APPLICATIONS OF NANO MATERIALS: ELECTRONICS, ENERGY AND ENVIRONMENT

Editors
V. RAJENDRAN
R. YUVAKKUMAR
K. THYAGARAJAH
K.E. GECKELER
EFFECT OF ZnO NANOPARTICLES ON STRUCTURAL, MECHANICAL, OPTICAL AND SURFACE PROPERTIES OF HPMC POLYMER FILMS

B. LAKSHMEESHA RAO, MAHADEVIAH1, S. ASHA, R. SOMASHEKAR2 AND SANGAPPA

Department of Studies in Physics, Mangalore University, Mangalagangothri, Mysore
1Department of Polymer Science, Sir MV PG Center, University of Mysore, Mandya, Mysore
2Department of Studies in Physics, University of Mysore, Manasagangothri, Mysore
E-mail: syhalabhavi@yahoo.co.in

ABSTRACT

The Zinc Oxide (ZnO) nano-particles were synthesized by electrochemical method. Then prepared nano-particles were dispersed in hydroxypropyl methylcellulose (HPMC) solution. The HPMC films were prepared by solution casting method and ZnO concentration was varied from 0.01 to 0.04%. The films were examined for structural, optical, mechanical and surface properties verifying how the addition of ZnO nano-particles affected the properties using X-ray diffraction (XRD), Ultra-Violet-Visible spectrophotometer (UV-Vis), Universal Testing Machine (UTM) and Atomic force microscopy (AFM). In general, addition of ZnO nano-particles negatively affected the performance of the HPMC films. The microstructural line parameters like <N>, g decreases with increasing concentration of ZnO nano-particles. A decrease of 30% in tensile strength, 37% in Young’s modulus, and 28% decrease in the elongation at break of the films was observed, when the ZnO concentration is 0.04%. Average surface roughness (Rₐ) of the film increases with ZnO concentration and 69% in 0.04% ZnO concentration.
**INTRODUCTION**

The addition of nano sized inorganic particles into polymer matrices, the new composites material will exhibit enhanced properties like physicochemical stability, high catalytic activity, effective antibacterial and bactericide function, intensive UV and infrared absorption, etc., which greatly differ from that of conventional materials. Researchers have studied the addition of nanoparticles to polymers to provide additional barrier or functional properties for food packaging purposes which include metal and metal oxide nanoparticles, nanofibres and nanotubes.[1] Silica nanoparticles were inserted into polypropylene or starch polymer matrices to improve mechanical or barrier properties of composites and biodegradable films.[2] Starch nanocrystals have been found to improve the mechanical properties of polymer films and inhibit there elongation.[3] Whiskers have also been incorporated into hydroxypropyl methylcellulose (HPMC) films and have been shown to improve mechanical and barrier properties.[4]

Hydroxypropyl methylcellulose is a biopolymer which has become a successful alternative material for two-piece capsule and is actually on the market. HPMC is also being adopted as a film coating or a sustained-release tablet material in the pharmaceutical field.[5] Researchers showed that Zinc Oxide (ZnO) nanoparticles have biodegradability and biocompatibility are potential useful for bio-applications.[6] In this paper Zinc Oxide (ZnO) nanoparticles were prepared and incorporated in hydroxypropyl methylcellulose films. The aim of the study was to investigate the effect of nano-ZnO particles on the HPMC films physical, optical, mechanical and surface properties. Hence in this paper we have carried out X-ray profile analysis to determine microstructural line parameters (<N>, g in % and Dₜ), optical band gap (E₉), tensile strength, elongation (%) and Young’s modulus and surface (Rₐ) roughness properties of ZnO incorporated HPMC polymer films.

**EXPERIMENTAL**

The metal wires (cathode electrode is platinum and Zinc metal rod is an anode) are used as electrodes. The experiment was run for 3–4 hrs with continuous stirring (40mA: 12V), the anodic dissolution of Zinc gives Zn (II) ions which are electrochemically reacted with aqueous NaHCO₃ (0.5%) to form Zn (II) oxide. The solid obtained was washed with deionised water till complete removal of unreacted NaHCO₃. The wet powder was then dried at a temperature 250°C–400°C for dehydration and removal of hydroxides to get ZnO. The synthesis takes place at the electrode -electrode interface or closed to the electrode within the electrical double layer.[7] The HPMC polymer films were prepared by solution casting method and concentration of ZnO varied from 0.01 to 0.04%.

The X-ray diffractograms (XRD) of the ZnO dispersed polymer samples were recorded using Rigaku Miniflex-II X-ray diffractometer with Ni filtered, CuKα radiation of wavelength λ = 1.5406 Å, with a graphite monochromator. The scattered beam was focused on a detector. The samples were scanned in the 2θ range 10–50° with a scanning speed and step size of 1°/min and 0.02°. Ultraviolet-visible (UV-Vis) absorption spectra of were recorded using a SHIMADZU UV–1800, UV-Vis spectrophotometer in the wavelength range 190–800 nm, at
room temperature. The mechanical properties of polymer samples were measured with Universal Testing Machine (Lloyd Instruments, UK, 5kN load cell). Each sample was tested at the specifications of 50 mm of gauge length, with the crosshead speed of 20mm/min at room temperature. A model LRX Plus was used to determine the maximum tensile strength (TS), maximum percentage elongation at break (%), and elastic modulus (or Young’s modulus). The surface morphology of polymer samples was carried out using Nanosurf easyscan2, Atomic Force Microscope (AFM-Switzerland) in contact mode with a scanner size of 12 µm × 12 µm.

RESULTS AND DISCUSSION

Wide angle X-ray diffractograms for pure and ZnO incorporated HPMC films are given in Figure 1. Wide angle X-ray scattering patterns of these films show that broad peak corresponding to the Bragg’s angle \( 2\theta = 22.2^\circ \). The microstructural parameters such as \( <N> \), \( (g) \), and \( D_s \) are determined by matching the simulated intensity profile, using equations [8] with the experimental data for all the samples studied here and the obtained results are tabulated in Table 1. For the sake of completeness, we have reproduced in Figure 2 the simulated and experimental intensity profiles for some of the ZnO incorporated HPMC films. From Table 1, the following results emerge. They are: 1. Reduction of crystal size with the incorporation of ZnO has been observed. This indicated that the addition of nanoparticles increases the disorderliness in the polymer network of HPMC. This is due to the weakening of van der Waal’s forces between the polymer molecules. 2. This decrease in crystal size is in consonance with the observed physical property like tensile strength that has also decreased. The reason for such changes can be attributed to indiscriminate dispersed nanoparticles in the matrix of HPMC, which generally tends to lower the short range interaction between the layers of HPMC, leading to increase in disorder in the lattice. These changes result in more broadening of
Table 1: Microstructural Parameters of ZnO Incorporated Polymer Samples Computed by Exponential Distribution Function

<table>
<thead>
<tr>
<th>Samples</th>
<th>$d_{hl}$ (Å)</th>
<th>&lt;$N&gt;$</th>
<th>g in %</th>
<th>Delta</th>
<th>$D_1$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>4.307</td>
<td>4.41±0.21</td>
<td>0.4±0.02</td>
<td>0.049</td>
<td>18.99</td>
</tr>
<tr>
<td>0.01%</td>
<td>4.241</td>
<td>3.63±0.16</td>
<td>0.3±0.01</td>
<td>0.045</td>
<td>15.39</td>
</tr>
<tr>
<td>0.02%</td>
<td>4.213</td>
<td>3.17±0.11</td>
<td>0.3±0.01</td>
<td>0.049</td>
<td>13.36</td>
</tr>
<tr>
<td>0.03%</td>
<td>4.253</td>
<td>2.55±0.15</td>
<td>0.3±0.02</td>
<td>0.053</td>
<td>10.85</td>
</tr>
<tr>
<td>0.04%</td>
<td>4.212</td>
<td>2.23±0.09</td>
<td>0.2±0.01</td>
<td>0.042</td>
<td>09.39</td>
</tr>
</tbody>
</table>

Fig. 3: Stress vs Strain Curves

Fig. 4: UV-Vis Scans

X-ray Bragg reflections and hence, decrease in microstructural parameters. On a macroscopic scale, these affect the physical parameters like tensile strength and percentage of elongation.

Tensile properties were calculated from the plot of stress (tensile force/initial cross-sectional area) versus strain (extension as a fraction of the original length) given in Figure 3. The mechanical properties were analyzed as a function of ZnO concentrations. The tensile strength in pure film was 59.12±4.18 MPa and in 0.01% ZnO sample it was 55.43± MPa. The extent of reduction in tensile strength is varying and we observed 30.46% reduction in 0.04% concentration. The decreasing trend of tensile strength was due to non-alignment of nanoparticles and strong surface interaction. Elastic modulus (Young’s modulus) goes on decreasing as the concentration changes and 37% reduction in 0.04% ZnO concentration. We observed that percentage of elongation at break decreases with increasing ZnO concentration. Contrary to the above results, we observe that the maximum load (N) increases with increasing concentration.

The UV-Vis spectrophotometric scans of virgin and ZnO incorporated polymer films are given in Figure 4. Figure shows the absorption decreases very sharply and come to the minimum absorption at $\lambda_g$. The values of $\lambda_g$ for virgin and ZnO with different concentrations are estimated as 400, 421, 391, 487 and 517 nm respectively. The optical band gap energy for the virgin as well as for ZnO incorporated samples has been calculated from the respective values
of $\lambda_g$ using the formula $E_g = \frac{hc}{\lambda_g}$. A shift in $\lambda_g$ towards higher wavelength indicates the decrease in $E_g$ of the ZnO dispersed samples. The microstructural modification produced in polymer matrix due ZnO dispersion would cause a change in the molecular structure of the polymer network. As a result a modification within the optical band gap was expected.

Figure 5 shows the topology and 3D AFM images of virgin and ZnO incorporated polymer samples. The surface topology parameters which are given in Table 2, presents some important physical scales, which are morphologically characterize the sample. The line roughness parameters ($R_a$ and $R_q$) and surface roughness parameters ($S_a$ and $S_q$) are the physical scales which describing the roughness degree of the samples. From the Table 2 it can be seen that all parameter increases as ZnO concentration increases. The roughness of HPMC films increases with ZnO concentration indicates non-alignment of nanoparticles in the polymer matrix. This fact is also evidenced by X-ray results as well as mechanical properties of the films.
CONCLUSIONS

We observe that there are changes, both microscopically and macroscopically, in HPMC films when ZnO nanoparticles are incorporated. These are quantified in terms of microcrystalline parameters and also physical parameters like tensile strength, percentage elongation, etc. We have also examined the reasons for such changes in terms of weakening of intermolecular van der Waal’s forces. The UV-VIS study shows the optical band gap decreases with increasing ZnO concentration. AFM study shows the surface roughness increases with increasing nanoparticles dispersion.

NOMENCLATURE

- $d_{hkl}$: Inter planar spacing, (Å).
- $<N>$: Crystallite size.
- $D_s$: Surface weighted crystallite size (Å).
- $E_g$: Optical energy gap, (eV).
- $g$: Planck’s constant, (J s).
- $c$: Speed of light, (m/s).
- $\lambda_g$: Absorption edge (nm).
- $R_a$: Average-line roughness (nm).
- $R_q$: Root mean square-line roughness, (nm).
- $S_a$: Average-surface roughness (nm).
- $S_q$: Root mean square-surface roughness (nm).

REFERENCES