

Surface Modification of ZnO Coated PMMA Film Using Low Temperature Plasma

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Abstract: Zinc Oxide Nano Particles were prepared by sol gel method. Nano particles of ZnO doped with PMMA (Poly Methyl Methacrylate) film was prepared by dip coating method. The ZnO nanoparticles doped PMMA film was exposed to DC glow discharge plasma for surface modification purposes. The plasma treated ZnO Nano / PMMA film was analyzed by FTIR spectrum, X-ray diffraction, scanning electron microscopy (SEM), and Energy dispersive spectrum, from the various results such as successfully functionalization, crystal structure and surface morphology and compared with untreated film.

Keywords: ZnO Nano particles, PMMA film, DC glow discharge plasma, Surface modification

1. Introduction

Polymer surface modification is an elegant method for generating functional polymer surfaces combined with the desirable attributes of bulk polymers. Modification techniques include plasma polymerization, plasma spray coating, ion implantation and ion-beam-assisted deposition, flame, corona treatment, photons, electron beams, X-rays. Key properties imparted by these technologies include wettability, adhesion, lubricity, chemical affinity and biocompatibility. Surface modification plays a very important role in many industrial end-use applications: electronics, packing, industrial, automotive and aerospace, storage, and medical devices. In fields such as protective coatings, adhesion, and biomaterials however, their surface properties are equally important for their success. Since polymers often do not possess the required surface properties for these, or similar applications, intensive research efforts have been made in recent years to develop surface treatment methods that alter and improve the chemical and physical properties of polymer surfaces. Improving adhesion characteristics, increasing hydrophobicity, introducing special functional groups on the surface, or modifying the surface morphology is an example for the purposes of these surface treatments. Firstly, some surface treatment methods are presented, that enable the alteration of chemical and physical properties of polymer surfaces with affecting their bulk properties. Secondly, surface modification by attachment of a monolayer or thin polymer film surface is discussed. In the present work ZnO Nano /PMMA films were treated with DC glow discharge plasma with an aim of improving the optical properties. The plasma treated ZnO Nano/PMMA film was characterized by the FTIR spectrum, X- Ray Diffraction, Scanning electron microscopy and Energy dispersive spectrum studies. These results such as crystal nature, functionalization, and surface morphology, elemental analysis of untreated film was compared with the plasma treated film.

2. Experimental and Methodology

2.1 Preparation of ZnO Nano/PMMA films

ZnO Nano particles doped with PMMA is obtained by magnetic stirring. A solution containing PMMA 150ml is added with synthesized ZnO Nano powder. The solution was then heated at a room temperature with constant stirring. After stirring for 2hrs, the glass substrate is dipped in the solution for 30mins. The films were prepared and allowed to annealing process. A well-dispersed film of ZnO Nano inserted into PMMA was obtained.

2.2 Plasma Exposure

The coated ZnO Nano PMMA films were exposed to DC glow discharge plasma was generated in a stainless steel chamber of 50cm length and 30cm internal diameter. Vacuum of 10^{-3} mbar was maintained inside the chamber using a vacuum pump. Required vacuum was maintained by fine control gas needle valve and the pirani gauge was used for pressure measurement. Circular shaped the electrodes made of aluminum have a diameter of 6cm were fixed inside the chamber. The electrodes were separated by a distance of 6cm. High tension DC power supply 1.5 kV was used. The films were placed perpendicular to the discharge axis between the parallel electrodes using a holder. After the plasma treatment the treated film was analyzed. The operating parameters influence the surface modification of the films is listed in Table (1).

Discharge potential	350-400V
Pressure	0.3mbar
Exposure time	5 mins
Electrode separation	6cm
Sample	ZnO Nano / PMMA film
Plasma gas	Atmospheric air

3. Results and Discussion

3.1 FTIR ANALYSIS ON ZnO COATED PMMA FILM:

The FTIR spectra of ZnO coated PMMA Film was recorded in the frequency region of $400\text{--}4000\text{cm}^{-1}$ using thermo Nicolet, Avatar 370 spectrometer a resolution of 0.9 cm^{-1} with scanning speed of 2 mm/s . and the recorded FTIR spectra is shown in figure(1). The following vibrational assignments are presented in Table (2).

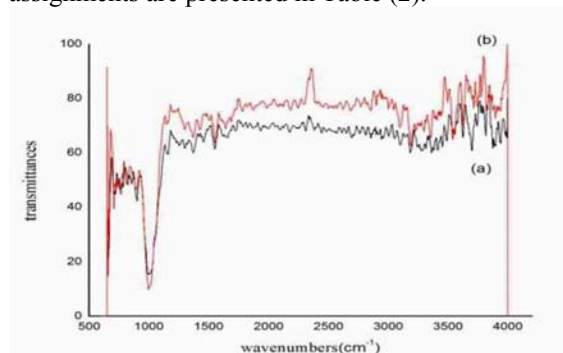


Figure 1: FTIR spectrum of ZnO coated PMMA Film (a) Untreated film (b) plasma treated film

Table 2: FTIR analysis on ZnO Coated PMMA Film

Literature (cm ⁻¹)	Untreated PMMA Film	Treated PMMA Film	Peak Characteristics
700-800	704.20	726.90	C-Cl Stretch
800	819.98	820.89	C-Cl Stretch
912-1141	901.02	882.18	(C-O-C) inplane, symmetric stretching
1000-1150	1148.01	1368.44	C-F Stretch
1376	1367.99	-	C-H Bending
1510	1553.23	1544.15	C=C-C Aromatic ring

3.2 X-RAY Diffraction Analysis

The X-Ray diffraction spectrum was analyzed by automated PAN analytical MPD diffract meter of wavelength $\lambda=1.5406\text{\AA}$. The XRD pattern for ZnO coated PMMA Film is shown in figure (2).

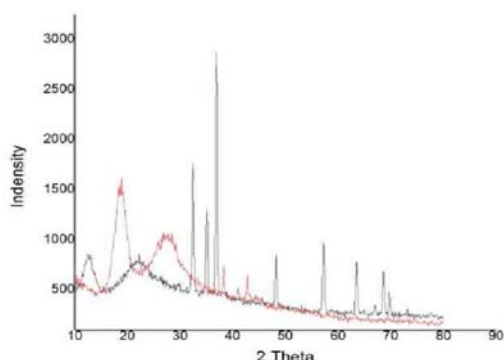


Figure 2: X-Ray Diffraction of ZnO coated PMMA Film

Clearly, the results indicates that there was a similar change in the shape or position of the diffraction peaks, except that the peaks were more intense in the plasma treated ZnO coated PMMA Film.

4. Scanning Electron Microscope Analysis

The morphology of the sample in micro Meter scale is shown in figure (3).

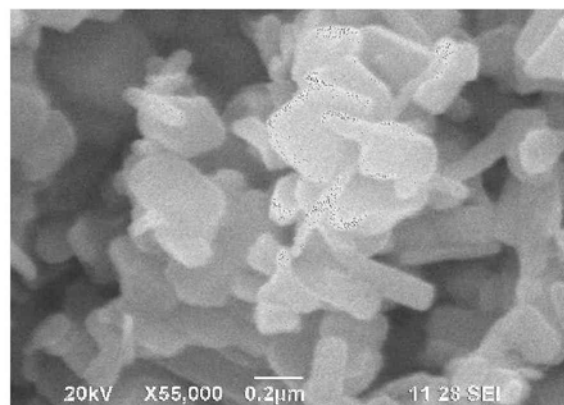


Figure 3: a) Untreated ZnO coated PMMA Film

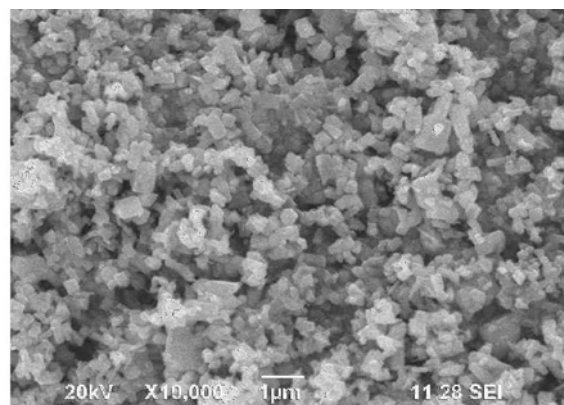


Figure 3: b) Untreated ZnO coated PMMA Film

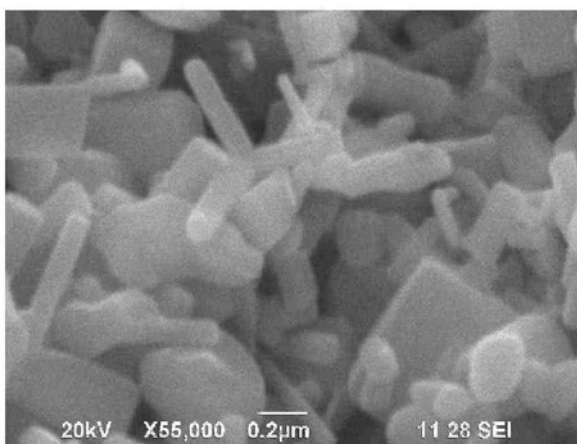


Figure 4: C) Plasma treated ZnO coated PMMA Film

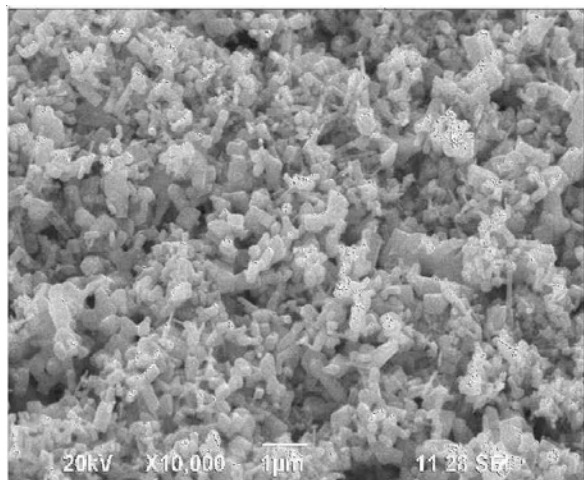


Figure 4: D) Plasma treated ZnO coated PMMA Film

The SEM image of untreated and plasma treated ZnO coated PMMA Film was analyzed. The ZnO coated image was clearly appeared. In addition to that some spots and small fragments were present. After plasma treatment the film surface was smooth and clean. The Surface roughness was increased, this may be caused by etching of the film surface was occur is shown in figure (4).

5. Energy Dispersive Spectrum Analysis

Elemental analysis was useful to identify the materials and its contaminants, as well as estimate their relative concentrations on the surface of the specimen. The energy spectrum is shown in figure(5).

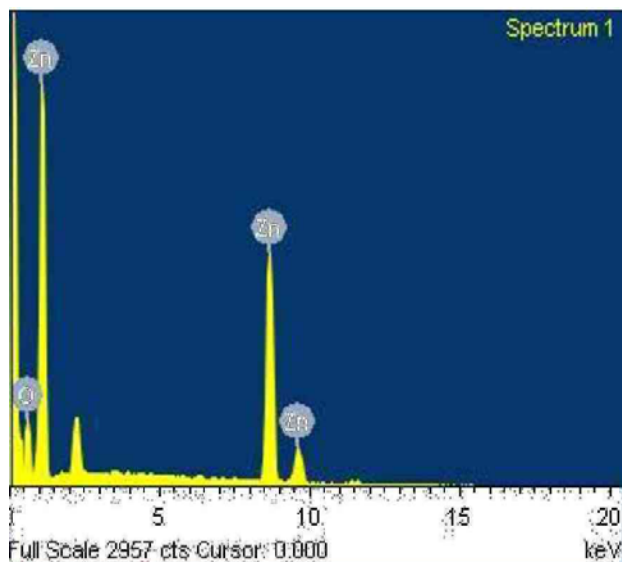


Figure 5: Energy Dispersive Spectrum

Table 3: Energy Dispersive Spectrum

Element	(keV)	Mass%	Atom%
Zn K	0.277	71.97	80.34
O K	0.525	20.05	16.8

In this study the presence of Zinc material was maximum number of atom and mass. Whereas the presence of Oxygen was minimum.

6. Conclusion

Low pressure glow discharge plasma treatment has been used to modify the polymer surface. It was found that the plasma treatment modified the surface. The spectral analysis shows that of the ZnO Nano /PMMA film the information related to the chemical spectroscopy have a various bonding nature corresponding to different frequencies. The FTIR Spectra shows absorption bonds increase in plasma treatment. When compared to untreated film. XRD characterization studies shows the increase in surface roughness and crystallinity of the film. The SEM results conform the change in surface morphology of the film by the localized ablation of the surface layer. EDX study was confirmed the presence of ZnO coated Polymer surface.

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