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Abstract. The mechanism of gas diffusivity in amine modified epoxy membranes is studied in the frame of free volume properties. Epoxy membranes with two different crosslinking densities and composite with Graphene nanoplatelets were prepared by solvent casting method. The free volume parameters measured by Positron Annihilation Spectroscopy (PAS) show inverse correlation with crosslinking density of the samples. The gas permeability and diffusivity for CO_2 have been studied by gas permeation measurements. The study reveals that the gas permeability and diffusivity change significantly as a function of crosslinking density, free volumes and structural relaxations of the molecular chains.

1. Introduction

Polymeric membranes are essential in applications where gas separation is required such as in the carbon dioxide capture and removal from natural gas mixtures [1]. Polyethylene based epoxy membranes are of interest due to their excellent mechanical strength and high thermal stability [2], ease processing and good compatibility with inorganic fillers [3,4] as well as for easy alteration of the microstructure by changing the crosslinking density. The effect of microstructural changes of the polymeric membranes is of fundamental importance to understand the gas transport mechanisms and the gas separation properties through the membranes. Aliphatic epoxy resins with low viscosity are of interest as gas separation membranes due to their ability to produce flexible polymeric networks with high thermal fluctuations [5]. The microstructure of epoxy networks can be tuned by changing the crosslinking density and the flexibility of the backbone chains [2]. In this paper, epoxy membranes with two different crosslinking densities as well as a composite membrane with Graphene nanoplatelets (GNP), have been prepared with the aim to study the influence of nanolevel molecular packing on the CO_2 gas permeability.

2. Experimental

The aliphatic epoxy resin, neo-pentyl glycol diglycidyl ether (NPGDE) with an epoxy equivalent weight of 145±5 g eq.$^{-1}$ was purchased from Sigma-Aldrich *S.r.l.* (Italy). The polyether diamines, namely Jeffamine D-230 (M. W. = 230 g; amine hydrogen equivalent weight = 59 g eq.$^{-1}$), and

Jeffamine ED-900 (M.W. = 900 g; amine hydrogen equivalent weight = 220 g eq.[-1]) were procured from Huntsman Chemical Co and used as curing agents.

The membranes were prepared by mixing 1:1 stoichiometric ratio of NPGDE epoxy and polyether diamines and hand-mixed vigorously for 10 minutes to ensure uniform mixing. For GNP composite sample (NPGD-900-5), 5 weight % of GNP platelets was added using mechanical stirrer at 100 rpm for 30 min, followed by sonication for 20 min to get fine dispersion in epoxy matrix. The mixture was then degassed for 15 min under vacuum to remove air bubbles. During the curing process, the samples were first cured at 323 K for 4 h, and then post-cured at 353 K for next 12 h. Samples with thickness in the order of 300µm and 2mm were used for gas permeation measurements and other structural characterization analysis, respectively. Fourier transform IR (FTIR) spectra were measured using TENSOR 27 apparatus to ensure about complete curing process. Differential scanning calorimetry (Perkin-Elmer DSC-8500) measurements were carried out to determine the glass transition temperature (T_g). X-ray diffraction (XRD) and Scanning electron microscopy (SEM) have been used to observe the morphology of GNP composite membrane. In the discussion, epoxy-Jeffamine D-230 and Jeffamine ED-900 networks will be referred as NPGD-230 and NPGED-900, respectively.

The PALS measurements were performed at 313 K using conventional fast–fast coincidence system with time resolution of 260ps. The positron source ^{22}Na (15 uCi), deposited on a 7 um thick Kapton film, was sandwiched between two stacks of epoxy sample. The membrane samples were 1.2cm X 1cm X 2mm in dimension. The positron lifetime spectra (3 X 10^6 counts each) were fitted in three discrete and continuous lifetime components by using routine PATFIT-88 [6] and LT9.0 [7] programs, respectively.

Samples shaped in form of discs with diameter of 1.1 cm were used for studying the gas transport process using gas phase permeation technique. The details about gas measurements and experimental apparatus are reported elsewhere [3,8]. Measurements were done at 313 K using CO_2 (purity > 99.99% mol) as test gas kept at pressure 600 mbar.

3. Results and discussion

The completion of curing process in all amine modified epoxy membranes were confirmed by FTIR measurements as shown in Figure 1. The disappearence of peaks at 757 (-CH_2), 838 (C-O-C), 908 cm^{-1} (C-O) from epoxy ring as well as appearence of peaks at 1650 (deformed N-H) and 3440 cm^{-1} (O-H) from diamine confirms the epoxy ring opening and complete crosslinking process. Nano level molecular packing in the membranes has been altered by using curing agents, namely D-230 and ED-900. The backbone chain length of these curing agents is in the order D-230 < ED-900 and hence the crosslinking density is assumed to vary inversely. The crosslinking densities have been calculated by
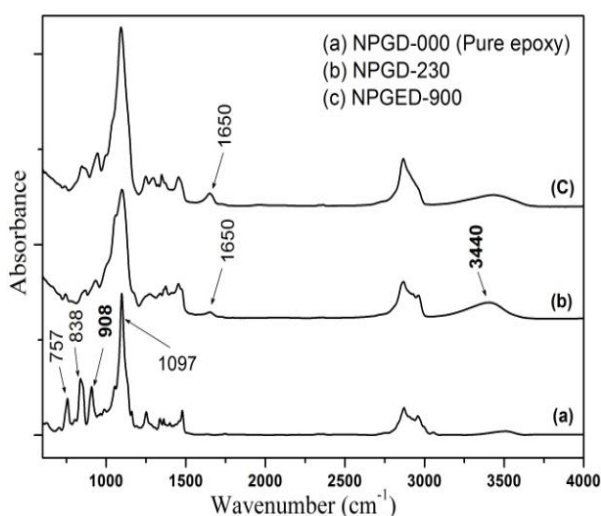

Figure 1. FTIR spectrum of amine-modified epoxy membranes after complete curing process
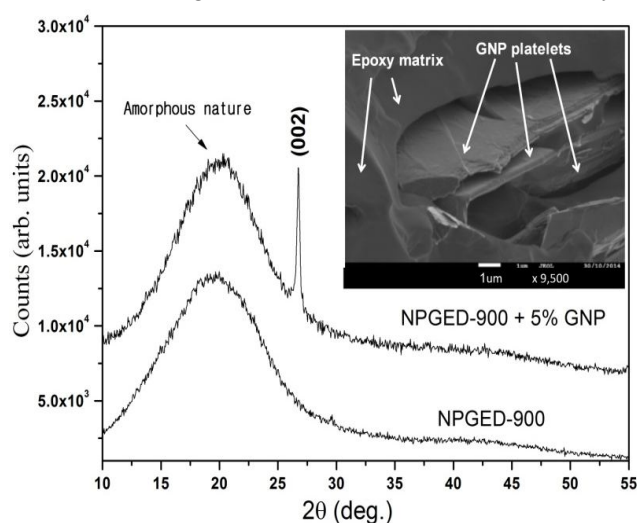

Figure 2. XRD patterns of pristine and composite membranes and SEM image of GNP composite.

reported method [9] and the values are mentioned in Table 1. The effect of crosslinking density on the T_g, attributed to the thermal relaxations in molecular chains, is one of the fundamental aspects in the structure-property relationships [2]. The lower T_g for NPGED-900 (227 K) compared with the T_g of NPGD-230 (273 K) shows that the NPGD-230 sample presents higher crosslinking density (χ = 1.67 sites/nm^3) and more rigid molecular chain packings than NPGED-900.

Table 1. Free volume and CO_2 gas transport parameters for pure epoxy membranes.

Sample at 313 K	Cross-linking density (χ), sites/nm^3	Free volume parameter				CO_2 Gas transport	
		o-Ps lifetime (τ_3), ns ($\pm$ 0.007)	o-Ps lifetime distribution (σ_3), ns	Free volume radius (R), nm	o-Ps Intensity (I_3), %	Permeability (Φ), mol/cm s Pa	Diffusivity (D), cm^2/s
NPGD-230	1.67	2.03	0.42 $\pm$ 0.03	0.29	23.73 $\pm$ 0.28	(8.36$\pm$0.20)X10^{-18}	(3.59$\pm$0.40)X10^{-8}
NPGED-900	0.90	2.56	0.57 $\pm$ 0.04	0.33	24.25 $\pm$ 0.27	(2.51$\pm$0.38)X10^{-16}	(6.67$\pm$1.00)X10^{-7}

CO_2 gas permeability and diffusivity in NPGD-230 and NPGED-900 membranes are reported in Table 1. From the results it is observed that CO_2 permeability diminishes with increasing crosslinking density of the epoxy membranes. NPGD-230 shows poor CO_2 gas permeability and diffusivity compared to NPGED-900. It seems that the rigid molecular chain packing in NPGD-230 membrane creates less diffusion channels for CO_2 gas molecules. In order to gain further insight into the effect of molecular chain packing on the CO_2 gas transport, we analyzed the free volume holes in the membrane microstructure, where the gas molecules are considered to jump for diffusion [10,11]. The free volume parameters (o-Ps lifetime, distribution and intensity) measured by PALS are reported in Table 1. The free volume radius (R) has been quantified using the semi-empirical Tau-Eldrup model [12,13]. It can be seen that free volume parameters are very well in aggreement with the microstructure of the membranes. NPGD-230 shows lower free volume radius and narrower o-Ps lifetime distribution (σ_3) compared to NPGED-900 due to its compact molecular chain networks. Therefore, it is understood that such compact molecular packings in the membrane provide less diffusion channels for gas molecules compared to the flexible networks present in the NPGED-900 membrane. It is proven that the NPGED-900 sample has ideal microstructure of polymer networks that facilitates the CO_2 gas permeabilty and diffusivity. There is no distinguishable change in the o-Ps intensity (I_3) which suggests the similar chemical nature in both membranes. It is attributed as the membrane chemical structure has no longer influence in gas transport results.

Polymer nanocomposites are interesting materials due to their enhanced properties with low amount of nanometer sized fillers. It is reported that the gas properties have been tailored by adding inorganic fillers in the polymeric membranes [3,14]. So we have prepared and studied a NPGED-900-5 nanocomposite membrane consisting of GNPs. In figure 2, XRD patterns of pristine and composite epoxy membranes confirm the amorphous nature of the materials with broad peak. The peak (002) at 2Θ = 26.7° (d-spacing, 0.34 nm) is related to the distance between two GNP layers. The presence of only (002) reflection indicates the GNPs surface is parallel to the surface of the membrane [3]. Such GNPs morphology has been also confirmed by SEM images as shown in figure 2 (inset). Although, the 5 wt% of GNPs incorporated inside the membrane, the free volume parameter and gas permeabilty values measured at 313 K for NPGED-900 and NPGED-900-5 membranes show no significant change. To understand such anomalous behaviour, we measure the free volume radius and CO_2 permeabilty as a function of temperature, as shown in figure 3 and 4, respectively. It is attributed that the present concentration of GNP nanostructures inside the membranes is no longer responsible for any microstructural changes in the membrane matrix and also have no physical or chemical interactions with CO_2 gas permeant molecules as seen no drastic change in the permeability parameter. This suggests that higher wt% of filler would be necessary to modify the CO_2 transport properties in the present membrane.
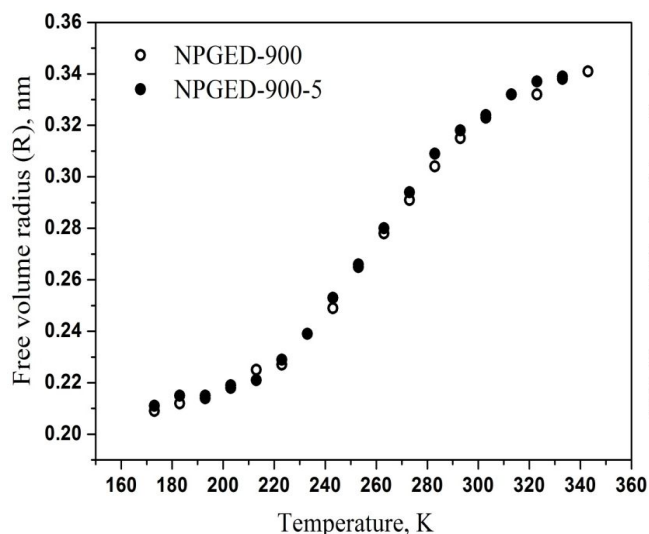
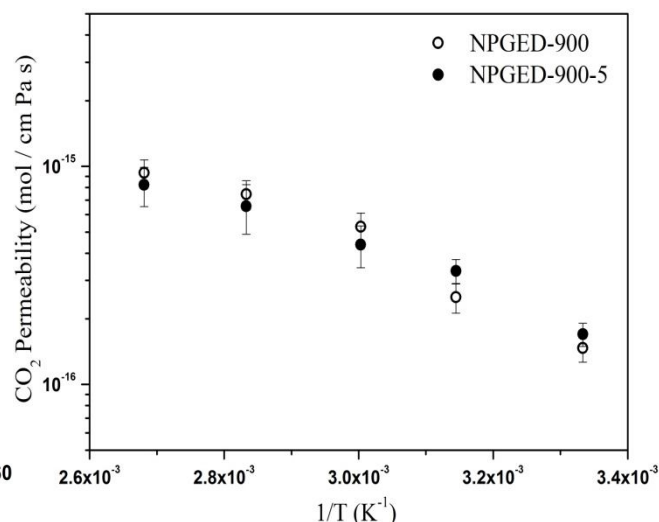**Figure 3.** Free volume radius as a function of temperatures from 173 K to 343 K

Figure 4. CO_2 permeability as a function of inverse temperatures from 293 K to 373 K

4. Conclusion

A good correlation between the average free volume properties measured by PALS and CO_2 gas permeability and diffusivity was found. The present study clearly reveals the influence of nanolevel molecular packing on the CO_2 gas diffusion. The membrane with low crosslinking density presents larger free volume spaces which acts like a diffusion channels for CO_2 gas permeant molecule. Composite membrane with 5wt% GNPs shows no significant change in CO_2 permeabilty which is in aggreement with the free volume results from PALS at different temperatures. Thus, the gas transport mechanism in polymeric membranes can be predicted by their free volume parameters.

References
[1]   Powell C E and Qiao G G 2006 *J. Membr. Sci.* **279** 1-49.
[2]   Patil P N, Rath S K, Sharma S K, Sudarshan K, Maheshwari P, Patri M, Praveen S, Khandelwal P and Pujari P K 2013 *Soft Matter* **9** 3589-3599.
[3]   Checchetto R, Miotello A, Nicolais L and Carotenuto G 2014 *J. Membr. Sci.* **463** 196-204.
[4]   Patil P N, Sudarshan K, Sharma S K, Maheshwari P, Rath S K and Pujari P K 2012 *Chem. Phys. Chem.* **13** 3916-3922.
[5]   Baker R W 2006 *Membrane Technology and Applications* (New York: John Wiley & Sons)
[6]   Kirkegaard P, Eldrup M, Morgensen O E and Pedersen N J 1981 *Comp. Phys. Comm.* **23** 307.
[7]   Kansy J 1996 *Nucl. Instrum. Methods Phys. Res. A* **374** 235-244.
[8]   Checchetto R, Bazzanella N, Patton B and Miotello A 2004 *Surf. Coat. Technol.* **177-178** 73.
[9]   Wang X and Zhou W 2002 *Macromolecules* **35** 6747-6750.
[10] Belov N A, Zharov A A, Shashkin A V, Shaikh M Q, Raetzke K and Yampolskii Yu P 2011 *J. Membr. Sci.* **383** 70-77.
[11] Nagel C, Günther-Schade K, Fritsch D, Strunskus T and Faupel F 2002 *Macromolecules* **35** 2071-2077.
[12] Tao S J 1972 *J. Chem. Phys.* **56** 5499–5510.
[13] Eldrup M, Lightbody D and Sherwood J N 1981 *Chem. Phys.* **63** 51–58.
[14] Sanip S M, Ismail A F, Goh P S, Soga T, Tanemura M and Yasuhiko H 2011 *Sep. Purif. Technol.* **78** 208-213.