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SYNTHESIS AND CHARACTERIZATION OF ECOFRIENDLY SOYPROTEIN CONCENTRATE/CLOISITE 30B NANOCOMPOSITES FOR FILM MAKING

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ABSTRACT

Biodegradable films of Soy Protein Concentrate (SPC) and Cloisite 30B (C 30B) have been prepared by melt extrusion method in which C 30B was used as a nanofiller. The structures and properties of the films were characterised by FTIR, XRD, SEM, TEM, TGA and tensile testing. Soy Protein Concentrate/Cloisite 30B hybrids showed an intercalated nanostructure due to the compatibility of the two components. The biodegradability of the films was investigated by three different methods like soil burial, compost burial and enzymatic degradation. In all the three methods the films containing C 30B clay were found to be more biodegradable than those SPC films without C30B.

KEY WORDS: **SPC, C 30B, nanocomposites, biodegradable.**

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INTRODUCTION

Recently human beings are highly benefited by the petrochemical-based polymers[1,2] ,however, there is a critical environmental issue as a result of the accumulation of the non-degradable plastic materials used for variety of disposable items. It is well documented that fossil resources are fast depleting, the price of petrol and its allied products is rocketing sky high, an alarming clarion call is being heard World over for environmental concern and sustainability. Therefore, recently bio based polymers has attracted the focus of research in diversified fields of science and technology[2-5]. Soy protein concentrate and Plasticized Soy Protein Concentrate (PSPC) are the most attractive and promising sources for biodegradable plastics among the others as it has low cost[6], biodegradability, renewability [6], and ease of chemical modifications [6] and plenty availability[7]. However, it has few disadvantages like water sensitivity [6], brittleness and poor mechanical properties[6] over the conventional synthetic thermoplastics. Now-a-days different physical and chemical approaches have been adopted to overcome these demerits. Cloisite 30B mineral is very popular for the synthesis of nanocomposites because of their small particle size, extremely large aspect ratio, and intercalation properties. The present investigation describes the fabrication of SPC clay nanocomposites via melt extrusion processing.

MATERIALS AND METHODS

Materials

Soy protein concentrate (SPC) was obtained from Archer Daniel, Midland Co. (Decatur, IL, USA) as a gift sample and used for the reaction. Cloisite 30B was purchased from Southern Clay Products, Austin, Texas. All other chemicals were used as analytical grade and purchased from Sigma Aldrich Company.

Sample Preparation

First, soy protein concentrate (SPC) and modified Cloisite 30B were dried for about 3 hrs at 65^{o}C (using a vacuum oven). SPC was pre-mixed with the C 30B in a beaker, with different C 30B concentrations like (2.5 wt%, 5 wt%, 7.5 wt% and 10 wt%). Then the powders were mixed with glycerol at a weight ratio of 70:30. These mixtures were fed to a two-roller extruder at 120°C. The mixing time was 5 min. Subsequently, the mixtures were compression-molded into dumbbell like pieces at 140 °C and 15 MPa for 10 min. The samples were stored in a desiccator before characterization.

Fourier transmission infrared spectroscopy (FTIR)

FTIR for SPC/Gly and SPC/Gly/C30B films were obtained on a Nicolet 5-5X C FTIR spectrometer by diffuse reflectance.

Mechanical Properties

The tensile properties of the specimen were measured on a universal testing machine (CMT4104, Shenzhen SANS Test Machine Co. Ltd, Shenzhen, China) with a tensile rate of 5 mm/min according to ISO527-3:1995(E). In all mechanical property measurements, five specimens were measured for each sample, and the results were averaged.

Scanning Electron Microscopy (SEM)

Liquid nitrogen was used for freezing the sample sheets and then snapped immediately and then the fractured surface was sputtered with gold and investigated with an Scanning electron microscope instrument (JSM-5900LV) using an acceleration voltage of 20 Kv.

X-ray Diffraction (XRD)

D8 Advance Diffractometer (Bruker, U.S.A.) equipped with a CuKα radiation source (λ = 0.154 nm) was used for X-ray diffraction (XRD) .The diffraction data were collected from 2θ = 1°−10° in a fixed time mode with a step interval of 0.02°.

Transmission Electron Microscopy (TEM)

The SPC/C 30B sample was cut into ultrathin films with the thickness of *ca.* 60 nm by using a microtome at normal temperature, and the ultrathin films were directly placed on the copper grids for TEM observation. Then the structure and morphology of the nano composites were visualized.

Thermogravimetric Analysis (TGA)

Perkin Elmer thermogravimetric analyzer (TGA-7) was used to analyse the TGA of the samples. The test samples (about 3 mg) were allowed to be heated at 50 °C to 800 °C at a heating rate of 20 K/min.

Enzymatic Testing

A mixture of DH_2O, α-amylase and β-amylase at certain specific ratio were placed in a conical flask. Then the specimens were cut at 4 X 4 cm square from the dried film and weighed using a digital balance. The flasks were incubated in a shaking incubator at a rate of 150 rpm for 50 hours at 45ºC. Then in order to remove the enzymatic mixture from the sample surface the samples were rinsed with distilled water and dried in a desiccator under vacuum for 24 hours before being weighed. The degree of enzymatic degradation [DED (%)] was calculated using the following Equation 1

$$\mathrm{DED}\,(\%) = \frac{W_I - W_H}{W_I} \times 100 \qquad (1)$$

Where W_H- dry weight of the specimen after the enzymatic treatment W_I- the initial dry weight of the specimen.

Soil and Compost Burial Test

The films were buried separately in soil and compost. First two different pots (capacity 10 L each) filled with soil and compost were taken. Then samples were cut into 25 × 40 mm pieces buried in the soil and compost at a depth of 15 cm in laboratory condition. Weight loss of the sample over time was used to indicate the degradation rate of the soil burial test.

The following formula (equation 2) was adopted for calculating the weight loss of the sample in every seven days from the starting day.

$$\text{Weight Loss}(\%) = \frac{w_i - w_d}{w_i} \times 100 \qquad (2)$$

Where W_d : dry weight of the film after being washed with distilled water Wi : the initial dry weight of the specimen

RESULTS AND DISCUSSION

XRD

Figure 1 shows the XRD patterns of SPC/C 30B nanocomposites with 2.5 wt%, 5wt%, 7.5 wt%, 10 wt% and pure C 30B. The basal spacing (*d*001) of C 30B was calculated to be 1.2 nm showing a sharp peak at 2θ= 7.3° by using Bragg's equation. The sharp peak of the clay disappears in the XRD patterns of SPC/C 30B nanocomposites with the increase concentration of C 30B content from 2.5% to 10 %, thus exfoliation between the polymer and the clay can be concluded. It confirms that C 30B could be easily intercalated or exfoliated with soy protein concentrate by simple melt extrusion [7].

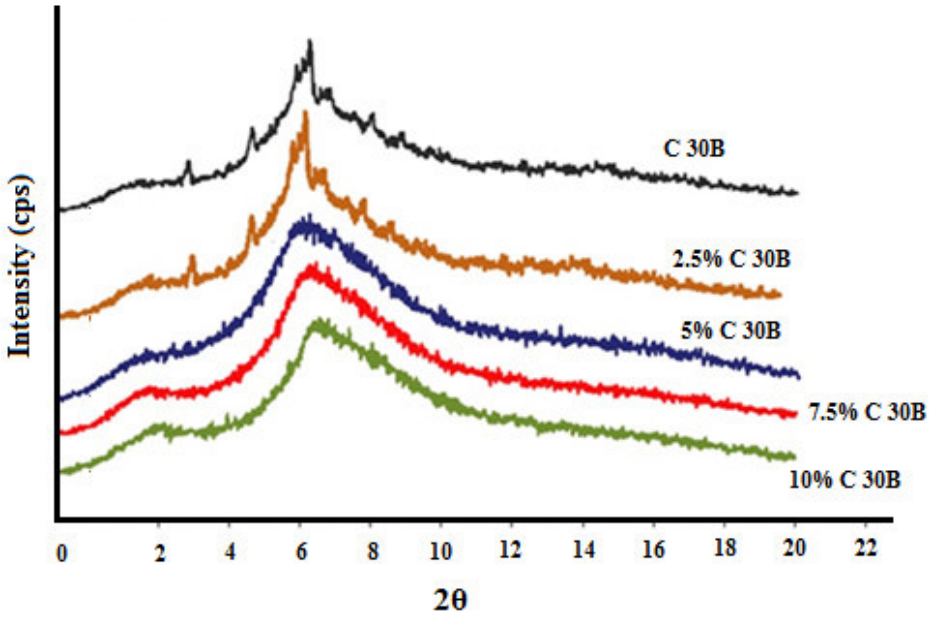

Figure 1
XRD patterns of SPC/C 30B sheets with various C 30B contents

FTIR

Figure 2(A) shows the IR spectra of glycerol, SPC and C 30B and figure 2 (B) shows SPC-Glycerol/C 30Bnanocomposites. In figure 2 (B) broad peaks in the range of 3440－3330 cm^{-1} can be seen. These peaks are the characteristics peaks of -OH stretching which indicates the presence of intermolecular hydrogen bond. Compared with SPC, glycerol and C 30B, the －OH peaks of SPC-glycerol- C 30B composites were less strong. This reduction of peak magnitude may attribute to the partial covering of SPC-glycerol composites by C 30B, and it was supported by SEM analysis (Fig. 3). The C－H stretching peaks near 3000 － 2800 cm^{-1} represent the structures of $CH_2$and CH3 and RCH_2 in soy protein concentrates. Glycerol and C 30B were hardly observed in SPC-glycerol and SPC-glycerol-C 30B composites, indicating the rearrangement of the groups on the surfaces of these composite films. However, the characteristic C=O stretching peak near 1650 cm^{-1} which was stronger in SPC-glycerol/C 30B composites than that in all other compounds in this study indicated the intermolecular rearrangements in SPC-glycerol/C 30B composites. Upon the formation of SPC films, the inter-molecular H-bonds played an important role [7,8].

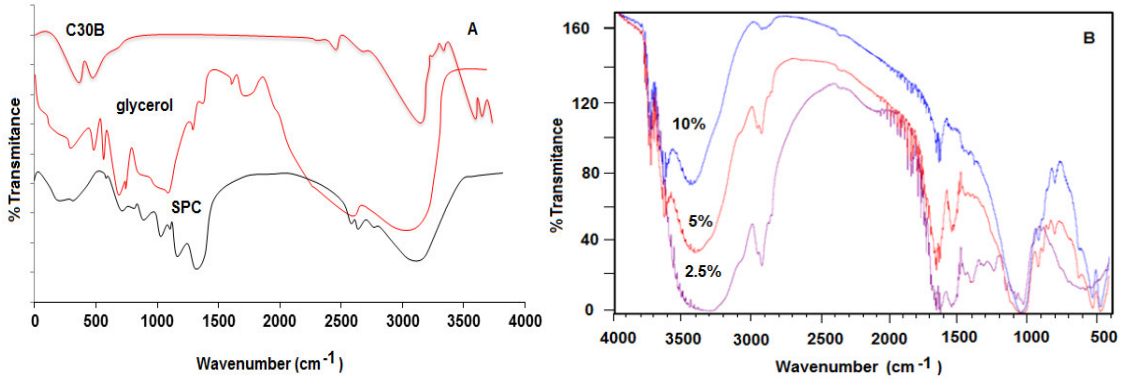

Figure 2

FT-IR spectra of (A) soy protein concentrate (SPC), glycerol and C 30B and (B) soy protein concentrate modified with glycerol and C 30B (SPC-Glycerol/C 30B)

SEM

The SEM images of fractured surfaces of the nanocomposites sheets are shown in Figure. 3. It clearly visualized the sizes and distributions of C 30B layers with the C 30B content 7.5 wt% and 10 wt%. The white strands in SEM images of 7.5% C 30B corresponds to C 30B platelets which are well dispersed it suggests the homogenised exfoliation of C 30B in 7.5% SPC-C 30B nanocomposite.The SEM images in 10% C 30B is found to be disorderly intercalated structure with aggregated clumps causing discontinuity in the polymer matrix, may be due to the presence of hydroxylated edge groups which interact strongly with each other. From the SEM results, we found exfoliated structure but at higher content of C 30B, an incomplete exfoliation is evident.

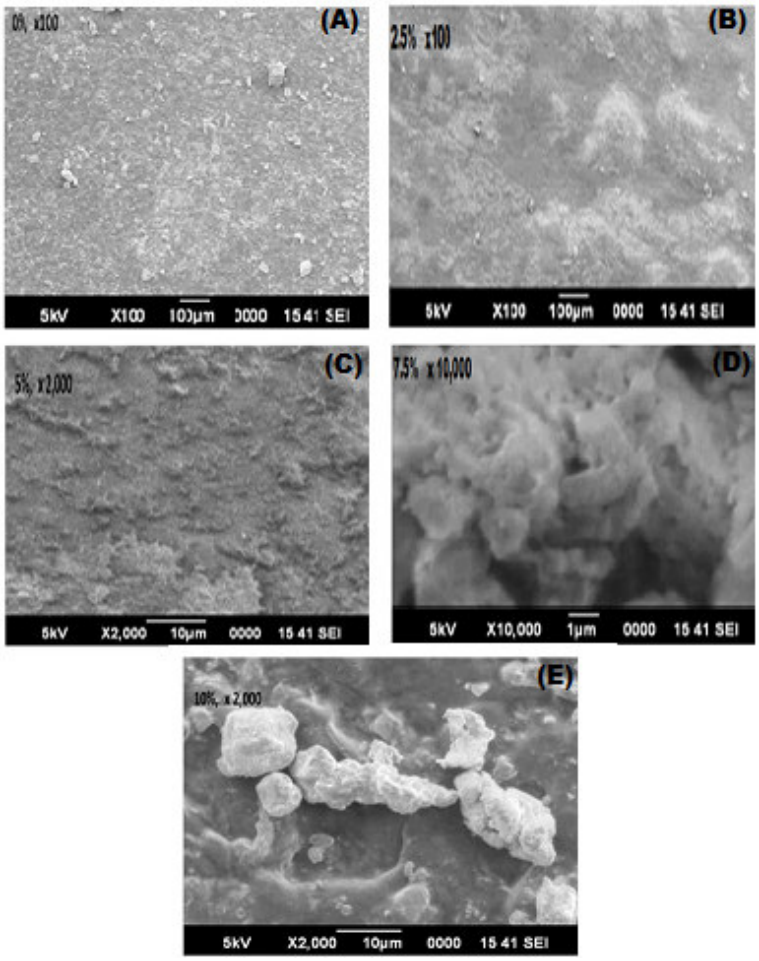

Figure 3

SEM images of SPC/C 30B plastics a) pure SPC; b) 2.5 wt% C 30B; c) 5 wt%, d) 7.5 wt%; e) 10wt% C 30B

TEM

Figure 4 presents the TEM images of SPC/clay nanocomposites with 5 wt% C 30B. From the TEM image, a very well dispersed layers of C 30B is observed in the SPC matrix which confirms the formation of exfoliation. Some aggregates with a dimension of about 20−50 nm are also observed (Fig. 4b), indicating an intercalated structure. TEM observation supports the results of the SEM and XRD. According to the evidence of XRD and TEM, the SPC/C 30B nanocomposites with exfoliated structure were obtained *via* a melt extrusion process. Moreover, these results obviously suggest a strong interfacial interaction between SPC and C 30B, including electrostatic interaction and/ hydrogen bonding.

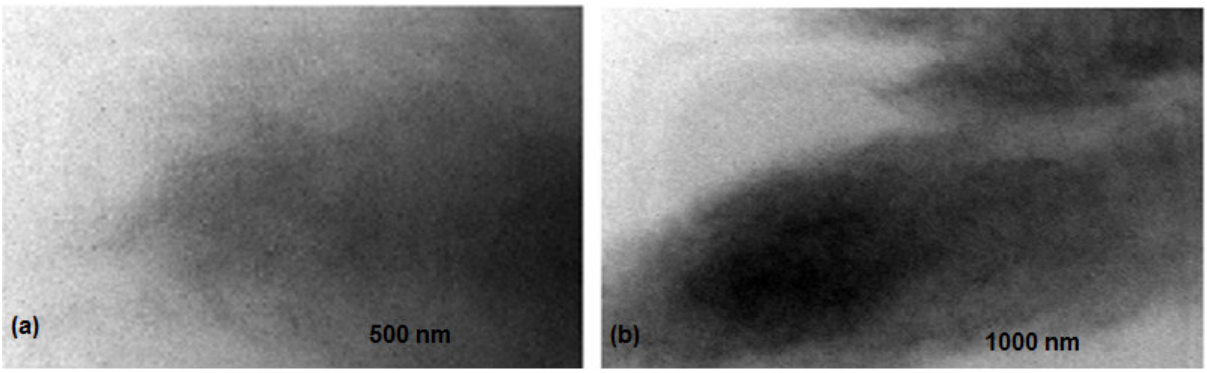

Figure 4

TEM images of SPC/C 30B films with 5 wt% C 30B with different magnifications

TGA

TGA data of SPC and SPC/C 30Bnanocomposites films with different clay contents of 0%, 2.5%, 5%, 7.5% and 10% are shown in figure 5. In all cases we found the thermal degradation of films in 3 steps between the temperature range of 100 to 900 ^{o}C. The first degradation occurred between 100 to 145 ^{o}C because of evaporation of water molecules from the films. Second thermal degradation occurred between 300 ^{o}C and 400 ^{o}C because of the decomposition of SPC and the organic modifier present in C 30B and loss of glycerol that was present in the films. A third step degradation was seen within the temperature range 520 to 750 ^{o}C. This is probably because of the oxidation of the sample under air flow. Interestingly with the increase of C 30B content, a delay in weight loss of the sample was observed at temperature more than 500 ^{o}C. The reason may be because of the enhancement of thermal stability with the incorporation of C 30 B [9-11].

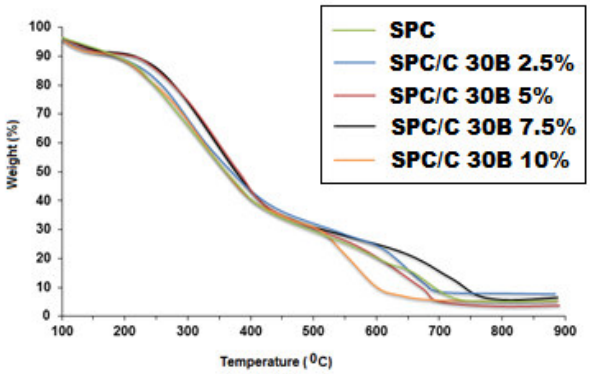

Figure 5

TGA curves of SPC/C 30B nanocomposites films with different C 30B contents

Enzymatic Testing

Figure 6(a) shows the weight loss of the film. With increasing C30B content in the SPC films an increase in degradation was found. The degradation rate of SPC film (without C 30B) was slower than that of SPC films (with C30B). Around 94% weight loss after 72hours of immersion was found as the absorption of enzymatic solution was directly proportional to the SPC content. Among the enzymes β-amylase and α-amylases, the later hydrolyse SPC more rapidly than former because it breaks the SPC molecule by attacking the main and branched chains. The hydrolysis of the SPC results a weaker interaction between SPC and C30B and thereby results in higher weight loss.

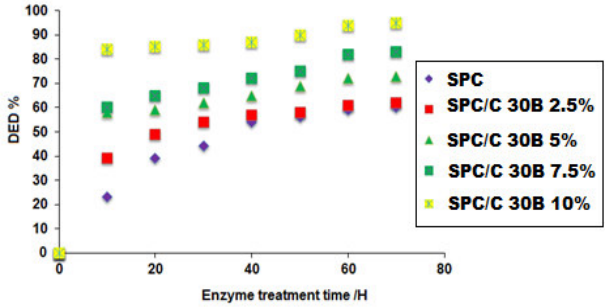

Figure 6(a)
Enzymatic degradation of SPC 100% and SPC/C30B films using α-amylase and β-amylase

Soil Burial Test

The biodegradability and burial time (both in soil and compost) are directly proportional to each other[12]. Almost 86% of biodegradation was observed after 10 weeks in both soil and compost (figure 6 (a) and (b)). Then the film continued to degrade and decompost at a slower rate because of the reduction of oxygen level and temperature in the film. In both the soil and compost, SPC/C30B sample showed the highest weight loss than pure SPC. C 30B has a major role in biodegradation of SPC film. The hydrolysability property of SPC films decreases with the increasing concentration of C 30B. So it shows a strong resistance against its degradation in soil burial test. But a 5–6% increase in the degradation rate was observed in case of compost burial. The presence of different types of organic matter in compost helped it to decompose largely through aerobic decomposition. Compost is made up of high nutrient content and hence can be used as a very good fertiliser and soil conditioner. Probably this high level of nutrients in the compost helps degrade the film more quickly by the microbes than soil.

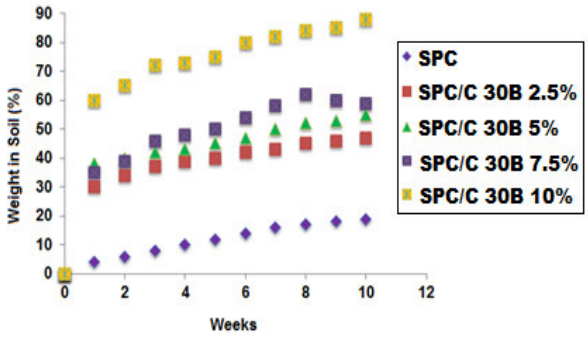

Figure 6(b)
Weight loss of SPC/C30B films after 10weeks in soil.

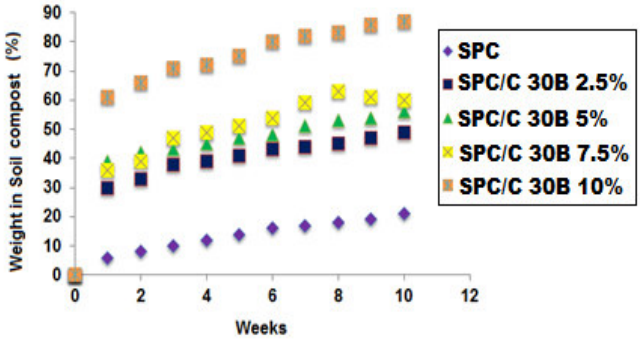

Figure 6(c)
Weight loss of SPC/C30B films after 10weeks in compost

Mechanical Properties and Thermal Stability

The tensile strength is improved from 22 MPa to 35 MPa, the maximum tensile strength occurs when the C 30B content is 5 wt%, and then the value decreases with the increase of C 30B content (Figure 7). The tensile modulus changes similarly with the tensile strength while the tensile modulus increases from 870MPa to 1342 MPa with the C 30B content increases from 0 wt% to 5 wt%, and then the value decreases with the increase of C 30B content, while the elongation at break gradually decreases with increasing C 30B content. The changes of mechanical properties can be described as the formation of intercalation and exfoliation of C 30B layers. Thus the tensile strength and tensile modulus increase

with the increase of C 30B content. However at higher content of clay, C 30B layers tend to aggregate as clusters which results in a decreased enhancement of tensile properties [13].

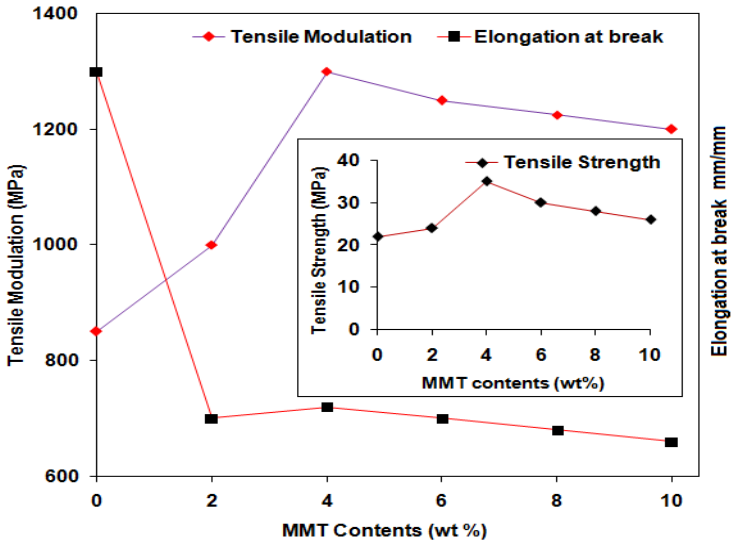

Figure 7

Effects of C 30B contents on tensile modulus, elongation at break and tensile strength

CONCLUSION

The SPC with C 30B has enhanced properties as compared to the SPC alone. The nanocomposites have been characterized by using FTIR, XRD, TEM, SEM and TGA, swelling studies and soil burial test methods to determine the characteristic properties of the nanocomposite materials. The addition of C30B to the SPC matrix increases the degradation rate of the sample. The degradation process increases with the increase in C30B content in the films. Thus SPC/C30B film has a great deal of future promise for potential application which will contribute to global sustainability.

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