MOLECULAR TRANSPORT OF CHLOROMETHANES THROUGH EPDM/PVC SYSTEMS

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ABSTRACT

The transport behavior of EPDM/PVC composites has been investigated using the three halogenated hydrocarbons; methylene chloride, chloroform and carbon tetrachloride, which are part of the homologous series of the chloromethanes, as probe molecules. Sulphur and peroxide were used for crosslinking the matrix. The dependence of the transport property on crosslink density, nature of penetrants and type of crosslinking system was studied. A peculiarity can be seen among the group of chloromethanes, i.e. sorption increases with increasing number of chlorine atoms or molar volume, as it would be predicted from simple solubility parameter considerations. The mechanism of transport was found to be deviated slightly from Fickian trend. The differences in the equilibrium uptake can be explained on the basis of morphological changes.

Key words: Swelling, Diffusion, Crosslinking, Composites.

INTRODUCTION

Long-term stability and performance of polymeric membranes in solvent and mixed solvent media can be reduced due to sorption and swelling of the membrane matrix. For this reason quantification of sorption and swelling is of major importance for the development of future applications of membrane processes in solvent and mixed solvent media. It is important to understand phenomena like swelling and sorption that contribute to a reduction of the life-time of the membrane. The transport phenomenon is a complex process with a variety of industrial applications. Solvent sorption and diffusion are the limiting factors of polymer end-use applications because these processes might change the mechanical properties and sometimes cause destruction in polymer structures. An investigation of the causes of such phenomena requires a thorough knowledge of the solvent-transport characteristics. Polymer composites have attracted in recent years a great deal of interest. In most cases, fillers are used as additives for improving the behavior of the host polymeric matrix[1].

Reports on the transport of small molecules into selected polymer membranes are available in the literature[2-9]. The sorption equilibria and kinetics of three volatile organic compounds (VOCs) -benzene, chloroform, and acetone- in a newly developed divinyl-terminated poly (dimethylsiloxane) (PDMS[vi]) -oligo polymer were studied[10]. The sorption uptake of each VOC by the polymer was measured gravimetrically at different VOC partial pressures at a constant temperature and at different temperatures between 24 and 50°C. The rate of VOC sorption was monitored until equilibrium was established. Jacob et al.[11], evaluated the water

absorption characteristics of the natural rubber composites with reference to fiber loading. The influence of temperature on water sorption of the composites is also analyzed. Moisture uptake was found to be dependent on the properties of the biofibers. The mechanism of diffusion in the gum sample was found to be Fickian in nature, while in the loaded composites, it was non-Fickian. Sisal and oil palm fibers were subjected to different treatments such as mercerization and silanation. The effect of chemical modification on moisture uptake was also analyzed. Chemical modification was seen to decrease the water uptake in the composites.

EXPERIMENTAL

Ethylene propylene diene monomer (EPDM) with an E/P ratio of 62/32 and a diene content of 3.92% was obtained from Herdilla Unimers, New Mumbai. Poly vinyl chloride (PVC) was obtained from Sigma Aldrich. The additives such as sulphur, dicumyl peroxide, zinc oxide, stearic acid, and mercapto benzothiazyl disulphide (MBTS) used were of commercial grade. The fuels were of commercial grade.

The composites EPDM/PVC with different PVC loading and crosslink systems were prepared on a two roll mixing mill (150 x 300 mm), with a nip gap of 1.3 mm and a friction ratio 1 : 1.4. The compounding formulations are given in Table 1. The different crosslinking systems in the study were sulphur (S) and peroxide (DCP). The cure characteristics of the compounds were determined according to ASTM d 2084 by using Zwick rheometer model ODR at 160°C. The composite membranes were compression moulded at 160 degree for optimum cure time using a hydraulic press having electrically heated platens, under a load of 30 tones.

Table 1: Formulation of Mixes (phr)

Ingredient	Vulcanizing system	
	Sulphur	**DCP**
EPDM	100	100
PVC (varying amount)	(0, 2.5, 5, 7.5, 10)	(0, 2.5, 5, 7.5, 10)
Zinc oxide	4	-
Stearic acid	2	-
MBTS	1.5	-
Sulphur (varying amount)	2,3	-
Dicumyl peroxide	-	4

Examination of sorption characteristics

For diffusion experiments, circular samples of diameter 19.6 mm and 2 mm thickness were punched out from the vulcanized sheets and were dried in vacuum desiccators over anhydrous $CaCl_2$ at room temperature for about 24 hours. The original weights and thickness of the samples were measured before sorption experiments. They were then immersed in solvents (15-20 mL) in closed diffusion bottles, kept at constant temperature in an air oven. The samples were removed from the bottles at periodic intervals of 30 minutes, dried for 5-10 s between filter papers to remove the excess solvent on their surfaces and weighed immediately using an electronic balance (Shimadzu, Libror AEU-210, Japan) that measured reproducibly within ± 0.0001 g. They were then placed back into the respective test bottles. The process was continued until equilibrium swelling was achieved. Since the weighing was done within 40 s, the error associated with the evaporation of solvents is negligible. The experiments were duplicates or triplicates in most cases and the deviation was within ± 0.08 to 0.1 mole percentage. The results of the sorption experiments have been expressed as moles of solvent taken by 0.1 Kg of the polymer blend sample, *Qt* (mol %).

$$Qt = \frac{\text{Mass of solvent sorbed/Molar mass of solvent}}{\text{Mass of polymer sample}} \times 100$$

Morphology

The samples for Field Emission Scanning Electron Microscopy (FESEM) were prepared by cryogenically fracturing them in liquid nitrogen. They were sputter coated with gold and morphology examination were performed on a scanning electron microscope (JEOL-JS IN-T330-A-SEM; ISS Group, Whittington, Manchester, U.K).

RESULTS AND DISCUSSION

Effect of PVC Loading

Fig. 1 shows the amount of carbon tetrachloride sorbed throughs pure EPDM and EPDM/PVC systems. It has been observed from the figure that pure EPDM shows higher sorprtion than the PVC loaded system due to the flexible nature of the chains that creates more free volume in the matrix. Adding rigid PVC to EPDM phase improves the barrier property due to the reduction in free volume or microvoids. Increase in PVC content also restricts the macromolecular chain mobility resulting in a tortuous path for the diffusion of the penetrants.
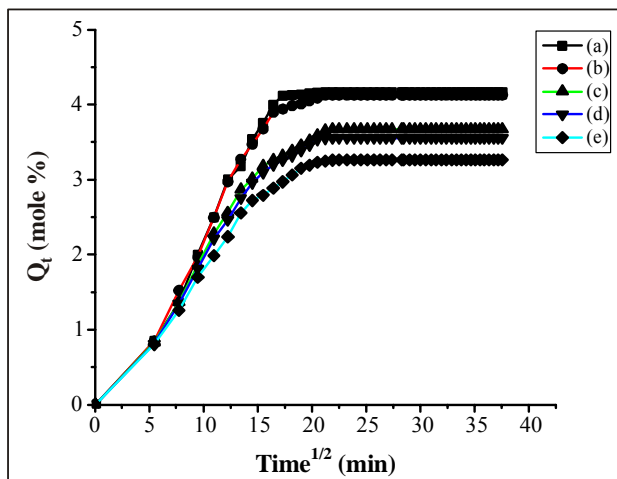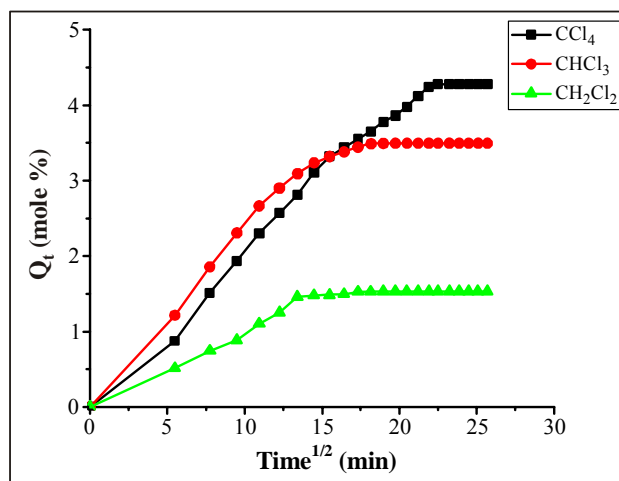

Fig. 1: Mole % uptake of CCl$_4$ in dynamically vulcanized EPDM/PVC composites:
(a) 100/0 EPDM/PVC, (b) 100/2.5 EPDM/PVC, (c) 100/5 EPDM/PVC,
(d) 100/7.5 EPDM/PVC and (e) 100/10 EPDM/PVC

Effect of penetrants

Fig. 2 shows the effect of penrtrant size on the sorption and diffusion of three chloromethanes through sulphur cured 100/5 EPDM/PVC composite It follows from the graph that the trend is in the order: carbon tetrachloride > chloroform > methylene chloride i.e., a systematic trend with penetrant size was not observed. The unusual behavior can be explained as follows:

The permeation through any matrix is a combination of sorption and diffusion. The kinetics of diffusion depends on the molecular mass of the solvent whereas sorption depends on the difference in the solubility parameter values[12]. The highest uptake exhibited by carbon tetrachloride is due to the dominance of the solubility parameter over the molecular mass of the solvent during transport. The smaller the difference in solubility parameter, the greater is the affinity of polymer towards the solvent. The Qt value of

methylene chloride is very low as solubility parameter value is far from EPDM. It exceeds size effect of methylene chloride on sorption. Between chloroform and carbon tetrachloride upto four hours, CCl_4 shows low Qt value due to the fact that the diffusion of the larger carbon tetrachloride has a retarding influence compared with chloroform[13]. When the sorption rate increases after that, the size effect is exceeded by solubility product i.e., sorption increases with increasing number of chlorine atoms or molar volume, as it would be predicted from simple solubility parameter considerations. So in chlorinated hydrocarbons, the main deciding factor is solubility parameter. A similar trend has been observed for poly (ethylene-co-vinyl acetate) membranes for aliphatic hydrocarbons[14].

**Fig. 2: Mole % uptake of chloromethanes in (sulphur cured) dynamically vulcanised
100/5 EPDM/PVC composite**

Effect of type of vulcanization

Fig. 3 shows the effect of the type of vulcanization techniques on the sorption behavior of EPDM/PVC membranes, using carbon tetra chloride as penetrant. It is observed that dynamically vulcanized samples showed a lower swelling compared to the corresponding statically vulcanized one. The dynamic vulcanization produces a fine dispersion[15] of the rigid PVC particles in EPDM matrix as shown in Fig. 4.
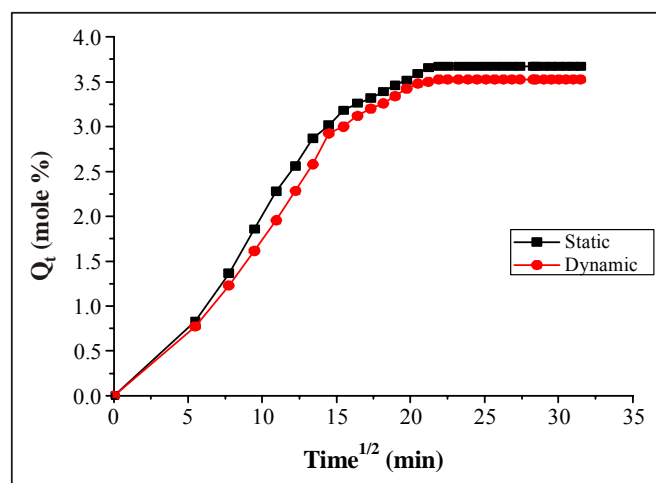
**Fig. 3: Effect of type of vulcanization on CCl_4 uptake in sulphur cured
100/5 EPDM/PVC composite**
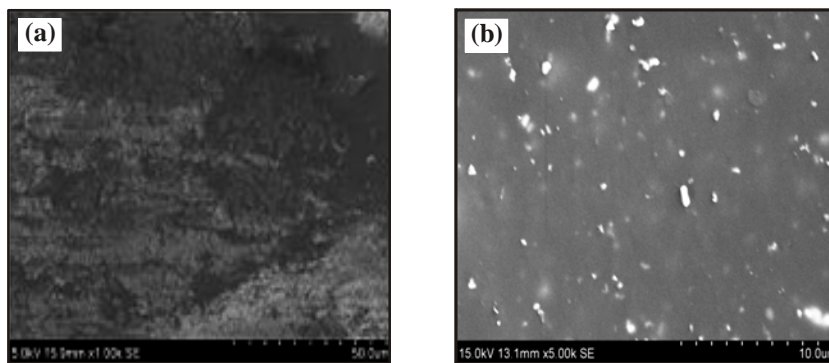
Fig. 4: Scanning electron micrographs of sulphur cured 100/7.5 EPDM/PVC composites;
(a) Statically vulcanized (b) Dynamically vulcanized.

Swelling mechanism

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

$$\text{Log } Q_t/Q_\infty = \log K + n \log t$$

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 solvent and polymer and on the structure of the polymer. The value of n determines the mode of diffusion mechanisms[16]. The values of n and K are given in Tables 2 and 3. Plots of log (Q_t/Q_∞) versus log t showed that the values of n were between 0.5 and 1 and this suggested that the mechanism of transport slightly deviates from normal Fickian behavior observed for conventional elastomers. There is no systematic variation in the value of 'n' with respect to PVC loading.

Table 2: Values of n and K for different PVC loading

| EPDM/PVC	n	K x 10^2 (g/g min^2)
100/0	0.661	2.32
100/2.5	0.697	1.99
100/5	0.613	3.04
100/7.5	0.636	2.76
100/10	0.578	3.65

Effect of concentration of sulphur

The Q_t decreases with increase in sulphur concentration. This is due to crosslinking of rubber phase and thereby exerting greater resistance to the flow of solvent. Fig. 5 shows the effect of sulphur concentration on sorption values of EPDM/PVC composite. The crosslink density increases with increase in sulphur concentration.

Effect of crosslinking system

It can be seen that the solvent uptake is higher in sulphur vulcanized system than peroxide cured system. This can be explained by the difference in the nature of the networks possible using sulphur and peroxide systems as can be seen from the Fig. 6. The mono, di and polysulphidic linkages in sulphur system

impart high chain flexibility to the polymer network when compared to the DCP system where only rigid C-C linkages are present.
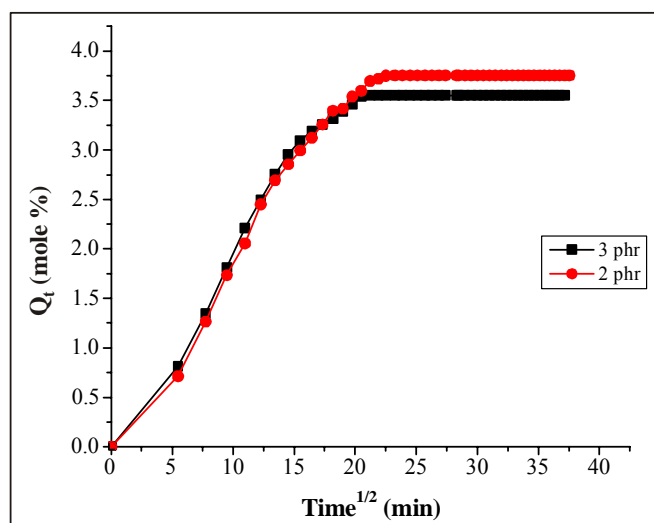
Fig. 5: Effect of sulphur concentration on CCl$_4$ uptake in 100/5 EPDM/PVC composite
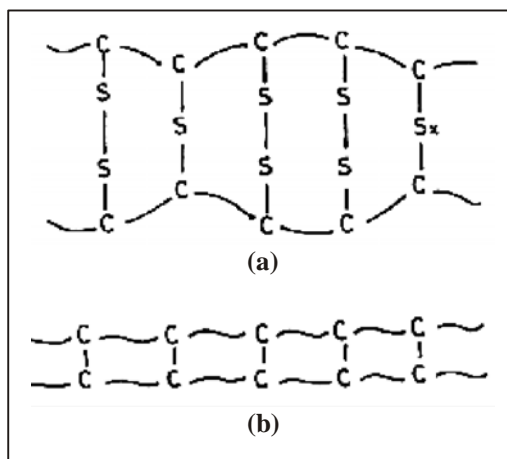
**Fig. 6: Structure of networks formed by different vulcanization techniques;
(a) sulphur (b) peroxide**

CONCLUSION

The transport characteristics of EPDM/PVC composites were studied using carbon tetrachloride, chloroform and methylene chloride as penetrants, with special reference to filler loading, crosslinking systems, concentration of sulphur and penetrant's nature. The diffusion of halogenated hydrocarbon solvents through EPDM/PVC composites revealed that the diffusion was found to decrease with an increase in PVC content, which was attributed to the rigid nature of PVC particles. The sample crosslinked by DCP showed the lowest equilibrium uptake compared to the sample with sulphur vulcanization mode. This can be explained in terms of the differences in the nature and distribution ofcrosslinks in the network. A peculiarity can be seen among the group of chloromethanes, i.e. methylene chloride, chloroform and carbon tetrachloride. Sorption increases with increasing number of chlorine atoms or molar volume, as it would be predicted from simple solubility parameter considerations. The values of n suggest that the mechanism of transport is anomalous.

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