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Interactions of some liquid fuels with EPDM/PVC system

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Abstract: *Composites based on Ethylene Propylene Diene Monomer (EPDM) and Poly Vinyl Chloride (PVC) has been prepared by static and dynamic vulcanization techniques. The effect of PVC as a filler on interactions of EPDM with three fuels viz; petrol, kerosene and diesel has been studied. The solvent transport was found to decrease with increase in PVC content in the composites. Diesel showed the lowest interaction with the composites compared to petrol and kerosene. The effect of cross linking system and the type of vulcanization on the swelling behavior has also been studied.*
Key words: *Polymer composites, interaction with fuels and factors affecting sorption.*

I. Introduction

Polymer and polymer composites are increasingly being used in a wide range of applications where long-term service in hostile environments is required. As a consequence, manufacturers of polymer-based materials are increasingly being asked for assurance of product lifetime, particularly for components, which cannot be easily inspected or may fail catastrophically in service. Understanding the mobility and distribution of penetrated molecules in polymeric systems is crucial for the success of a wide variety of applications of polymers. The mass transport process through filled polymer systems is influenced by factors such as nature of fillers, the degree of adhesion, their compatibility with the polymer matrix, nature of components, crosslink density and nature of penetrants. Swelling experiments are important because they give valuable information, about the service performance of composites in liquid environment, and to study the characteristics of rubber / fibre interface[1] . Lowering of equilibrium swelling in filled samples generally indicates an excellent filler-matrix adhesion. For all practical purposes, liquids that attack cross linked rubbers either degrade the rubber or cause swelling through absorption. A swollen elastomeric network is much weaker and more susceptible to damage, although in certain sealing applications, a small positive swell is beneficial for the retention of sealing force The significant role of fillers on the diffusion process has been identified by several researchers[2,3]. In the typical case, the crystals do not sorb or transmit penetrant molecules. Usually the continuous phase dominates the permeation process[4]. EPDM, a non polar polymer exhibits excellent resistance to ozone, water and chemicals while accommodating fillers/plasticizers and retaining desirable physical and mechanical properties[5] . Poly (vinyl chloride) is one of the most widely used polymers in many industrial applications[6] and is rigid. It is a chemically stable material and is resistant to acids, solvents and oil due to its polar nature. The transport property of EPDM can be considerably controlled by dispersing the PVC particles in the EPDM matrix.

The goal of the present work is to evaluate the performance of EPDM/PVC composite systems filled with different PVC loadings, in an atmosphere of petrol, diesel and kerosene, which are considered as possible threats to polymers when they are used in automotive applications. Special stress is being given to the effects of filler loading, rubber-filler interaction, vulcanizing system, type of vulcanization and penetrant size on the transport process.

There exist interesting reports on the molecular transport through different polymer membranes [7-9]. 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 diffusivity with an increase in the size of penetrant has been reported by many investigators[10,11].

II. Experimental Details

Materias

Ethylene propylene diene monomer (EPDM) [E/P ratio of 62/32 and a diene content of 3.92 % from Herdilla Unimers, New Mumbai,India]. Poly vinyl chloride (PVC) [Sigma Aldrich]. The additives such as sulphur,Dicumyl peroxide , zinc oxide, stearic acid, and mercapto benzothiazyl disulphide (MBTS) used were of commercial grade. The petrol, kerosene and diesel were used as received [Bharat Petroleum Corporation Limited, India].

Preparation Of The Membrane

The mixing of EPDM with PVC in different ratios was done on a two roll mixing mill (150 x300 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 composites of EPDM and PVC with various amounts of PVC and with 4 phr DCP were also prepared. The processing time after the addition of 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^{o} C The composite sheets were compression moulded at 160 degree for optimum cure time using a hydraulic press having electrically heated platens, under a load of 30 tones. Dynamically vulcanized samples were prepared by using Brabender Plasticorder Model PLE 331.The samples were compression moulded as in static vulcanization method.

Morpholoy

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).

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. Similar methodology has been adopted by several researchers [12-14]. 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, Q_t (mol%).

III. Results And Discussion

Effect Of Pvc Loading

Figure 1 shows the amount of diesel sorbed through statically vulcanised pure EPDM and 100/2.5 EPDM/ PVC system. It has been observed from the figure that EPDM membrane shows higher sorptrion 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 impermeable PVC particles. This restricts the path of solvent vapours. Similar results were reported earlier for other polymer systems [15,16].

Effect Of Amount Of Pvc

Figure 2 shows the swelling behaviour of different statically vulcanised composites in diesel. It can be seen that the diffusion of solvent decreases with increase in PVC content in the composite . This can be better understood by determining their swelling coefficient (α) values calculated using the equation[17]

$\alpha = M_\alpha - M_0/M_0.\rho$,

Where M_α is the mass of the swollen rubber sample at equilibrium saturation, Mo is the original mass of the composites and ρ is the solvent density. The swelling coefficient values of composites are give in Table 2. It has been found that the swelling coefficient value decreases with increase in PVC content, due to rigid nature of the PVC.

Nature Of Penetrants

The size, shape and side chain of the penetrant molecule is found to influence its rate of diffusion through the polymer membrane[18]. The effect of molecular weight of the three solvents on the mole percentage uptake by the EPDM/PVC (7.5 phr) sample at 28^{o}C is shown in Figure 3. There is a systematic trend in the sorption behaviour of liquids of different molecular weight. With an increase in molecular weight of the solvent molecules, there is a decrease in the values of Q_t and Q_∞ for all the systems. Petrol shows the maximum value of Q_∞ and diesel the minimum, among the solvents used in the work. Kerosene takes an intermediate position. An exactly similar trend is observed for all the compositions. This can be explained on the basis of free volume theory, according to which the diffusion rate of a molecule depends primarily on the ease with which the polymer chain segments exchange their positions with the penetrant molecules. As the penetrant size increases, the ease of exchange becomes less, particularly in the case of filled matrices.

Effect Of Crosslinking

Figure 4 shows the effect of cross-linking system on the sorption behavior of EPDM/ PVC membranes, cross-linked by two vulcanizing modes, viz., sulphur and DCP with diesel as probe molecule. It is observed that the liquid sorption behavior decreases from sulphur to DCP. This can be explained by the nature of the cross chemical bonds introduced between the macromolecular chains during vulcanization. The sulphur vulcanization introduces mono sulphidic and poly sulphidic linkages between the chains. The polysulphidic linkages between the rubber chains give overall flexibility for the network and help to accommodate more solvent between the rubber chains. The DCP which introduces only C-C linkages, do not allow the chains to rearrange easily under solvent stress. This accounts for the lowest solvent uptake by DCP cured systems [19]. A schematic representation of the networks formed by different cross linking systems has been given in Figure 5.

IV. Conclusion

The transport characteristics of EPDM/PVC composites, vulcanized by DCP and sulphur have been studied. The solvent transport has been found to be decreased with an increase in PVC content in the composites. The observations have been explained in terms of their morphology, using scanning electron micrographs. The DCP system showed lower solvent uptake than sulphur system which can be explained by the difference in the nature of the cross chemical bonds introduced between the macromolecular chains during vulcanization.

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Table 1. Details of formulation of mixes (phr)

Ingredients	Vulcanizing system	
	Sulphur	DCP
EPDM	100.00	100.00
PVC	Varying amounts (2.5,5, 7.5, 10)	Varying amounts (2.5,5, 7.5, 10)
ZnO	4	-
Stearic caid	2	-
MBTS*	1.5	-
Sulphur	3	-
DCP	-	4

*****Mercaptobenzothiazyl disulphide

Table 2. Swelling coefficient values (in diesel).

EPDM/PVC	A
100/0	0.0042
100/2.5	0.0039
100/5	0.0036
100/7.5	0.0028
100/10	0.0025

Figure Captions

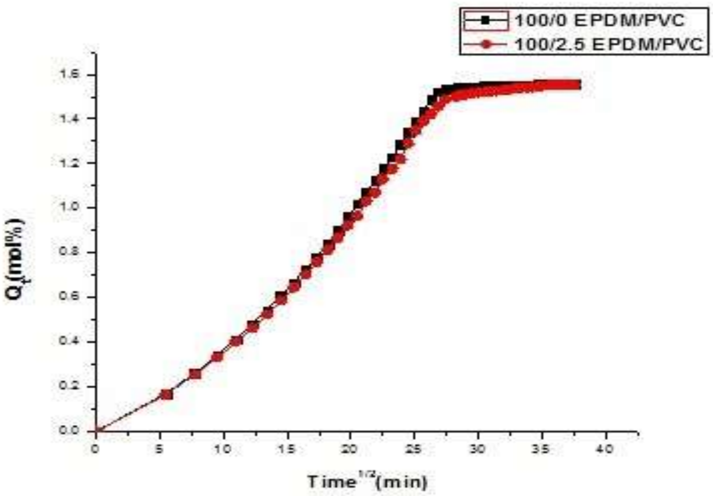

FIGURE 1. Effect of PVC loading on mole percentage deisel uptake by statically vulcanised pure EPDM and EPDM/PVC (2.5phr) composite

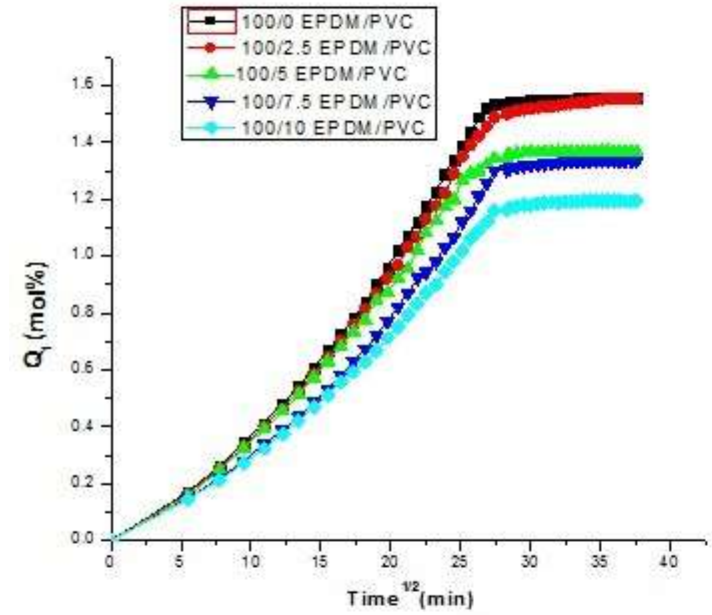

FIGURE 2. The mole percentage deisel uptake by statically vulcanised EPDM and EPDM/PVC composites

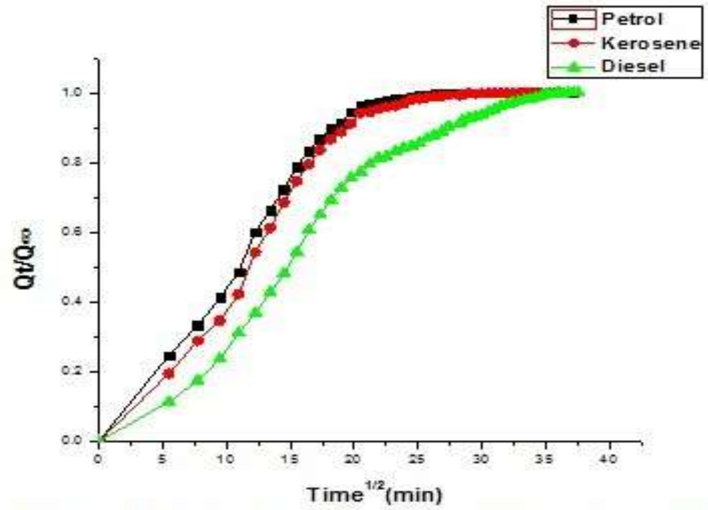

FIGURE 3. The mole percentage uptake by dynamically vulcanised 100/7.5 EPDM/PVC in petrol,kerosene and diesel