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Synthesis and Structural, Vibrational and Optical Properties of Cellulose Nanofiber/Polyaniline Film Composite

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Abstract

In-situ chemical oxidative polymerization of aniline mixed in cellulose nanofiber (CNF) suspension (that was isolated from jute fibers) was done to synthesize polyaniline (PANI)/CNF composite films, using aniline monomer as the starting material. During this synthesis, $K_2Cr_2O_7$ acted as an oxidant, while HCl worked as solvent for $K_2Cr_2O_7$ as well as for nanocellulose-aniline mixture. Different aniline concentrations were taken. The composite was characterized for its crystalline properties using X-ray diffraction (XRD), supported by Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy, which revealed the presence of bonding among C, O, H, N, etc., constituent elements. The result shows the decrement in crystalline properties as the concentration of aniline decreases. The composites will be used for electrical and mechanical measurements in future.

Keywords

Composite, X-ray diffraction, Suspension, Polymerization, Polyaniline, Cellulose

Introduction

All types of conducting polymers have received increasing attention during the last decades because of their unique properties. Among these, PANI is widely used and popular for its ease of synthesis, good electrical conductivity, environmental stability, low cost, and excellent redox reversibility properties. It has potential applications in anti-static agent, sensors, electrodes, electro chromic displays, rechargeable batteries, corrosion protection, etc. [1]. The conductive nature of PANI shows high potential for a variety of additional applications such as gas sensors, super capacitors, lithium-ion batteries and photovoltaic cells among the others. Due to poor mechanical properties of this polymer, it restricts to use this in its pure form. Therefore, the study of composite materials containing PANI is a rapidly developing subject of research. To overcome poor mechanical strength, one effective way is to produce its blends with neutral polymers and other materials which have great mechanical and good processing properties. Cellulose nano-derivatives are considered to be suitable for this purpose and are thus quite often used in combination with PANI to prepare nanocomposites. This mechanically strong nanomaterial will be covered with intrinsically conductive polymers to impart electrical conductivity. Such nanocomposites have the important characteristic advantages of neutral behavior, capacity for transparent film formation, low and economic cost.

In this regard, the present work is focused on the synthesis and characteriza-

tion of PANI synthesized with CNFs using chemical oxidation method, which is an easy and simple to use method [2]. The samples were then characterized for their crystalline behavior, vibrational properties using various techniques.

Experimentation

Materials

Aniline ($C_6H_5NH_2$), ethanol (CH_3CH_2OH), acetone (CH_3COCH_3), hydrochloric acid (HCl), Potassium dichromate ($K_2Cr_2O_7$) and CNFs suspension were used as the starting materials.

Synthesis of CNFs

The CNFs were synthesized using jute fibers. Following simple steps were followed to obtained it. To reduce the length of the fiber, jute fiber was chopped into small pieces and then grinded in a mixture jar for about 15 min. 1 g of chopped jute fibers were dissolved in 14 ml of nitric acid in a three neck round bottom flask. The chopped jute fibers with 1.96 g of sodium nitrate was completely drowned in nitric acid. The stoppers were used to seal the mouth of the flask, so that it will not allow red fumes to form inside the round bottom flask. The container flask was kept under 60 °C for 12 h to conclude the reaction. Then after duration of 12 h, 150 ml distilled water was added up into it to quench and stop the reaction. The flask containing solution was kept at rest for 2 h at room temperature for equilibration. Centrifugation of solution was then done at 2500 rpm for 10 min to separate the extra amount of acid from it. With 2:1 ethanol/water mixture, the washing was carried out by centrifuging at 2500 rpm and this step is performed again till pH became neutral. CNFs were isolated from ethanol/water mixture combination, then 50 ml distilled water was mixed into it and kept in centrifuge tube at 2 °C till used.

Synthesis of PANI-CNF composite films

To prepare the composite films using chemical oxidation method, 50 ml cellulose was added in 2 ml of aniline monomer (in liquid form) by magnetic stirring for a few hours. This mixture was then dissolved in 50 ml of 1 M HCl solution. On the other hand, initiator solution was made by dissolving 6.25 g $K_2Cr_2O_7$ into 50 ml of 1 M HCl solution. The two solutions were then slowly mixed at room temperature to initiate the polymerization process. After the polymerization, the sample was filtered, and washing was done using acetone. Then this polymer composite was pressed into films and the films were dried in oven, after which it was used for characterization. The same procedure was done by taking 5 ml of aniline monomer. Two films were obtained using this process containing different percentage of aniline monomer [3].

Characterization

For structural characterization, PROTO AXRD Benchtop Diffractometer with Cu-Kα_1 radiation of wavelength λ = 1.5406 Å was used to obtain XRD spectrum of prepared composite films. FTIR of the samples were obtained by using ALPHA ECO-ATR FTIR spectrometer instrument at room temperature in the wave number range of 4000 - 500 cm^{-1} with a resolution of 4 cm^{-1}. Raman spectroscopy measurements were performed on Horiba Jobin Yvon HR800 make micro-Raman instrument with 632.8 nm incident wavelength from a He-Ne laser.

Results and Discussion

Figure 1a and 1b show the XRD spectra of PANI-CNF composite films which are synthesized by chemical oxidation method. The diffraction peaks at 2θ positions of 11.74°, 15.31°, 20.7°, 25.4°, 27.09°, 29.14°, 31.2°, 33.4° show crystalline nature of the composite [4]. The degree of crystallinity for a polymer is defined by equation 1 [5].

$$Degree\ of\ crytallinity = \frac{Area\ of\ crytalline\ peaks}{Area\ of\ all\ peaks}\ x\ 100\% \quad (1)$$

As per the equation, the calculated degree of crystallinity was found to be decreased from 48% to 42% as we increase the aniline concentration in the sample. The degree of crystallinity was calculated, and it is found that the crystalline nature has decreased.

The FTIR spectrum of PANI-CNF composite is shown in figure 2. The peak assignment based on literature survey reveals that the band observed at 3616 cm^{-1} and 3656 cm^{-1} is assigned to -OH stretching mode of vibrations, the band at 1741cm^{-1} can be attributed to C=O stretching, the band which is observed at 3064 cm^{-1} and 3094 cm^{-1} correspond to -CH stretching, the band at 3025 cm^{-1}, 1623 cm^{-1} and 1625 cm^{-1} correspond to the alkyl group (C-C), the bond at 1508 cm^{-1} attributes to C=C stretching peak of quinine ring, the bond at 1346 cm^{-1} correspond to bending vibrations of C-H (N= quinine =N), bond at 1200 cm^{-1} and 1198 cm^{-1} correspond to

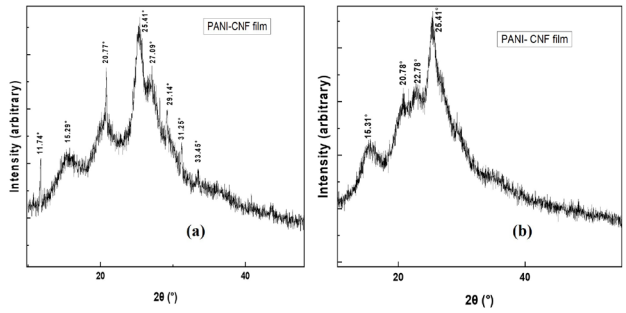

Figure 1: XRD patterns of PANI-CNF composite film containing **(a)** 5 ml and **(b)** 2 ml aniline.

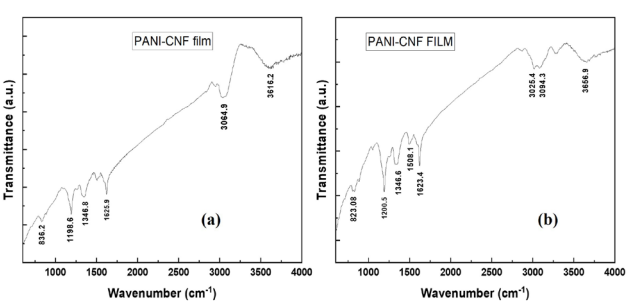

Figure 2: FTIR spectrum of PANI-CNF composite film containing **(a)** 2 ml and **(b)** 5 ml aniline.

C-O stretching. At lower wave number side, the band at 836 cm^{-1} is allocated to β-glycosidic linkages between glucose units of cellulose [2, 3]. Apart from these characteristic bands, no other peak is observed, confirming the purity of the samples. Also, the band positions do not change when the data for pure PANI and composites are compared although a slight change in the absorbance is seen, which suggests that when composite is made, original PANI vibrational bands are not broken due to incorporation of cellulose and its properties are retained, which is an advantage [3] that the host is intact to some extent.

For the efficient study of interactions between the components in polymer blends, Raman spectroscopy is very effective tool used in the microscope mode (Figure 3). In the Raman spectra of the composite film prepared using 1 M HCl shows a sharp peak at 1623 cm^{-1} (arising from C-C benzenoid ring, stretching vibrations) and the peak position at 1490 cm^{-1} (due to C=N stretching vibrations in quinonoid units) [6]. Also, the band positions do not change significantly when the data for both the composites films are compared, indicating that incorporation of CNFs does not lead to modifications in the vibrational properties of original PANI host, which is an obvious advantage in applications where properties of PANI are also important [3].

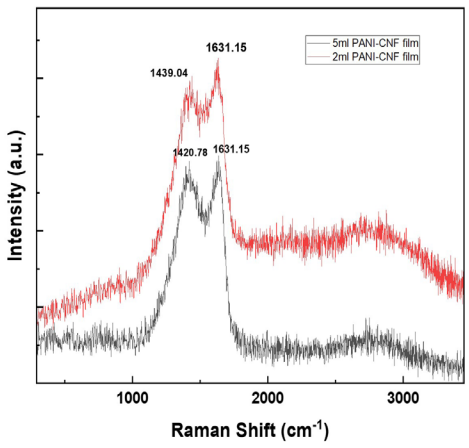

Figure 3: Raman spectra of PANI-CNF composite film containing 5 ml and 2 ml aniline.

Conclusion

These results confirm that the PANI in both samples is in its green conducting form. The PANI-CNF composite films were successfully synthesized by the chemical oxidation polymerization process of aniline. The structural analysis of composite films was analyzed using XRD, which showed that the composite formation extends crystallinity to PANI exhibiting well-defined crystalline peaks after incorporating cellulose in PANI. The interaction among elements of cellulose and PANI has been analyzed by FTIR spectroscopy and by Raman spectroscopy. The composite with less amount of PANI shows better crystalline properties.

Acknowledgments

None.

Conflict of Interest

None.

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