Conclusion and Future Outlook

Summary

The major conclusions of the results of the previous chapters are presented here. Investigation mainly emphasized on the development of the new membranes and their applications to solvent transport, vapour transport, pervaporation separation and gas permeation. The transport features of these membranes towards penetrants, which are extensively used in industry, were studied in detail. Besides this, an outlook of the future studies to be done for the present work is given in this chapter.
10.1. Conclusion

Transport of gases, vapours and liquids through polymers is an important and in some cases, the controlling factor in a number of important applications, such as protective coatings, membrane separation processes and packaging for foods and beverages. A deep understanding of the intrinsic as well as extrinsic factors controlling the transport process is highly essential to achieve significant improvement in these areas and to develop new ones. Poly (ethylene-co-vinyl acetate) (EVA) was vulcanized by dicumyl peroxide (DCP) and benzoyl peroxide (BP). Membranes with different amounts of crosslinker and gum samples were prepared for the present work. A new class of membranes, EVA/clay nanocomposites were also prepared. Cloisite Na⁺ was used as the nano clay. It has no organic modifier. The thesis presents the detailed investigation of the transport of organic solvents, vapours and gaseous molecules through these membranes. The results have been explained in terms of different kinetic and thermodynamic parameters. The introductory chapter provides an overview of the fundamentals of transport phenomena and membrane based transport process. The factors affecting the transport process and transport through various polymeric systems are included. The characteristics of various permeants like gas, liquid and vapour are discussed briefly. The details of the materials used and experimental techniques adopted in the present investigation are explained in detail.
The transport characteristics of uncrosslinked and dicumyl peroxide crosslinked EVA membranes were examined using benzene, toluene and xylene as probe molecules in the temperature range of 28-70°C. The significant increase in solvent sorption with the introduction of dicumyl peroxide has been explained on the basis of decrease in crystallinity. The above observation was complemented by X-ray diffraction analysis (XRD) of the samples. But the equilibrium uptake ($Q_\infty$) decreased with the increase in the extent of crosslinking and also with the increase in the molecular mass of the penetrant. The mechanism of transport has been found to deviate from the regular Fickian behaviour. The experimental sorption data were compared with theoretical predictions. The diffusion process is well explained by the first order kinetics. The sorption behaviour of EVA samples was supported by transmission electron microscopic (TEM) studies.

The transport of aliphatic hydrocarbons viz. n-pentane, n-hexane and n-heptane through EVA membranes has been studied and it can be seen that transport follows a similar trend to that of aromatic hydrocarbons. The examination of the influence of crosslinking density on diffusion behaviour of polymer showed that the sorption decreases with increase in crosslink density. n-Heptane has been found to show comparatively higher interaction with EVA samples. The penetrant nature was explained on the basis of polymer-solvent interaction parameter. The diffusion coefficient, sorption constant and permeability coefficient values decreased with
increase in dicumyl peroxide content of the matrix. Temperature was found to activate the diffusion process in EVA which was supported by the higher intrinsic diffusion coefficient values \((D')\) and increase in slopes of the linear portion of the sorption curves at higher temperatures. High activation energy value observed for the sample with maximum dicumyl peroxide content \((D_8\) system) is due to the presence of its high crosslink density. The positive value of heat of sorption indicated that Henry’s law of sorption predominates. The entropy of sorption was estimated using the vant Hoff’s relationship. Network structure was analysed by calculating the molar mass between crosslinks \((M_c)\). \(M_c\) value of the samples is found to decrease with increase in dicumyl peroxide content in the samples, complementing the solvent uptake behaviour. The phantom and affine models were used to analyse the deformation of the network during swelling. It was found that affine model agrees well with the experiment.

The transport of dichloromethane, chloroform and carbon tetrachloride through dicumyl peroxide and benzoyl peroxide crosslinked EVA membranes, has been investigated. A significant reduction in diffusion rate and solvent uptake were observed for dicumyl peroxide modified membranes. Among the three penetrants, chloroform showed the highest equilibrium uptake. The higher interaction of chloroform with crosslinked system can be explained on the basis of the solubility parameters of the solvent and polymer. The swelling coefficient value of benzoyl peroxide sample was higher than the dicumyl peroxide crosslinked sample. The
intrinsic diffusion coefficient values were estimated and the values are higher for benzoyl peroxide samples. The activation energy for diffusion was calculated. Sorption, desorption, resorption and redesorption studies revealed that crosslinked samples are stable in an environment of organic liquids. The tensile behaviour of dicumyl peroxide modified sample has been found to be higher than that of benzoyl peroxide modified sample. It also reveals that the stress required to break the samples increases with increase in dicumyl peroxide content. The degree of crosslinking determined by swelling was in agreement with the observed properties. The measurement of glass transition temperature and scanning electron microscopic studies also supported the different behaviour of benzoyl peroxide and dicumyl peroxide crosslinked samples.

The feasibility of pervaporation technique for the separation of organic liquid mixtures using EVA membranes has been examined. The pervaporation performance for the separation of aromatic hydrocarbon/alcohol mixtures has been investigated. It is observed that the membrane exhibits permselectivity towards aromatic hydrocarbons, due to the closer solubility parameter values. However, uncrosslinked samples did not show any hydrocarbon selectivity. Dicumyl peroxide modified membranes showed a higher selectivity than benzoyl peroxide modified ones. The differences in the pervaporation performance of the membranes can be explained on the basis of the crystallinity and crosslink density.
It was observed that the membrane performance was strongly influenced by the feed mixture composition. For all mixtures, both flux and wt% of hydrocarbon in the permeate increased with increasing hydrocarbon content in the feed. Benzene-alcohol mixtures showed higher flux and separation factor than toluene-alcohol mixtures. In the case of toluene-methanol mixtures, the fluxes were higher than toluene-ethanol mixtures but selectivity was higher for toluene-ethanol mixtures. The separation factor of the membrane was independent of the thickness while the flux decreased with increase in membrane thickness.

Dicumyl peroxide modified membranes showed CCl₄ selectivity from CCl₄-acetone mixtures. But uncrosslinked membranes did not show CCl₄ selectivity. Pervaporation of chloroform-acetone mixture having a composition near azeotropie region showed high flux and selectivity. The high values for flux and selectivity shows that dicumyl peroxide modified membranes are effective in pervaporation separation.

Transport of chlorinated hydrocarbon vapours through EVA membrane has shown that the permeation behaviour depends strongly on the structure of the material. Uncrosslinked EVA membranes showed the least permeability. When crosslinked by dicumyl peroxide or benzoyl peroxide, the permeability was increased due to the reduction in crystallinity. Benzoyl peroxide crosslinked samples showed maximum permeability than dicumyl peroxide samples. This result was complemented by differential scanning calorimetric (DSC) analysis.
Development of membranes with high permeability and high permselectivity has become an active field of investigation because of the increased interest in the membrane process for gas separations. The oxygen and nitrogen permeability and O$_2$/N$_2$ selectivity of EVA membranes were investigated. Benzoyl peroxide crosslinked EVA membranes showed highest oxygen permeability. Also, membranes with high O$_2$ permeability showed low selectivity. Dicumyl peroxide modified membranes showed highest O$_2$/N$_2$ selectivity. The covalent radii of nitrogen gas molecule are higher than oxygen gas molecule and hence nitrogen gas showed reduced permeability. The permeation behaviour of EVA samples can be explained on the basis of the availability of free volume in the matrix. The free volume analysis was carried out with positron annihilation life time spectroscopy.

The wide application of membranes for pervaporation and gas separation has resulted in the investigation of new polymeric membranes with good permeability and selectivity. Recently polymer-clay nanocomposites have received greater interest because these material exhibits improved mechanical properties, decreased gas permeability and less swelling. EVA/clay nanocomposite membranes were prepared and their transport features were investigated in detail. These membranes were characterised by X-ray diffraction technique. The dispersion of layered silicates in the matrix was analysed using transmission electron microscopic analysis (TEM). The effect of free volume on the transport was investigated by
positron annihilation lifetime spectroscopy (PALS). Nanocomposite membranes with 3 wt% of clay showed good dispersion of nano particles resulting in an exfoliated structure. The dispersion of nano particles decreased with increase in the percentage of filler. At higher concentration, the clay particles agglomerate. PALS measurement showed that composites with 3 wt% of filler possess minimum free volume and increases with increase in clay content.

The transport characteristics of these membranes were analysed using aromatic hydrocarbons as probe molecules. Nano clay composite membranes showed reduced solvent uptake due to the enhanced polymer/filler interaction. The free volume of nanocomposite membranes decreased in the presence of layered silicates. The solvent uptake tendency increased with increase in weight percentage of the filler. This is due to the reduction in polymer/filler interactions resulting in the aggregation of filler particles. The above observations were complemented by X-ray diffraction analysis and transmission electron microscopic analysis. The mechanism of sorption was found to be anomalous. It was also found that the transport through nanocomposite membrane is temperature activated.

EVA/clay nanocomposites showed a far superior membrane selectivity than the unfilled ones. Membranes with 3 wt% filler showed maximum selectivity towards chloroform from chloroform-acetone mixtures. An increase in flux and decrease in selectivity was observed when the clay
content was higher than 3wt%. It was found that membrane selectivity dominates the evaporative selectivity and these developed new membranes can be effectively used for the azeotropic separation.

The diffusion of organic vapours through EVA/clay nanocomposites has been investigated. EVA nanocomposites showed a decrease in vapour permeability than unmodified ones. Increase in effective penetration path due to the very large aspect ratio of silicate layers was responsible for the reduced vapour permeability. It was found that EVA nanocomposite membranes showed improved mechanical property.

The gas transport properties of nano filled membranes were investigated using permeant gases such as $O_2$ and $N_2$. Due to enhanced polymer/filler interaction the nanocomposites exhibited lower permeability. The maximum barrier characteristics were observed at a lower filler loading. The size of the penetrant gas molecules affected the permeability coefficient.

Finally it is important to mention that the crosslinked EVA membranes and the nanostructured membranes could be used successfully for the selective separation of liquid mixtures, gases and as barrier membranes towards liquids, gases and vapours.

10.2 Future Outlook

The research work carried out so far on the transport of organic liquids through EVA and nanocomposite membranes provide necessary
informations for developing economically viable permselective polymer membranes. The output of the study can be applied to different polymeric systems. The work completed so far offers many interesting extensions to it. The following studies are proposed for future.

The theoretical background gained from this study can be applied to characterise the diffusion and equilibrium sorption of several polymers. The transport characteristics of different grades of EVA can be analysed.

The development of synthetic polymeric membranes is closely linked to the progress of separation industry. The membranes are used to separate and modify the permeate stream. This technology could revolutionise the biochemical, and other chemical industries. The use of EVA membranes for the separation of ethanol-water and removal of organics from water using pervaporation is another area of interest.

EVA offers a good barrier for many gases. Hence studies can be directed towards the gas permeability of poisonous gases.

Another inspiring prospect is the modification of EVA matrices with other modified clay particles. Their transport characteristics will be highly interesting.