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ZnO Nano Composites Polystyrene Membranes: Plasma Treatment & Characterization

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***Abstract*— Systematic study was carried out to characterize the effects of Nitrogen ion plasma on nanocomposite polymer membranes. 10-25 nm sized nanoparticles of ZnO are synthesized by chemical route and characterized by TEM. Solution casting method was used for synthesis of ZnO nanocomposite and polymeric membranes of 40 micron were prepared. Glow discharge low temperature nitrogen ion plasma treatment was done for these membranes. These membranes were characterized before plasma treatment and after plasma to make comparative study by different technique such as optical microscopy, Scanning electron microscope (SEM), Atomic Force Microscope (AFM), Optical Absorbance Spectroscopy. Surface roughness was found to be increased after plasma treatment and hence applicable in many biomedical applications.**

Keywords*— *Synthetic Membrane, Plasma Treatment, Ion Energy, Plasma Etching, Biomedical applications.

I. INTRODUCTION

Polymers have become very important materials in modern manufacturing processes and offer wide varieties of chemical and mechanical properties applicable in numerous applications [1-3]. It is well known that permanent bonding, coating, printing etc. are difficult on many polymers without surface pre-treatment. Therefore, after the surface treatment of polymers they have significant benefits in the specific requirements of surface properties while retaining bulk mechanical properties [4, 5]. The physical and chemical surface modifications of polymeric materials without alteration of the bulk properties are of great interest in many applications [6- 8].The complex nature of plasma due to presence of ions, neutrals and radiation in the discharge makes low-temperature plasmas widely useful in a growing number of materials fabrication processes including the etching of complex patterns and surface modifications of polymeric membranes [9].

Due to many interesting properties of ZnO nanoparticles it has gained great interests to scientists and researchers around the world. ZnO can be simply used as the filler for coatings on plastics/polymers and rubbers resultant improved performance in UV-shielding [10], dynamic fracture toughness [11], flame retardant and optical transparency [12].

Nano composites in principle can be formed from clays and organoclays in a number of ways including various in situ polymerization [13]. Small addition of nano-particles in polymers has potential to drastically transform the properties of the host polymer [14]. These Polymer nanocomposites have many diverse applications like flame resistance [15], dye-sensitized solar cells [16], bound catalysts [17], cosmetic applications [18], nanomedicine [19] and many others biomedical applications [20]. Thus polymer nanocomposites represent a new alternative to conventionally filled polymers [21].

But many of these applications especially biomedical applications are depend on surface roughness i.e. high surface roughness is required for many biomedical applications. Low temperature plasma treatment offers high roughness to material surfaces. Hence in this paper a systematic study was carried out to characterize the effects of Nitrogen ion plasma on nano composite polymer membranes. 10-25 nm sized ZnO nanoparticles of are synthesized by chemical route and characterized by TEM. Solution casting method was used for synthesis of ZnO nanocomposite and polymeric membranes of 40 micron were prepared. Glow discharge low temperature nitrogen ion plasma treatment was done for these membranes. These membranes were characterized before plasma treatment and after plasma to make comparative study by different technique such as optical microscopy, Scanning electron microscope (SEM), Atomic Force Microscope (AFM).

II. EXPERIMENTAL

ZnO nanoparticles are synthesized by using chemical method as described by Agarwal et. al. [20, 22]. Polystyrene (PS) granules were used to prepare flat sheet membranes by solution cast method. Dichloromethane of extra pure grade was used as a solvent for preparing membranes. Solution-casting method was used for preparation of 5% ZnO doped polystyrene membranes. Polystyrene granules are weighed and dissolved in dichloromethane (CH_2Cl_2). Agitation of solution is important, since solvent penetration is very slow for high molecular weight polymers and a viscous coating is usually formed over each particle. Solution was stirred by magnetic stirrer to ensure the uniform dissolution and to enhance the rate of dissolution. Process is carried out at room temperature for around 2-3 hours till a clear solution is formed. ZnO nanoparticles were dispersed in dichloromethane (CH_2Cl_2) by ultra-sonication and this solution was mixed with polymer solution and stirrer for one hour. This solution was then put into flat-bottomed Petri-dishes floating on mercury to ensure uniform thickness of the membranes. The solvent was allowed to evaporate slowly over a period of 3-4 h. The films so obtained were peeled off using forceps. Nitrogen ion plasma treatment was done for these membranes at 10-1 mb pressure. Low temperature nitrogen ions plasma was generated by using 1KV power supply with plasma current of 0.2 mA.

The particle size and morphology of ZnO NPs are determined by transmission electron microscopy (TEM). The imaging is performed using a Technika TEM instrument operating at 200 kV. Optical Absorbance Spectroscopy was performed for membranes by using a double beam UV-Vis spectrophotometer (Shimadzu 2100). LABOMED optical microscope is used for the imaging and micrographs (at 100X magnifications) are stored in computer through CCD camera which is attached to the computer with standard software (Pixel View). While SEM analysis was done using scanning electron microscope (Carl ZEISS EVOR -18) operated at 20kV. Surface topography and roughness analysis of the plasma-treated nanocomposite surfaces was carried out means of atomic force microscopy (AFM- Nanosurf easy scane 2).

III. RESULT AND DISCUSSIONS

Synthesized ZnO NPs are dried and re-dispersed in acetone by ultra-sonication. Fig 1 shows TEM image of ZnO NPs synthesized having spherical shape and particle size ranging from 10-25 nm. Individual particles in TEM images can be identified easily that shows no aggregations in ZnO NPs.

40 µm, 5% ZnO Nanocomposite PS membranes were synthesized using solution casting method and low temperature nitrogen ion plasma treatment was done. Plasma treatment consists of a source chamber with the complete power supply and connected to a vacuum system. The N_2 gas used for generating plasma is admitted into source chamber using a flow controller and plasma is generated by applying high voltage DC power between two electrodes. This glow discharge plasma is quite homogenous & magnetically confined at low-pressure. The other energetic species like radicals, electrons and meta-stable photons in short-wave UV range may also present with nitrogen ions in this plasma.

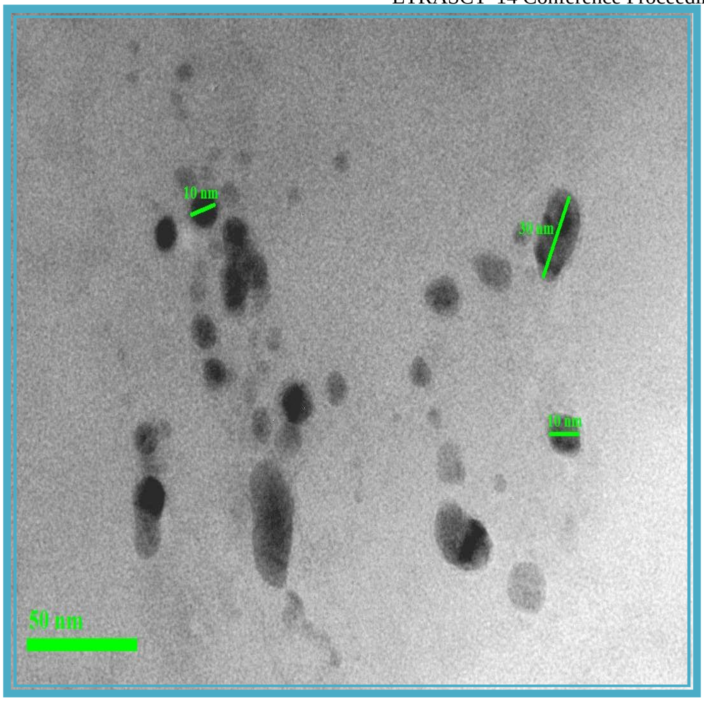
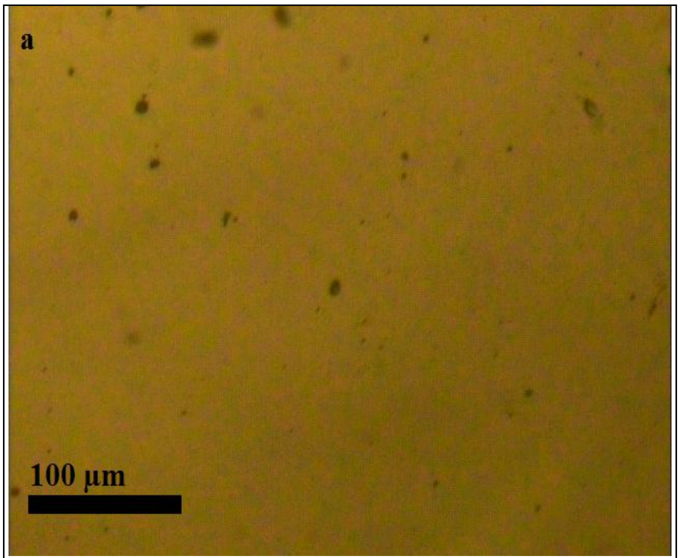
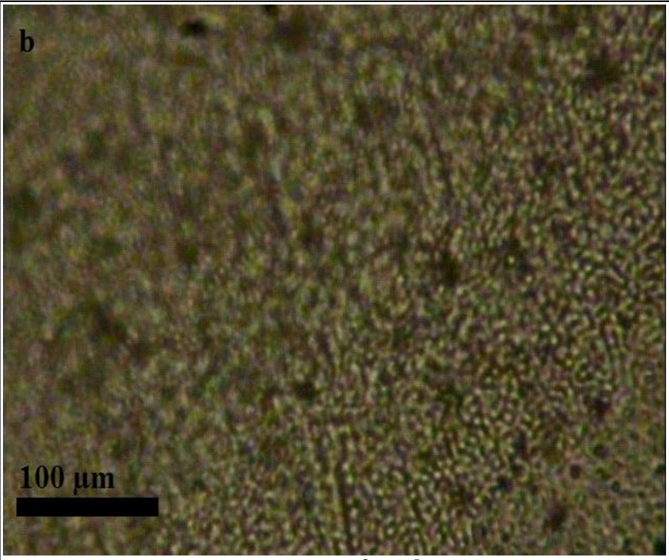


Fig. 1. Transmission electron micrographs (TEM) of ZnO NPs synthesized, having spherical shape and particle size ranging from 10-25 nm.

Effect of nitrogen plasma treatment/modification on the surface of nanocomposite membrane is primarily investigated by optical microscope at higher dimension (100 X magnifications) as shown in Figure 2. This shows surface morphology and surface roughness increased after plasma treatment. Nano composites are further investigated at lower dimensions (higher magnifications) by SEM, there also higher roughness was observed after plasma treatment that shows applicability of nitrogen plasma for modulation of surface properties of polymers.

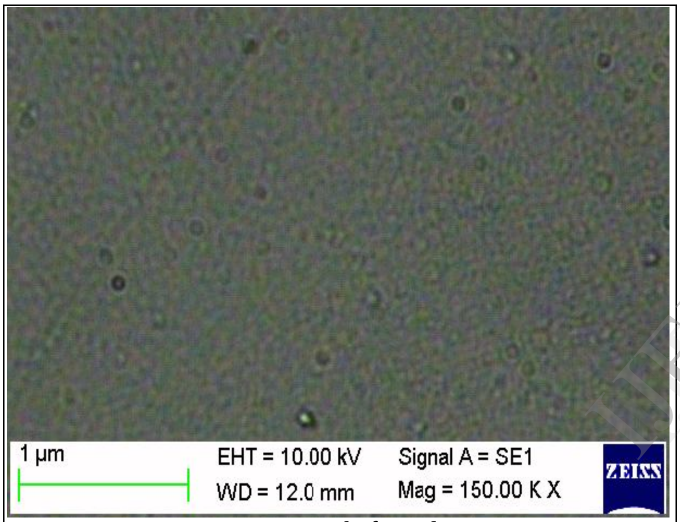


Zno PS Nanocomposite before plasma treatment

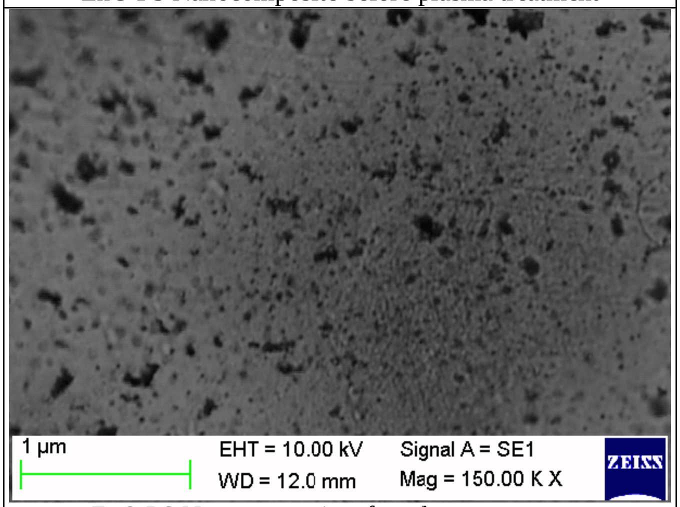


Zno PS Nanocomposite after plasma treatment

Fig. 2. Optical microscope images of (a) 5 % ZnO doped PS membrane (b) 5% ZnO doped Plasma Treated Membrane.



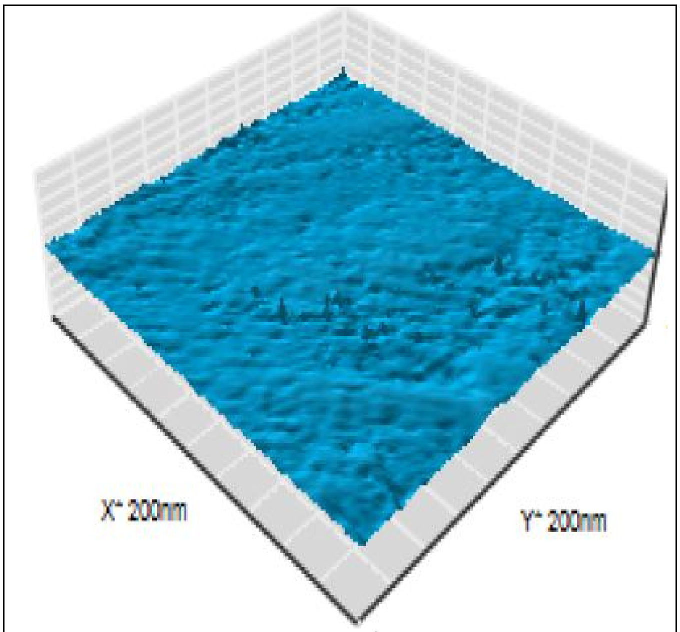
ZnO PS Nanocomposite before plasma treatment



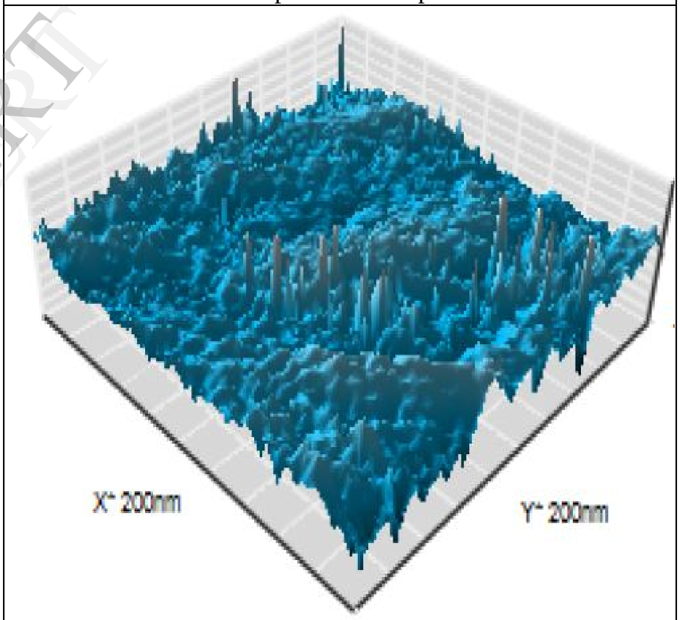
ZnO PS Nanocomposite after plasma treatment

Fig. 3. SEM images of (a) 5 % ZnO doped PS membrane (b) 5% ZnO doped Plasma Treated Membrane.

We have also investigated surface morphologies and topography before and after plasma treatment for ZnO nanocomposite polystyrene membranes using AFM. AFM topography images of these films are shown in Fig. 4. Here also high roughness was observed after plasma treatment i.e. plasma treatment improve its porosity of membranes.



ZnO PS Nanocomposite before plasma treatment



ZnO PS Nanocomposite after plasma treatment

Fig. 4. AFM images of (a) 5 % ZnO doped PS membrane (b) 5% ZnO doped Plasma Treated Membrane.

Fig. 5 shows the optical absorbance spectra in the wavelength range of 300–800 nm for Nano composite ZnO, polystyrene membranes before and after plasma treatment. It was inferred from the spectra found that plasma treatment decrease optical transmission of nanocomposite and material become more opaque after plasma treatment.

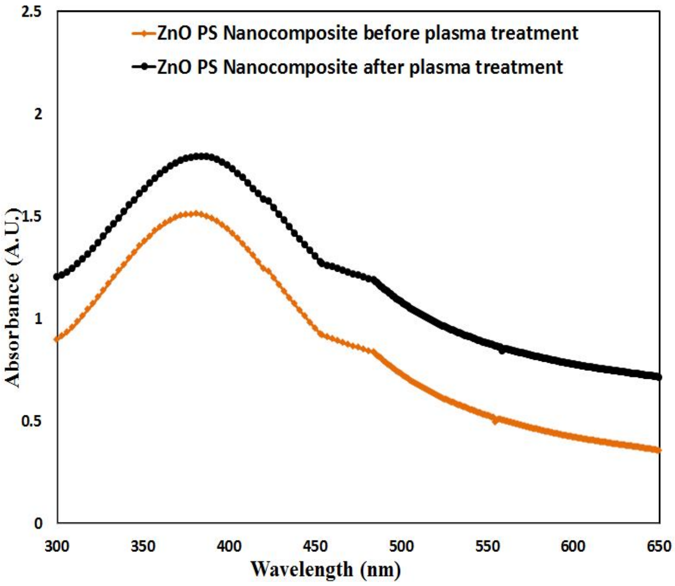


Fig.5. Optical absorbance spectra of Nano composite ZnO membranes before and after plasma treatment.

IV. SUMMARY AND CONCLUSIONS

Nanoparticles of ZnO having spherical shape and particle size ranging from 10-25 nm are synthesized using chemical method. 5% ZnO Polystyrene nanocomposite membranes are prepared by solution cast method. These membranes are exposed with low temperature glow discharge nitrogen plasma for improving the surface properties and activation. An increase in surface roughness and topography has been observed after plasma treatment. So that this technique can be used to prepare nanocomposite membranes with desired surface properties, important in many biomedical applications.

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