

Synthesis, Characterization and Physico–Chemical Properties of Nano Zinc Oxide and PVA Composites

Rashmi S. H., G. M. Madhu, A. A. Kittur, R. Suresh

Abstract—Polymer nanocomposites represent a new class of materials in which nanomaterials act as the reinforcing material in composites, wherein small additions of nanomaterials lead to large enhancements in thermal, optical and mechanical properties. A boost in these properties is due to the large interfacial area per unit volume or weight of the nanoparticles and the interactions between the particle and the polymer. Micro sized particles used as reinforcing agents scatter light, thus reducing light transmittance and optical clarity. Efficient nanoparticle dispersion combined with good polymer–particle interfacial adhesion eliminates scattering and allows the exciting possibility of developing strong yet transparent films, coatings and membranes. This paper aims at synthesising zinc oxide nanoparticles which are reinforced in poly vinyl alcohol (PVA) polymer. The mechanical properties showed that the tensile strength of the PVA nanocomposites increases with the increase in the amount of nanoparticles.

Keywords—Glutaraldehyde, polymer nanocomposites, poly vinyl alcohol, zinc oxide.

I. INTRODUCTION

THE field of nanotechnology is one of the most popular areas for current research and development basically in all the technical disciplines. Nanotechnology is not new to polymer science as prior studies, before the age of nanotechnology involved nanoscale dimensions but were not specifically referred to as nanotechnology until recently. Over the last decade, Polymer Nano-Composites (PNCs) have been one of the most extensively examined areas of polymeric nanomaterials. These efforts have lead to numerous commercial successes, innovative approaches for fabricating and tailoring hybrid materials, and important fundamental insights on the behavior of polymers in confined environments [1].

The synthesis of polymer nano-composites is an integral aspect of polymer nanotechnology. By introducing the nanometric inorganic compounds, the properties of polymers improve and hence this has lot of applications depending upon the inorganic material present in the polymers [2]. Solvent casting is one of the easiest and time saving methods for the synthesis of polymer nano-composites. The objective of this

study was to develop nano polymer composite films and to evaluate their physico–chemical properties by various techniques.

Polymer nano-composites are the materials in which nanoscopic inorganic particles, typically 10-100 Å at least in one dimension, are dispersed in an organic polymer matrix in order to improve the performance properties of the polymer dramatically. Polymer nano-composites exhibit stiffness, strength and dimensional stability in two dimensions (rather than one). Due to nanometer length scale which minimizes scattering of light, nano-composites are usually transparent.

Inorganic nanoparticles can be introduced into the matrix of a host polymer either by some suitable chemical route or by an electrochemical incorporation technique. The mechanical, electrical, thermal, optical, electrochemical and catalytic properties of the nano-composites will differ markedly from that of the component materials.

Because of the nanoscale structure of dispersion, nano-composites possess unique mechanical, chemical and thermal properties, e.g. excellent mechanical strength and stiffness, enhanced gas barrier behavior, good flame retardancy, and increased solvent resistance when compared to the pristine polymers [3].

In the present study we have made an effort to synthesize and characterize nanomaterials of zinc oxide. By dispersing them in PVA, the mixed matrix membranes were prepared and their properties were studied to give more light on other suitable applications.

II. EXPERIMENTAL

A. Materials

PVA (Molecular weight $\approx 125,000$) was obtained from S.D. fine chemicals, Mumbai, India; Zinc acetate dihydrate was obtained from Merck; Potassium hydroxide, Methanol, PVA and Glutaraldehyde were procured from S.d. fine chemicals, Mumbai, India; Double distilled water was used throughout the experiment.

B. Preparation of Zinc Oxide Nano Particles (ZnO)

Zinc oxide was prepared by precipitation method using zinc acetate dihydrate and potassium hydroxide as described by Radzimska et al. [4]. A solution was prepared by dissolving 5% of potassium hydroxide in methanol. Similarly another solution of 5% zinc acetate dihydrate was prepared by heating up to 60°C for a period of 15min. To this, 5% methanolic potassium hydroxide was added dropwise till the product precipitates. It is then filtered and the solid product was separated and heated to 250°C for 60 minutes.

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C. Preparation of Pure PVA

Poly vinyl alcohol (5gm) was dissolved in 95ml of deaerated distilled water with constant stirring for about 24 hrs at 60°C temperature. This was filtered using a glass disc filter to remove the undissolved residue particles. To this 1ml of glutaraldehyde was added at 100°C for in-situ cross linking and stirred for 1hr. at the same temperature. The solution was kept overnight so as to remove the air bubbles. The resulting clear solution was cast onto a glass plate with the aid of a casting knife in a dust free environment. After being dried in air for about 48 hrs, the membrane was peeled off.

D. Preparation of Poly Vinyl Alcohol-Zinc Oxide Nanocomposites

5% Poly vinyl alcohol (PVA) solution was prepared by dissolving 5g of PVA in 95g of distilled water and stirring overnight at 60°C. Polymer nano-composite membranes were prepared by dispersing 0.1, 0.15, 0.2 and 0.25g of zinc oxide nanoparticles respectively in 5% of polymer solution and stirring the solution over night. The clear solution thus obtained was casted on a previously cleaned glass plate by solution casting technique.

It is known that glutaraldehyde (GA) is a highly efficient cross linking agent for PVA [5]. To improve the performance properties of PVA membranes and to study the effect of nanoparticles as well as cross linking agent on PVA, we have also prepared cross linked PVA composite membranes by cross linking with GA in presence of 0.5ml of 1:1 hydrochloric acid. The membranes were casted on glass plate by following the same procedure as in case of plane membranes.

III. CHARACTERIZATION

A. Scanning Electron Microscopy (SEM)

The morphology of the prepared sample was analyzed by JEOL – JSM - 400A, Tokyo, Japan, Scanning Electron Microscope. Before photographing, the samples were vacuum - dried and coated with a conductive layer (400 Å) of sputtered gold.

B. Wide angle X-ray Diffraction (WAXD)

Wide angle X-ray diffraction is a proven tool to study crystal lattice arrangements and yields very useful information on degree of sample crystallinity [6]. WAXRD of the nanomaterial was studied at room temperature using Rigaku Miniflex 600 X-ray diffractometer. The X-ray source was nickel-filtered Cu-K α radiation (40 kV, 30 mA). The dried powder was mounted on a sample holder and scanned in the reflection mode at an angle 2 θ over a range from 30° to 90° at a speed of 8°/min.

IV. RESULTS AND DISCUSSIONS

A. Scanning Electron Microscopy

Fig. 1 shows the SEM image of ZnO nanoparticles, which indicates that the ZnO nanoparticles have flaky shape. They

have distributed throughout the polymer matrix without affecting the morphology.

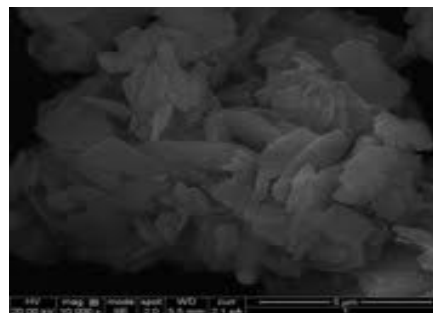


Fig. 1 SEM image of ZnO nanoparticles

B. X-Ray Diffraction

Degree of crystallinity of the nanomaterials was studied by WAXRD and the resulting diffraction patterns are given in Fig. 2. The X-ray pattern of PVA shows a typical peak at around $2\theta = 31^\circ$, indicating that cross linked PVA contains both crystalline and amorphous domains in the nano material.

Fig. 2 shows the XRD pattern of the ZnO nanoparticles annealed at 250°C. The diffraction pattern can be indexed to the hexagonal ZnO phase (Wurtzite Structure) by comparison with the data obtained from JCPDS card 36-1451. However, the XRD patterns of the nanoparticles are considerably broadened due to the very small size of these particles. The strong and narrow diffraction peaks indicated that the product has good crystallinity.

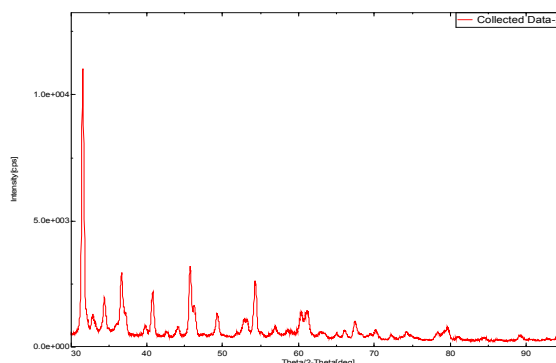


Fig. 2 WAXRD pattern of ZnO nanoparticles

C. Study of Rheological Properties

The composite films were cut into strips of 25mm width and introduced into the tensile testing machine. Then it is subjected to the study of the tensile strength and elongation at break. The point of breakage was noted by the digital meter.

$$\text{Elongation} = \left(\frac{\text{Final Reading} - \text{Initial Reading}}{\text{Initial Reading}} \right)$$

The data thus obtained are tabulated in Table I.

TABLE I
TENSILE STRENGTH AND % ELONGATION OF VARIOUS PVA
NANOCOMPOSITES

Nano composite	Tensile Strength (kg/in)	Tensile strength (N/cm)	% Elongation
Pure PVA	3.64	14.0584	86.6
PVA+ 0.1g ZnO	3.94	15.2170	110
PVA+ 0.15g ZnO	4.05	15.6419	160
PVA+ 0.2g ZnO	4.63	17.8819	213
PVA + 0.25g ZnO	7.39	28.5416	155
PVA+GA	4.89	18.8861	143
PVA+ 0.1g ZnO+ GA	5.69	21.9759	173
PVA+ 0.15g ZnO+ GA	7.68	29.6616	194
PVA+ 0.2g ZnO+ GA	8.95	34.5666	220
PVA+ 0.25g ZnO+ GA	9.07	35.0301	236

The graph of tensile strength vs. composition of PVA nano composites is plotted in Fig. 3.

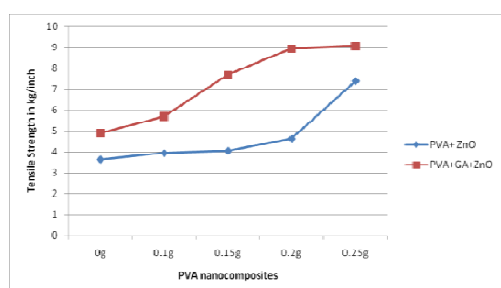


Fig. 3 Tensile strength v/s composition of PVA nanocomposites

From the above (Fig. 3), it is clearly observed that the tensile strength of all the membranes increased as the nanoparticles are increased in the PVA matrix. There is a sudden increase in 0.25g ZnO loaded PVA membrane than 0.2g ZnO indicating that the membranes with highest load of ZnO nanoparticles have higher tensile strength. On the other hand in case of cross linked PVA nanocomposites, the tensile strength steeply increases as the nanoparticles are increasing in the matrix. It reaches to saturation after 0.20gm nano particles loaded.

The graph of percentage elongation vs. composition of PVA is plotted in Fig. 4.

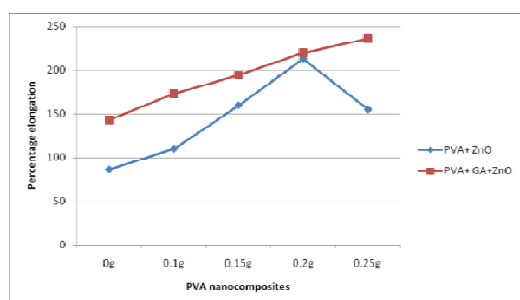


Fig. 4 Elongation of PVA nanocomposites

From the above (Fig. 4), it is observed that the percentage elongation steeply increased as the content of nanoparticles

increases in the matrix up to 0.2g and then it decreased suddenly indicating that % elongation of membrane (0.25g loaded) collapses. In case of cross linked PVA nanocomposite membranes % elongation shows an exponential increasing trend as the nanoparticles in the PVA matrix increases. The percentage elongation for PVA - ZnO with glutaraldehyde shows an increasing trend as the composition of PVA - ZnO composite increases.

V. CONCLUSION

The tensile strength of the PVA nanocomposite increases with the increase in the amount of nanoparticles. Addition of Glutaraldehyde adds to the tensile strength of PVA [7]. Maximum elongation was observed when the composition of ZnO nanoparticles was 0.2g (when no glutaraldehyde was added). The presence of glutaraldehyde increased the elongation at break as compared to the absence of glutaraldehyde.

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