

TRANSPORT OF METHYL METHACRYLATE MONOMER THROUGH NATURAL RUBBER

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ABSTRACT:

The diffusion and transport of inhibitor-free methyl methacrylate monomer through cross linked 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 cross links 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 cross links 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 cross linking 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.

Keywords: *HPLC, PDA, stability indication method, drug.*

1. 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 satisfactory 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 Harrogopad 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 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 c-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, acrylonitrile, 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 v are determined. Efforts are also made to investigate the morphology of the NR network in equilibrium swelling state. Thermodynamic parameters are also computed.

2. MATERIALS ARE USED:

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.

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.

3. PROPOSED METHODOLOGY:

Sorption curves were analysed to obtain conclusions from the diffusion experiments. Figures 1, 2 and 3 show the diffusion curves of NR cross linked 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 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.

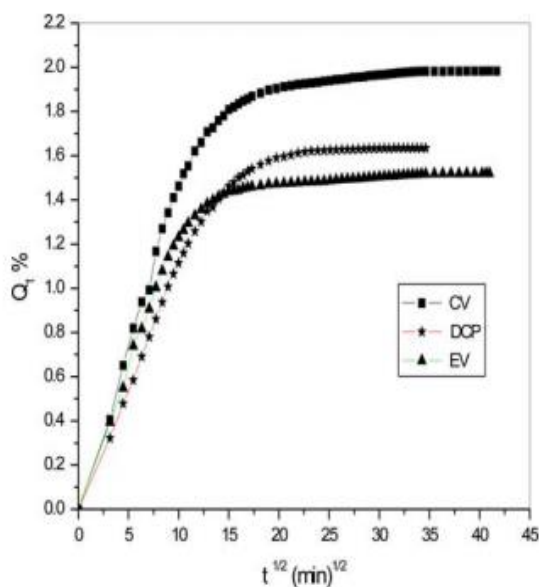


Fig.3.1. Sorption curves showing the mole percent uptake of optimum cured CV, DCP and EV at 25 C.

5. CONCLUSION:

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 v 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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