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# Sorption and diffusion of aromatic solvents through linear low density polyethylene–ethylene vinyl acetate blend membranes

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**Abstract** An investigation has been made for understanding the transport behaviour of organic solvents through linear low-density polyethylene (LLDPE)/ethylene vinyl acetate (EVA) blend membranes with special reference to the effects of blend ratio, concentration of cross-linking agent, penetrant size and temperature. Attempts have been made to relate the transport parameter with the morphology of the blend. The various transport parameters such as diffusion coefficient (D), permeation coefficient (P) and sorption coefficients (S) were evaluated at different diffusion conditions. The results were compared with theoretical predictions and found that the diffusion process follows anomolous type behaviour. The blends show dispersed/matrix and co-continuous phase morphologies depending on the composition. Dynamic vulcanization leads to fine and uniform distribution of the dispersed domains with a stable morphology. Among the blends $E_{70}$ sample shows the maximum solvent uptake and $E_{30}$ the minimum. The solvent uptake of blend varies with concentration of cross-linking agent. Molecular size of the solvent is a decisive factor in the solvent uptake. The rate of sorption and maximum solvent uptake increase with increase of temperature. Irrespective of the solvents used, the maximum solvent uptake increases with increase of temperature. The observed sorptivity, diffusivity and permeability are associated with cross-link densities of different samples. The D, S and P values increase with increase of EVA content in the blend.

## Introduction

The technological and industrial progress in the field of polymer blends during the last two decades points to the importance of blending technique to develop a new material with excellent properties at affordable cost. The diffusion and sorption of small organic molecules into polymer blend membranes is a complex process. While considering the various properties of a blend, the miscibility of the components is of great importance. The transport properties are strongly dependant on the miscibility of the blend. The blends may be either heterogeneous or homogeneous. In homogeneous blends the transport phenomenon is affected by the interaction between the component polymers [1–3], whereas the interfacial phenomena and the rubbery or glassy nature of the phases are important in heterogeneous blends [4]. Study of this process is important for the understanding of polymer properties ranging from processing and production to end use and shelf life. Understanding the mobility and distribution of organic solvent molecules in polymeric systems is crucial to the success of wide

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variety of applications of polymers. The use of polymers as barrier layers, cable coatings, food packaging [5], encapsulation of electronic circuits [6], controlled drug release [7] reverse osmosis [8–10], pervaporation separation [11], microelectronics [12] etc. is extremely widespread. It is quite essential to evaluate the dimensional stability of the polymeric materials in the presence of aggressive liquids. The diffusion process is also important because the permeating molecule can be used as a molecular probe to determine the polymer morphology.

The polymer–solvent interaction has been extensively studied and reviewed by many researchers [13–18]. Rate of diffusion through a polymer depends on the polymer structure, type of cross-linking, cross-linking density, size of the penetrants, temperature, etc. Harogoppad and Aminabhavi [19] investigated the transport of organic liquids through a series of polymeric membranes and found that swelling depends on the polymer structure. Barrer and co-workers [20] followed the effect of cross-linking density on diffusion. Harrogoppad and Amminabhavi [21] studied the effect of penetrant size on diffusion and found that equilibrium sorption of the sorbents decreases with the increasing penetrant molecular size. Our research group [22–24] studied the transport and sorption of various organic liquids through a variety of polymer system.

In the last two decades the increase in the applications of polymer blends has grown up to a very high level. Studies have been concentrated on polymer blends [25–27]. The transport phenomena in polymer blends can be used to as a characterization technique for understanding the morphology and miscibility of the system. The transport properties of polymer blends depend on the miscibility of the component polymers and morphology of the blend systems [25]. Cates and White [28–30] first reported the sorption behaviour in polymer blends. They investigated the water sorption characteristics of polyacrylonitrile (PAN)/cellulose, PAN/silk, and PAN/cellulose acetate blends. The sorption of water in PAN/cellulose and PAN/cellulose acetate varied linearly with blend composition, whereas the blend of PAN/silk exhibited complicated sorption behaviour. Hopfenberg and co-workers [31–34] systematically examined the effects of temperature, penetrant activity, blend composition, and thermal history on the sorption kinetics of *n*-hexane in polystyrene/poly (2,6-dimethyl 1,4-phenylene oxide). Varghese et al. studied the transport properties of blends of ethylene co-vinyl acetate/acrylonitrile butadiene rubber (EVA/NBR) [35] blends. Thomas and co-workers studied the diffusion and transport phenomena in nitrile rubber/polypropylene (NBR/PP) blends [36]. Marais et al. [37] reported that the addition of glassy PVC to EVA copolymer reduced water and gas permeability and increased the selectivity of the membrane. Cabasso et al. [38] studied the sorption of benzene cyclohexane mixtures in polymer blend membranes of poly(phosphorates) and acetyl cellulose. It was found that the blend selectively absorbs benzene from benzene–cyclohexane mixture. Aminabhavi and co-workers made a series of studies on the molecular transport characteristics of EPM/PP thermoplastics rubber blends [39–42]. The permeability of polyethylene/nylon blends to *n*-heptane, methyl salicilate and methyl alcohol has been reported [43]. The transport properties of small organic molecules in poly (vinyl chloride) (PVC)/atactic poly (methyl methacrylate) (PMMA) has been studied by Pavlovska and Raka [44]. Recently various researchers have conducted a lot of research works to study the transport properties of different blend membranes [45–57].

EVA is a random copolymer of ethylene and vinyl acetate, which finds many applications. This polymer is extensively used in many engineering and industrial areas because of its toughness, chemical resistance, intrinsic flexibility, excellent processability, etc. The copolymer has been used in many biomedical applications due to its chemical stability, biocompatibility and biological inertness. Earlier, Thomas and co-workers [58] have shown that the EVA membranes can be successfully used for pervaporation separation of liquid mixtures. Linear low-density polyethylene (LLDPE) is a thermoplastic with excellent properties including good mechanical properties. We have already reported on the morphology, mechanical properties, rheological properties, melt elasticity, dynamic mechanical properties, crystallinity and electrical properties of these blends.

To our knowledge till date no studies have been reported on the transport characteristics of LLDPE/EVA blends. The aim of the present work is to investigate the diffusion and sorption behaviour of aromatic hydrocarbons through cross-linked LLDPE/EVA blends .The effects of blend composition, concentration of cross-linking agent, penetrant size and temperature on the diffusion process have been investigated.

## Experimental

### Materials and blend preparation

Details of the polymer viz. Butene co monomer based linear low-density polyethylene (LLDPE-Reclair F19010) and Ethylene vinyl acetate (EVA-Piolene

1802) of vinyl acetate content (18%) are given in Table 1.

The blends of LLDPE/EVA were prepared in a Brabender plasticorder at 125 °C at a rotor speed of 60 rpm. The LLDPE was first melted for 2 min, and then EVA was added and mixed for 4 min. The total mixing time was 6 min in all cases. The DCP crosslinked EVA/LLDPE blends were also prepared in the same Brabender plasticorder by melt mixing. The dynamically vulcanized 30/70 EVA/LLDPE blends were prepared by melt mixing EVA (30 parts) and LLDPE (70 parts) with DCP wt% (based on the weight of EVA) 0, 1, 2, 3 and 4 and they are designated as 3E, $3EC_1$, $3EC_2$, $3EC_3$, $3EC_4$, respectively. The notations $E_{100}$, $E_{70}$, $E_{50}$ and $E_{30}$ denote EVA/LLDPE blends with 100/0, 70/30, 50/50, 30/70 compositions, respectively.

### Sorption experiments

Circular samples were cut out from the compression moulded samples using a sharp-edged steel die of 20-mm diameter. The sample thickness was measured at several points with an accuracy of ±0.01 mm using a micrometer screw gauge. Previously weighed samples were soaked in sorption bottles kept at constant temperature in an air oven. At regular intervals, the samples were taken out; the wet surfaces were dried using tissue paper and weighed in an electronic balance. The samples after weighing were placed back into the original test bottles. The weighing was continued to equilibrium. Experiments were conducted at 32, 45 and 60 °C. The results of mass uptake of the liquid by the polymer samples were expressed as moles of liquid sorbed per g of the membrane material.

$$Q_t\,\text{mol/g} = \frac{\text{Mass of the solvent uptake at equilibrium}}{\text{Molar mass of the solvent} \times \text{Mass of the polymer}} \tag{1}$$

### Phase morphology

The phase morphology was studied using cryogenically fractured samples. By immersing the samples in liquid nitrogen, a brittle fracture is obtained avoiding large deformations in the surface to be examined. The fractured ends of the samples were kept immersed in $CCl_4$ and the EVA phase was preferentially etched out. The fracture surfaces were dried, sputter coated with gold and scanned by using scanning electron microscope, JEOL JSM 500 °C.

## Results and discussions

### Morphology of uncrosslinked blends

The morphology generation during melt mixing of immiscible polymers involves processes such as liquid drop stretching into threads, breakup of the threads into smaller droplets, and coalescence of the droplets into larger ones. The balance of these competing processes determines the final particle size of the blends, which results upon solidification of the blends.

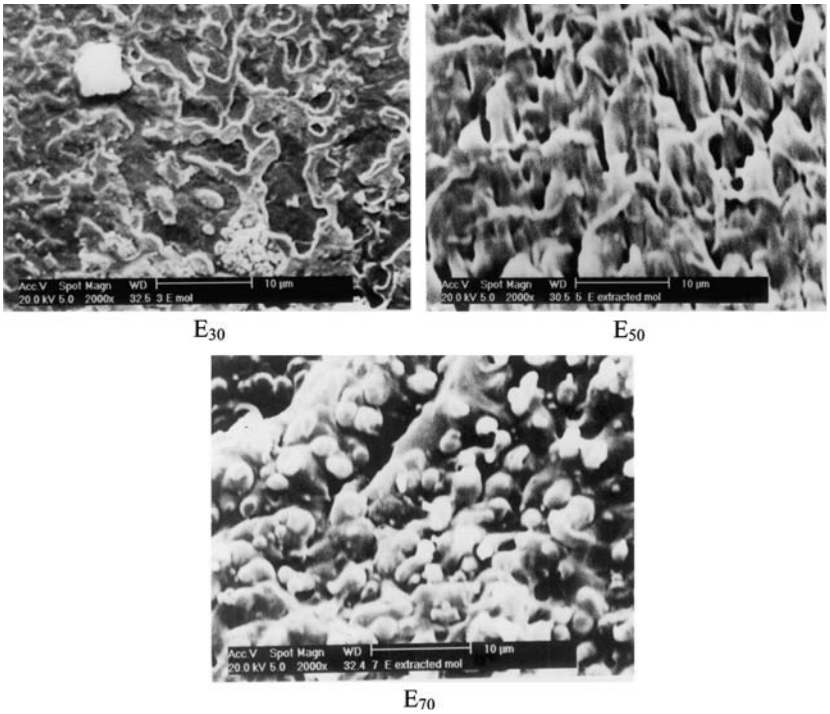
The scanning electron micrographs of $E_{30}$, $E_{50}$ and $E_{70}$ blends are shown in Fig. 1. It is observed that in $E_{30}$ blend EVA exists as dispersed domains in continuous LLDPE phase. When the proportion of EVA increases there is onset of co-continuity. A clear interpenetrating co-continuous morphology is obtained for $E_{50}$. Upto $E_{60}$ the co-continuous morphology has been observed. In the case of $E_{70}$ a phase inversion occurs where EVA forms the continuous phase and LLDPE exists as dispersed spherical domains.

### Morphology of dynamically vulcanised blends

The physical properties of thermoplastic elastomers can be improved by vulcanisation of the rubber phase during mixing. This process, which is known as dynamic vulcanisation, leads to a stable morphology,

**Table 1** Details of materials used

| Materials | Characteristics | Procured from |
|---|---|---|
| Linear low density polyethylene (Reclair F 19010) | Grade: F 19010<br>Melt flow index (g/10 min): 0.9<br>Density (kg/m$^3$): 920 | Reliance Industries Ltd. Hazira, Gujarath, India |
| Poly(ethylene-co-vinyl acetate)–Piolene (1802) | Vinyl acetate (%): 18<br>Melt flow index (g/10 min): 2.00<br>Intrinsic viscosity (m$^3$/kg): $0.17 \times 10^{-4}$<br>Density (kg/m$^3$): 937 | Polyolefins Industries Ltd. Chennai, India |



$E_{30}$ $E_{50}$

$E_{70}$

**Fig. 1** SEM photographs of morphology of blends $E_{30}$, $E_{50}$ and $E_{70}$

which is having a uniform and fine distribution of the dispersed phase. The morphology of the DCP vulcanised 30/70 EVA/LLDPE system is shown in Fig. 2. In the DCP cured system the distribution of domains are more fine and uniform. The dispersed domain diameter and interfacial area per unit volume of $E_{30}$ blends cross-linked with different concentration of DCP are given in Table 2. The size of the dispersed domain decreases considerably due to vulcanisation and thereby interfacial area increases.

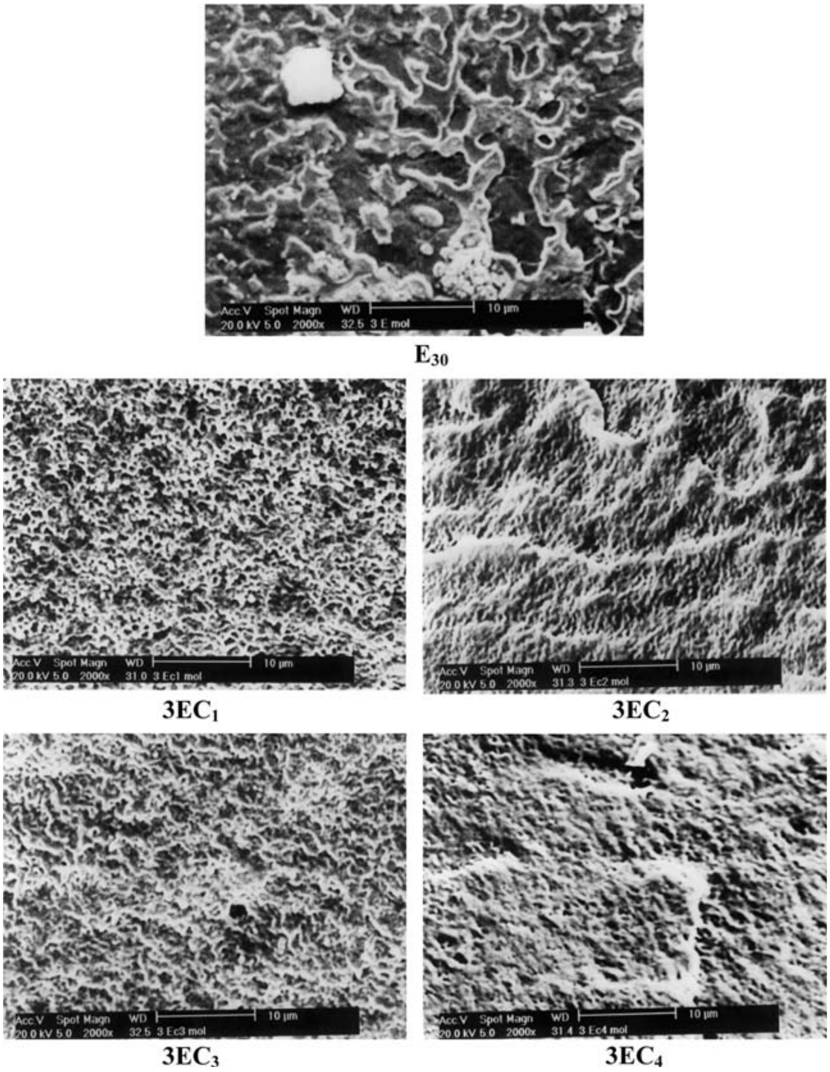
## Effect of blend composition

The sorption behaviour of LLDPE/EVA blends in benzene in presence of a cross-linking agent (peroxide 2 phr) is displayed in Fig. 3. We would like to mention that the uncross-linked blends could not be used for diffusion studies due to their dissolution. In Fig. 3, it is obvious that $E_{30}$, $E_{50}$ and $E_{70}$ blends show almost similar sorption behaviour even though the maximum solvent uptake values are different. The $E_{70}$ sample shows the maximum solvent uptake and $E_{30}$ the minimum. The maximum solvent uptake increases with increase in volume fraction of EVA. This is due to the increasing chain flexibility with increasing volume fraction of EVA in the blend. The chain flexibility increases due to low crystallinity of EVA, which is more amorphous. Morphology of the blends also influences the transport behaviour. The two-phase morphology of $E_{30}$ blend makes a tortuous path for the penetrant and hence the net solvent uptake is low. The morphology of $E_{50}$ is co-continuous and in $E_{70}$ phase inversion occurs and EVA becomes the continuous phase. In both cases EVA becomes continuous phase, and the system exhibits increased passage of the penetrant. This leads to an easier transport of the solvent and hence the uptake is high. Tortuous diffusion is usually observed in heterogeneous systems in which there are regions that support fast diffusion and regions that support slow diffusion or act as barriers. A schematic representation of the transport of solvent through LLDPE/EVA blends is shown in Fig. 4. In $E_{30}$ the more crystalline LLDPE is the continuous phase and EVA exists as dispersed domains. This morphology offers a tortuous path to the solvent molecules and therefore the uptake will be minimum. In $E_{50}$ EVA also becomes continuous and the uptake of solvent increases. In $E_{70,}$ EVA is the continuous phase, which leads to maximum uptake of solvent. Wide angle X-ray scattering (WAXS) analysis [59] provides enough explanation on the crystalline nature of these blends.

## Effect of concentration of cross-linking agent

The influence of concentration of cross-linking agent on the solvent sorption behaviour of $E_{30}$ blend in benzene is shown in Fig. 5. It is clear from the figure that the solvent uptake of $E_{30}$ blend varies with increase in

**Fig. 2** Scanning electron micrographs of DCP vulcanised $E_{30}$ blends



$E_{30}$

$3EC_1$ $3EC_2$

$3EC_3$ $3EC_4$

the concentration of cross-linking agent. $E_{30}$ blend samples with 3 phr of cross-linking agent showed the lowest uptake and 1 phr of cross-linking agent showed the highest uptake. Normally one expects a decrease in solvent uptake with increase in concentration of cross-linking agent. This can be explained on the basis of the cross-link density ($n_1$) of samples prepared. The degree of cross-linking ($n_1$) can be estimated using the following equation, [60]

**Table 2** Dispersed domain diameter and interfacial area/unit volume of $E_{30}$ blend and the cross-linked samples

| Sample | Dn (µm) | Interfacial area/unit volume ($\mu m^{-1}$) | Inter particle distance (µm) |
|---|---|---|---|
| 3E | 3.44 | 0.517 | 0.71 |
| $3EC_1$ | 0.86 | 2.07 | 0.18 |
| $3EC_2$ | 0.68 | 2.614 | 0.14 |
| $3EC_3$ | 0.65 | 2.734 | 0.13 |
| $3EC_4$ | 0.58 | 3.064 | 0.12 |

i.e.,

$$n_1 = 1/2M_c \tag{2}$$

where $M_c$ is the molar mass between crosslinks ($M_c$). $M_c$ can be determined using the following Flory–Rehner equation [60]

$$M_c = \frac{-\rho_p V_s V_r^{1/3}}{\left[\ln(1 - V_r) + V_r + \chi V_r^2\right]} \tag{3}$$

where $\rho_p$ is the density of polymer, $V_s$ molar volume of solvent, $V_r$ the volume fraction of rubber in the swollen sample and $\chi$ the Flory–Huggins interaction parameter. $\chi$ is calculated by the following equation [61]

$$\chi = \beta + V_s/RT(\delta_s - \delta_p)^2 \tag{4}$$

where $\beta$ is the lattice constant [considered as zero as per reference [62], $V_s$ the molar volume of solvent, $\delta_s$

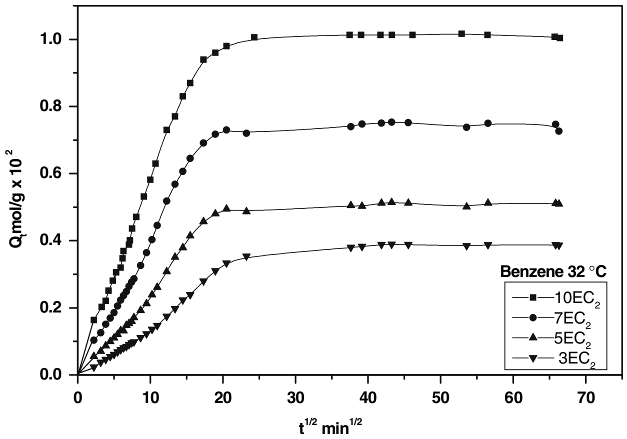


**Fig. 3** Mole percent benzene uptake of LLDPE/EVA blends

and $\delta_p$ the solubility parameters of solvent and polymer, respectively.

The $n_1$ values are $1.0728 \times 10^3$, $1.084 \times 10^3$ and $1.3928 \times 10^3$ mol/m$^3$, respectively for 3EC$_1$, 3EC$_2$ and 3EC$_3$. Crosslink density is lowest for 3EC$_1$ and highest for 3EC$_3$. Therefore 3EC$_1$ and 3EC$_3$ have the highest and lowest solvent uptake values, respectively. Therefore the solvent uptake decreases in the order 3EC$_1$ > 3EC$_2$ > 3EC$_3$. The variation of maximum solvent uptake with concentration of cross-linking agent is shown in Fig. 6.

### Effect of penetrant size

The penetrants, benzene, toluene and xylene were used to study the effect of molecular size. The influence of penetrant size on the sorption behaviour of the blend is shown in Fig. 7. It is observed that the maximum solvent uptake decreases as the molecular size increases from benzene to xylene. This behaviour can be explained on the basis of interaction between the polymer and solvent. It is found that as the solubility parameter between polymer and solvent becomes close to one another, the solubility of the latter in the polymer becomes high. The $\chi$ values calculated using Eq. (4) for solvents benzene, toluene, and xylene are 0.813, 1.24 and 1.33, respectively. The increasing $\chi$ values support the observed trend in penetrant uptake. It is evident from the values that as the molecular size increase the interaction between the polymer and solvent decreases from benzene to xylene. Therefore the solvent uptake took place accordingly.

### Effect of temperature

The diffusion experiments were conducted at 32, 45 and 60 °C. The effect of temperature on solvent sorption is displayed in Fig. 8. The rate of sorption and maximum solvent uptake increase with increase of temperature. The variation of maximum solvent uptake with increase in temperature is shown in Fig. 9. Irrespective of the solvents used, the maximum solvent uptake increases with increase of temperature.

### Diffusivity, sorptivity and permeability

The diffusivity was calculated using the relation [63]

$$\frac{Q_t}{Q_\infty} = \sum_{n=0}^{n=\infty} 8/(2n+1)^2\,\pi^2 e - \left\{(2n+1)^2\,\pi^2\,Dt/h^2\right\} \tag{5}$$

where t is the time and h the initial sample thickness. This equation can be readily solved, but is instructive to examine the short-time limiting expression as well

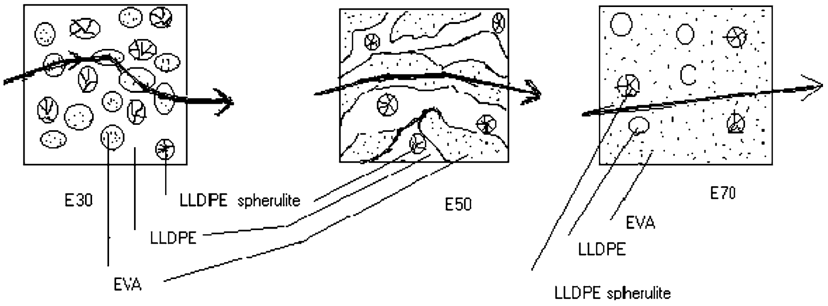
$$\frac{Q_t}{Q_\infty} = \frac{[4]}{\pi^2}\,\frac{[Dt]^{1/2}}{h^2} \tag{6}$$

A single master curve is obtained from a plot of $Q_t$ versus $t^{½}$, which is initially linear. Thus D can be calculated from a rearrangement of Eq. (6) as [63]

$$D = \pi\,(h\,\theta/4Q_\infty)^2 \tag{7}$$

where $\theta$ is the slope of the linear portion of the sorption curve $Q_t$ versus $t^{½}$. Sorption coefficient (S) is a thermodynamic parameter, which depends on the

**Fig. 4** Schematic representation of the transport of solvent through LLDPE/EVA blends



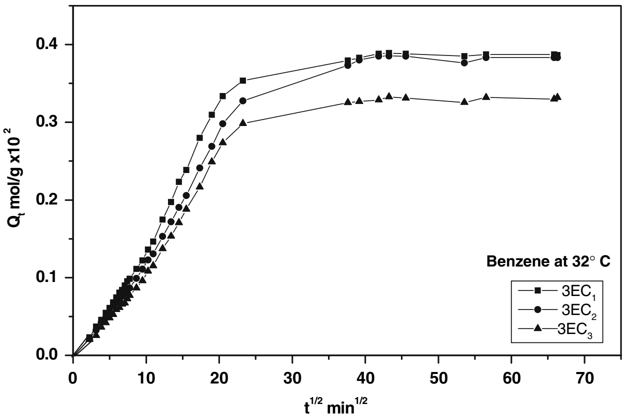


**Fig. 5** Effect of concentration of crosslinking agent on the mole percent benzene uptake of LLDPE/EVA blends

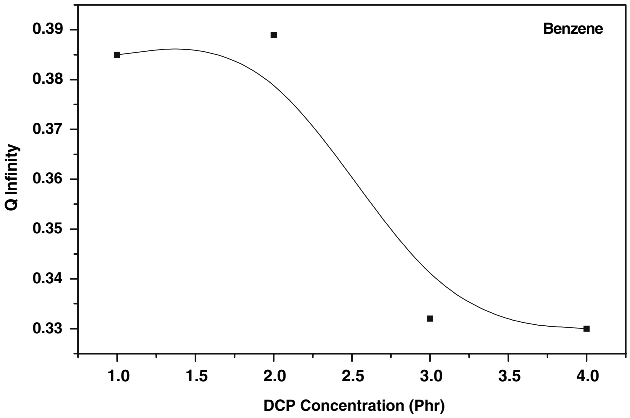


**Fig. 6** Variation of Maximum solvent uptake with concentration of crosslinking agent

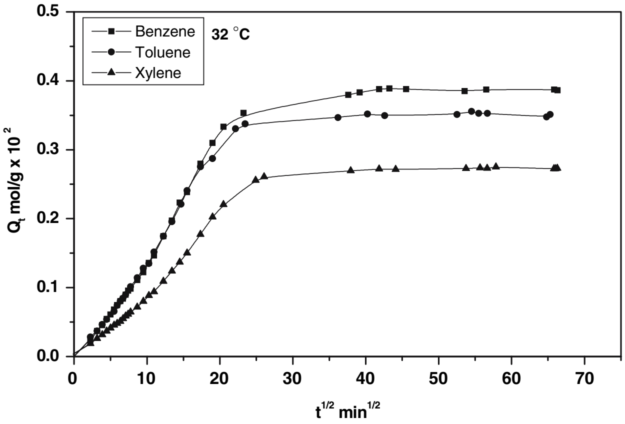


**Fig. 7** Mole percent solvent uptake of $3EC_2$ in aromatic hydrocarbons

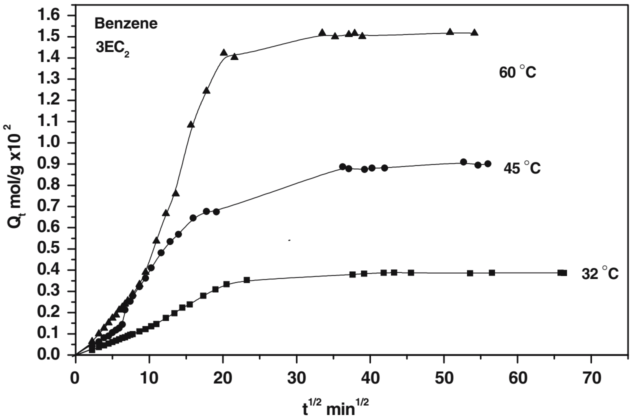


**Fig. 8** Mole percent benzene uptake of $3EC_2$ at different temperatures

strength of the interactions in the polymer/penetrant mixture. Sorption describes the initial penetration and dispersal of permeant molecules into the polymer matrix. It is calculated from the equilibrium swelling using the equation [63].

$$S = M_\infty / M_0 \tag{8}$$

Permeability is a combination of sorption and diffusion processes and hence the permeability of solvent molecules into polymer membrane depends upon both diffusivity and sorptivity. P can be determined from the following empirical relation. [64]

$$P = DS \tag{9}$$

The calculated values of D, S and P values are given in Table 3a–d. The values for D, S and P for cross-linked 30EVA/70LLDPE systems are given in Table 3a. The value of D is lowest for $3EC_3$ and highest for $3EC_1$. Values of D vary in the order $3EC_3 < 3EC_2 < 3EC_1$. The values of S and P are also varying in the same trend. These trends are in agreement with the variation of solvent uptake as reported earlier. The observed sorptivity, diffusivity and permeability are associated with cross-link densities of different samples. $3EC_1$ is the system, which has the minimum cross-link density, and the $3EC_3$ is the system which posses maximum cross link density.

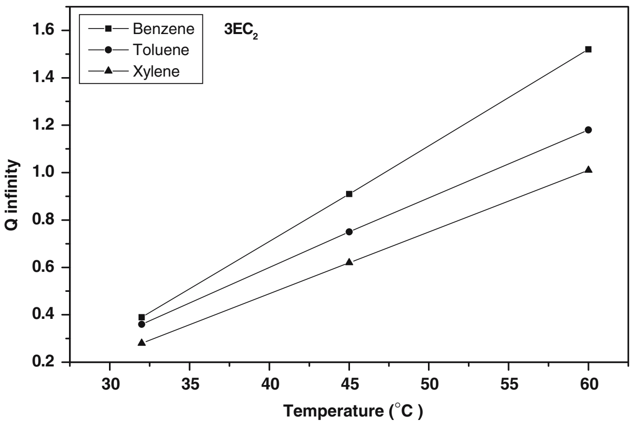


**Fig. 9** Variation of maximum solvent uptake with temperature

**Table 3** Variation of D, S & P with (a) concentration of DCP [in benzene at 32 °C], (b) blend ratio [in benzene at 32 °C], (c) penetrant size (3EC$_2$ at 32 °C) and (d) temperature (3EC$_2$ in Benzene)

| | D × $10^3$ m$^2$/s | S g/g | P × $10^4$ m$^2$/s |
|---|---|---|---|
| (a) Sample | | | |
| 3EC$_1$ | 1.580 | 0.304 | 4.480 |
| 3EC$_2$ | 1.462 | 0.301 | 4.401 |
| 3EC$_3$ | 1.432 | 0.259 | 3.712 |
| (b) Sample | | | |
| 3EC$_2$ | 1.580 | 0.304 | 4.800 |
| 5EC$_2$ | 1.969 | 0.402 | 7.907 |
| 7EC$_2$ | 2.624 | 0.588 | 15.43 |
| (c) Solvent | | | |
| Benzene | 1.580 | 0.304 | 4.800 |
| Toluene | 1.647 | 0.328 | 5.400 |
| Xylene | 1.057 | 0.292 | 3.087 |
| (d) Temperature (°C) | | | |
| 32 | 1.580 | 0.304 | 0.480 |
| 45 | 1.532 | 0.711 | 1.089 |
| 60 | 0.897 | 1.185 | 1.063 |

The variation of D, S and P with respect to blend composition is shown in Table 3b. The D, S and P values increase with increase of EVA content in the blend. This is due to the increased flexibility with increase in EVA content. The variation of D and P values with volume fraction of EVA at a concentration of cross-linking agent at 2 phr is given in Fig. 10. It was found that D and P values increase with increasing volume fraction of EVA. Table 3c gives the values of D, S and P with the influence of penetrant size. With increasing molecular size of the penetrant from benzene to xylene through toluene, D, S and P values decrease with molecular size. Sorptivity and diffusivity decrease due to the low polymer solvent interaction and thereby permeability also decreases. The effect of temperature on diffusivity is given in Table 3d. Sorptivity increases where as diffusivity decreases but the overall permeability increases with increase of temperature. With increasing temperature solvent sorption at the membrane surface as well as segmental mobility increases and resultantly sorptivity and overall permeability increase.

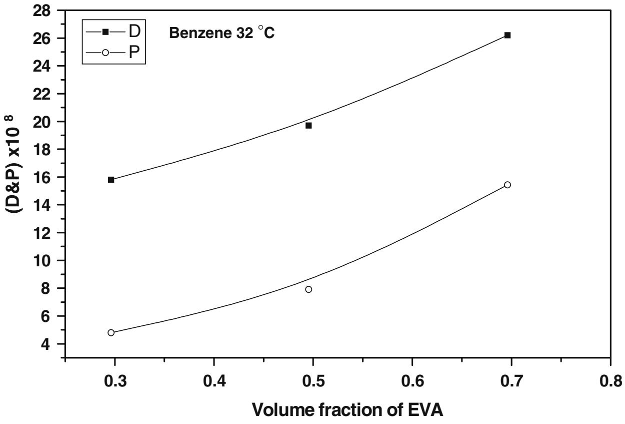


**Fig. 10** Variation of diffusion coefficient and permeation coefficient with volume fraction of EVA

## Mechanism of transport

The results of the sorption experiments were analysed using the empirical relation [65].

$$\log Q_t/Q_\infty = \log K + n \log t \tag{10}$$

where $Q_t$ is the mole per cent sorption at time t and $Q_\infty$ is the mole per cent sorption at equilibrium. The term k depends upon structural features of polymer, besides its interaction with the solvent. n gives an idea about the mechanism of sorption.

When n = 0.5, the mechanism of sorption is termed as Fickian, and this occurs when the rate of diffusion of permeant molecules is much less than the polymer segmental mobility. If n = 1, the mechanism of sorption is non-Fickian. This arises when the rate of diffusion of permeant molecules is much greater than polymer segmental mobility. And if n lies between 0.5 and 1, then the mechanism of sorption follows an anomalous trend. Here, the permeant mobility and polymer segment relaxation rates are similar. By regression analysis, the values of n and k are obtained as slope and intercept, respectively and are placed in Table 4a–c. The correlation coefficient values are found to be 0.999. The values of n range from 0.45 to 0.63 and it evidently imply that the mechanism of sorption follows an anomalous trend. The n values of EVA/LLDPE samples vulcanised at different concentration of peroxide (Table 4a), different

**Table 4** Variation of n & k with (a) DCP concentration (in benzene at 32 °C), (b) blend ratio (in benzene at 32 °C) and (c) penetrant size (3EC$_2$ at 32 °C)

| | n | k × $10^2$ (g/g min$^n$) |
|---|---|---|
| (a) Sample | | |
| 3EC$_1$ | 0.599 | 2.11 |
| 3EC$_2$ | 0.630 | 2.33 |
| 3EC$_3$ | 0.561 | 2.33 |
| (b) Blend ratio | | |
| 3EC$_2$ | 0.630 | 2.33 |
| 5EC$_2$ | 0.450 | 5.05 |
| 7EC$_2$ | 0.417 | 6.65 |
| (c) Solvent | | |
| Benzene | 0.630 | 2.33 |
| Toluene | 0.515 | 3.30 |
| Xylene | 0.490 | 3.08 |

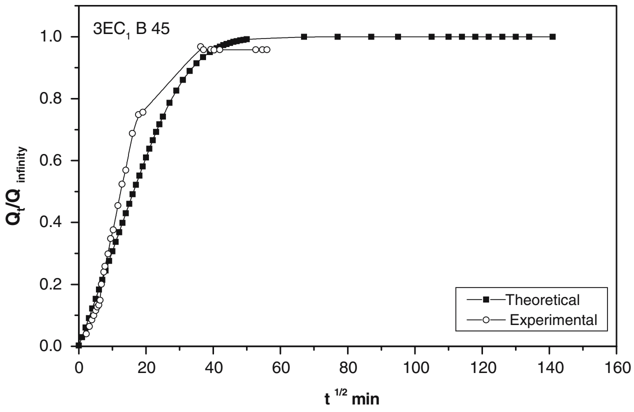


**Fig. 11** Comparison of experimental diffusion results of $3EC_1$ with that of theoretical prediction

blend compositions (Table 4b), and in different solvents (Table 4c), fall in the above range and hence possess a tendency to show anomalous sorption behaviour. This is clearly understood from the initial portions of Figs. 7 and 8. It is sigmoidal in nature. Sigmoidal nature of diffusion curve shows that diffusion mechanism varies from Fickian to anomalous. Thomas and co-workers have earlier reported on such kind of diffusion in blends [66]. According to Southern and Thomas [67] this kind of behaviour is because when a polymer interacts with solvents, the surface of the polymer sample immediately swells, but the swelling in the lateral expansion is prevented by the underlying unswollen material. Thus a two dimensional compressional stress is produced in the surface. The swelling stresses are either relaxed or dissipated by further swelling and rearrangement of segments. This sigmoidal nature is associated with the time taken by the polymer segments to respond to the swelling stress and rearrange themselves to accommodate the penetrant molecules. The values of k are found to increase with increasing concentration of cross-linking agent (Table 4a), blend composition (Table 4b) and penetrant size (Table 4c).

### Comparison with theory

The experimental diffusion results were compared with theoretical predictions using Eq. (5) [68]. The experimentally determined values of diffusion coefficients (D) were substituted in the equation and the representative of the resulting curves is shown in Fig. 11. The figure represents the behaviour of $3EC_1$. The initial portion of the curve is in agreement with the corresponding theoretical curve. However, some deviation is observed at longer times. All other samples exhibit similar sorption behaviour.

## Conclusion

The effects of blend composition on the transport behaviour of crosslinked EVA/LLDPE blends have been investigated. The solvent uptake increases with increase of EVA content in the blend. This is due to the overall increase in flexibility as well as the morphology of the blend. The 30/70 EVA/LLDPE blend exhibited dispersed matrix morphology. The permeable EVA exists as a dispersed phase in continuous LLDPE matrix. The two-phase morphology of 30/70 EVA/LLDPE blend makes a tortuous path for the penetrant and hence the net solvent uptake is low. In 50/50 EVA/LLDPE blend and 70/30 EVA/LLDPE blend, EVA becomes continuous and thereby the passage of the penetrant becomes easier and hence the uptake is high. Variation of solvent uptake with increase in concentration of cross-linking agent is examined. The 30/70 EVA/LLDPE blend samples with 3 phr of cross-linking agent showed the lowest uptake and 1 phr of cross-linking agent showed the highest uptake. 30/70 EVA/LLDPE blend with 2 phr of cross-linking agent showed intermediate solvent uptake values. This is because of the difference in cross-linking densities in the samples. Further, the various transport parameters such as diffusion coefficient, permeation coefficient and sorption coefficients were found to vary with blend composition, concentration of cross-linking agent, penetrant size, temperature etc. The maximum solvent uptake decreases as the molecular size increases from benzene to xylene. The rate of sorption and maximum solvent uptake increase with increase of temperature. The experimental diffusion results were found to be in agreement with the theoretical predictions.

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