CHAPTER 6

CONCLUSION AND FUTURE SCOPES

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6.1. Conclusion

The proposed study has identified the effect of modified polymer membrane over the transport of gas flux. The basic objective of the research was to fabricate the polycarbonate membrane and various modifications which can fulfill the desired gas transport properties. The improvement of gas transport properties, mainly the permeability coefficient which causes the reverse effect on the separation factor. It was aimed to improve selectivity of desired gas pairs with gain in the permeability coefficient. To tend over the tradeoff relationship, basic need of the research work was to design the system for gas permeability testing with minimum operating cost. This need has been fulfilled by development of constant pressure/variable volume set-up. The system consist the test equipment with standard material and the output results also matched with the reported data. The cost-effective and reliable technique of preparing blend and composite membrane provides the comfort way to membrane fabrication. The whole experimental part with necessary technical parameters is described in detail in **Chapter 2**. The additional characterization techniques and the equipment functions give additional information about the membranes. Various modifications during membrane synthesis influence the emerging idea in membrane technology. **Chapter 3** focusses the alteration made over the membrane morphology by thin film deposition using metal and metal alloy. The metallic barrier has emended the transport behaviors of the polymer membrane as particularly for nitrogen separation from methane gas is one of the fruitful results of this modification. Although there is reduction in the selectivity for some gas pairs by layered PC membrane, it can be applicable where desired gas transport is required. Thus, one of the objectives of the study to tend towards Robeson upper bound line could have accomplished. In addition, the alloy coating has also improved the plasticization effect for CO_2 gas and the feed pressure has improved the CO_2 separation from other gasses.

Another modification in the polymer matrix is observed by the incorporation of nanofiller. Silica nanofiller dispersion in polycarbonate was synthesized by simple solution cast method and agglomeration of nanofiller was eliminated by ultra-sonication up to some extent. **Chapter 4** focusses on the hydrogen transport behavior by metal coated, mixed matrix and pure PC membranes. The modification has provided the transport to the hydrogen gas molecules to permeate through the membrane. Palladium is considered a best tool for hydrogen transport as it provides ultrahigh purity gas. Their alloy has improved the transport with maintaining the separation factor of H_2 over CO_2. Moreover, Iridium metal coating provided better adhesion with polymer surface. The metallic coating provides platform for physiochemical process which can influence sorption parameter. Metal/alloy coting has improved hydrogen permeability compare to that of pure PC. For polymer-nanoparticle system, where the particle size is in nanometer range exists poor bandage with polymer matrix. The large spacing between the nanoparticles is also responsible for desire gas transport [1]. As nonporous silica particles are mixed with the polymer composition, it does not directly contribute the gas transport properties. It alters molecular chain packing of its mobile segments which results in improved permeation and selectivity. The presence of silica nanofillers has altered the morphology of membrane matrix at the filler/polymer interface promoting amorphous region of the MMM. Moreover, the mean distance between the chain segments is increased due to reduction of polymer chain packing density at the organic/inorganic interface. Membrane stiffness ascribed to improve tortuosity and restriction to segmental mobility results in diffusivity selectivity by disturbing chain packing [2, 3]. The solubility factor can be influenced by change in the backbone stiffness of MMM. The silica particle loading has also significantly affected the gas permeation and at the high silica loading, it may raise the nonlinear expansion of the free volume [4]. The membrane hybridization by MMM have potential to accomplish requirements of gas separation applications. The new emerging approach provides feasibility to execute features from both the organic/inorganic phases. The contemporary study points that although there is an obstacle in the successful introduction of silica fillers in to polymer matrix but the separation factor remains almost unchanged for H_2/CO_2 gas pair. The transient interface region at filler/polymer interface exist particular importance to the separation performance.

The introduction of silica filler in to blend polymer matrix has rewarded potential to alter the transport routs of the penetrant. The blend matrix has influenced the gas permeation whereas the blend composites have reduced permeability coefficient compared to the same blend ratio as described in **Chapter 5**. Oxygen permeability for polymer nanocomposite of pure polymer is increased in remarkable amount compared to reported values. The selectivity of H_2/CO_2 gas pair is more influenced by the modification while for other gas pairs it reduces by the modified membranes. The nanofillers dispersed within the crosslinked regions of the blend matrix generate blockage within the tiny area. Therefore, penetrant diffusion is resisted by these obstacles which in turn to reduce gas transmission. To overcome the difficulty, the filler composition can be modified or somehow porous filler content can be introduced instead of the nonporous fillers. Moreover, the shape of the inorganic particles also play vital role. As it forms blockages between the crosslinked structures, it may restrict to particular gas molecules. The spherical fillers do not allow the penetrant to bypass whereas in the form of nanofiber or oval shaped fillers may leave some negligible void to bypass the gas molecules only to the specific shapes and size. The modification of surface functional group of the filler can induce higher polymer/particle interface region causing strong impact in fractional free volume [5, 6].

6.2. Future scopes

Using metal oxide nanoparticles such as MgO and TiO_2 as fillers can exhibit high affinity to particular gas molecules based on their interaction facilitate transport routs to the penetrant [2]. Thus, the separation factor can be influenced in future scopes. In addition, chemically modified nanofiller also improve the transport routs. As reported by Aghaei et al. fumed silica disperse homogeneously in the polymer matrix producing high percentage of void within the volume and facilitates CO_2 permeability with its selectivity over nitrogen and methane gas [7]. It forms uniform stability in the blend matrix due to its oblong shape and forms good adhesion with host polymer matrix. In SEM analysis, the surface ruptures do not occur on fumed silica dispersed in MMM because of the oblong shape of the filler particles. Additionally, the smoothness of the modified silica helps it to form good adhesion with the host polymer. Fumed silica having high surface coverage of silanol group which provides good interaction with blend matrix. Thus the modification of fillers content makes it as attractive candidate for future scope [8].

By this extensive research, the expectations are accomplished up to some extend as per the permeability point of view but as per the selectivity point of view it hiders for particular gas pairs due to several factors such as the membrane processing issue, filler agglomeration and its shape and unfavorable orientation of silica nanoparticles within the cross linked matrix. Thus the filler interaction with the host materials must be improved for commercial applications of MMM. Chemical modifications such as introduction of functional group may provide necessary chemical affinity to the penetrant in MMMs [2]. The nanofiller dispersed MMMs provide additional diffusion routs to facilitate gas transportations through the membrane. Thus one of the gas transport parameters, the diffusion coefficient is responsible in the improvement of gas permeability. But another one, solubility also performs important role to alter the gas permeability. The introduction of metallic barrier to the polymer matrix can change the sorption of gas molecules which overall reflects in its permeation. Thus the metallic coating over the PNC membrane can improve diffusivity, the kinetic parameter and solubility, the thermodynamic parameter of the resultant membrane. The resultant membrane promotes to bypass condensable gasses through it which may lead to enhance separation of such gasses from the gas mixture. As the gas solubility is promoted by rubbery polymer and diffusivity is influenced by glassy polymers, by compounding both type of membrane material selectivity can be enhanced for specific gas pair. Rubbery polymeric materials are competitive in membrane processing applications due to their quality to separate the gas species as per their condensability. For separation of N_2 from CH_4, alone the glassy or rubbery polymer membrane does not reflect fruitful result because dense structure of glassy polymer promotes permeability of nitrogen whereas flexible rubbery polymers allow methane to permeate [9, 10].

Nowadays, reverse selective membranes for gas and vapor separation applications have reward the attention for industrial applications. Such membrane induces faster permeation of larger gas molecule rather than the smaller one. Such membranes can modify sorption capacity of large condensable molecule instead of providing facilitate transport to the smaller penetrants for diffusion. The additional modifications on the proposed membrane materials can make them compete with the reverse selective membrane [11]. The composite form of organic and inorganic materials has also a potential to surpass the separation benefits exhibited in polymer frame. The unique mechanism of the hybridization allows the current research to apply it in its particular field applications. Currently the membrane technology is running with membrane fabrication processing and contributing to develop highly affordable membrane compositions which can cross the Robeson upper bound limit of 2008 and tending to form new upper bound. Moreover, Penetrant interaction with the target materials should not be underestimated. Therefore, the main future perspective of the field is to understand the interaction of particular penetrant with the target membrane composition. The integration of organic/inorganic compositions presents not only the basic research of the field but also provide their multifunctional nature. Thus they offer great prospects for their applications in extremely diverse fields. Productive insights in the near future are possible with the upgradations of membrane fabrications techniques and introduction of modified materials compositions.

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