

Facile Preparation and Characterization of Chitin- Polyaniline Nanocomposite

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ABSTRACT

Chitin/Polyaniline nanofiber composite films have been prepared by solution casting. Polyaniline self assembled nanofibers (PANF) were synthesized by direct mixed oxidation performed in an aqueous HCl (1M HCl) in the presence of ammonium peroxodisulfate as oxidant. Dedoped nanofibers were homogeneously dispersed in N,N-dimethylacetamide by the aid of ultrasonication and then mixed with chitin solution made in the 5% LiCl/ N,N-dimethylacetamide solvent system according to pre determined weight ratios. The characterization of the composites were done by X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), Differential scanning calorimetry (DSC), Thermogravimetric analysis (TGA) and Field Emission Scanning Electron Microscopy (FESEM). No observable interaction has been noted from FTIR studies which indicate polyaniline nanofibers are physically entrapped in the chitin matrix. When compared to pure chitin, thermal studies show that the overall decomposition rate of composites is decreased due to the incorporation of polyaniline nanofiber into the chitin matrix. FESEM results show that polyaniline has nanofiber morphology and composites have continuous homogenous structure.

Keywords: Chitin, FESEM, Nanocomposite, Polyaniline nanofiber, Thermal studies.

I. INTRODUCTION

Polyaniline (PANI) is one of the most promising electrically conducting polymers because of its good combination of low cost, stability and conductivity [1,2]. Nonetheless, its poor solubility and mechanical properties imply difficulties in possible practical uses of this unique material. In addition, conducting polymer composites with common insulating polymers have emerged out as alternate materials which combine metal-like electrical conductivity with good mechanical properties of conventional polymers [3]. Out of which, nanocomposite of biopolymers such as chitin, cellulose etc with organic/ inorganic materials as filler opens a new window for the enhancement of multifunctional properties [4-6]. Nanocomposites with an organized structure usually provide a new functional hybrid, with complementary properties over their single component counterparts, which have attracted considerable attention for their potential applications in various fields [7,8]. Thus, processible PANI and its composites have great potential use in a vast number of applications [9]. On the other hand, polymer matrix itself might be protected against degradation when blended with conducting polymers.

In this work, dedoped polyaniline nanofibers (PANF) were synthesized through direct mixed polymerization and subsequently blended with an insulating host, chitin, a well known biopolymer to produce composite films with low PANF loads.

II. MATERIALS

All chemicals used in the experiments were analytical grade reagents, and were used without further purification. Chitin from shrimp shells having molecular weight 400,000g/mol was obtained from HiMedia Laboratories Pvt Ltd, Mumbai, India. N,N-Dimethyl acetamide (DMAc), Aniline, Ammonium peroxodisulphate, Hydrochloric acid, Acetone and Lithium chloride (LiCl) were purchased from Merck, Germany. Aniline was distilled under reduced pressure prior to use.

III. PREPARATION OF CHITIN/POLYANILINE NANOFIBER COMPOSITE

All experiments were conducted under air atmosphere. Polyaniline nanofibers were synthesized by rapid mixing reaction [10-12]. Polyaniline nanofiber sample was collected as a deep blue powder. The yield obtained was 25%. Required amount of polyaniline nanofiber sample was dedoped with 1M ammonium hydroxide solution and washed several times until the filtrate became colourless. Dedoped polyaniline nanofiber was dried under vacuum at 60 °C.

Dedoped nanofibers were homogeneously dispersed in N,N-dimethylacetamide with the aid of ultrasonication and then mixed with chitin solution made in the 5% LiCl/ N,N-dimethylacetamide solvent system according to pre determined weight ratios (0.5%, 1% and 5% of polyaniline nanofiber) and named as CHPA 0.5, CHPA 1 and CHPA 5 respectively. The system allowed to stir for 6 hours and then casted on a petridish and kept in an oven at 60 °C for 24hrs to get dried films. Dried films were washed several times with distilled water to remove LiCl and then again dried in an oven at 60 °C.

IV. CHARACTERIZATION

Infrared spectra were measured with KBr-supported sample of chitin and Chitin/polyaniline nanofiber composite over the frequency range 4000–400 cm⁻¹ at resolution of 4 cm⁻¹ using a model IR Prestige-21 FTIR spectrophotometer, Shimadzu. X ray diffraction (XRD) patterns were recorded in the range of $2\theta = 5^\circ$ to 50° on a Rigaku X-ray diffractometer operated at a voltage of 40 kV and a current of 30mA with Cu K α ($\lambda = 1.5405 \text{ \AA}$) radiation. Differential scanning calorimetric analysis (DSC) was carried out with a Shimadzu 60 plus instrument (Japan) at a scan rate of 10 °C min⁻¹ from room temperature to 450 °C under nitrogen atmosphere. Thermal gravimetric analysis (TGA) was performed under nitrogen atmosphere at a flow rate of pure nitrogen gas 100 ml/min., heating rate was 10°C/min. from ambient up to 500°C using TA SDT Q600 instrument (Dupont). SEM of the pure polyaniline nanofiber and polyaniline-chitin nanocomposite was recorded using CARL ZEISS ΣIGMA Field Emission Scanning Microscope (FESEM).

V. RESULTS AND DISCUSSION

X-ray diffraction pattern (Fig. 1) of polyaniline nanofiber emeraldine base has a broad amorphous peak centered at $2\theta \sim 22^\circ$ with a shoulder at $2\theta \sim 15^\circ$. Because of the amorphous nature of polyaniline, crystalline nature decreases with increasing polyaniline content in the composite. Significant peaks of chitin are observed at about $2\theta = 9.2, 12.8, 19.6, 23.4, 26, 39^\circ$. It is noted that intensity of chitin peak at 19.6° decreases as the percentage of polyaniline increases in the composite.

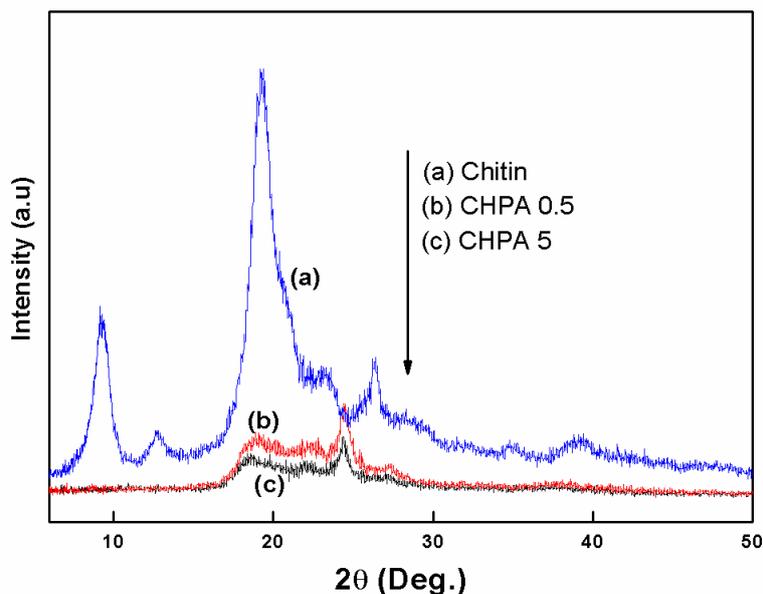


Figure 1. XRD pattern of Chitin and Chitin/polyaniline nanocomposites.

FTIR spectra (Fig. 2) of both the pure chitin and Chitin/polyaniline nanocomposite show broad band at $\sim 3448 \text{ cm}^{-1}$ and $\sim 3271 \text{ cm}^{-1}$ due to OH stretching and NH stretching respectively. The band at $\sim 1562 \text{ cm}^{-1}$ is assigned to NH bending (amide II) while the small peak at $\sim 1656 \text{ cm}^{-1}$ is attributed to the C=O stretching (amide I). The bands at ~ 2926 , ~ 1317 and $\sim 1262 \text{ cm}^{-1}$ are assigned to CH_2 bending due to pyranose ring. The band at $\sim 1378 \text{ cm}^{-1}$ is due to CH_3 wagging [13, 14]. There were no observable peak shifts in chitin/polyaniline nanocomposite compared to pure chitin.

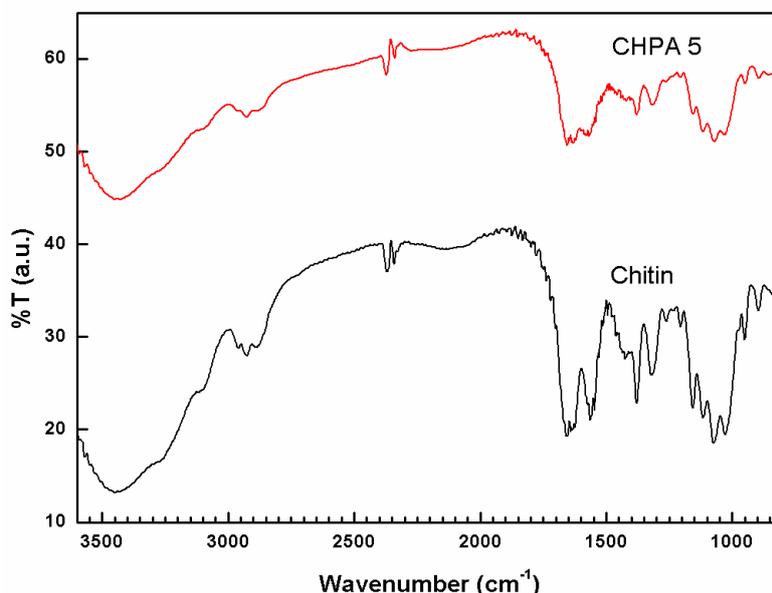


Figure 2. FTIR spectra of Chitin and Chitin/polyaniline nanocomposite.

DSC and TGA thermograms of the blends are given in Fig.3 and Fig.4 respectively. The broad endothermic peak between 35°C and 150°C , in DSC is due to the moisture and bound water present in the sample [15]. This is supported by the initial weight loss in TGA thermograms (Fig. 4). A small endothermic peak near 240°C is

observed due to local relaxation of the backbone chain of chitin and not due to Tg [16]. From TG analysis of the composites, one can see that the weight loss is reduced when compared to pure chitin.

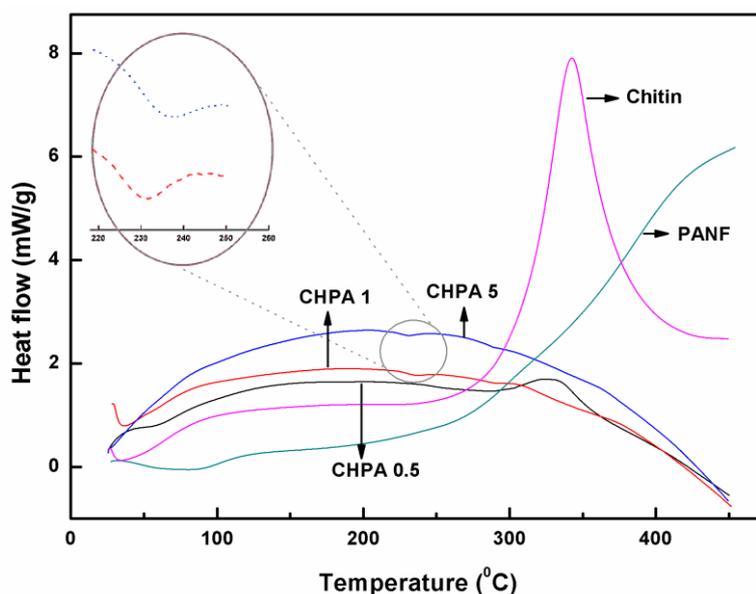


Figure 3. DSC thermograms of chitin, Polyanilie nanofiber (PANF) and Chitin/polyaniline nanocomposites

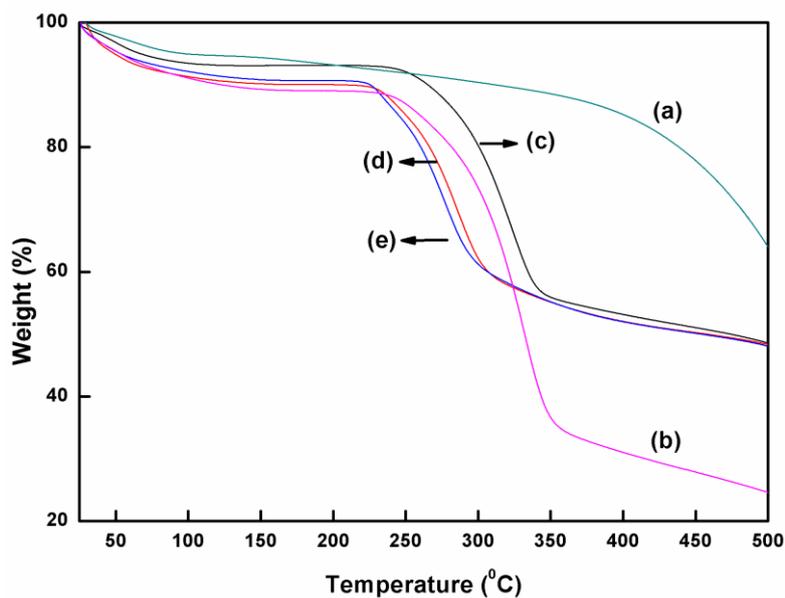


Figure 4. TGA thermograms of (a) Polyanilie nanofiber; (b) chitin and ((c) – CHPA 0.5, (d)- CHPA 1 and (e)- CHPA 5) Chitin/polyaniline nanocomposites

Field Emission Scanning Electron Microscopy (FESEM) images of prepared polyaniline and chitin-polyaniline nanofiber composite (CHPA 5) are shown in Fig. 5. It is noted that polyaniline nanofiber prepared has an average diameter of 62 nm. FESEM image of composite shows homogeneity and continuous structure (Fig. 5 (b)).

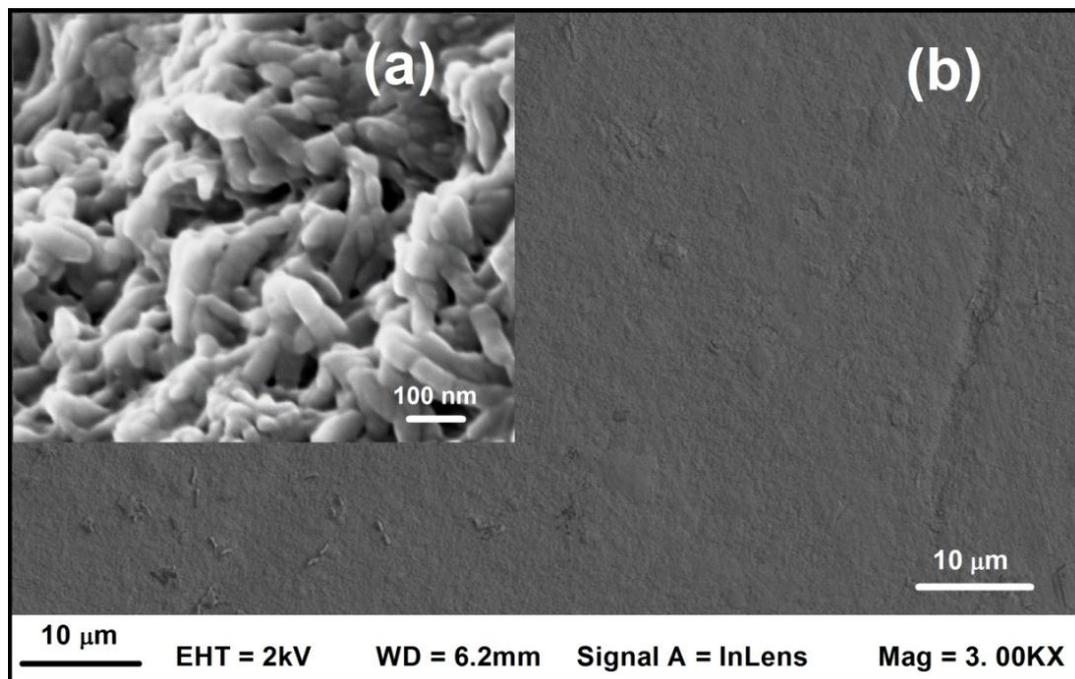


Figure 5. Field Emission Scanning Electron Microscopy (FESEM) image of (a) Polyaniline nanofiber; (b) Surface morphology of 5% polyaniline nanofiber dispersed chitin composite (CHPA 5)

VI. CONCLUSION

In this work, novel chitin/ polyaniline nanocomposite is synthesized successfully. XRD studies confirm that crystallinity decreases with increase in polyaniline content in the composite. FTIR spectra of pure chitin and nanocomposite show that there is no chemical interaction between polyaniline nanofiber and Chitin in the composite. Polyaniline nanofibers are physically entrapped in the chitin matrix. Thermal studies show that the prepared nanocomposites have improved thermal stability when compared to pure chitin even at lower percentage of polyaniline nanofiber. Morphology of polyaniline and composites show that prepared polyaniline have fibrous structure and the composite surface is having continuous, homogeneous structure.

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