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THERMAL, MORPHOLOGICAL AND TOPOGRAPHIC CHARACTERIZATION OF A BIODEGRADABLE POLY(3-HYDROXYBUTYRATE-CO-3-HYDROXYVALERATE)/ POLYANILINE.CSA FILM COMPOSITES

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Abstract: Poly (3-hydroxybutyrate-co- 3-hydroxyvalerate)(PHBV) and polyaniline (Pani) were mixed in different weight ratios i.e. 100:0, 0.05, 1.5, 2.5, 3.5 and 5 to produce composite films. Polyaniline (PANI) synthesized by emulsion polymerization technique using an aqueous solution of CSA, ammonium persulfate and aniline monomer In order to evaluate the influence of Pani. CSA addition on the final Thermal, morphological, and topographic PHBV. complete microstructural, and thermal properties of Α characterization of films of PHBV/Pani blends has been performed. The following characterization techniques were employed: Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analyses (TGA-DTA), scanning electron microscopy (SEM), simultaneous. It has been observed that the micro- structure of PHBV/Pani.CSA was remarkably affected by blending composition. In order to study the surface topography of the PHBV and its composition with Pani.CSA, the surface of the prepared films were explored by an atomic force microscope (AFM).

Keywords: Biodegradable, Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV, . Polyaniline, PANI.



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1. Introduction

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a biodegradable and biocompatible thermoplastic aliphatic polyester, produced by bacteria fermentation and can be easily degraded within 3-9 months under environmental conditions[1,2]. PHBV has been used in a variety of applications including drug delivery system[3], tissue engineering[4], packaging[5], plastic containers and bottles[6]. However The more usage of PHBV is hindered by several drawbacks such as brittleness, high material cost, poor thermal stability and low mechanical properties[7]. To overcome these limitations in properties, incorporation of other polymers into the PHBV to form composites has received attention recently.

A. Bianco et al [8] had prepared composites of poly (3-hydroxybutyrateco-3-hydroxyvalerate) (PHBV) and polyethylene oxide (PEO) bv electrospinning in order to evaluate the influence of PEO addition on the final properties of PHBV. All electrospun mats consisted of randomly oriented fibers with average size ranged between 0.5 µm and 2.6 µm and the microstructure of PHBV/PEO was remarkably affected by blend composition. Z. Qiu et al [9] had reported the preparation of Biodegradable polymer composites of poly(3-hydroxybutyrate-co-hydroxyvalerate) (PHBV) and poly(3-caprolactone) (PCL) with the ratio of PHBV/PCL ranging from 80/20-20/80 by co-dissolving the two polyesters in chloroform and casting the mixture. Differential scanning calorimetry and optical microscopy were used to investigate the miscibility and crystallization of PHBV/PCL blends. Results indicated that PHBV is immiscible with PCL and the crystallization rate of PHBV decreased with increasing PCL. R. Fryczkowski et al [10] had prepared spinning fluid contained poly(3 hydroxybutyrate) (PHB) and polyaniline (Pani). Fibers were produced from the solutions in different solvents by electrospinning and then they were characterized in terms of morphology, spectroscopic and thermal properties. Among the numerous conducting polymer polyaniline (Pani) is one of the most popular due to its unique electrical properties, environmental stability and facile synthesis process. Pani has numerous potential applications in the different areas such as solar cell[11], sensors[12], light emitting diodes[13], rechargeable batteries[14], membranes[15] and non-linear optical devices[16].

In the present work camphor sulfonic acid doped polyaniline (Pani. CSA) was utilized as second components to blend with PHBV in order to produce composite films to evaluate the influence of Pani. CSA addition on the final Thermal, morphological, and crystallite properties of PHBV.



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2. Synthesis of camphor sulfonic acid doped polyaniline (Pani.CSA)

The Pani.CSA is synthesized by emulsion polymerization technique [17] using an aqueous solution of CSA, ammonium persulfate and aniline monomer. Initially equal molar ratio of CSA and aniline (0.05 mol) will introduce into 300 mL of distilled water under constant stirring until homogenization occurred. The mixture will kept at 0 °C and an aqueous solution containing 0.02 mol of ammonium persulfate in 20 mL of water will slowly introduced to the solution over a period of 30 minutes to avoid over heating the reaction mixture. The polymerization will be terminated by pouring the emulsion into acetone. The precipitated Pani. CSA salt as a dark green powder is filtered and washed several times with distilled water/ acetone in order to remove unreacted protonic acid and oxidizing agent.

3. Preparation of PHBV/Pani. CSA based biodegradable films composites

The stock solutions of PHBV, Pani.CSA are prepared by dissolving a known amount of each in chloroform. Then prepared solutions will be combined in various PHBV: Pani.CSA ratios. By this way different solution will be made and each of them subsequently casted to produce biodegradable film composites.



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Figure1. Chemical structure of Poly (3-hydroxybutyrate-co- 3hydroxyvalerate)(PHBV). Polyaniline (PANI) and camphor sulfonic acid (CSA).

4. Instruments

Transmission FTIR spectra of hybrid composites were recorded with Perkin Elmer 2000 FTIR spectrophotometer at room temperature. The samples were scanned from 4000 to 400 cm^{-1} . All the spectra were collected after an average of 16 scans for each specimen.

The thermal stability of specimens was tested using PERKIN ELMER TGA7 1991 thermogravimetric analyzer from ambient temperature to 900°C at a heating rate of 20°C/min under nitrogen gas. The morphological features of each sample were obtained using a QUANTA FEG 650 2012 field emission scanning electron microscopy (FESEM). The samples were prepared with chromium coating for the measurements. AFM images of thin PHBV/Pani films were obtained using the atomic force microscopy Dimension EDGE, BRUKER model.

5. Results and discussion

The structures of the prepared PHBV/ pani.CSA composite, PHBV and pani.CSA were characterized by FTIR spectroscopy as shown in Figure 2. In the spectrum of PHBV, the strong absorption peak at approximately 1726 cm $^{-1}$ was associated with the carbonyl (C=O) groups the intensity of these peaks seems to be decreased with increase the loading of PANI, this phenomena was showed in the peaks of –OH groups. Based on these observations, one can assumes that there seems to be some kind of interaction between PHBV and pani.CSA.



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Figure 2. FTIR spectroscopy of the prepared PHBV/ pani.CSA composite, PHBV and pani.CSA

The films were also examined using DSC, at temperatures ranging from 30 to 850 °C. The thermograms are showing in Figure 3. Generally, the thermograms looks like similar, one thermal effect is visible, which is related to the melting of crystallites in polymer matrixes. Remarkably, the melting temperature decreases as the pani.CSA content increases. For 2.5% pani.CSA, it is higher by 20 °C as compared with pure PHBV.





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Figure 3. Differential scanning calorimetry (DSC) curve of PHBV (A) and 0.05% (A1), 2.50% (A3), 5% (A5) of PHBV/pani.CSA.

Degradation temperatures for the PHBV and PHBV/ pani.CSA, obtained by TGA curves are shown in Figure 4. Thermal degradation of the samples can be observed. Another effect observed in thermal examination is increased thermal resistance of the films containing pani.CSA. Pure PHBV thermogram shows a fast degradation of the sample above 200 °C. This stops entirely when a minimum amount of pani.CSA has been added. As pani.CSA content increases, the effect continues, which became lower degradation. Based on these observations, one can adopt that there seems to be some kind of interaction between PHBV and pani.CSA, which, rises the melting temperature and enhances the thermal resistance of the pani.CSA.



Figure 4. Thermogravimetric curves of PHBV (A) and 0.05% (A1), 2.50% (A3), 5% (A5) of PHBV/pani.CSA.

The micrographs of pure PHBV and with the different compositions of PHBV/ pani.CSA are showing in Figure 5. It can be observed that micrographs presented a porous morphology on the upper surface, and the distribution of the porous increased with the increase of the pani.CSA concentration.



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Figure 5. Micrographs of pure PHBV (A) and in the different compositions 0.05% (A1), 2.5% (A3) and 5% (A5) of PHBV/ pani.CSA films.

The microparticles were spherically shaped with a rough surface observed by SEM photomicrographs for the edge of PHBV/1.5% pani.CSA film Figure 6. From the micrographs there are no separated phase and stranger particles which revealed homogenous phase is established. This observation enhanced that some kind of chemical interaction between PHBV and pani.CSA may be occur.



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Figure 6. SEM photomicrographs of PHBV/1.5% pani.CSA film's edge

In order to study the surface topography of the PHBV and its composition with Pani.CSA, the surface of the prepared films were explored by an atomic force microscope (AFM). AFM images of the PHBV and PHBV/Pani.CSA are shown in Figure 7. The PHBV film surface (Figure 7.A) shows white areas representing the crystalline regions while the remaining is expected to be an amorphous region. The root mean square roughness (R_q) and mean average roughness (R_a) of the samples shown in table 1. PHBV film showed highest surface roughness. With addition of Pani.CSA in PHBV the surface roughness decreases impressively. PHBV with 5 % Pani.CSA (A5) has the least value in both R_a and R_q in compare to other composites.

Polymer & composites	R _a (nm)	R _q (nm)
PHBV	259	326
A2	178	260
A5	56	72

Table 1. Mean roughness R_a and root-mean square roughness R_q determined from AFM image for PHBV film and its composition with Pani.CSA.



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Figure 7. Topographic AFM images of pure PHBV (A), PHBV/1.5% Pani.CSA (A2) and PHBV/5% Pani.CSA (A5).

6. Conclusion

The Pani.CSA is synthesized by emulsion polymerization technique, Poly (3-hydroxybutyrate-co- 3-hydroxyvalerate)(PHBV)and polyaniline (Pani) were mixed in different weight ratios i.e. 100:0, 0.05, 1.5, 2.5, 3.5 and 5 to produced composite films. Based on FTIR observations, we can conclude that there seems to be some kind of chemical interaction between PHBV and pani.CSA. The films thermograms looks like similar. one thermal effect is visible, which is related to the melting of crystallites in polymer matrixes. Remarkably, the melting temperature decreases as the pani.CSA content increases. As pani.CSA content increase, the effect continues, which became lower degradation. It can be observed that SEM micrographs showed a porous morphology on the upper surface, and the distribution of the porous increased with the increase of the pani.CSA concentration. From the micrographs there are no separated phase and stranger particles which revealed homogenuoce phase is established. With addition of Pani.CSA in PHBV the surface roughness decreases. PHBV with 5 % Pani.CSA (A5) has the least value in both Ra and Rg in compare to other composites.

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