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Biodegradation Studies of Chitosan-Polycaprolactone (PCL) Nanocomposite In Soil Burial Test

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Abstract: In this study, chitosan-PCL/C30B blend films were prepared using the solvent evaporation method. Chitosan (CS) and PCL with different ratios were blended solution by solvent evaporation method. Nanoclay was incorporated in the formulation as a matrix material component which also plays the role of a co-emulsifier in the nanocomposite preparation. Morphology and structure characterization of nanocomposites were investigated by Fourier Transmission Infra Red Spectroscopy (FTIR), Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD) respectively. The biodegradability of the films was investigated based on burial in soil and compost.

Key words: Chitosan · PCL · MMT · Nano composites · Biodegradability

INTRODUCTION

The use of synthetic polymer materials has caused significant environmental problems. Solid waste from these materials is a major contributor to environmental pollution because it can take up to a thousand years to degrade. Therefore, a great deal of attention has been given to the development of various biodegradable materials to overcome this serious problem. The development of environmental friendly polymer materials can be classified into two categories based on the raw material used: degradable synthetic polymers and renewable natural polymers [1]. Renewable natural polymer resources include starch, cellulose and chitosan. These materials have been tested alone and in combination with plastic to enhance the plastic properties and biodegradation potential of the product [2-4].

Chitosan, a natural linear biopolyaminosaccharide, is obtained by alkaline deacetylation of chitin, which is the second abundant polysaccharide next to cellulose [5-6]. Chitin is the principal component of protective cuticles of crustaceans such as crabs, shrimps, prawns, lobsters and cell walls of some fungi such as aspergillus and mucor. Chitin is a straight homopolymer composed of b-(1,4)-linked N-acetyl-glucosamine units while chitosan comprises of copolymers of glucosamine and N-acetyl-glucosamine [7,8].Chitosan has one primary amino and two free hydroxyl groups for each C6 building unit.

Polycaprolactone (PCL), semi-crystalline and resorbable aliphatic polyester, has found various biomedical applications such as sutures, drug delivery systems and scaffolds in tissue engineering, due to its soft-and hard-tissue compatible properties and biodegradation characteristic. It is an FDA approved biomaterial, currently used in drug delivery and sutures [9]. Its low melting point (60°C) allows easy processing and it is biodegradable by hydrolysis. Although PCL has been widely used as a matrix material, its applications are frequently limited by several drawbacks including limited bio-regulatory activity; hydrophobicity [10]; neutral charge distribution; slow rate of degradation and acidic degradation products. In addition, like other synthetic biodegradable polyesters, PCL is costly and therefore its applications are restricted to some extent. Numerous efforts have been focused on overcoming these drawbacks. One of common strategies is to blend PCL with other natural biopolymers, including starch, zein, cellulose and chitosan [9]. Application of PCL for controlled drug delivery systems has a draw back of slow degradation rate in-vivo due to its high crystallinity and hydrophobicity. It has been reported the biodegradability of PCL can be enhanced by co-polymerizing [11] or blending with a variety of other polymers [12]. Enhancement of hydrophilicity of PCL has been achieved by the chemical blending with natural polymer such as chitosan [10].

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Experimental

Materials: Chitosan (CS) (Degree of Deacetylation = 95% determined by ^{1}H NMR) was purchased from India Sea Foods, Kerela. Polycaprolactone (PCL) was purchased from Solvay Interox, USA. Cloisite 30B was procured from Southern Clay Products, USA. Acetic acid, NaH_2 PO_4, NaOH and other chemicals were used as analytical grade and purchased from Sigma Aldrich Company.

Synthesis of Chitosan / PCL Nanocomposites: Chitosan was dissolved in 0.5M acetic acid and PCL in glacial acetic acid. To prepare sterile 1% (w/v) chitosan solutions, chitosan suspension in water was first autoclaved (at 121° C in a wet cycle for 20 min) and then dissolved by adding acetic acid equivalent to 0.5M in a sterile laminar flow hood. In order to get chitosan / PCL (80: 20) ratio, 4 ml of 1% chitosan solution was added to 10 ml of 0.1 % PCL solution. The mixtures were stirred at room temperature for 2 hours to obtain homogeneous solutions. Calculated amount of C30B was added to this slurry (1%, 2.5% and 5%). The mixture was stirred for 8hours at room temperature till a homogenate composite is formed.

Characterization

Fourier Transmission Infra Red Spectroscopy (FTIR): The FTIR spectrum of the Chitosan-PCL blends was obtained using a BIORAD-FTS-7PC type FTIR spectrophotometer.

X-Ray Diffraction (XRD): The change in gallery height of the blend was investigated by WAXD experiments, which were carried out using a X-ray diffractometer (BEDE D-3 system) with Cu Kα radiation at a generator voltage of 40 kV and a generator current of 100 mA. Samples were scanned from 2è = 1-10° at a scanning rate of 2 °/min.

Scanning Electron Microscopy (SEM): The blending of the Chitosan-PCL Nanocomposites containing different concentrations was characterized using SEM (440, Leica Cambridge Ltd., Cambridge, UK). The powdered specimens were placed on the Cambridge standard aluminium specimen mounts (pin type) with double-sided adhesive electrically conductive carbon tape (SPI Supplies, West Chester, PA). The specimen mounts were then coated with 60% Gold and 40% Palladium for 30 seconds with 45 mA current in a sputter coater (Desk II, Denton Vacuum, Moorestown, NJ). The coated specimens were then observed on the SEM using an accelerating voltage of 20 kV at a tilt angle of 30° to observe the microstructure of the chitosan-PCL composite blends.

Soil Burial Test: Two different pots were filled to their approximate capacity of 10 L with soil and compost. The samples were cut into 30 × 50 mm pieces and buried in the soil at a depth of 10 cm. The soil was placed in the laboratory and the moisture of the soil was maintained by sprinkling water at regular time intervals. The excess water was drained through a hole at the bottom of the pot. The degradation of the samples was determined at regular time intervals (7 days) by carefully removing the sample from the soil and washing it gently with distilled water to remove soil from the film. The sample was dried under vacuum until a constant weight was obtained. Weight loss of the sample over time was used to indicate the degradation rate of the soil burial test.

The soil burial test was studied by evaluating the weight loss of the film over time. The weight loss was determined every seven days from the starting day and was calculated using Equation

$$\text{Weight Lose}(\%) = \frac{w_i - w_d}{w_i} \times 100$$

Where *Wd* is the dry weight of the film after being washed with distilled water and *Wi* is the initial dry weight of the specimen.

RESULTS AND DISCUSSION

Fourier Transmission Infra Red Spectroscopy (FTIR): Fig. 1 shows the FTIR spectra of chitosan, (CS), polycaprolactone (PCL) and chitosan-polycaprolactone (CS-PCL) blend. Chitosan is an amino glucose characterized by a small proportion of amide groups via an amide linkage with acetic acid. In the IR spectrum, powder chitosan exhibited a broad peak at 3432 cm^{-1}, which is assigned to the N-H and hydrogen bonded O-H stretch vibrational frequencies, while a sharp (shoulder) peak at 3611 cm^{-1} is that of free O-H bond stretch of glucopyranose units [13]. Further, in the C-H stretch region of FTIR spectrum, the higher the asymmetric and the lower intensity peak at 2858 cm^{-1} is assigned to the symmetric modes of CH_2. In addition, the characteristic band due to CH_2 scissoring, which usually occurs at 1466 cm^{-1} was also present in the sample. Since the grade of chitosan used in the present study was =90% deacetylated, an amide bond peak was present in the spectra and the C=O stretch of amide bond was observed at 1661 cm^{-1}. The peaks at 1551 and 1598 cm^{-1} were assigned to strong N-H bending vibrations of secondary amide, which usually occur in the range of 1640 to 1550 cm^{-1} as strong band.

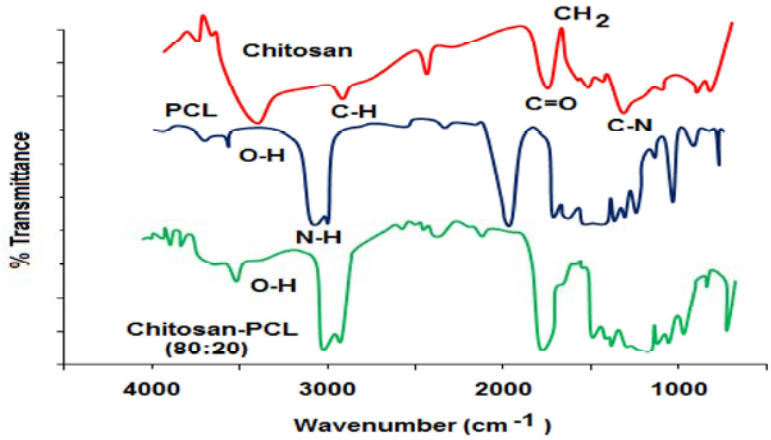

Fig. 1: FTIR spectra of Chitosan, (CS), Polycaprolactone (PCL) and Chitosan-Polycaprolactone (CS-PCL) blend

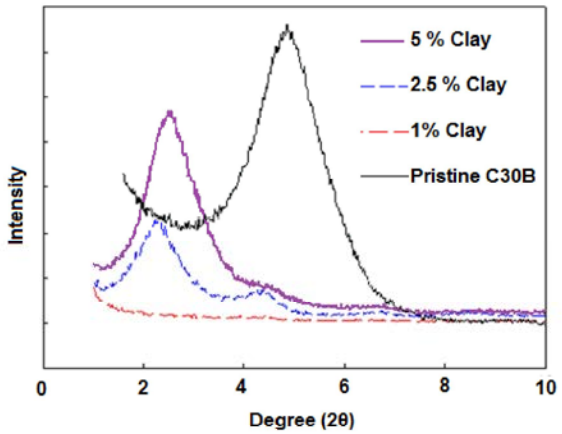

Fig. 2: X-ray diffraction patterns of (a) Pristine C30B (b) chitosan –PCL (80:20)1% clay (c) chitosan –PCL (80:20)2.5%clay, chitosan –PCL (80:20)5%clay.

The IR spectra shows the characteristic peaks of both polymers i.e., chitosan and PCL (3300-370, 1724, 852-1481 and 721 cm^{-1}). Furthermore, the IR spectra of Chitosan/PCL produced peaks between 3200 and 3700 cm^{-1}, which were much more intense than the stretching absorbance at 3000-3600 cm^{-1} observed in the absence of chitosan. Additionally, the spectrum in Fig.2.30. identifies differences in absorbance intensity at 1651cm^{-1} (primary amide, secondary amide) and 1591 cm^{-1} (non-acylated primary amide).

X-ray Diffraction Analysis: The XRD patterns of closite 30B along with chitosan-PCL/ C 30B nanocomposites are furnished in Figure. 2. From the figure it is ascertained that the peak corresponding to the basal spacing of the organoclay appears at 4.74A° with the corresponding (d_{001}) spacing 1.9nm. For the 1 wt % 30B nanocomposites, we did not see any noticeable peaks of 30B in the low angle range and this confirmed the exfoliated structure of silicate layers of C 30B in the PCL matrix after the mixing. For 2.5 wt % C 30B hybrids, a broad peak at 4.6A° and for 5 wt % a peak at 3.02 A°, much lower than that of closite 30B, was observed, indicating that intercalation of 30B occurred together with some exfoliation. The results in Figure 2.31. shows that intercalation and/or exfoliation of cloisite 30B could be accomplished by mixing in an internal mixer. In summary, during the mixing process of the polymer matrix and organoclay, the fracturing process of the organoclay particles takes place first; that is, external platelets are subjected to dynamic high shear forces that ultimately cause their delamination from the stack of layers building the organoclay particles and then an onion-like delamination process continues to disperse the platelets of silicate into the polymer matrix [14-17]. In the chitosan-PCL/ C 30B nanocomposites, these two steps are also presumed to have taken place.

Scanning Electron Microscopy (SEM): SEM has been employed for the observation of the surface morphology of the different chitosan/PCL nanocomposites. The microstructure obtained by SEM for the chitosan/PCL nanocomposites prepared by mixing, showed that PCL nanoparticles (with irregular forms) are relatively well dispersed in the chitosan matrix. Fig. 2. Shows that chitosan/PCL nanocomposites is homogenous at low concentration 3% C30 B, 5% C30 B.As the concentration of the nanoclay increases from 1% to 5% the homogeneity of the surfaces increases because of the intercalation of the nanoparticles along the polymer matrix This might enhance the surface modification [17].

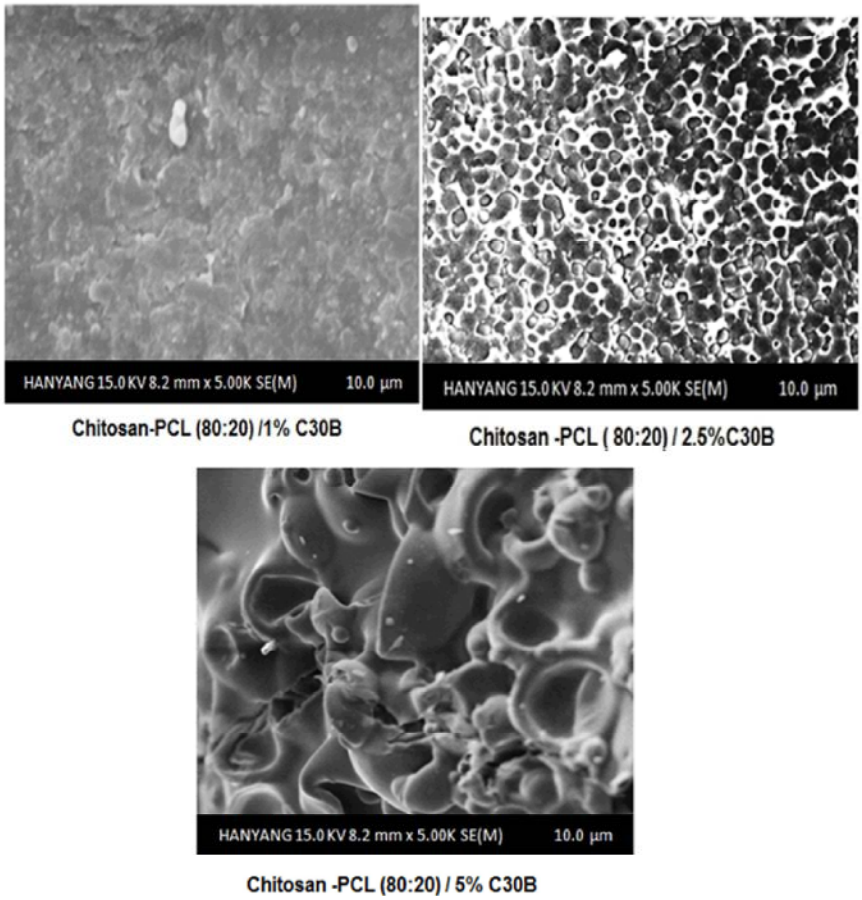

Fig. 3: Scanning Electron Microscope of Chitosan/PCL nanocomposites (A) Chitosan –PCL (80:20)1% C 30B (B) chitosan –PCL (80:20)2.5% C 30B (C) chitosan –PCL (80:20) 5% C 30B

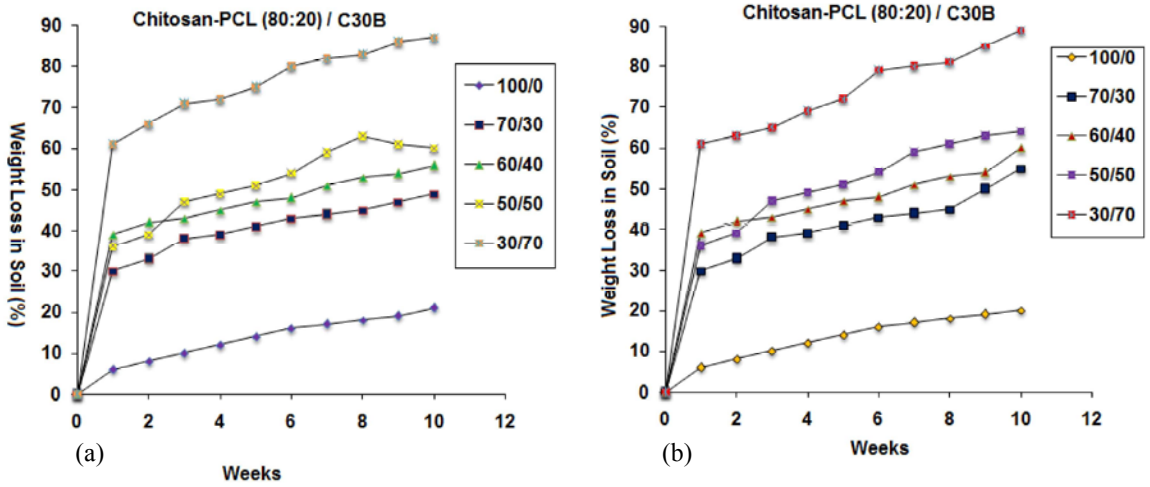

Fig. 4a,b: a) Weight loss of Chitosan-PCL/C30B after 8 weeks in soil.
b) Weight loss of Chitosan-PCL/C30B after 8 weeks in compost.

Soil Burial Test: Figures 4a and 4b show the weight loss of the pure chitosan and chitosan-PCL/C30B films in soil and compost, respectively. In the figures, the biodegradability increased up to 85% as the burial time increased in both the soil and compost for 8 weeks. All of the films in soil and compost degraded rapidly in the first 7 days. This rapid degradation was due to the composting process, which occurred in two main stages: an active composting stage and a curing period. In the first stage, the temperature rose and remained elevated as long as there was available oxygen, which resulted in strong microbial activity [18].

In the second stage, the temperature decreased but the film continued to compost at a slower rate. In both the soil and compost, the 30/70 chitosan-PCL/C30B sample showed the highest weight loss while pure chitosan showed the lowest weight loss over time. This finding was attributed to the C30B content in the film because C30B is more biodegradable than pure chitosan. The chitosan, which is biodegradable due to its high hydrolysability, exhibited a higher resistance against soil burial degradation. The addition of compost resulted in an approximate 2–3% increase in the degradation rate. Compost is composed of organic materials derived from plant and animal matter that have been decomposed largely through aerobic decomposition. It can be rich in nutrients. The compost itself is beneficial for the land in many ways because it can act as a soil conditioner, a fertiliser, an addition of vital humus or humic acids and a natural pesticide for soil. The nutrients in the compost can degrade the film more rapidly than unamended soil.

As shown in Figure 6, for the duration of 14 to 30 days, the weight loss was slightly lower but the composting process did not stop at a particular point. Rather, it continued slowly until the last remaining nutrients were consumed by the remaining micro-organisms and almost all of the carbon had been converted into carbon dioxide.

CONCLUSION

The last two decades of the twentieth century saw a paradigm shift from biostable biomaterials to biodegradable (hydrolytically and enzymatically degradable) biomaterials for medical and related applications. The current trend predicts that in the next couple of years, many of the permanent prosthetic devices used for temporary therapeutic applications will be replaced by biodegradable devices that could help the body to repair and regenerate the damaged tissues. Chitosan is a natural biodegradable polymer where as polycaprolactone is a synthetic biopolymer. Novel nanocomposites of chitosan-PCL blended with MMT (Cloisite 30B) (CS/

PCL/MMT) were Prepared and Characterized by FTIR spectroscopy, X-ray diffractometry and scanning electron microscopy. From the XRD analysis it is evident that probably the chitosan-PCLcomposite did not enter sufficiently into the layers of clay structures. The obtained results can be summarised as follows: the addition of chitosan to the PCL-C30B matrix increases the degradation rate of the sample. The degradation process increases as the C30B content increases.

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