanized, Conventional vulcanized and Peroxide vulcanized SBR samples at 30°C.

From the figure, it is clear that Qt (mol%) values decreases in the order efficient vulcanized system > conventional vulcanized system > Dicumyl peroxide vulcanized systems (EV> CV> DCP). The difference in the solvent uptake value for SBR vulcanized with different vulcanizing systems may be due to the formation of different types of bonds between rubber chains during vulcanization. The Figure 2 depicts the general structural features of vulcanized networks. [16]
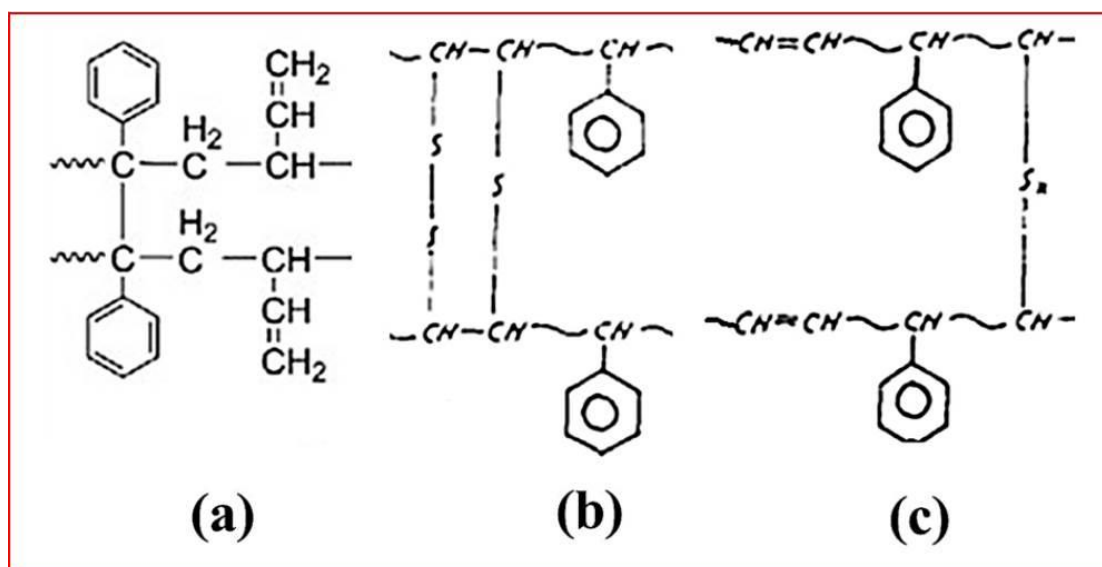
Figure2.Scheme showing the general features of vulcanized SBR network (all systems included).

The peroxide vulcanized sample contains only C-C linkages (a) with lowest solvent uptake, since they contain most rigid cross links which are resistant to permanent mobility. Contrary to our expectations, effectively vulcanized samples showed the highest amount of solvent uptake even though it contains mostly monosulphidic and disulphidic linkages (b),whereas SBR vulcanized with conventional system showed lower solvent uptake than EV systems even though it possess highly flexible polysulphidic linkages (c). However the observed anomaly could be explained on the basis of volume fraction of solvent swollen rubber (Vr) and can be determined using the relation.[17]

$$V_r = 1/\{1 + \left(\rho_p/\rho_s\right)\left(M_\alpha/M_0\right) - \left(\rho_p/\rho_s\right)\} \qquad (2)$$

M_∞ is the mass of solvent taken up at equilibrium and M_0 is the initial mass of polymeric sample. ρ_p and ρ_s represent the densities of polymer and solvent respectively. The **table3** shows the value of volume fraction of swollen rubber and in the order DCP> CV> EV.

Table3. Volume fraction of swollen SBR

Solvent	EV system	CV system	DCP system
MMA	0.4769	0.5213	0.5813

Volume fraction of swollen rubber is proportional to crosslink density. It can be concluded that as the volume fraction value decreases the crosslink density also decreases. As a result solvent uptake behavior follows the order DCP< CV< EV.

3.2. Effect of crosslink density

The nature of interlocking is the one of the major controlling factors in the physico–mechanical and thermal properties of polymers. The assessment of the interaction of polymer with solvent is very much essential to understand the extent of interlocking. The cross-linking content in polymer can act as one of the controlling factor in its transport behavior. Here we consider the sorption behavior of 1phr, 2phr and 4phr SBR (peroxide vulcanized) samples in MMA. Result can be depicted in the Fig .3. As the crosslink density increases, penetration of solvent is hindered by excess crosslinks in the system. This conclusion is crystal clear from the Figure3.
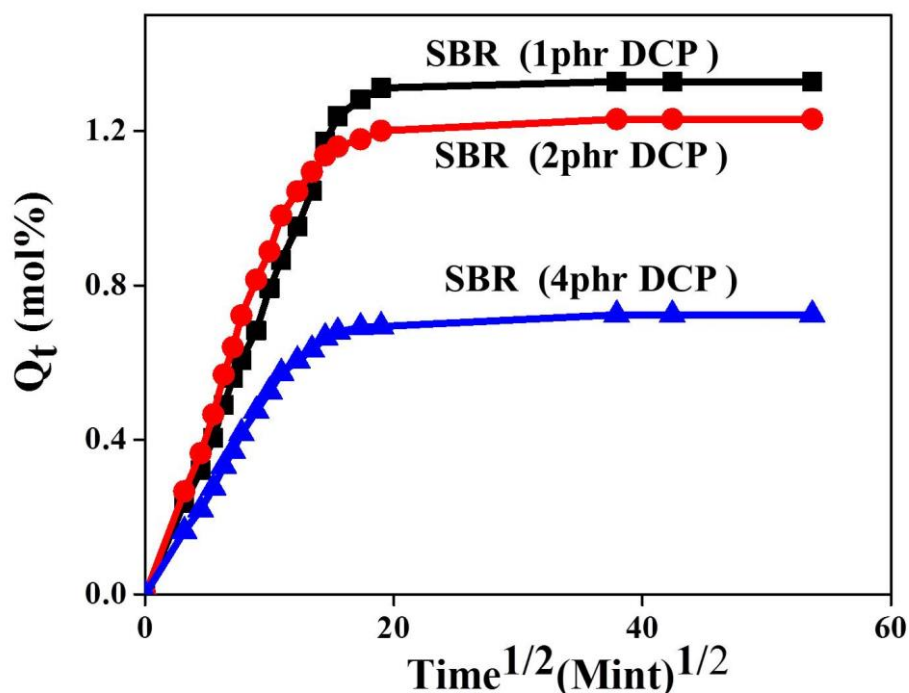

Figure3. Sorption curve showing the mole per cent uptake of optimum cured 1phr, 2phr and 4phr peroxide Vulcanized SBR samples at 30°C.

3.3 Effect of Penetrant Size

There is a systematic trend of sorption behavior of liquids of different molecular sizes.[18] With an increasing size of the solvent molecules (Methyl methacrylate [MMA] to Glycidyl methacrylate [GMA]), there is a decrease in the value of Qt mol%, when these liquids flowing through the 1phr peroxide SBR sample. As the penetrant size increases, corresponding Q_∞-value decreases. By increasing the size of penetrant, the resistance offered by the polymer to the transport of the solvents through the matrix is enhanced. Therefore, the uptake was low for penetrants of higher size. In other words, the high molecular weight solvent shows the lowest uptake and the low molecular weight shows the highest uptake. The increase in uptake with decrease in penetrant size may be due to the lower activation energy required for the activation of the diffusion process. It is clear from the Fig:4.
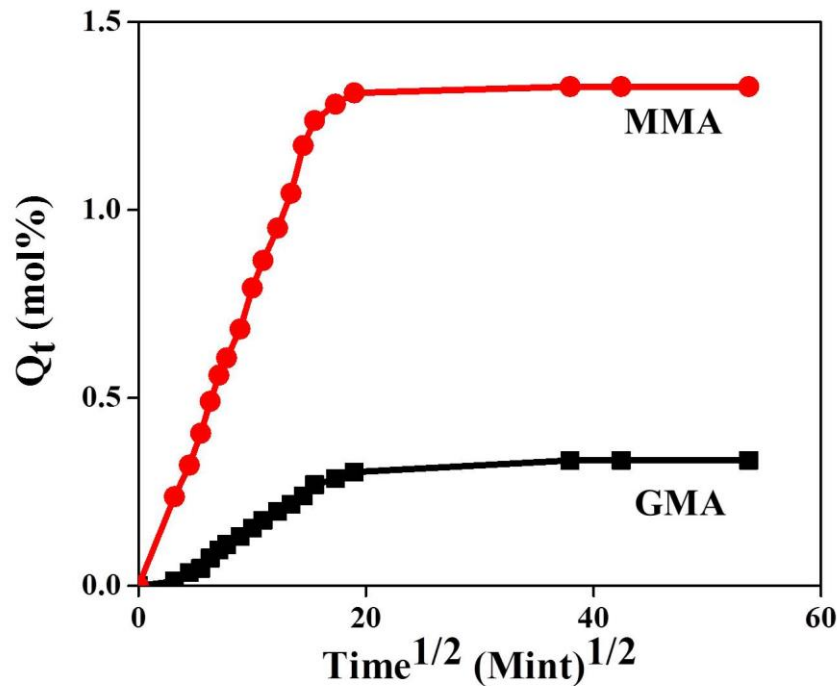
Figure4. Sorption curve showing the mole per cent uptake of MMA and GMA through optimum cured SBR (1phr peroxide Vulcanized) sample at 30°C.

3.4 .Effect of polymer matrix

Here we compare the sorption behavior of MMA through 1phr NR and 1phr SBR (both are peroxide vulcanized) samples. The results are depicted in the Figure 5.
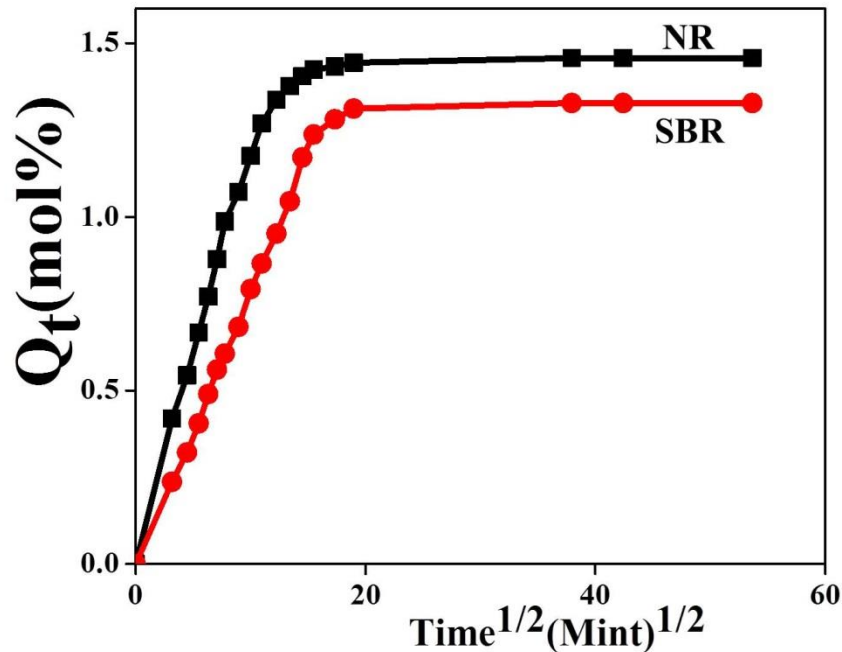

Figure5. Sorption curve showing the mole per cent uptake of MMA through optimum cured 1phr NR and 1phr SBR (peroxide vulcanized) samples at 30°C.

NR sample possess high Q_t value than SBR sample because bulkier benzene side rings in SBR hinders the solvent penetration. Shape and orientation of functional groups in polymer matrix have deciding role in its transport behavior.

3.5. Effect of thickness of polymer Matrix

Here we compare the sorption behavior of 1phr peroxide SBR samples with variable thickness (0.8mm,2mm and 6mm) and are depicted in Fig:6 .As the thickness of the sample decreases rate of sorption increases .This tendency follows Fick's laws of diffusion.[19]
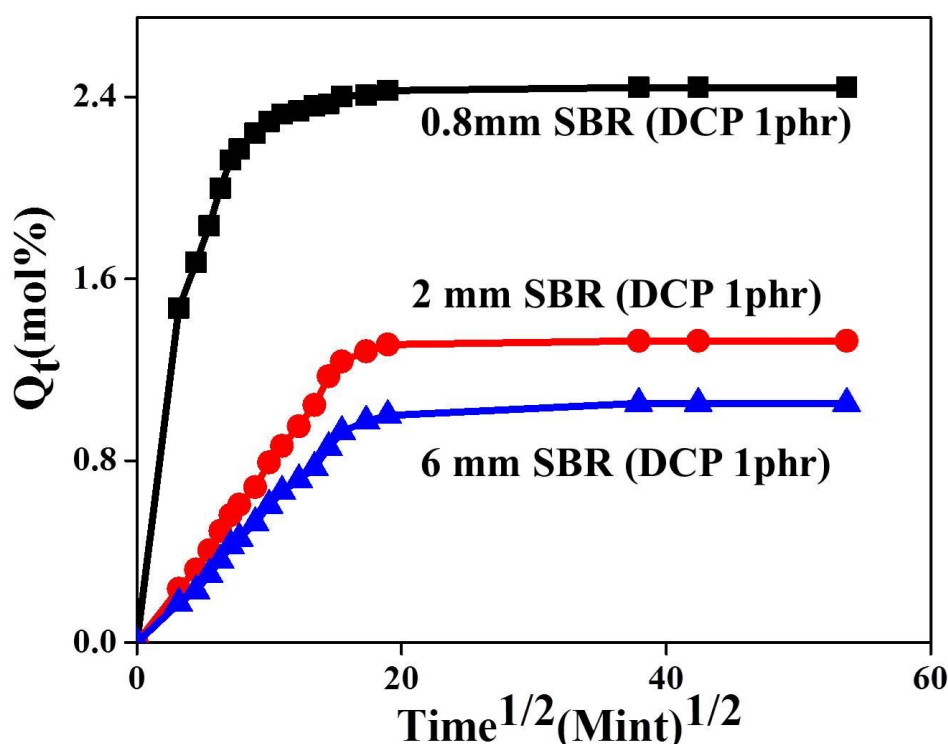

Fig:6. Sorption curve showing the mole per cent uptake of MMA through optimum cured 1phr SBR (peroxide vulcanized) samples with variable thickness at 30°C.

3.6. Effect of temperature

Diffusion of MMA through SBR sample was conducted at 30, 40 and 50°C in order to study the effect of temperature on the diffusion phenomenon in SBR.As the temperature increases the rate of diffusion increases. The Q_∞ values show increased solvent uptake with increasing temperature. This is mainly due to two reasons. As the temperature enhances, there is an increase in free volume of the SBR system leading to an increase in segmental motion of the polymer matrix. The gain in kinetic energy by the solvent molecules is resulted from the increased number of collisions. It is also found that the slope of the linear portion increases with temperature showing that the transport properties are temperature dependent. The effect of temperature on diffusion is clearly proved in Fig:7.
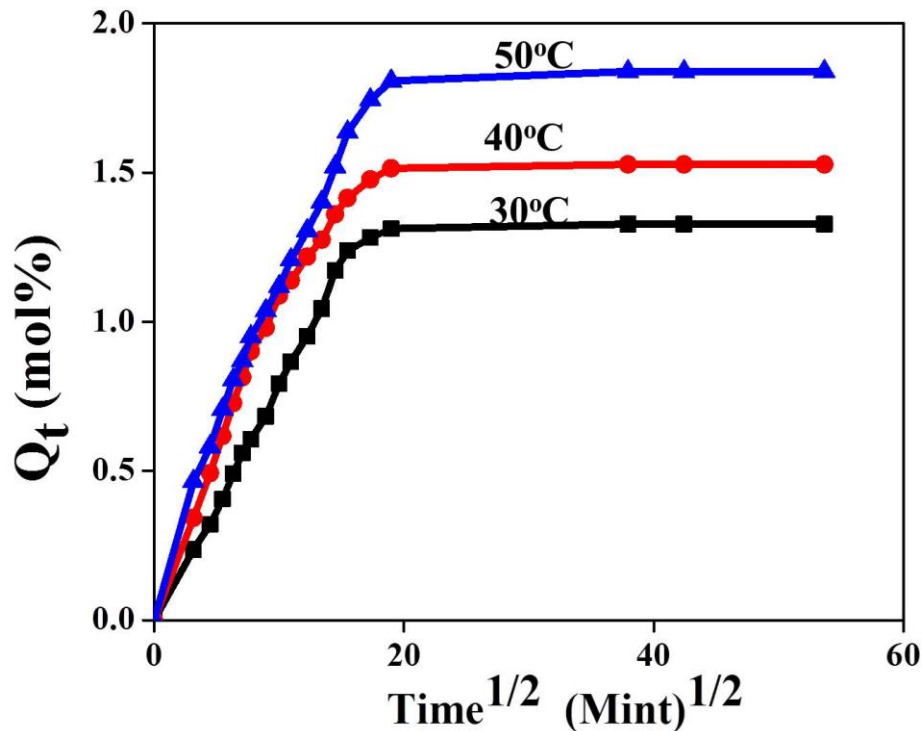
Fig:7. Sorption curve showing the mole per cent uptake of MMA through optimum cured 1phr SBR (peroxide vulcanized) samples at different temperatures.

3.7 Transport Mechanism
The transport properties of polymeric membranes can be followed by the empirical equation [20],

$$log\left(Q_t/Q_\infty\right) = log k + n log t \qquad (3)$$

Where Q_t and Q_∞ are the mol % increase in uptake at time t and at equilibrium respectively. k is a constant. The value of n and k are determined by linear regression analysis. In all cases the correlation coefficients were found to be 0.99

The slope of the plot of $log\left(Q_t/Q_\infty\right)$ versus $log t$ gives the value of **n** which indicates the mechanism of transport and its Y intercept gives the value of k which depends upon the structural significance of polymer as well as its interaction with solvent.

The value of "n" gives an insight into the mode of transport and its relations with relaxation of polymer chains.[21] This information can be summarized as follows. When value of n = 0.5, the rate of diffusion of solvent molecules (r_1) is less than that of the rate of relaxation of polymer chains (r_2) and is called Fickian mode of transport. When r_1 is greater than r_2, it adopts non-Fickian mode of transport with n =1. If n varies from 0.5 to1, the system adopts anomalous mode of transport where r_1 is approximately equal to r_2.

'n' and 'k' values at different temperature for SBR(peroxide vulcanized) samples are summarized in the table 4.

Table4. Values of n and k for MMA through SBR at different temperatures

System	Solvent	Temperature	n values	k values
SBR (peroxide-1phr)	MMA	30°C	0.5126	-1.292

SBR (peroxide-1phr)	MMA	40°C	0.4981	-0.2661
SBR(peroxide-1phr)	MMA	50°C	0.5081	-0.3821

In all the conditions, transport of MMA through peroxide vulcanized SBR system follows Fickian mode of transport. The Fick's laws are usually followed by rubbery polymers. Here SBR does not show deviation from accepted law. There is no regular trend in 'K' values.

4. Conclusions

In conclusion, this study on the diffusion of MMA monomer through SBR shows following interesting results. Among different vulcanization systems of SBR, the sorption rate is in the order efficient vulcanized system > conventional vulcanized system > Dicumyl peroxide vulcanized systems (EV> CV> DCP). As the crosslink density of a particular vulcanized system increases, the rate of diffusion decreases. The diffusion rate of solvent through SBR system decreases with enhancement in the size of penetran . For the same vulcanized system, NR poses high sorption rate than SBR system. As the thickness of the SBR sample decreases, its sorption rate increases. The diffusion of MMA through SBR is a temperature dependent process and as the temperature increases, rate of diffusion increases. Diffusion of MMA through peroxide vulcanized SBR samples follow Fickian mode of transport. From the above results, we can conclude that sorption of MMA in SBR can take place successfully and are governed by existing laws of diffusion. This study could be act as a pretest for the synthesis of IPN   based on SBR and PMMA.

Acknowledgements

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