

A NEW BIOPOLYMER-BASED POLYCAPROLACTONE/STARCH MODIFIED CLAY NANOCOMPOSITE

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Biopolymer nanocomposite was successfully prepared by the melt blending method. Fatty hydroxamic acid (FHA), synthesized from triacylglycerides of vegetable oil, has been used as an organic compound to modify natural clay, sodium montmorillonite (Na-MMT) for production of polycaprolactone/corn starch (PCL/CS) nanocomposite. The product was characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). An improvement in compatibility was obtained with 2% modified clay (OMMT). Moreover, an increase in the tensile strength of the blend and elongation at break was observed. The nanocomposite shows higher biodegradability and thermal stability in comparison with those of the PCL/CS blend.

Keywords: polycaprolactone, starch, degradation, nanocomposite

INTRODUCTION

PCL is a biodegradable polyester with a low melting point, compared to other polyesters. It has attracted much attention, due to the increasing interest in environment protection. PCL undergoes autocatalysed bulk hydrolysis and can be fully degraded by microorganisms in soils within 2 years.¹ In addition to food packaging materials, it can be used in different biomedical applications, such as in tissue engineering and drug delivery.²⁻⁴ However, the relatively high price of PCL restricts its application. Reducing of its cost has therefore been attempted by blending PCL with cheaper biodegradable polymers, such as starch, to obtain a competitive price. Besides helping to lower the cost, starch develops biodegradable properties of PCL.⁵⁻¹⁴

Starch is a renewable, biodegradable and available polymer. It is a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds.

Plants, such as rice, wheat, potato, tapioca and corn, are used to produce starch.¹⁵

Because of the poor compatibility between PCL and starch, attempts have been made to enhance their properties using a crosslinker, compatibilizer or coupling agent.¹⁶⁻¹⁸ These modifiers are considered not attractive because

they are toxic, non-environmentally friendly, or/and expensive.

Lately, the application of organo-modified clay in polymer/starch blends has been of great interest. Clay is hydrophilic in nature, but can be modified by a cation exchange process using alkylammonium or phosphonium cation to reduce its hydrophilicity.¹⁹⁻²⁴ The incorporation of organoclays in a polymer to produce a nanocomposite is one of the means to modify the property balance of the polymer. Improvements in thermal stability, physical and mechanical properties can be achieved by the addition of 2-5 wt% of organoclays, in comparison with the neat polymer.²⁵⁻²⁸

Kalambur and Rizvi reported that the addition of 1-5% modified clay improved the tensile strength of a PCL/wheat starch blend.²⁹ The compatibility of PCL/tapioca starch blend was enhanced by incorporating 1% organoclay into the blend. Improvements in tensile strength and elongation at break were also observed.³⁰

In this study, fatty hydroxamic acid (FHA) synthesized from vegetable oil was used for modification of the montmorillonite clay. The presence of long-chain fatty acids (mainly 16 and 18 carbon atoms) in FHA containing O and N

donor sets suggests that FHA should be very useful as surfactant for clay modification. The use of FHA reduces the dependence on petroleum-based surfactants. The present study also discusses the preparation and characterization of new biopolymer nanocomposites based on PCL/corn starch modified montmorillonite.

EXPERIMENTAL

Materials

Corn starch with starch particles of 5-20 μm size and surface area of $1.79 \text{ m}^2 \text{ g}^{-1}$ was purchased from Amylum, Slovakia. Glycerol was supplied by Merck, Germany. Polycaprolactone (CAPA 650) with number-average molecular weight of 50,000 was supplied by Solvay Caprolactone, England. Clay (MMT) with a cation exchange capacity of 119 meq/100 g was obtained from Kunimine Ind. Co., Japan. FHA was synthesized according to the procedure published by our group.³¹ Silver nitrate and concentrated hydrochloric acid were purchased from BDH, England. Sodium montmorillonite (Kunipia F) was obtained from Kunimine Ind. Co. Japan.

Preparation of organoclay

Organoclay was prepared by a cationic exchange process, where Na^+ in the montmorillonite was exchanged with alkylammonium ion of FHA. Typically, 4.00 g of sodium montmorillonite (Na-MMT) was stirred vigorously in 600 ml of hot distilled water for one hour to form a clay suspension. Subsequently, a designated amount of fatty nitrogen compounds in 400 mL of hot water were added and the desired amount of concentrated hydrochloride acid (HCl) was added into the clay suspension containing fatty nitrogen compounds. After being stirred vigorously for one hour at 80 °C, the organoclay suspension was filtered and washed with distilled water until no chloride was detected with a 1.0 M silver nitrate solution. It was then dried at 60 °C for 72 h. The dried organoclay was then ground to the particle size of less than 100 μm for the preparation of the nanocomposite.

Preparation of PCL/starch-OMMT nanocomposite

A mixture of starch, glycerol and water in the weight ratio of 5:1:4, respectively, was stored in a tightly sealed polyethylene plastic bag for 24 h to let the plasticizers (water and glycerol) to be absorbed by the starch granules.³⁰ A Thermo Haake Polydrive internal mixer at 120 °C with 100 rpm rotor speed for 10 min was used to blend the PCL and starch in the ratio of 70:30, using six different contents (0.5, 1, 2, 3, 4 or 5) per hundred plastic (php) of OMMT. The compounds were then moulded in an electrically heated hydraulic press at 130 °C for 10 min and a pressure of 150 kg/cm². At the end of the moulding

time, the compounds were immediately cooled for 5 min.

Characterization

Measurements of tensile properties

The tensile strength, tensile modulus, and elongation at the break were measured by using an Instron Universal Testing Machine 4301 at 5 mm min⁻¹ of crosshead speed, in accordance with ASTM D638.³² Seven samples were used for the tensile test and an average of five results was taken as the resultant value.

X-Ray diffraction (XRD) analysis

X-Ray diffraction study was carried out using a Shimadzu XRD 6000 diffractometer with CuK radiation ($\lambda = 0.15406 \text{ nm}$). The diffractogram was scanned in the ranges from 2 to 10° at a scan rate of 1° min⁻¹.

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of the samples were recorded by the FTIR spectrophotometer (Perkin Elmer FT-IR-Spectrum BX, USA), using the KBr disc technique.

Thermogravimetric analysis (TGA)

The thermal stability of the samples was studied by using a Perkin Elmer model TGA 7 Thermo gravimetry analyzer. The samples were heated from 35 to 800 °C with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere with a nitrogen flow rate of 20 mL min⁻¹.

Transmission electron microscopy (TEM)

The dispersion of clay was studied by using energy filtering transmission electron microscopy (EFTEM). TEM pictures were taken in a LEO 912 AB EFTEM with an acceleration voltage of 120 keV. The specimens were prepared using an Ultracut E (Reichert and Jung) cryomicrotome. Thin sections of about 100 nm were cut with a diamond knife at -120 °C.

Biodegradation test

The biodegradability of the PLC, PCL/CS blend and the PCL/CS-OMMT nanocomposite was determined as per ASTM D5338-92. A mixture of mature compost (200 g, wet weight) and the plastics (5%, on a dry basis) was introduced and incubated at 58 °C. The moisture content of the compost was maintained at 65%. CO₂ produced from the compost was absorbed by a 0.4 N potassium hydroxide and 2 N barium chloride mixture solution, and was quantified by titrating the solution with 0.2 N HCl.

RESULTS AND DISCUSSION

The weight ratio of the PCL/CS blend was fixed at 70:30 according to preliminary investigation which gave the highest tensile strength and elongation at break of the blend.

Therefore, this ratio was chosen in subsequent experiments.

Table 1 shows the effect of clay content on the tensile strength properties of the PCL/CS-OMMT nanocomposite. The tensile strength of the PCL/CS blend decreases to 14.21 MPa, compared to that of the neat PCL (39.98 MPa). The addition of 0.5, 1 or 2 php of OMMT into the PCL/CS blend increases the tensile strength. The highest tensile strength (26.36 MPa) is observed with 2 php of OMMT. This result is 13% and 40% higher than those reported by Then³⁰ and McGlashan and Halley,³³ respectively. Interfacial adhesion was increased by incorporating OMMT in the polymer blend, which plays an influential

role in causing compatibilization at a molecular level.²⁷ Further increase of OMMT content decreases the tensile strength due to the decrease of the PCL/CS chains interacting with the clay as the clay coagglomerates. The increase of the OMMT content also increases the modulus of the PCL/CS nanocomposites. The PCL/CS blend exhibits an elongation at break value of 127.35%. It increases to 997.68% with the addition of 0.5 php OMMT. The highest elongation at break (1621.34%) is observed with 2 php OMMT. However, further addition of OMMT causes the decrease of elongation at break, and makes the blend more brittle.³⁴ The tensile specimens were prepared as shown in Figure 1.

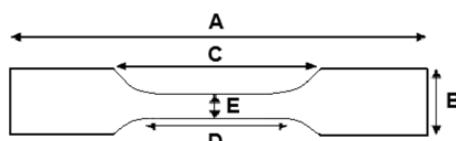


Figure 1: Dumbbell dimension diagram for tensile test; A, length of test specimen (75 mm), B, width of test specimen (12.5 mm), C, length (25 mm), D, length of bench marker (20 mm), and E, width (4 mm).

Table 1
Tensile properties of PCL, PCL/CS blend and PCL/CS-OMMT nanocomposite

Sample	Tensile strength, MPa	Modulus, MPa	Elongation at break, %
PCL	39.98 ± 1.92	148.23 ± 5.87	1.906 ± 1.42
PCL/CS	14.21 ± 0.85	151.21 ± 3.92	127.35 ± 2.89
PCL/CS/0.5 php OMMT	18.32 ± 0.91	187.18 ± 6.84	997.68 ± 6.28
PCL/CS/1.0 php OMMT	21.29 ± 1.32	198.91 ± 7.12	1380.70 ± 8.63
PCL/CS/2.0 php OMMT	26.36 ± 1.87	201.18 ± 7.71	1621.34 ± 9.32
PCL/CS/3.0 php OMMT	17.03 ± 0.85	205.35 ± 9.33	348.42 ± 8.12
PCL/CS/4.0 php OMMT	15.46 ± 0.72	219.23 ± 10.11	168.19 ± 7.59
PCL/CS/5.0 php OMMT	14.16 ± 0.64	232.18 ± 9.84	121.27 ± 6.96

The XRD patterns of NaMMT, OMMT, and PCL/TS-OMMT nanocomposite are shown in Table 2. NaMMT shows a peak at $2\theta=7.19^\circ$. According to Bragg's law, ($n\lambda=2d \sin\theta$), which provides the condition for a plane wave to be diffracted by a family of lattice planes: d refers to the distance of two consecutive clay layers, where λ is the wavelength of the intercept X-rays at the incident angle θ , this peak assigns the interlayer distance of the natural montmorillonite with a basal spacing of 1.23 nm. NaMMT was surface treated with FHA as an intercalation agent through a cation exchange process, which converted it from the normally hydrophilic silicate surface to an organophilic one. In the preparation of OMMT, the optimum amount of

FHA and HCl to reach maximum d-spacing was reported in our previous paper.²⁸ It was found that the maximum d-spacing was achieved when the amounts of FHA and HCl were 4.50g and 16mL, respectively. The d-spacing of FHA-MMT increases from 1.23 to 2.89 nm, indicating that the FHA was successfully intercalated into the NaMMT galleries. This result is in agreement with that reported in a previous paper.²⁸ In the nanocomposite where the NaMMT surface was pretreated with FHA, the d-spacing of the OMMT increased to 3.27 nm. The increase in the d-spacing of OMMT suggests that an intercalated type nanocomposite was formed. Figure 2 shows a schematic drawing of clay modification with FHA and PCL/CS clay nanocomposite.

Table 2
Diffraction angle and basal spacing of natural clay (NaMMT), modified clays with the FHA-MMT and PCL/CS-OMMT nanocomposite

Sample	Exchanged cation	2 Theta, degree	d-spacing, nm
Na-MMT	Na ⁺	7.19	1.23
FHA-MMT	RCO-N ⁺ H ₂ OH	3.05	2.89
PCL/CS-FHA-MMT	-	2.69	3.27

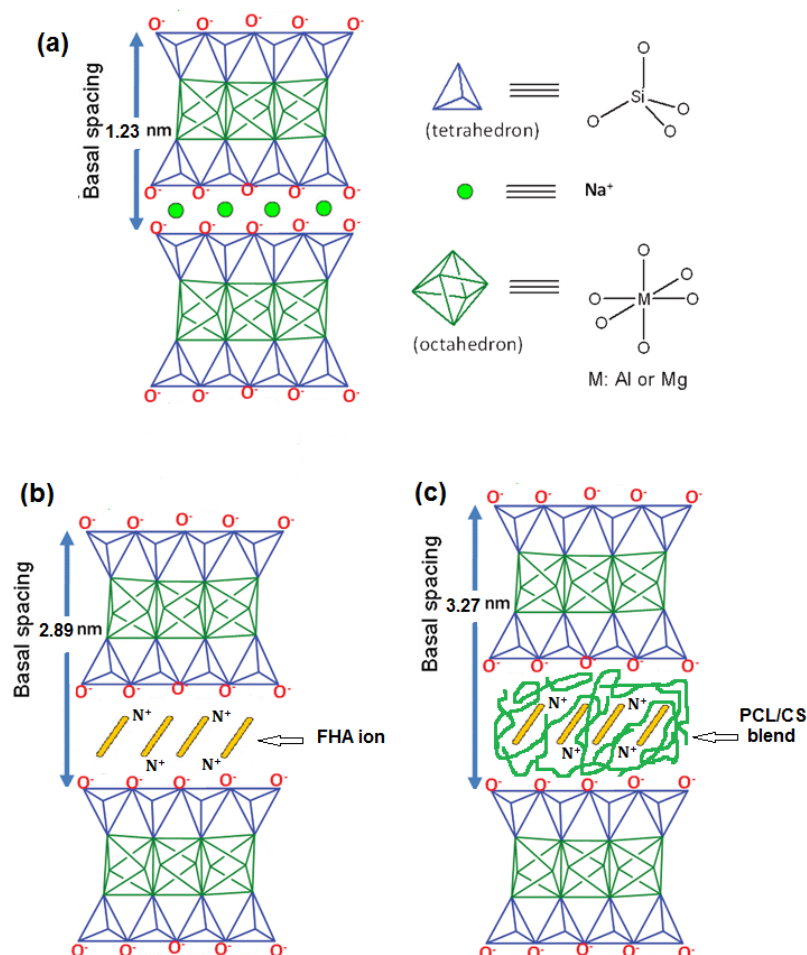


Figure 2: Layered silicate: (a) unmodified sodium montmorillonite, (b) sodium montmorillonite modified by FHA and (c) PCL/CS nanocomposite

Figure 3 shows the FTIR spectra of CS, PCL and PCL/CS blend and PCL/CS-OMMT nanocomposite. The CS spectrum illustrates the following characteristic bands: O-H stretching at around 3400 cm⁻¹, C-H stretching at 2861 and 2923 cm⁻¹, O-H bending vibrations of adsorbed water at 1639cm⁻¹, CH bending at 1461cm⁻¹, O-H bending at 1240-1204 cm⁻¹, C-O stretching of C-O-H at 960 and 1190 cm⁻¹ and C-O-C bond stretching of the anhydroglucose ring at 925cm⁻¹. The PCL spectrum displays typical bands at 2923 and 2854 cm⁻¹, attributed to CH stretching

vibrations, and at 1756 and 1555 cm⁻¹, associated with carbonyl adsorption and C-O stretching, respectively. The spectrum of the PCL/CS blend shows the characteristic adsorption of each polymer with no shift band frequencies, indicating that there are no strong molecular interactions between the components. This result is in agreement with that reported by Ciardelli.³⁵ The same observation was made regarding the PCL/CS-OMMT nanocomposite spectrum.³⁰

The biodegradation of PCL, PCL/CS blend and its nanocomposite was studied by the weight

loss in the compost. The weight changes of the PCL/CS blend and the PCL/CS-OMMT nanocomposite in the compost at 58 °C are shown in Table 3. The biodegradability of the neat PCL blend increases with increasing incubation time after blending with CS. It is clearly seen that the biodegradability is significantly enhanced

(20.51% weight loss) after 60 days. The same behavior was observed for the biodegradability of the PCL/CS-OMMT nanocomposite. A higher percentage (31.42 weight loss) was recorded, compared to the biodegradability of the PCL/CS blend, especially after 60 days.

Table 3
Time dependence of PCL, PCL/CS blend and PCL/CS-OMMT nanocomposite weight loss at 58 °C

Sample	Weight loss, %				
	5 days	10 days	20 days	30 days	60 days
PCL	0.21	0.42	0.74	1.09	5.16
PCL/CS	1.15	1.53	196	2.17	20.51
PCL/CS-OMMT	1.75	2.81	3.10	5.81	31.42

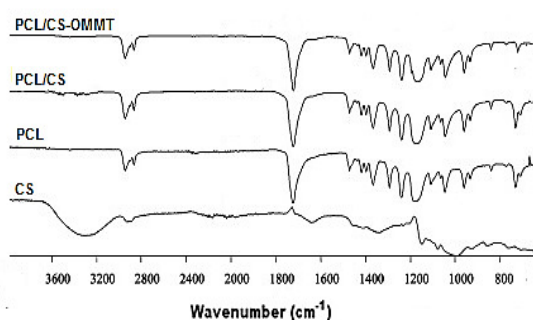


Figure 3: FTIR spectra for pure components, blend and nanocomposite

The TGA curves of the PCL, CS, PCL/CS blend and PCL/CS-OMMT nanocomposite are presented in Figure 4. It can be seen that the onset of PCL and CS thermal degradation is at temperatures of about 306 and 240 °C, respectively. The PCL/CS-OMMT nanocomposite curve exhibits a lower weight loss

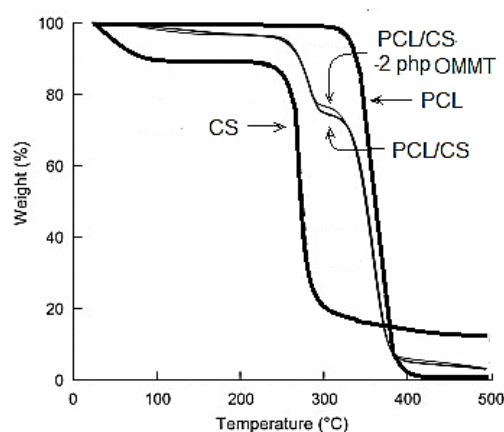


Figure 4: TGA thermograms of PCL, CS, PCL/CS blend and PCL/CS-OMMT nanocomposite

(73.8%), compared to the PCL/CS blend (66.4%) at about 306°C. The presence of FHA-MMT dispersed homogeneously in the PCL/CS sheet acts as a barrier hindering the permeability of volatile degradation products out from the material and helps delay the degradation of the nanocomposites.²⁸

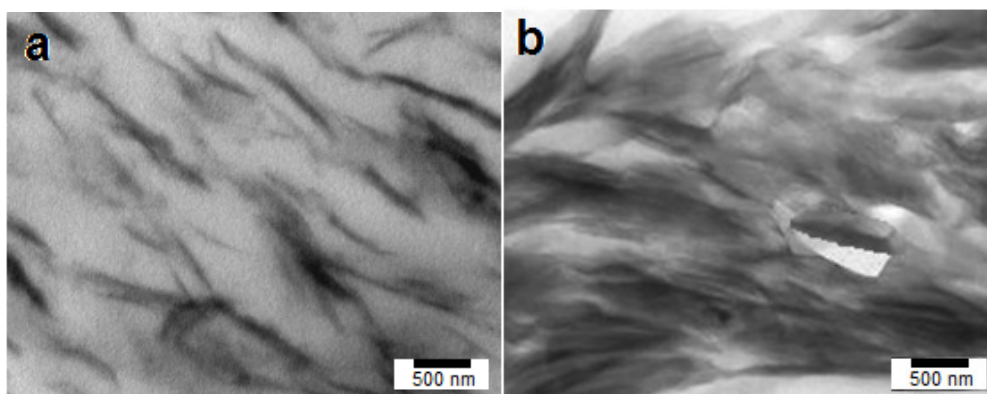


Figure 5: TEM micrographs of (a) PCL/CS/2 php OMMT and (b) PCL/CS/2 php OMMT composites

Figure 5 shows the TEM micrographs of the PCL/CS blend reinforced with 2 php OMMT (Figure 3a) and with 3 php OMMT (Figure 3b). The dark lines correspond to the thickness of the clay layers. It was observed that the 2 php OMMT is quite dispersed in the PCL/CS matrix. The related structure can be referred to as both intercalated and exfoliated lamellae. Agglomerates tend to form rapidly with the increase of the OMMT content to 3 php.

CONCLUSION

A new biopolymer nanocomposite was prepared by incorporating 2 php of FHA-MMT in the PCL/CS blend. The XRD technique and TEM analysis confirm the resulting nanocomposite. The product represents a good candidate to produce disposable packaging, as it presents good mechanical and thermal properties and processability. Another advantage is that it is created from renewable, biodegradable and easily available raw materials, and is environmentally friendly, thus solving the problem of plastic waste. The surfactant (FHA) used in this study for clay modification will reduce the dependence on petroleum-based surfactants.

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