Effect on Nano-porosity and Thermal Stability of Polymethyl-methacrylate Polymer Membranes by Titanium Oxide Nanoparticle Dispersion.

Subhash Chandra
Department of Physics
University of Rajasthan, Jaipur (India)
E-mail: subbichandra@gmail.com. Mob +919928153253
YK Vijay
Vivekananda Global University
Jagatpura, Jaipur (India)
E-mail: vijayyk@gmail.com, Mob +919461302757

Abstract— The control over nanoporosity in polymers with thermal stability could be achieved by nanoparticle dispersion in the polymer matrix. Titanium oxide (TiO_2) nanoparticles dispersed Polymethyl-methacrylate nanocomposite membranes were prepared using solution casting method and these prepared membranes were characterized for nanoporosity using Doppler broadening positron annihilation spectroscopy (DBPAS) and scanning electron microscopy (SEM), Thermo-gravimetric measurements were carried out using simultaneous thermo-gravimetric analyzer (STA); It is found that as nanoparticle weight percentage (wt.%) increases at lower filler concentrations of TiO_2- in nanocomposite systems the nanoporosity increases, while at higher filler concentrations nanoporosity decreases, the thermal stability of these composites doesn't deteriorate by TiO_2 nanoparticle loading.

keywords— Doppler broadening positron annihilation spectroscopy, Nanocomposite, Nanoparticle, Nanoporosity, Weight percentage.

1 Introduction

THE membrane technology has been proven to be quite versatile technology for the separation applications in the past few decades. The polymeric membranes have been shown many advantages over other inorganic membranes in various industrial processes like, no phase changes or chemical additives; modular which is easy to scale up, simple in operation, relatively low energy consumption, etc. Therefore, membranes are being widely used in various fields such as water treatment [1],[2], gas purification or separation [3], food processing technology [4], pharmaceutical industries [5] and environmental protection [6]. Polymeric membranes have become more favourite of the researchers due to their better pore forming control and low cost manufacturing [7]. Having all these advantages polymer membranes also have some disadvantages in which membrane fouling is the biggest of all during filtration process [8], [9]. Addition of various types of nanoparticles has been in focus to overcome this disadvantage and improve the membrane performance.

Polymer composite membranes have been established to be the most promising candidate in water and waste water treatment technologies [10] Addition of inorganic nanoparticles to the polymeric membranes has been shown an interesting approach to improve chemical, physical and separation properties of Polymer membranes by the incorporation of both inorganic and organic material properties to the same membrane hence these nanocomposite membranes show better permeability, selectivity and mechanical and thermal strength [11]. Polymer inorganic nanoparticle composite materials also called nanocomposites, are defined as the inorganic nanoparticles are dispersed uniformaly in the polymer matrix [12], [13]. Titanium dioxide have been in the centre of attraction due to its unique properties as photo catalyst, oxygen sensor, to decompose organic compounds and can be used in filtration membranes to overcome membrane fouling [14], [16] Studies on organic solvent filtration membranes of polyimide have shown that presence of TiO_2 in polymeric membranes resulted in decreased porosity of the membranes. Nanofiltration experiments showed that TiO2 nanoparticles are helpful in preventing the porous structure from collapsing and therefore, reduce flux decline. Incorporation of TiO2 nanoparticles into the membranes enhanced the hydrophilicity and mechanical strength of the membranes [17].

In this work we report a novel method to control the nanoporosity present in the PMMA membrane by dispersion of titanium oxide nanoparticles. Different weight percentages of nanoparticles were dispersed in the polymer matrix using solution casting method. The thermo-gravimetric analysis of as prepared composite membranes was also performed.

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2. Experimental

2.1 Membrane Preparation

The PMMA was supplied by HiMedia Laboratories Pvt. Ltd., Mumbai (India) and TiO_2 nanoparticles were supplied by Nano Research Lab, Jamshedpur(India).The PMMA, TiO2 nanocomposite membranes were prepared by solution casting method [18] as shown in figure 2.1.1.

Dichloromethane was used as a solvent [19]. Different weight percentages (0.0%, 0.1%, 0.2%, 0.5%, 1%, and 2%) of TiO2 nanoparticles were dispersed in solvent, 10 minute ultrasonication was performed using ultrasonic bath sonicator for de-agglomeration of TiO_2 nanoparticles. After that PMMA polymer granules were added and dissolved in this dichloromethane-TiO_2 solution using magnetic stirrer for 8 hours, 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 membranes were peeled off. The whole scheme of the membrane preparation method is shown in figure 2.1.1

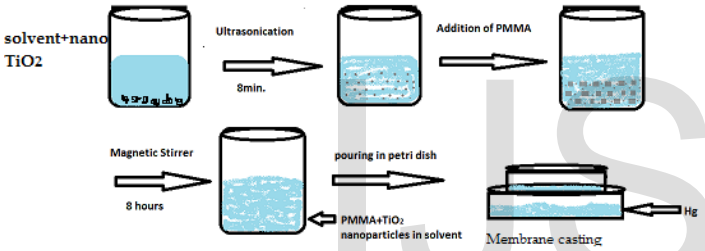


Figure: 2.1.1 schematic diagram of solution casting method.

2.2 DBPAS measurements

To study the change in nanoporosity of PMMA nanocomposite membranes an in situ DBPAS set up shown in figure 2.2.1 has been used.

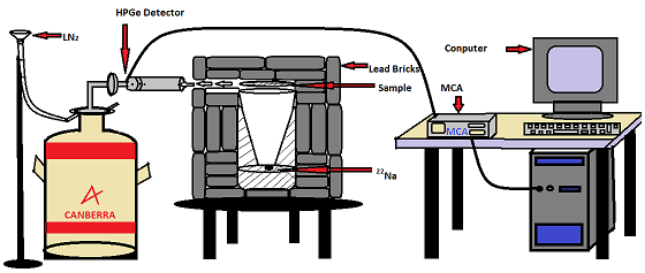


Figure: 2.2.1 Schematic figure of in situ DBPAS setup.

The DBPAS setup consists of an HPGe detector supplied by Canberra inc. the detector has an energy resolution of 1.3 keV at 511 keV energy. In this DBPAS setup ^{22}Na (35 mCi) radioisotope of sodium has been used as positron source. The source has been shielded by lead bricks to avoid gamma ray exposure to the persons who performed the experiment. The S-parameter and W-parameter are calculated from observed spectrum of annihilation radiation, using SP program. The S-parameter is the ratio of the central region of the 511 keV photo to peak to the total peak and the W-parameter is the ratio of the wing regions of both sides of the 511 keV photo peak to the total peak.

The S-parameter is sensitive to annihilation of positron/positronium (bound pair of electron and positron in material) with low momentum electrons hence the S-parameter is affected by the size and number of open volume/nanopore present in the sample.

2.3 SEM measurements

The cross sectional SEM measurements were carried out using Bruker Nova Nano SEM machine available at MRC, MNIT, Jaipur (India). The samples were prepared using liquid nitrogen for viewing cross sectional open volume structures of the nanocomposite membranes.

2.4 Thermo-gravimetric analysis

Thermo-gravimetric analysis were carried out using simultaneous thermo-gravimetric analyzer, HITACHI STA 7300 machine to study the thermal decomposition or the thermal stability of the nanocomposite membranes and the weight loss of the composite membrane was measured with increase in temperature.

3 Results and discussion

3.1 Nanoporosity investigation using DBPAS and SEM

The results of DBPAS measurements of S-parameter for nanocomposite membranes are shown in figure 3.1.1 from the graph it is clear that as the weight percentage of the TiO_2 nanoparticles increased in PMMA polymer matrix the S-parameter increases at lower TiO_2 nanoparticle filler concentration (0.0wt% to 0.5wt%) while as the TiO_2 nanoparticle filler concentration is increased further the S-parameter decreases.

These results are in accordance with previously studied Polymer-TiO_2 nanocomposite system [20] and can be attributed to increased nanoporosity by TiO_2 nanoparticle addition to the PMMA polymer matrix. This increased nanoporosity at lower filler concentration can be seen as a consequence of creation of nano-void due to polymer chain breaking in the nanocomposites. The decreased nanoporosity at higher concentration of nanoparticles caused by nanopore clogging due to excess nanoparticles present in the polymer matrix.

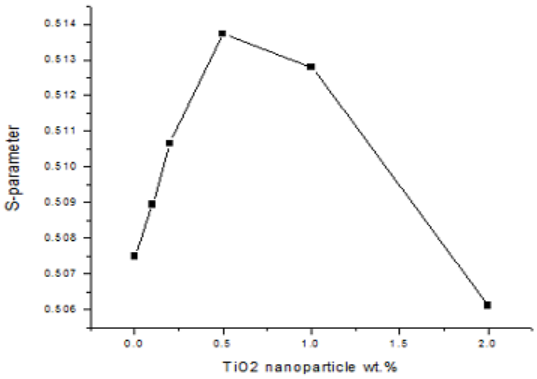


Figure: 3.1.1 Variation of S-parameter with TiO_2 wt%.

The cross sectional SEM measurements as shown in figure 3.1.2 give similar results for all the composite membranes and are in good agreement to the DBPAS results.

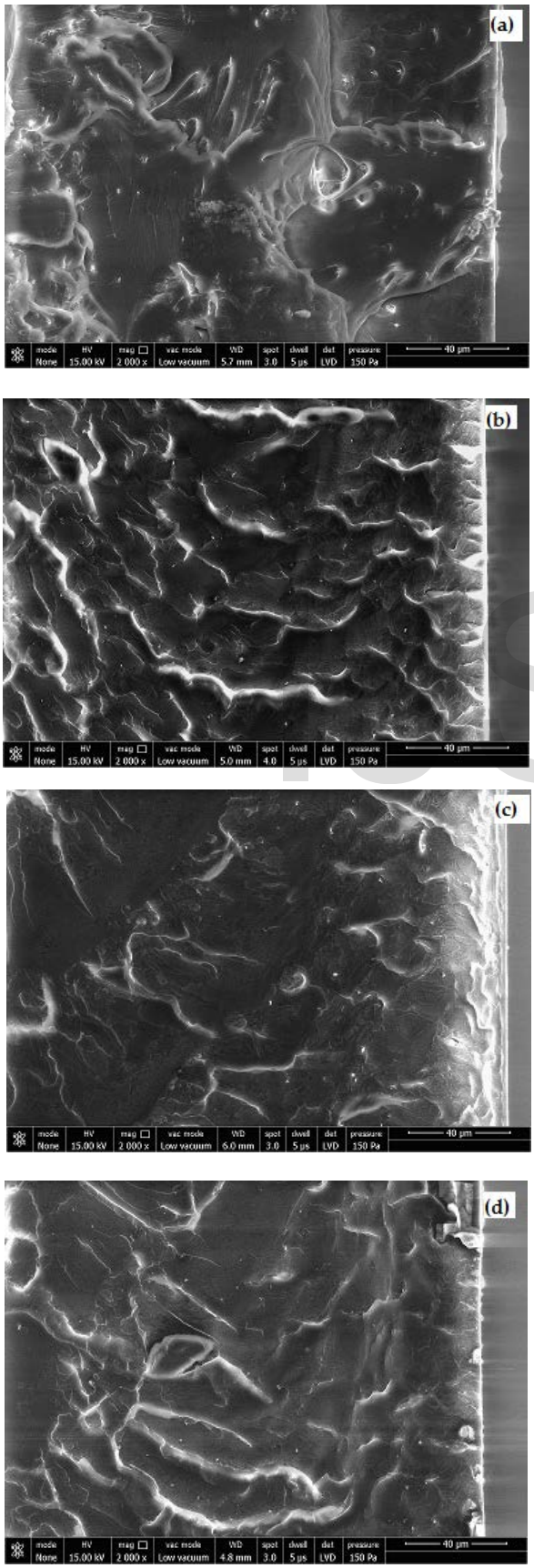
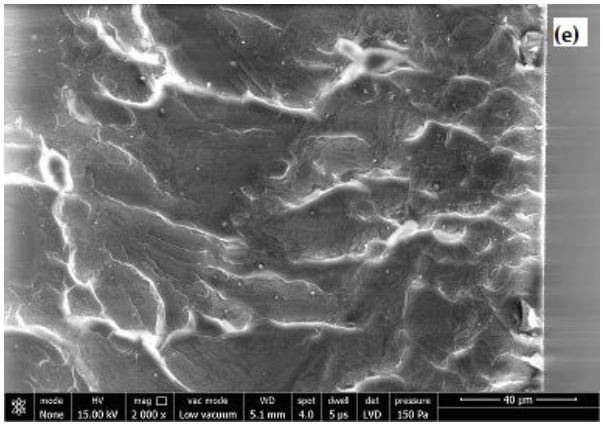


Figure: 3.1.2 Cross sectional SEM images of nanocomposite membranes (a) PMMA+0.0 wt% TiO_2, (b) PMMA+0.1 wt.% TiO_2 (c) PMMA+0.5 wt.% TiO_2 (d) PMMA+1% TiO_2 (e) PMMA+2% TiO_2.



3.2 Thermo-gravimetric analysis

The percentage weight loss of nanocomposite membranes for different compositions are measured with temperature and results are plotted in figure 3.2.1 it is clear from the results that for all the nanocomposite membranes the dominant weight loss occurs between 300°C to 400°C it is also seen that the on-set of thermal decomposition is almost at the same temperature in all the nanocomposite membranes.

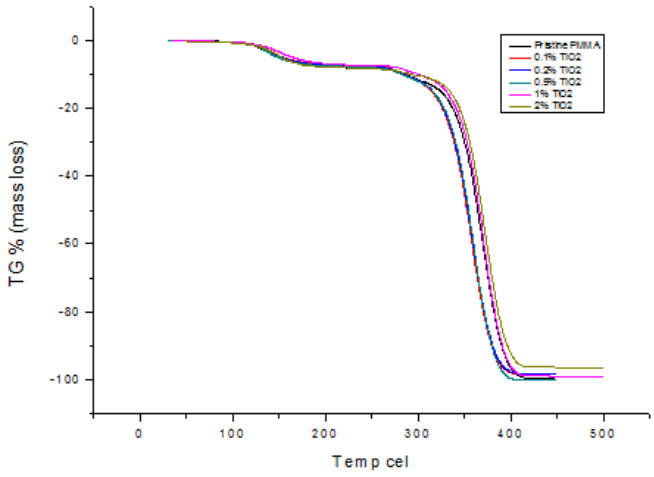


Figure: 3.2.1 Weight loss curve of nanocomposite membrane.

4 Conclusions

The addition of TiO_2 nanoparticles to PMMA polymeric membranes is a novel method to control the nanoporosity present in the polymeric membranes. At very low concentrations of TiO_2 nanoparticle the nanoporosity increased and run throughout the membrane and at higher filler concentration

the nanoporosity decrease; these composite membranes could be useful in nano-filtration and nano-seperation experiments. These composite membranes shows similar thermal stability which implies that the thermal stability of these nanocomposites is not deteriorated at low filler concentrations.

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