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Organic vapor permeation through membranes based on ethylene propylene diene monomer and polyvinyl chloride

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Abstract

Composite membranes based on ethylene propylene diene monomer (EPDM) and polyvinyl chloride (PVC) has been prepared. The vapor permeation studies were conducted with aromatic hydrocarbons and aliphatic alcohols for the membrane characterization. Special attention has been given to the amount of PVC in the membrane, size of penetrant and also type of vulcanization. The permeability was found to decrease with increase in PVC content due to the stiff and rigid nature of PVC. The field emission scanning electron microscopy of the membranes showed a two-phase morphology. Here, the PVC is dispersed in the continuous EPDM phase. It was found that the permeability decreased with increase in the size of the penetrant. Different types of miscible liquid mixtures have been analyzed for finding out the separation efficiency of the membranes. In the case of benzene/propanol mixture, it has been found that when the concentration of benzene increases, the vapor permeation rate increases, indicating high interaction of benzene toward the composites.

Keywords

Polymer composite membranes, permeation separation, characterization

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Introduction

The investigation on permeability and selectivity of a membrane is important to understand its fundamental functions for practical applications.[1-3] Permeation process through any material is a combination of sorption and diffusion and occurs by a solution-diffusion mechanism,[4] which can lead to useful levels of selectivity. Each component in the vapor feed dissolves in the membrane polymer at its upstream surface, much like gases dissolve in liquids, then diffuse through the polymer layer along a concentration gradient to the opposite surface where they 'evaporate' into the downstream gas phase.[5] The components in the membranes usually consist of separate phases and so the material needs to be treated as a composite. The presence of crystallinity reduces permeability, and good membranes should be capable of high fluxes. The usual physical picture is to think of a semi-crystalline polymer in terms of a simple two-phase model; one phase being amorphous and the other being crystalline. Usually, the continuous phase dominates the permeation process.[6]

Vapor permeation process has now emerged as a new industrial technology and is considered as an attractive alternative to pervaporation.[7] The process offers the unique feature of studying the transport process of a single permeant through a dense membrane under various upstream activities and promises greater simplicity in technical design and significant opportunities for energy savings. Using this technique, even difficult separation of azeotropic mixture can be performed. This process offers direct practical conclusion for the understanding and rational design of volatile organic components' (VOCs) vapor recovery from contaminated air stream and is more advantageous than classical VOC control process. In order to obtain a good permeation rate and a high degree of separation for a feed mixture, it is essential to choose the right membrane as well as the optimum operating conditions. Since usually a single polymer does not possess the optimum properties for a given separation, new membranes have to be developed to achieve the desired balance of properties.[8] Novel membranes can be prepared by various methods like copolymerization, blending and use of thin film composites.

There exist interesting reports on the vapor permeation through different polymer membranes.[9-11] It has been reported that the permeation depends upon a number of factors like composition, method of formation, type of cross-linking agents used, nature and size of the penetrants, temperature, etc. For example, a decrease in the diffusivity with an increase in the size of penetrant has been reported by many investigators.[12-14] Haraya and Hwang[15] have conducted permeation studies in a series of polymers for selecting appropriate polymers for the separation of O_2/Ar mixtures. Masoud et al.[16] studied gas barrier properties of PP/ethylene propylene diene monomer (EPDM) blend composite and found that the permeability decreased with PP content in the composite. Anil et al.[17] studied the permeability of n-alkanes through EVA membranes and found that the rate increased with the introduction of cross-links to a certain extent due to the 1 increase in free volume of the crystalline polymer. Sowmya et al.[18] tested composite membranes for recovering VOCs from dilute aqueous solutions and found that this method can offer potentially cleaner and cost-effective means of recovering VOCs from contaminated streams.

EPDM, a nonpolar polymer, exhibits excellent resistance to ozone, water, acids and alkalies, while accommodating fillers/plasticizers and retaining desirable physical and mechanical properties.[19] These characteristics have allowed EPDM to be employed as a membrane material for separation operations, which primarily include separation of organics from aqueous stream. However, it performs poorly when exposed to oil and solvents. The other component polyvinyl chloride (PVC) is one of the most widely used polymers in many industrial applications.[20] PVC possesses a low level of crystallinity and derives its rigidity as a plastic from its high glass transition temperature. It is a chemically stable material and is resistant to acids, solvents and oil due to its polar nature. The barrier property of EPDM can be considerably controlled by dispersing the PVC particles in the EPDM matrix.

The objective of the present work is to investigate the permeating capabilities of organic liquid vapors, both aromatic and aliphatic through EPDM/PVC composite membranes, with particular attention to the effect of PVC loading, penetrant size and type of vulcanizing method. Different types of miscible liquid mixtures, including azeotropes, have been analyzed for finding out the separation efficiency of the membrane.

Experimental details

Materials

EPDM with an E/P ratio of 62/32 and a diene content of 3.92% was obtained from Herdilla 2
Unimers (Navi Mumbai, India). PVC was obtained from Sigma Aldrich. The additives such as sulfur, zinc oxide, stearic acid and mercapto benzothiazyl disulfide (MBTS) used were of commercial grade. The solvents benzene, toluene, xylene, 1-propanol and 2-propanol were obtained from Nice chemicals (Cochin, India). They were distilled twice before use to ensure purity.

Preparation of membranes

The mixing of EPDM with PVC in different ratios was done on a two roll mixing mill (150 300 mm), with a nip gap of 1.3 mm and a friction ratio of 1:1.4. The EPDM was masticated for 2 min and PVC powder was then added. After 4 min, other ingredients were added in the following order: zinc oxide, stearic acid, MBTS and sulfur. The processing time after the addition of each component was about 2 min. Details of formulations are given in Table 1. The cure characteristics of the compounds were determined according to ASTM D2084 using Zwick rheometer
3 model ODR at 160 C. The composite membranes were compression moulded at 160 for optimum cure time using a hydraulic press having electrically heated platens, under a load of 30 tons. The average thickness of the membranes was 0.23-0.25 mm. Dynamically vulcanized samples were prepared using Brabender Plasticorder Model PLE 331. The samples were compression moulded as in static vulcanization method.

Table 1. Formulation of mixes (phr)

Ingredients	Amount (g)
EPDM	100
PVC	Varying amounts (2.5, 5, 7.5 and 10)
ZnO	4
Stearic acid	2
MBTS	1.5
S	3

EPDM: ethylene propylene diene monomer; PVC: polyvinyl chloride; ZnO: zinc oxide; MBTS: mercaptobenzothiazyl disulfide; S: sulfur.

Vapor permeability

The vapor permeability was determined at room temperature by the measurement of the weight loss of small vials filled with solvents and tightly closed by a membrane of 0.23-0.25 mm thick. The weight loss was proportional to the time, area of membrane and pressure inside and outside of the vials (considered zero outside) and inversely proportional to the thickness of the membrane. The results of the vapor permeation results were expressed by plotting the amount of vapor permeated, M_t versus square root of time, t. The experiments were conducted in triplicates in most cases and the deviation was within +0.001-0.003 mole percentage.

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 was performed on a scanning electron microscope (JEOL-JS IN-T330-A-SEM; ISS Group, Whittington, Manchester, UK).

Results and discussion

Effect of PVC loading

Figure 1 shows the amount of benzene vapors permeated through pure EPDM and 100/2.5 EPDM/PVC system. It has been observed from the figure that EPDM membrane shows higher permeability than the PVC loaded system due to the flexible nature of the chains that creates more free volume in the matrix. Adding PVC to EPDM phase improves the barrier property due to the combination of two phenomena: the decrease in the area available for diffusion as a result of impermeable PVC occupying free volume and the increase in the distance a molecule must travel to cross the film as a result of the tortuous path it follows around the impermeable PVC particles. Figure 2 shows a schematic representation of permeability through pure EPDM and EPDM/PVC composites. Figure 3(a) and (b) show the FESEM of pure EPDM and EPDM/PVC 100/2.5 systems, respectively. Figure clearly shows the PVC domains that distributed in the

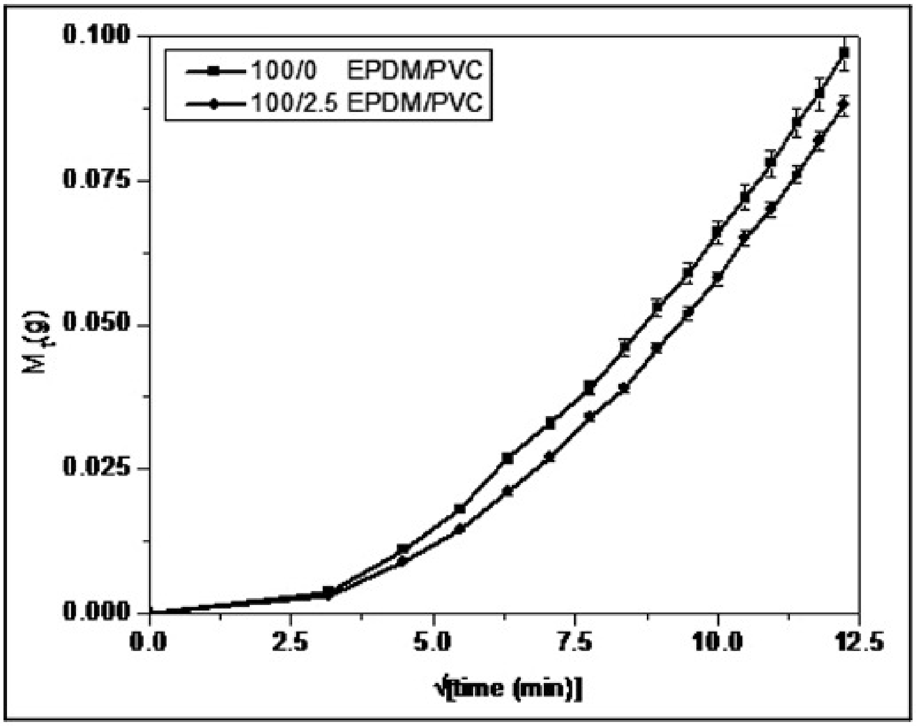

Figure 1. Effect of PVC loading in EPDM on vapor permeation of benzene. PVC: polyvinyl chloride; EPDM: ethylene propylene diene monomer.

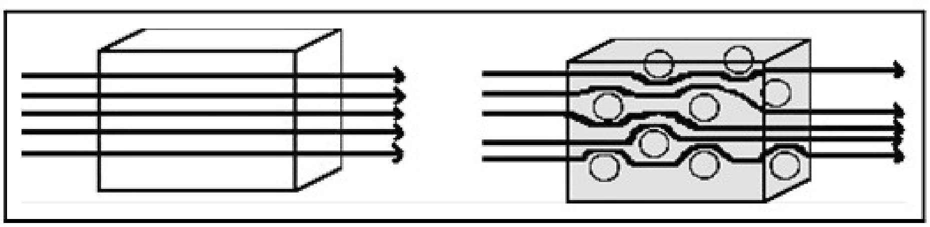

Figure 2. Schematic representation of permeation through (a) pure EPDM and (b) EPDM/PVC composite. PVC: polyvinyl chloride; EPDM: ethylene propylene diene monomer.

EPDM matrix. This restricts the path of solvent vapors. Similar results were reported earlier.[21-23]

Effect of amount of PVC

Figure 4 shows the amount of benzene permeated through membranes with varying amount of PVC. It can be seen that the vapor permeation decreases with increase in PVC content in the composite up to 7.5 phr PVC and then the permeability increases in 10 phr

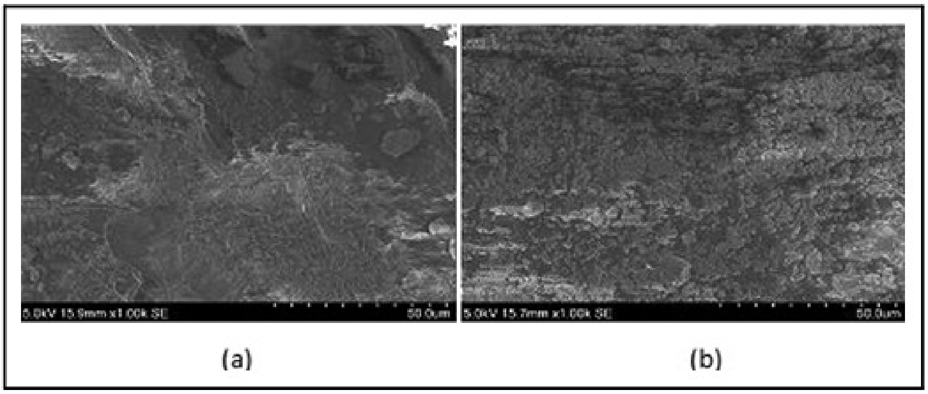

Figure 3. Field emission scanning electron micrograph of (a) 100/0 EPDM/PVC composites. PVC: polyvinyl chloride; EPDM: ethylene propylene diene monomer.

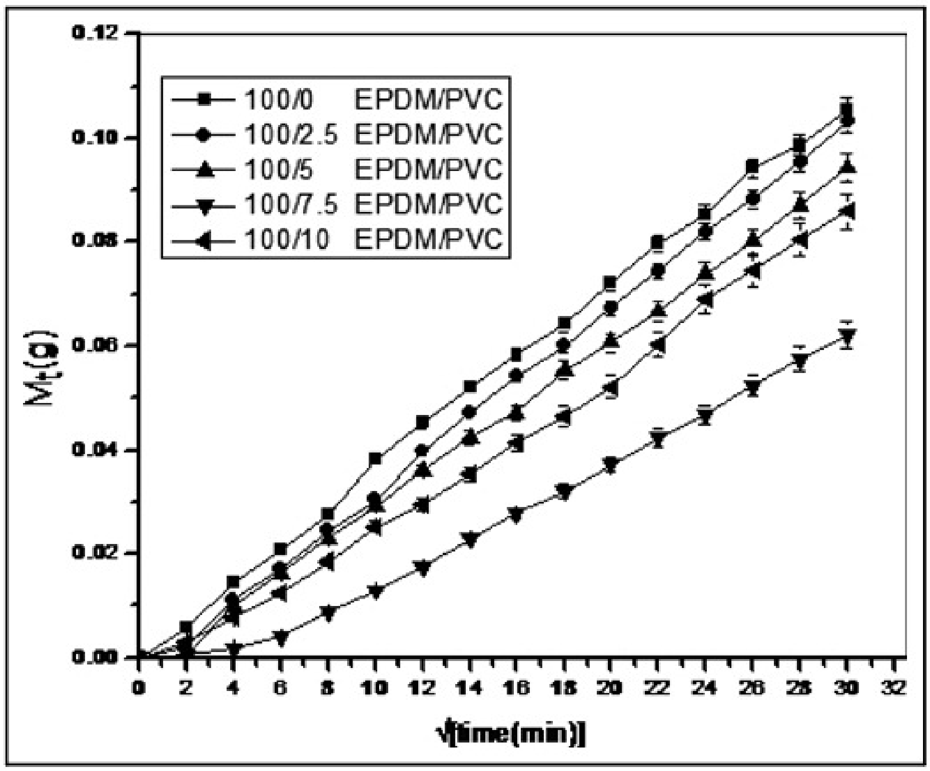

Figure 4. Effect of the amount of PVC on the vapor permeation of benzene through EPDM/PVC composite. PVC: polyvinyl chloride; EPDM: ethylene propylene diene monomer.

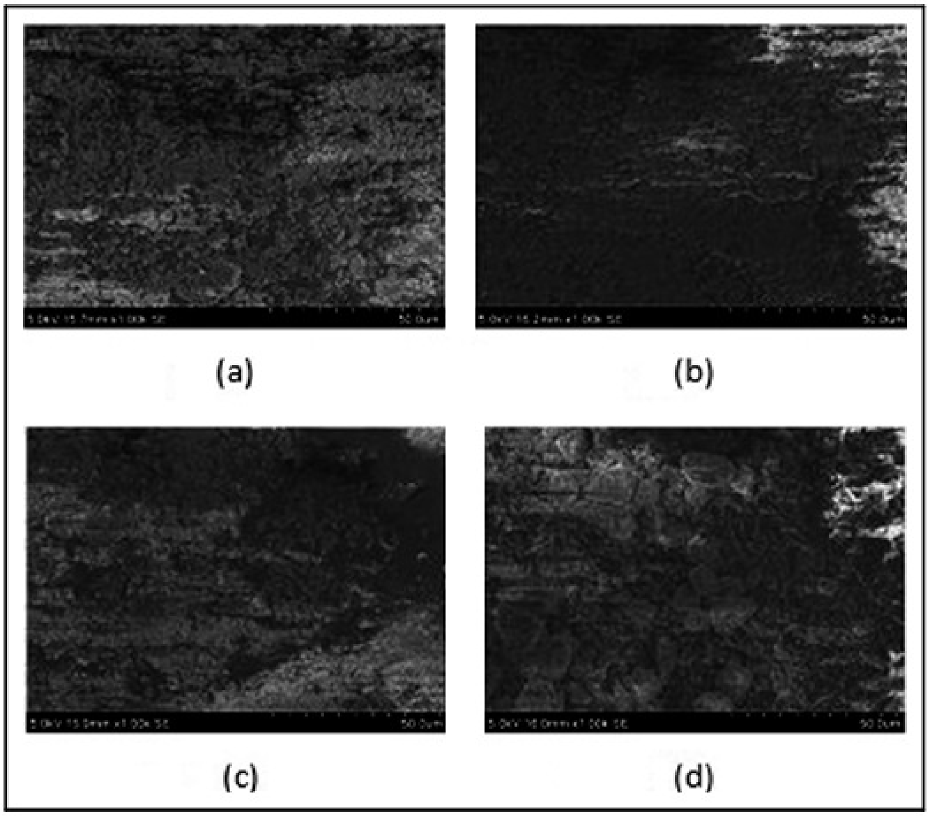

Figure 5. Field emission scanning electron micrograph of EPDM/PVC composites. (a) 100/2.5 EPDM/PVC, (b) 100/5 EPDM/PVC, (c) 100/7.5 EPDM/PVC and (d) 100/10 EPDM/PVC. PVC: polyvinyl chloride; EPDM: ethylene propylene diene monomer.

PVC. This may be due to the optimum loading in 7.5 phr PVC and the nonuniformity after the optimum loading. Figure 5(a) to (d) shows the FESEM of 2.5, 5, 7.5 and 10 phr PVC, respectively, in EPDM matrix. It is clear from the figure that the uniformity of the dispersed PVC particles increases up to 7.5 phr. After that the dispersion of PVC in EPDM matrix is nonuniform. In 100/10 EPDM/PVC, agglomeration of the dispersed domains occurs. This makes the particles larger and nonuniform, leading to an unstable morphology. Here, voids tend to occur at interface which leads to an increase in free volume.

Nature of the penetrants

The size, shape and side chain of the penetrant molecule is found to influence its rate of permeation through the polymer membrane.[24] The vapor permeation curves of EPDM/PVC (5 phr) for the three aromatic solvents, benzene, toluene and xylene is given in

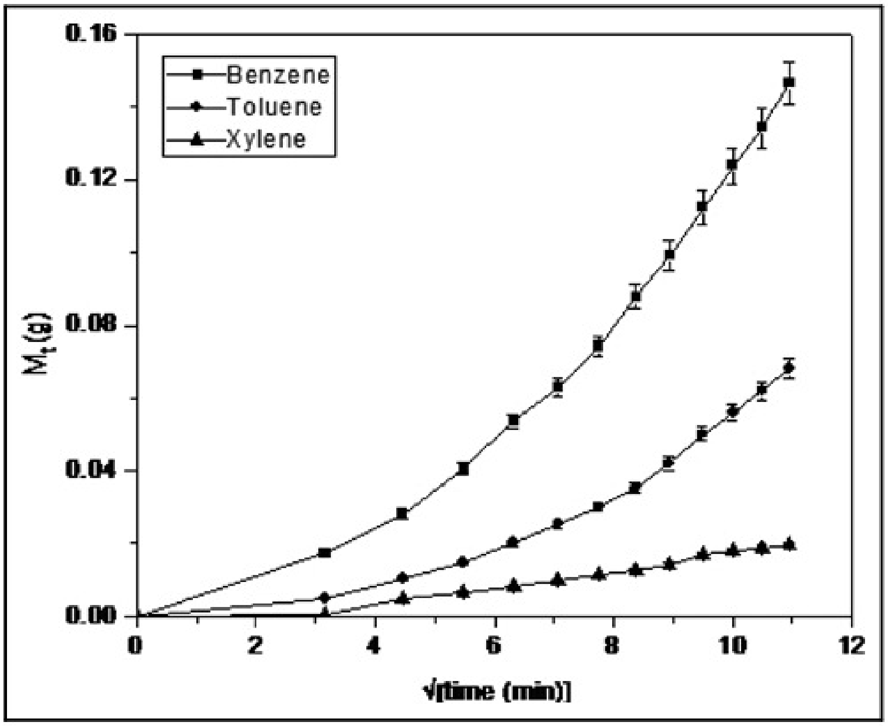

Figure 6. Effect of different penetrants on the vapor permeation through 100/5 EPDM/PVC composite membrane. PVC: polyvinyl chloride; EPDM: ethylene propylene diene monomer.

Figure 6. As expected, when the size of the permeant molecule increases, the permeation rate of the solvent vapors decreases. The order of permeation is benzene > toluene > xylene. Figure 7 shows the difference in vapor permeation of 1-propanol and 2-propanol; molecules having same molecular weight but different structures. It has been found that 1-propanol has greater permeation compared with 2-propanol.This can be due to the CH_3- side chain of 2-propanol, that cannot easily pass through the matrix.

Effect of liquid mixtures

Figure 8 shows the difference in permeability between benzene and 1-propanol vapors through 100/5 EPDM/PVC membrane. In all cases, pure benzene permeates at a higher rate than pure propanol. Figure 9 shows the effect of benzene/propanol mixtures on the vapor permeation behavior of 100/5 EPDM/PVC composite membrane. It has been found that 100% benzene permeates at a higher rate than 100% propanol. This clearly indicates the high interaction of benzene with the EPDM/PVC membrane than propanol. This can be explained by their solubility parameter values [EPDM: 8.6, benzene: 9.15 and 1-propanol: 11.97 in $(cal/cc)^{1/2}$]. The polymer-solvent interaction will be high if their solubility parameter values were closer. From the figure, it has been found that

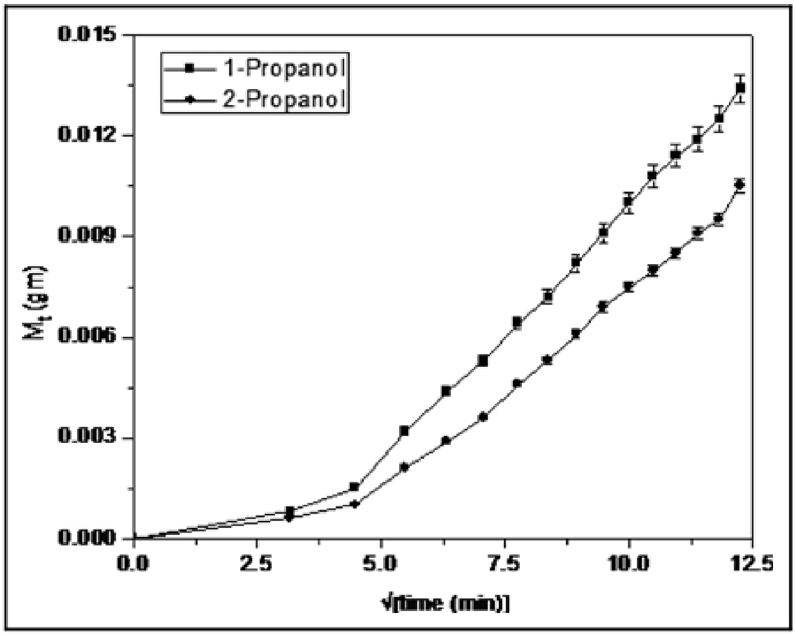

Figure 7. Permeation of propan-1-ol and propan-2-ol through 100/5 EPDM/PVC composite membrane. PVC: polyvinyl chloride; EPDM: ethylene propylene diene monomer.

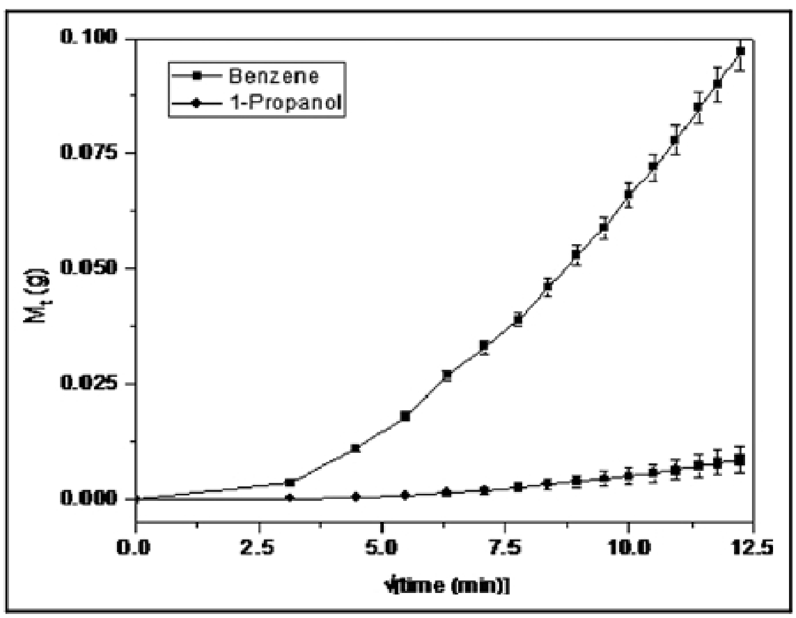

Figure 8. Permeability of 100/5 EPDM/PVC membrane for propan-1-ol and benzene. PVC: polyvinyl chloride; EPDM: ethylene propylene diene monomer.

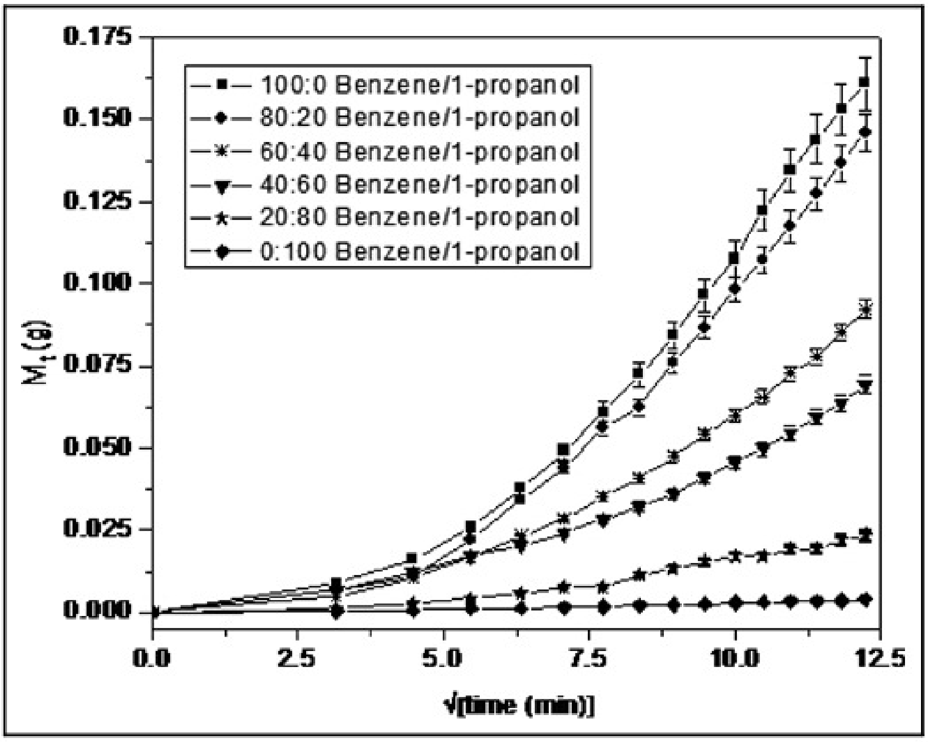

Figure 9. Effect of liquid mixture compositions on the permeability of 100/5 EPDM/PVC composite membrane. PVC: polyvinyl chloride; EPDM: ethylene propylene diene monomer.

as the propanol content in the mixture increases, the M_t values have been found to decrease. This clearly indicates the higher permeability of benzene than propanol through EPDM/PVC membrane. Figure 10 shows the permeation of azeotropic mixtures of benzene/1-propanol and benzene/2-propanol. The liquid mixture composition was analyzed by an Abbe refractometer upon completion of the vapor permeation studies. It was found that after 2½ h, the concentrations of benzene in the permeate decreased from 82% to 78% and from 58% to 55.5%, respectively.

Effect of type of vulcanization

Figure 11 shows the effect of the type of vulcanization techniques on the permeation behavior of 100/5 EPDM/PVC membranes, using benzene as a permeant. It is observed that dynamically vulcanized samples showed a lower permeation compared with the corresponding statically vulcanized one. The dynamic vulcanization produces a fine dispersion[25] of the rigid PVC particles in EPDM matrix as can be seen from FESEM in Figure 12. This generates a matrix with relatively lower free volume for solvent permeation.

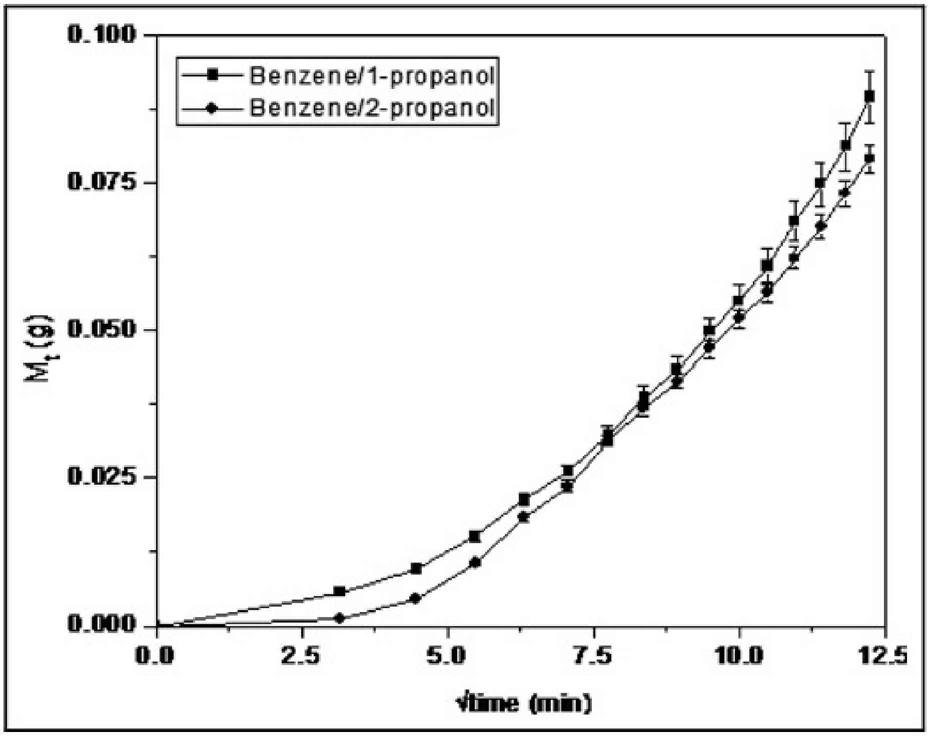

Figure 10. Permeation of azeotropic mixtures of benzene/1-propanol and benzene/2-propanol.

Conclusion

Permeation of three organic solvent vapors, namely, benzene, toluene, xylene and
5 propanol through EPDM and EPDM/PVC composites has been studied. The reduction in
the rate of solvent vapor permeation through the membrane with increase in PVC content has been attributed to the stiff and rigid nature of the PVC. The morphology of the composites is complementary to the observations. Of the three aromatic vapors used, the trend is in the order: benzene > toluene > xylene. This is in accordance with their molecular size. The vapor permeability decreases with increase in chain length and with the introduction of side chain in isomeric solvents. In the case of benzene/propanol mixtures, it has been found that when propanol content increases, the vapor permeation rate decreases. This indicates less interaction of propanol toward EPDM/PVC membranes, which can be explained by their solubility parameter values. Thus, membranes separate mixtures by discriminating the components on the basis of physical or chemical attributes, such as molecular size, charge or solubility. Dynamically vulcanized samples showed enhanced permeation compared with the corresponding statically vulcanized composites.

Azeotropes at the azeotropic point give vapor of the same composition as the azeotropic liquid and thus cannot be further concentrated by normal distillation no matter

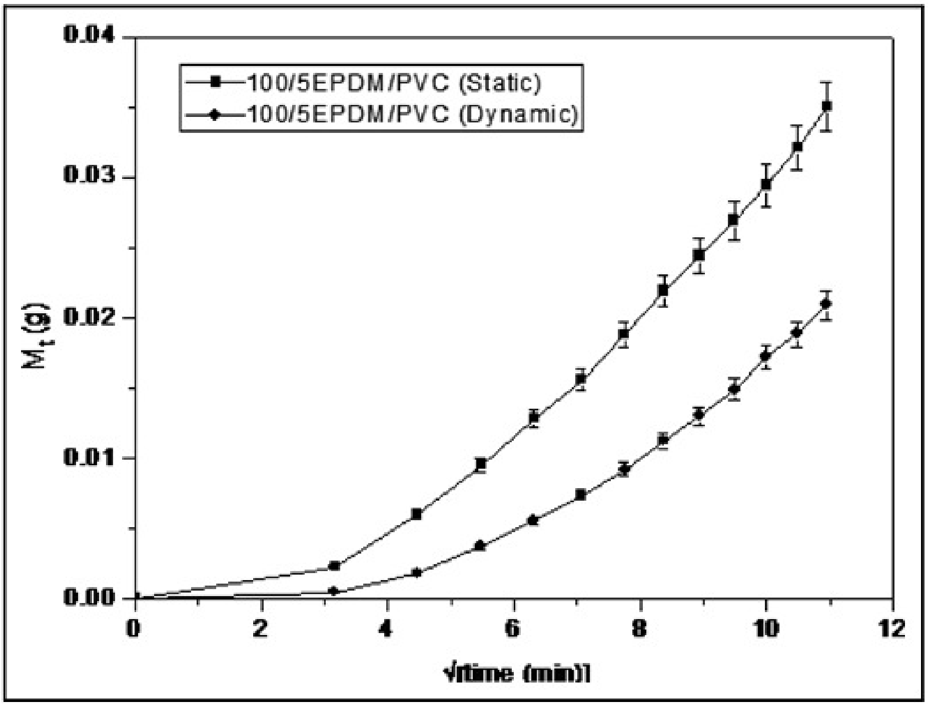

Figure 11. Effect of the type of vulcanization techniques on benzene permeation behavior of 100/5 EPDM/PVC composite membranes. PVC: polyvinyl chloride; EPDM: ethylene propylene diene monomer.

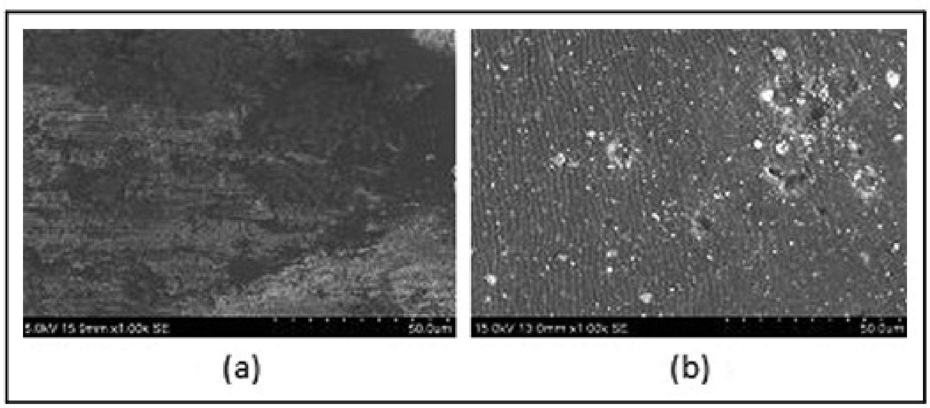

Figure 12. FESEM of 100/7.5 EPDM/PVC composites prepared by (a) static and (b) dynamic vulcanization. PVC: polyvinyl chloride; EPDM: ethylene propylene diene monomer; FESEM: field

4 emission scanning electron microscopy.

how efficient is the fractionating column used. Thus, an alternative means to effect the separation of such mixture is highly desirable.

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