BIODEGRADABLE POLYESTER / CRYSTALLINE NANOCELLULOSE NANOCOMPOSITES FOR BIOMEDICAL APPLICATIONS: PREPARATION AND CHARACTERIZATION.

A. Butron, O. Llorente, J. Fernandez, E. Meaurio, JR. Sarasua

Department of Mining-Metallurgy Engineering and Materials Science, POLYMAT, University of the Basque Country (UPV/EHU), School of Engineering, Alameda de Urquijo s/n, Bilbao, Spain, amaia.butron@eu.eus

ABSTRACT

The use of biodegradable polymers in biomedicine is rising and polymer matrices loaded with reinforcements can be good candidates for temporary implants and tissue engineering scaffolds. In this work poly (ethylene brassylate) (PEB) was reinforced with cellulose nanocrystals (CNC), in order to achieve a biocompatible material with superior mechanical properties than the neat polymer. PEB/CNC composites were characterized through calorimetry, thermogravimetry and tensile tests in order to determine the effect CNC reinforcement in the thermal and mechanical properties. The Young´s modulus was found to increase about 20 % with just an addition of 2.5 wt% CNC; higher contents of reinforcement resulted in a decrease of ductility of the composites. The thermal analyses suggest lack of interaction between PEB and CNC at their interphase.

INTRODUCTION

Nanocelluloses are classified in three groups: (1) cellulose nanocrystals (CNC) or nanocrystalline cellulose, which has been used in this project; (2) cellulose nanofibrils (CNF), nanofibrillated cellulose (NFC) or cellulose nanofibers; and (3) bacterial cellulose (BC) or microbial cellulose [1]. The CNC is achieved by an acid hydrolysis process, disturbing the hydrogen bonds in the fine fibers of the pulp of cellulose and thus fragmenting the amorphous zones. Well defined crystalline rods are produced. The acid used in the treatment defines the colloidal stability of the nanoparticles, since each acid confers different functional groups [2]. The mechanical properties of the CNC depend to a great extent on the concentration of the acid used to carry out the hydrolysis reaction.

Crystalline nanocellulose is thermally stable, a critical property in composite melt production. However, the degradation temperature is reduced in the hydrolysis process in sulfuric acid: the cellulose decomposes at 330-340°C and the crystalline particles at 215-220°C [3].

The biological properties of nanocelluloses are essential if they are intended to be used in biological tissues, but there are few research works on this topic. The CNCs prove to be biocompatible, with hardly any body rejection in vivo, but the human body is not capable of degrading them, which always implies some incompatibility. It would also be of interest to know its hemocompatibility and toxicity, both very scarcely studied, but with positive results so far. [1]

Poly (ethylene brassylate) (PEB) or poly (ethylene tridecanedioate) is a polyester with properties similar to poly (ε-caprolactone) (PCL), with a glass transition temperature (Tg) of -27 °C and a melting temperature (Tm) of 70 ºC. The price of ethylene brassylate monomer is low, much more than that of PCL, which is already among the cheapest biodegradable polyesters [4] [5] [6].

The maximum thermal degradation of this polymer occurs at approximately 425 °C, starting at about 325 °C. The deformation at break is above 900%, its tensile strength is about 26 MPa, and its yield point is around 11 MPa [5] [6].

Compared with traditional composites, nanocomposites usually exhibit superior thermal, mechanical and barrier properties with lower reinforcing loads. A number of medical products based on biodegradable polymers has now reached the stage of clinical use. Biodegradable polyesters, in general, and especially polylactides and polylactones, are the most widely used biopolymers in medical applications [7]. Commercially important examples are Dexon™, used to produce sutures composed of poly (glycolic acid) (PGA), La**cto**mer™ surgical staples composed of PGA and poly (L-lactic acid) (PLLA), angioplasty plugs from PGA and poly (D,L lactic acid) (PDLLA), and many others [8].

The novelty of this work consists in the preparation and characterization of novel composites of PEB with CNC as reinforcement. The initial idea is to improve the overall mechanical properties of neat PEB since CNC are much more rigid and strong than the polymer. Besides, resulting biocompatible and biodegradable, these composites will be potentially of used as biomedical implants of for tissue engineering.

1. METHODS AND MATERIALS

1.1. MATERIALS

The PEB which has been used as the base material [10] was synthesized in our laboratory. Ethylene Brassylate monomer (purity> 95%) was supplied by Sigma Aldrich (W354309) and bismuth triphenyl catalyst (Ph3B) was obtained from Gelest; both were used for polymerization.

The nanocrystalline cellulose used in this project has a hydrodynamic diameter of approximately 150 nm, according to the data provided by Alberta Innovates Technology Futures. It is whitish and is presented as agglomerated flakes.

Chloroform as organic solvent, methanol to precipitate-purify the polymer and 1-Hexanol to control the molecular weight were also used.

1.2. COMPOSITE PREPARATION

Films of PEB/CNC composites were prepared with CNC compositions ranging fron 0.5 to 50 wt% (see Table 1). PEB was dissolved in chloroform and the CNC were dispersed in the appropriate ratios and sonicated. To obtain films of uniform thickness, the cast film composites were compression molded in a Collin P 200 at 175 ° C and 250 bar pressure for 15 seconds. Then, the molds were slowly cooled to 35 ° C to ensure correct crystallization.

1.3. CHARACTERIZATION

1.3.1 DSC

Melt pressed fims were analyzed by Differential Scanning Calorimetry (DSC) in a Q200 model from TA Instruments. Samples, weighing between 6 and 9 mg were cut from the films and encapsulated in aluminum pans.

Samples were first scanned from room temperature to 130 ° C at a rate of 20 °C / min. Then they were quenched to -80 ºC, cool down at the maximum speed allowed by the equipment, and finally a second heating scan was performed from -80 ºC to 130 ºC at 20 °C / min.

1.3.2 TENSILE TESTS

The mechanical properties of the composites were analyzed from tensile tests carried out on six specimens for each composition. These tests were carried out on an Instron model 5565. Specimens were cut in 8 x 1 cm sizes and the distance between fastenings was 5 cm.

1.3.3 THERMOGRAVIMETRY

To study the thermal degradation of the composites~~, a~~ thermogravimetric analysis (TGA) was carried out in a TGA Q50-0545 from TA Instruments. The results are presented as mass loss curves and their corresponding derivative curves. Sample weights were in the 10 - 15 mg range and were put in ceramic crucibles that were heated from 25 to 700 °C at a rate of 5 °C / min.

2. RESULTS AND DISCUSSION

2.1. DSC analysis

Figure 1 shows the heat flow in the first scan of the curves of the composite samples containing 0, 2.5, 5, 10, 15, 20, 30, 40 and 50 wt% nanocellulose. The melting enthalpies were obtained from this Figure and were corrected to a pure polymer basis (see Table 1). As can be seen the corrected values for composites nearly matches the value obtained for pure PEB.

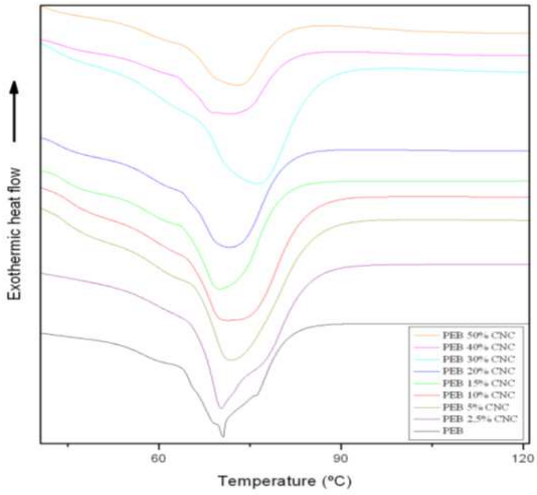

Figure 1. *First DSC scans. Melting enthalpies (exothermic heat flow against temperature) for the investigated composites.*

PEB/CNC Compositions	First scan		Second scan			
	Tm (°C)	ΔHm (J/g)	Tg (°C)	ΔCp (J/g)	Tm (°C)	ΔHm (J/g)
PEB	70.6	89.3	-27.6	0.313	69.7	90.7
PEB/2.5% CNC	70.3	94.7	-31.1	0.309	69.9	94.4
PEB/ 5% CNC	71.6	89.5	-25.6	0.296	72.9	95.0
PEB/ 10% CNC	70.7	100.0	-28.5	0.259	72.5	92.5
PEB/ 15% CNC	69.6	89.8	-32.2	0.250	70.3	92.9
PEB/ 20% CNC	71.2	92.8	-29.2	0.243	70.9	94.8
PEB/ 30% CNC	76.7	92.9	-24.2	0.160	75.7	89.0
PEB/ 40% CNC	71,6	88,7	-30,6	0,158	72,1	92,0
PEB/ 50% CNC	74.3	91.8	-32.2	0.120	73.8	89.3

Table 1. *Melting temperature, melting enthalpy, glass transition temperature and specific heat of the different concentrations of CNC*

Table 1 shows the melting enthalpy (ΔHm) and temperature (Tm) of neat PEB and its CNC composites obtained during the first heating scan. The glass transition temperatures (Tg) and its specific heats associated (ΔCp) are also shown; these were obtained during the second heating scan.

From these data it can be seen that Tm remains approximately constant at 72° C, ΔHm reaches values in the range of 90 and 95 J/g and Tg is located at about -30°

C. Regarding the specific heat (ΔCp), its value decreases as expected with the addition of CNCs, its value being 0.313 J/g for pure PEB, and 0.120 J/g for the 50 wt% CNC composite.

2.2. TENSILE TESTS

Figure 2 shows the stress-strain curves obtained from the tensile tests for the different composites. As can be seen, composites with CNC compositions below 20 wt% show high ductility and can achieve break strain values of up to 700%. PEB composites with higher CNC contents than 30 wt. % CNC, however, hardly attain the yield point and therefore show brittle behavior.

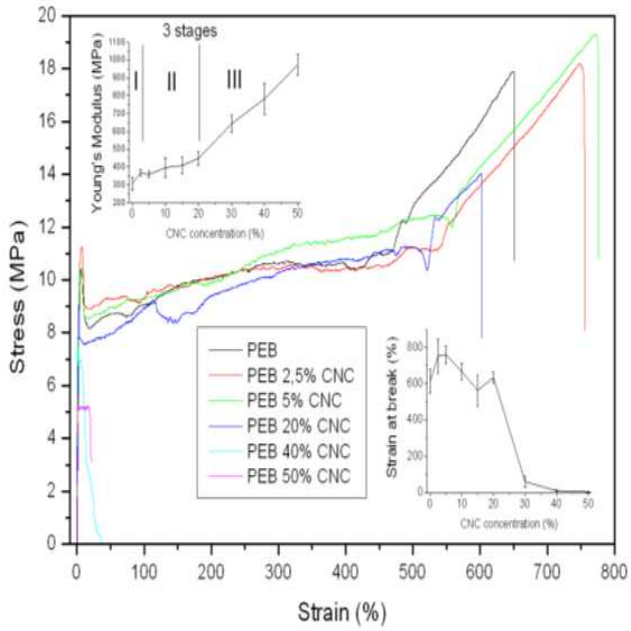

***Figure 2**. Nominal stress-strain curves for PEB/CNC composites*

The mean values, and corresponding deviations, of the yield stress (σ_y) and strain (ε_y) and the elastic modulus or Young's modulus (E) are shown in the Table 2. The elastic modulus increases markedly, being almost 320% higher in the CNC 50 wt% composite with regard to neat PEB. The evolution of Young´s modulus with CNC wt. % of these composites can be divided into three stages (Figure 2). In the first stage, corresponding to CNC contents below 2.5%, E grows abruptly, then in the second stage stabilizes to a value close to 400 MPa and finally, in the third stage, from 20 wt. % CNC another important increase occurs. The latter suggests interaction between cellulose nanocrystals within possible agglomerates.

PEB/CNC	σ_y (MPa)	ε_y (%)	E (MPa)
PEB	10.7 ± 0,3	6.5	307 ± 37
PEB/2.5% CNC	11.4 ± 0,6	7.4	368 ± 18
PEB/ 5% CNC	10.2 ± 0,5	5.8	359 ± 16
PEB/ 10% CNC	11.2 ± 1,9	5.2	397 ± 55
PEB/ 15% CNC	9.3 ± 0,6	3.3	409 ± 46
PEB/ 20% CNC	10.0 ± 0,8	3.2	449 ± 38
PEB/ 30% CNC	9.8 ± 0,5	1.9	643 ± 47
PEB/ 40% CNC	7.1 ± 0,8	1.0	784 ± 86
PEB/ 50% CNC	-	-	974 ± 59

***Table 2**. Mechanical properties of different concentrations of CNC copolymers*

Figure 3 shows the stress-strain behavior of neat PEB and its CNC composites at low strains. A slope increase is clearly observed in the lineal region as CNC content added to PEB increases. In addition the yield stress increases and a significant reduction of yielding area is observed with adding CNC contents. Finally, the 50% CNC composite does not attain the yield point and therefore breaks in brittle mode in the linear region.

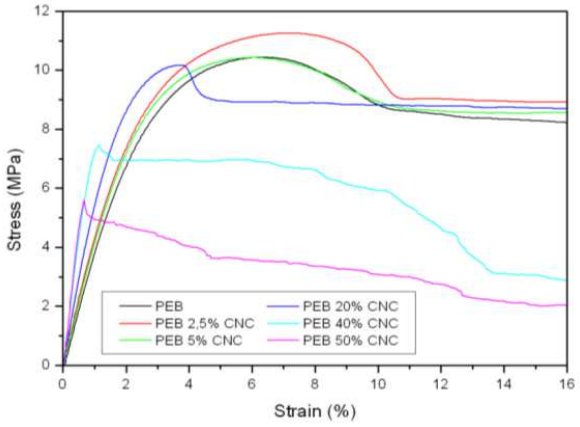

***Figure 3.** Creep stress and zone of elastic behavior of the different concentrations*

2.3. TGA

Figure 4 shows the thermal degradation curves of the PEB composite samples containing 0, 10, 30, 50 and 100 wt% CNC. As can be seen, degradation begins at about 250 °C for all samples, except for PEB, which begins to degrade at 300 °C. Mass loss ends in all cases at about 500 °C save for neat CNC whose curve drops at lower temperature leaving a residue of the initial CNC mass. In this figure also two steep drops can be detected, which can be associated to two different stages of degradation, the former at lower temperature corresponding to CNC degradation and the latter at higher temperature corresponding to PEB. As expected, as the CNC content in composites increases, the first mass drop increases in intensity.

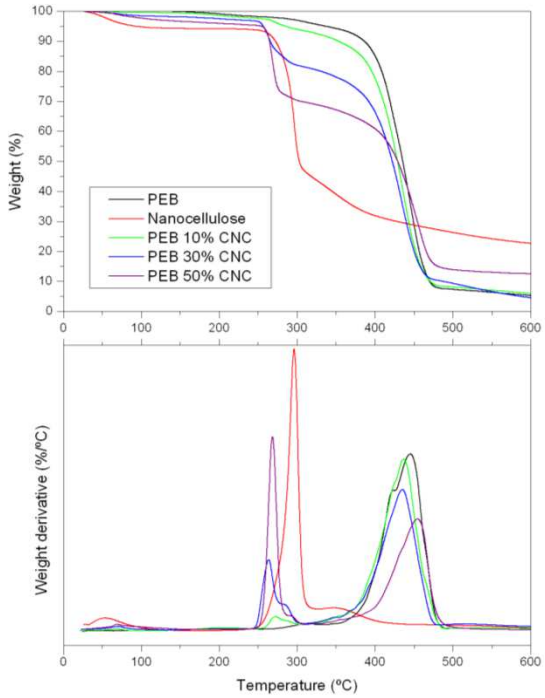

Figure 4. *Weight loss and its derivative for 0, 10, 30, 50 and 100 CNC wt%.*

Figure 4 shows also (below) the derivative curves. The CNC show its maximum degradation rate at 296 °C whereas that of PEB occurs at 445 °C. Overall the curves show the expected shapes according to composite materials composition. This additivity suggests the lack of interaction between PEB and CNC.

3. CONCLUSIONS

- CNC seem well dispersed in PEB since the good reproducibility of results obtained from different samples is consistent with homogeneous dispersions.

- Since both components of composites degrade as would do if they were isolated, the thermal degradation analysis suggests lack of interactions between CNC and PEB and therefore the existence of a pure physical mixture.

- Thermal properties of PEB are not significantly altered when CNC is added suggesting also lack of interaction at PEB-CNC interfaces.

- Increasing the CNC content in PEB composites, elastic modulus and the tensile strength increase. Particularly relevant is the composite containing 2.5 wt.% since Young´s modulus shows the largest increase over PEB without losing ductility. This is therefore the optimal CNC content and reveals the possibility of using CNC composites as neat PEB alternatives with an increment of stiffness.

- At CNC contents higher than 20 wt% load, the modulus increases higher than expected, which suggests interactions between CNC forming agglomerates.

- The higher CNC content in composites the greater the brittleness. Particularly, ductility is highly reduced above 20 wt% CNC contents suggesting the existence of CNC agglomerates above this content.

- The degradation temperature in PEB/CNC composites is reduced to 250 °C; this reduction of thermal stability with regard to neat PEB should be considered during processing operations.

- PBC/CNC nanocomposites show a significant improvement of stiffness and strength related properties and therefore can be considered potential material candidates for bone tissue temporary implants.

Acknowledgments

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