INFLUENCE OF DYNAMIC VULCANIZATION TECHNIQUE ON THE PERMEATION PROPERTY OF ETHYLENE PROPYLENE DIENE MONOMER RUBBER/POLY VINYL CHLORIDE COMPOSITE MEMBRANES

C. P. MOHAMED KUTTY[*], M. SUNIL KUMAR[a] and M. JAHFAR[b]

Department of Chemistry, P. S. M. O. College, Tirurangadi, MALAPPURAM – 676 306 (Kerala) INDIA
[a]Department of Chemistry, National Institute of Technology Calicut, CALICUT – 673601 (Kerala) INDIA
[b]Department of Chemistry, Farook College, CALICUT - 673632 (Kerala) INDIA

ABSTRACT

Composite membranes based on ethylene propylene diene monomer (EPDM) and poly vinyl chloride (PVC) has been prepared by dynamically and statically vulcanization techniques. The mechanical property and organic solvent vapour permeation characteristics of two composites, one statically cross linked and the other dynamically cross linked EPDM/PVC composite membranes has been measured. The dynamically vulcanized membrane exhibited better mechanical and enhanced barrier properties compared to the corresponding statically vulcanized sample. The polymer composition strongly affects the final membrane properties and can be used for optimizing conflicting properties like permeability and mechanical stability. The experimental observations have been correlated with the phase morphology of the membranes using scanning electron micrographs.

Key words: Permeation study, Mechanical properties, Vulcanization.

INTRODUCTION

Permeation process through any material is a combination of sorption and diffusion and occurs by a solution-diffusion mechanism, which can lead to useful levels of selectivity. Each component in the vapour 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 down stream gas phase[1]. The presence of crystallinity enhances barrier property and good membranes should be capable of high fluxes. The usual physical picture is to think of a semicrystalline polymer in terms of a simple two-phase model; one phase being amorphous and the other

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[*]Author for correspondence

being crystalline. In the typical case, the crystals do not sorb or transmit penetrant molecules. Usually the continuous phase dominates the permeation process. Vapor transport offers one the unique ability to study structure–property relationships in polymers. Transport of small molecules through the polymeric membrane influences several industrial processes[2]. The membrane morphology dictates the mode of permeation and separation[3].

Interesting reports on the interaction of polymer composites with different liquids exist in literature. For example, Anusree et al.[4] studied the organic vapour permeation through TPEs and found that the permeability was found to decrease with increase in semi-crystalline EVA. Haraya and Hwang[5] have conducted permeation studies in a series of polymers for selecting appropriate polymers for the separation of O_2/Ar mixtures. Asalatha et al.[6] found that the overall performance of thermoplastic elastomers was enhanced upon dynamic vulcanization.

Ethylene propylene diene monomer (EPDM), a terpolymer of ethylene, propylene and a non–conjugated diene, is one of the most versatile elastomers in commercial use. The main attributes of EPDM are its outstanding resistance to oxidation, ozone and the effects of weathering[7]. These characteristics have allowed EPDM to be employed as a membrane material for separation operations. However, it performs poorly when exposed to oil and solvents. PVC is a normal impact, high corrosion resistant polyvinyl chloride. Because of its exceptional corrosion resistance, it is ideally suited for applications where maximum chemical resistance is necessary. Its high strength-to-weight ratio, cost efficiency, ease of fabrication and economic balance make it the material of choice. Loading of filler particles into a polymer matrix is known to affect mechanical and vapour permeation propereties of composite polymers[8].

The objective of the present work is to investigate the influence of dynamic vulcanization on the mechanical properties of the polymer and the permeating capabilities of organic liquid vapours, both; aromatic and aliphatic through EPDM/PVC composite membranes, prepared by static and dynamic vulcanization methods.

EXPERIMENTAL

Materials

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

toluene, xylene, 1-propanol and 2-propanol (Nice chemicals, Cochin, India) were used. These 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 x 300 mm), with a nip gap of 1.3 mm and a friction ratio 1 : 1 : 4. The EPDM was masticated for two minutes and PVC powder then added. After 4 minutes, other ingredients were added in the following order: zinc oxide, stearic acid, MBTS and sulphur. The processing time after each component added was about 2 minutes. Details of formulations are given in Table 1. 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 plates, under a load of 30 tones. The average thickness of the membranes was 0.23-0.25 mm. Dynamically vulcanized samples were prepared by using Brabender Plasticorder Model PLE 331. The samples were compression moulded as in static vulcanization method.

Vapour permeability

The vapour permeability was determined by the measurement of the weight loss of small vials filled with solvents and tightly closed by the membrane. The weight loss was proportional to the time, area of membrane and pressure inside and outside of the vials (considered zero outside) and inversly 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, verses square root of time, t. The experiments were triplicates in all cases and the deviation was within $\pm$ 0.001 to 0.003 mole percentage.

Investigation of mechanical properties

The test specimens were dried at 60°C for 3 hours to remove moisture prior to the tests. Tensile testing of the samples was done at 25 ± 2°C according to ASTM D-412 (2002) test method using dumb-bell shaped test specimens at a cross head speed of 500 mm/min using a universal testing machine (Tinius Olsen H10KS (USA)). Tensile strength was calculated using the equation -

$$\text{Tensile strength} \ = \ \frac{\text{Load at failure (N)}}{\text{Area of cross section (mm}^2)} \qquad \qquad \text{...(1)}$$

Morphology

The samples for scanning electron microscopy (SEM) (JEOL-JS IN-T330-A_SEM; ISS Group, Whittington,Manchester, U.K) were prepared by cryogenically fracturing them in liquid nitrogen. They were sputter coated with gold and SEM examination were performed.

RESULTS AND DISCUSSION

Permeation property

Fig. 1 shows the effect of the type of vulcanization techniques on the permeation behavior of 100/5 EPDM/PVC membranes, using benzene as permeant. In all cases, pure EPDM membranes show 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 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 the impermeable PVC particles. It is observed that dynamically vulcanized samples showed a lower permeation compared to the corresponding statically vulcanized one. The dynamic vulcanization produces a fine dispersion[8] of the rigid PVC particles in EPDM matrix. This generates a matrix with relatively lower free volume for molecular transport transport. Fig. 2 shows a schematic representations of permeability through pure EPDM and EPDM/PVC composites.
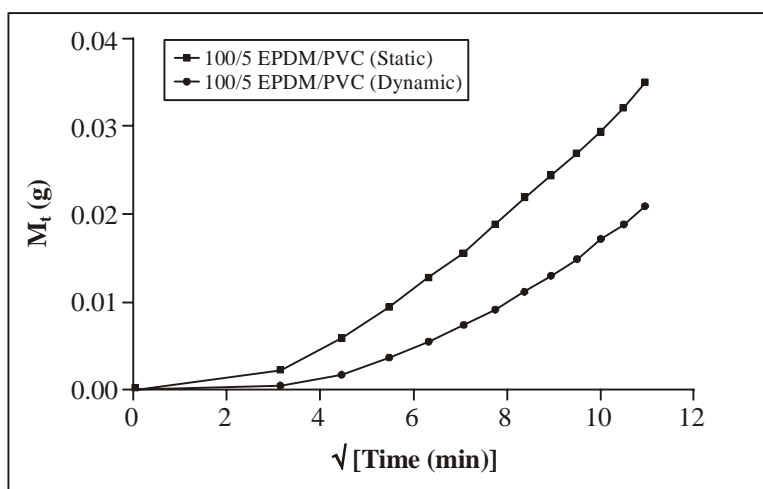

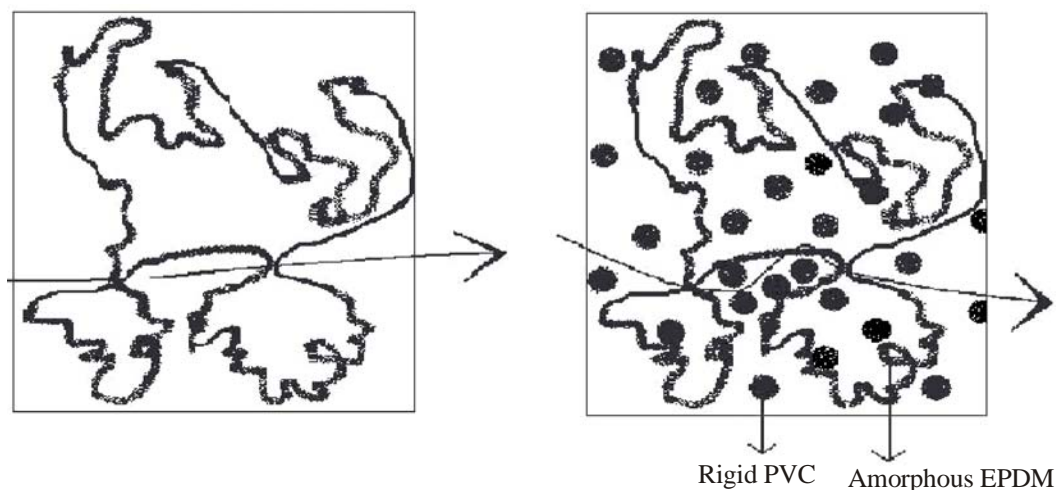**Fig. 1: Effect of type of vulcanization technique on the permeability of benzene**

Rigid PVC   Amorphous EPDM

Fig. 2: Schematic representation of permeation through pure EPDM and EPDM/PVC composites

Mechanical properties

The tensile strength increases with PVC loading upto 7.5 phr (optimized sample) and then show a decrease in the value, in both; statically and dynamically vulcanized samples. Dynamically vulcanized samples exhibit higher tensile strength than conventional vulcanized samples, as can be seen from the Fig. 3. This is due to the fine particle size of the dispersed phase, which is clear from the morphology.
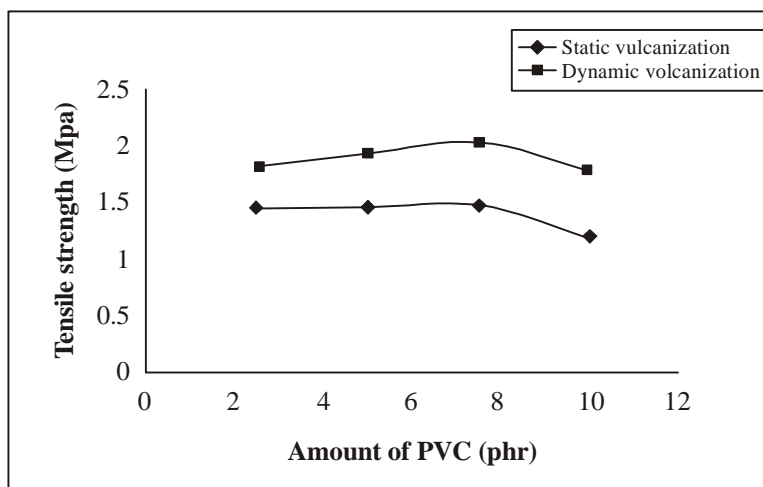

Fig. 3: Variation of Tensile strength with PVC loading

Morphology

The SEM photographs of staically vulcanized EPDM/PVC composites are shown in Fig. 4 (a to e). In all the samples, the minor PVC component forms a distinct phase dispersed in the continuous EPDM phase. In 100/2.5 EPDM/PVC, the PVC particles are randomly dispersed as domains in the continuous EPDM matrix as shown in the figure. 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 non-uniform. That may be the reason for maximum torque value for 7.5 phr samples. In 100/10 EPDM/PVC, agglomeration of the dispersed domains occurs. This makes the particles larger and non-uniform, leading to an unstable morphology. Here, voids tend to occur at interface which leads to an increase in free volume. In 100/2.5 EPDM/PVC, the rigid and stiff PVC particles act as a filler. This filler occupies the free volume of the EPDM matrix and restricting the permeability (increasing the path length for diffusion) of EPDM chains.
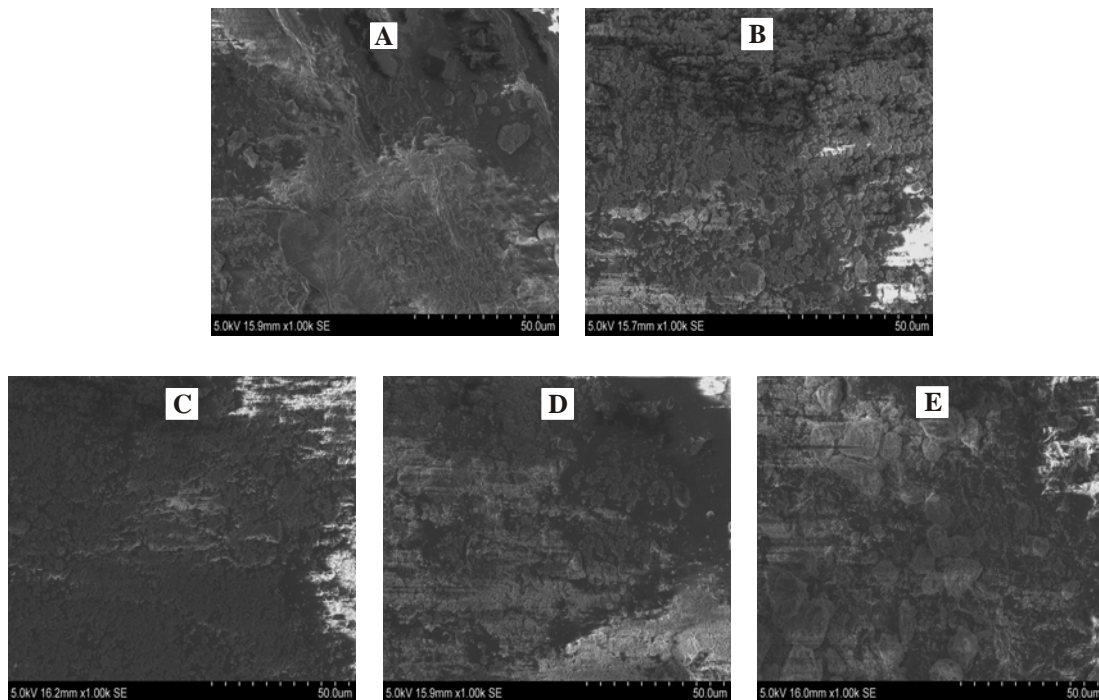

Fig. 4: SEM photographs of statically vulcanized EPDM/PVC composites
(a) 100/0 EPDM/PVC, (b) 100/2.5 EPDM/PVC, (c) 100/5 EPDM/PVC,
(d) 100/7.5 EPDM/PVC and (e) 100/10 EPDM/PVC

The SEM photographs of dynamically vulcanized EPDM/PVC composites are shown in Fig. 5 (a to e). Here also, the minor PVC component forms a distinct phase dispersed in the continuous EPDM phase. It can be seen that dynamic vulcanization has improved the morphology of the system, i.e., a uniform and fine dispersion of PVC particles in EPDM matrix is obtained[9].
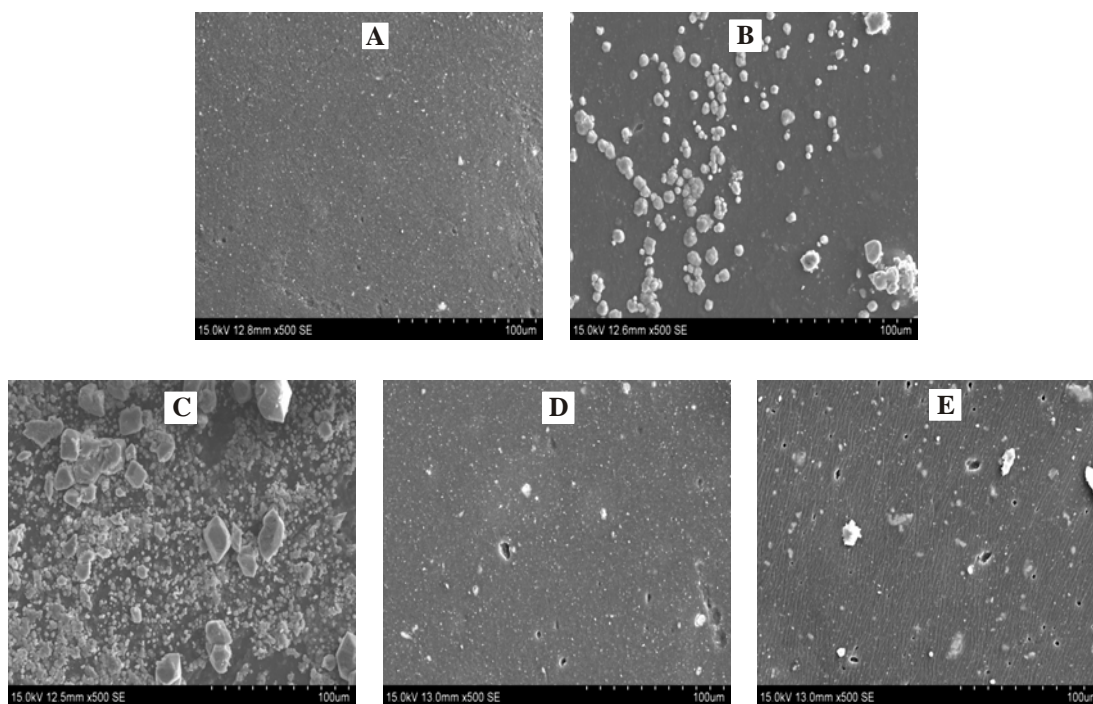

**Fig. 5: SEM photographs of dynamically vulcanized EPDM/PVC composites
(a) 100/0 EPDM/PVC, (b) 100/2.5 EPDM/PVC, (c) 100/5 EPDM/PVC
(d) 100/7.5 EPDM/PVC and (e) 100/10 EPDM/PVC**

CONCLUSION

An analysis of the transport of hydrocarbons through ethylene propylene diene monomer rubber/poly vinyl chloride composite membranes showed us how the permeation behavior varied according to the structure and morphology of the material under study ? Composite membranes were subjected to solvent transport studies. The solvent uptake increased with EPDM content and decreased with PVC content. The behavior varied with the morphology. The effects of blend ratio and dynamic vulcanization on the vapor permeation behavior of EPDM/PVC composites were investigated in detail. The results from the vapor permeation studies were complimentary to those of the morphology studies.

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