Doppler Broadening Positron Annihilation Study of Aluminium Oxide Nanoparticle Embedded Polymethyl-methacrylate

Subhash Chandra, YK Vijay

Abstract—Incorporation of inorganic nanoparticles to the polymeric membrane can serve to achieve tunable nanoporosity, and provides good control over pore size as well as pore distribution in the polymer matrix, In this paper we give the Doppler broadening positron annihilation spectroscopy (DBPAS) analysis of aluminium oxide nanoparticle embedded polymethyl-methacrylate (PMMA) polymeric membranes.The DBPAS is a powerful nondestructive technique to characterize nanoporous structures of polymeric membranes We have prepared nanocomposite membranes of PMMA and aluminium oxide nanoparticles by solution casting method with 0%, 0.2%,0.5% and 1%; weight percent loadings of nanoparticles.DBPAS is used to measure S parameters for the nanocomposite membranes. As the weight percentage of nanoparticles is increased the S parameter increases due to increased free volume at higher concentrations.

Index terms— Aluminium oxide nanoparticles, Doppler broadening positron annihilation spectroscopy, Nanocomposite, Polymethyl-methacrylate, , S parameter, Weight percent.

1 INTRODUCTION

THE Doppler broadening positron annihilation spectroscopy has been established as a useful technique in characterization of open volumes and nano-porous structures in the polymeric materials. Other techniques like scanning electron microscopy, transmission electron microscopy, gas diffusion studies etc. are available for porosity characterization but they are not non-destructive or cost effective and provide limited information about the nano porosity in the samples, however positron annihilation technology provides quite dependable information about the variation of porosity in the samples at nano and subnano level, at present it is the only technique which can directly measure free volumes present in the samples at the atomic scales through its unique way in which the S parameter is quite sensitive to any kind of free volume enteties present in the polymer composite. The positron can have three different forms in polymer material; free positron, para Positronium, ortho Positronium. The Doppler broadened annihilation peak contains the information of momentum distribution of electrons annihilating with these three different species. In DBPAS one can measure the S parameter which correspond to fraction of low momentum annihilation of electron positron pair, p- Positronium being a short lived state annihilates with its own bound electron with low momentum and comprises to the central region of the 511 keV peak; since self annihilation probability of ortho Positronium increases by increasing free volume in material the S parameter which is the ratio of the central low momentum region to the entire photo peak is used to charecterize porous structure of the sample.[1-2]

Polymer and inorganic nanoparticle composite membranes have attracted the researchers due to their improved physical and chemical properties as well as separation properties in gas separation processes, addition of inorganic nanoparticles to the polymer matrix can serve to achieve tunable nano porosity in the polymeric membranes[3], dispersion of metal oxide/ceramic nano particle to the polymer matrix causes change in pore size as well as pore concentration throughout the composite membrane which in turn can affect the selectivity and the permeability of the polymer membrane in gas separation applications. These polymer nanocomposite membranes could be used to incorporate the properties of both the organic and inorganic materials. Previously Yan et al. have prepared Al_2O_3-PVDF nanocomposite membranes by phase inversion mechanism and found that the latter contains large number of micropores and have the possibility for finger like pores to communicate with each other [4].

2 EXPERIMENTAL

2.1 Membrane Preparation

The PMMA was supplied by HiMedia Laboratories Pvt. Ltd., Mumbai (India) and aluminium oxide nanoparticles were supplied by Nano Research Lab, Jamshedpur(India).The PMMA aluminium oxide nanocomposite membranes were prepared by solution casting method discussed by Shweta et al. [5] For this dichloromethane is used as a solvent [6] Different weight percentages of aluminium oxide(0.0%,0.2%, 0.5%, 1%) nanoparticles were dispersed in PMMA-dichloromethane solution using magnetic stirrer for 8 hours, 10 minute ultrasonication was performed using ultrasonic bath sonicator for even dispersion of nanoparticles in the solution, thus prepared solutions were poured in a flat bottom petri dish, floating on mercury to obtain membranes of even thickness, the solution was left in petri dish for 24 hours to let the solvent evaporate at room temperature, after that the homogeneous composite membrane was peeled off.

2.2 DBPAS measurements

To characterize the nanocomposite membranes we are using an in situ DBPAS set up shown in fig. 2.2.1, in this set up an HPGe detector is being used; which has an energy resolution of 1.3keV at 511keV. The energy calibration of the detector was done using ^{137}Cs, ^{60}Co and ^{22}Na radioactive sources as calibration sources.

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Fig. 2.2.1 Photograph of in situ DBPAS set up.

35mCi, ^{22}Na(half life 2.6 years) radioisotope is used as a positron source in the set up whose decay scheme is given in fig. 2.2.2, this source is heavily shielded by lead bricks; a slit is made through these lead bricks to make a beam of annihilation radiation to be detected by HPGe detector.

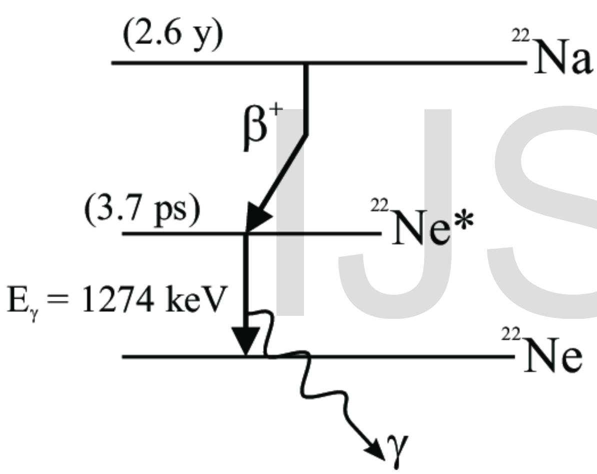


Fig. 2.2.2 Decay scheme of ^{22}Na radioisotope [7]

Composite membranes loaded with different weight percentages of aluminium oxide nanoparticles were measured for DBPAS measurements each for 10 hours and spectrum were recorded using Genie-2k software.

3 RESULT AND DISCUSSION

The SP program [8] is used to evaluate the S parameters with Gaussian fitting. It is observed that S parameter shown in fig. 3.1 for the nanocomposite membranes for lower concentration of nanoparticle loading there does not change much, for higher concentration of nanoparticle loading wt.% (1%) the S parameter decreases rapidly. Since the S parameter is defined as the ratio of the central low momentum region to the entire 511keV photo peak; in the context of the present study the change in S parameter is associated with the change in size and concentration of the free volume holes in the nanocomposite membranes. at lower concentration the nanoporosity is not much affected by nanoparticle addition while for higher nanoparticle concentration the nanoporosity decreased by pore clogging due to excess nanoparticle concentration.

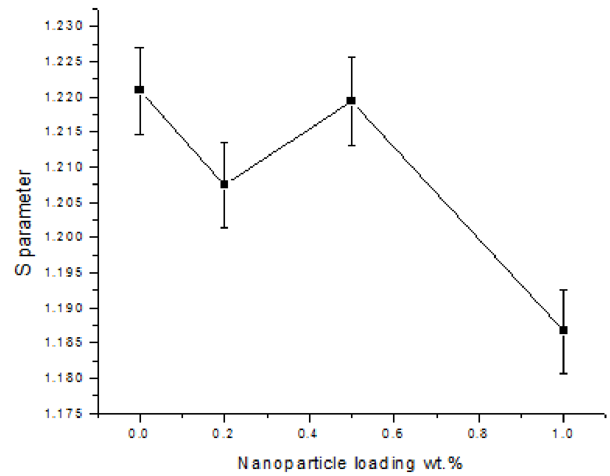
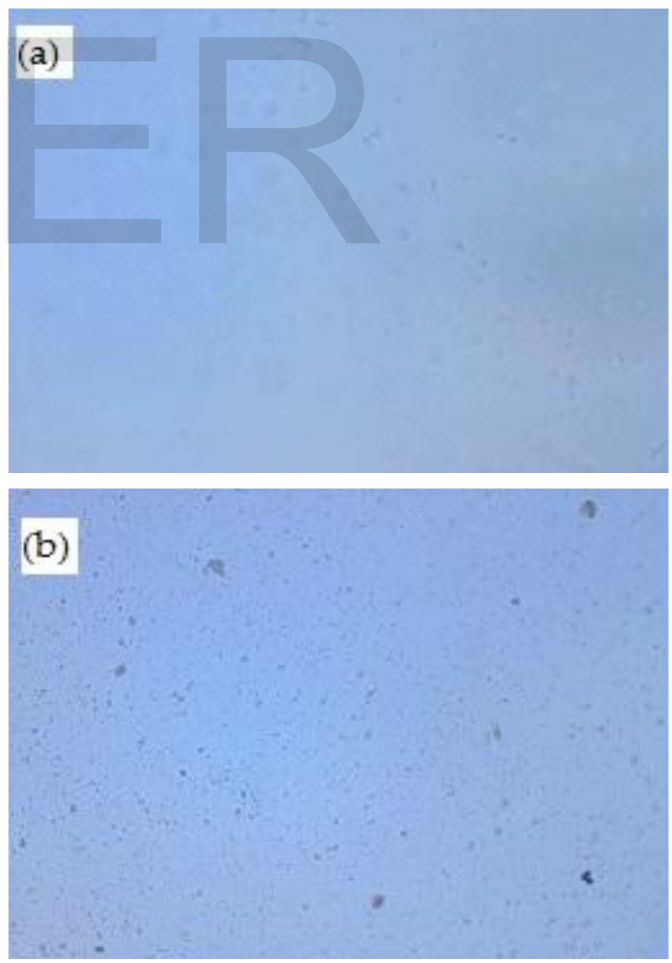


Fig.3.1 Variation of S parameter for nano composite mem -brane with nano particle loading wt. %.



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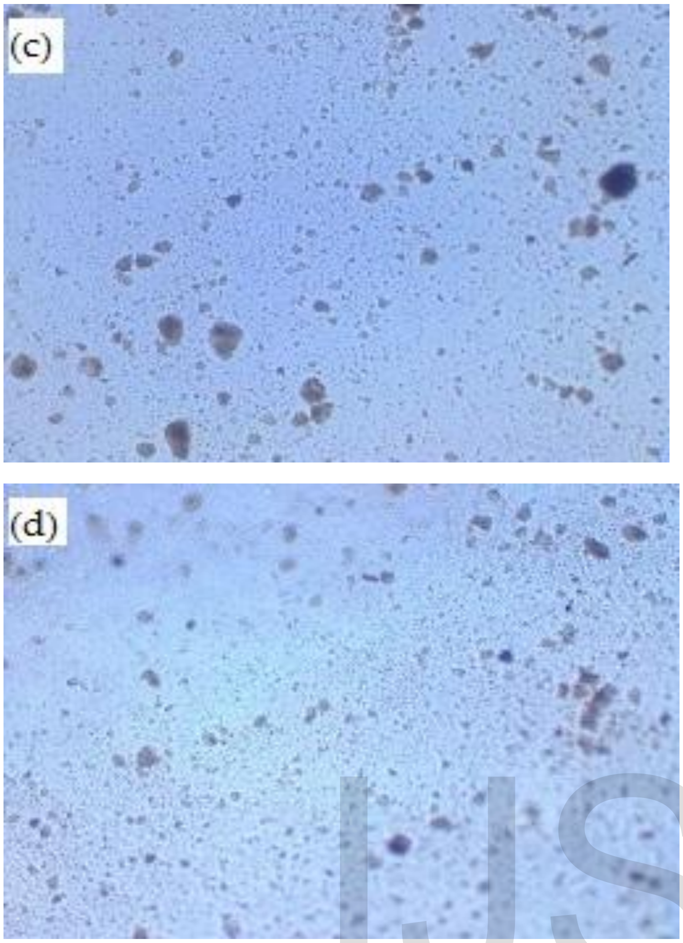

Fig. 3.2 Optical micrographs of nanocomposite membranes (a) pristine PMMA, (b) PMMA+0.1 wt.% nanoparticles, (c) PMMA+0.2 wt.% nanoparticles, (d) PMMA+0.5 wt.% nanoparticles, (e) PMMA+1.0 wt.% nanoparticles.

4 CONCLUSIONS

Addition of Aluminium oxide nanoparticles to the polymer matrix can serve for tuning nanoporosity at higher concentrations while at lower nanoparticle loading one can change other physical properties without compromising nanoporosity present in the polymer, DBPAS technique can be used as a cost effective direct method to sense any kind of free volume present in the composite membranes.

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