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Poly(-caprolactone)-based biocomposites reinforced with nanocrystalline cellulose grafted with poly(L-lactic acid)

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Poly(ϵ -caprolactone)-based biocomposites reinforced with nanocrystalline cellulose grafted with poly(L-lactic acid)

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Abstract. The modification of nanocrystalline cellulose with poly(L-lactic acid) was carried out using the "grafting from" approach based on the ring-opening polymerization of L-lactide initiated with cellulose hydroxyls. The modification was proved by FTIR spectroscopy, thermogravimetric analysis and dynamic light scattering. Samples of native and modified cellulose were applied as fillers for poly(ϵ -caprolactone) films that were studied for their mechanical properties. A significant increase of Young's modulus was observed for composite material based on PCL containing nanocrystalline cellulose modified with poly(L-lactic acid).

1. Introduction

Currently, the polyester-based materials are widely used for many applications such as food industry, surgery, drug delivery and regenerative medicine [1]. Poly(lactic acid) (PLA), poly(glycolic acid) (PGA), poly(ϵ -caprolactone) (PCL), poly(ω -pentadecalactone) (PDL) and their copolymers are biodegradable and one of the most commercially competitive polyesters. The major drawback of polyesters in biomedicine is their hydrophobicity, which results in uncontrollable fouling of proteins on the surface of materials upon contact with biological fluids and tissues [2]. In turn, it leads to uncontrollable cell-material interactions effects [3]. Thus the material hydrophilization is needed to improve its biological properties. These could be tuned by surface modification [4] or by addition of the special fillers [5,6], which change also the bulk properties of the materials, such as mechanical properties. To improve the mechanical properties, the polyester materials are usually reinforced with synthetic or mineral nanofillers [6,7].

In last decade, the natural polymers are received much attention due to their availability from renewable resources, which is in accordance with the Principles of Green Chemistry. Currently, the micro- and nanocrystalline cellulose (MCC or NCC) are widely considered as fillers in polymer matrices to develop fully renewable and biocompatible materials [8]. However, the application of pure cellulose micro/nanocrystals as fillers to polyesters is accompanied with the interfacial incompatibility between the hydrophobic polymer matrix and the hydrophilic cellulose [9]. This drawback could be surmounted *via* cellulose nanocrystals surface chemical modification. In particular, the adsorption of poly(ethylene glycol) (PEG) on NCC surface [10] and covalent modification of NCC surface with PLA [9] has been recently reported. In this work, we focused on preparation of the composite material



based on PCL filled with NCC bearing poly(L-lactic acid) (PLLA) and study of PLLA attachment effect on the properties of formed composite material.

2. Results and Discussion

2.1. Grafting of PLLA from NCC via ring-opening polymerization of L-lactide

The modification of NCC surface by PLLA was carried out using the grafting-from strategy. In this case, the hydroxylic groups of NCC acted as initiators for ring-opening polymerization of L-lactide (Fig. 1). The characteristics of NCC are given in Tables 1 and 2. Grafting procedure was carried out both in suspension and in bulk. NCC and monomer were dried in vacuum before polymerization. The NCC/L-lactide ratio was 2 (wt/wt), but $[L\text{-lactide}]/[Sn(Oct)_2]$ ratio was equal to 14. Other experimental conditions can be found in Fig. 1. The yield of grafted polymer was equal to 20% for in bulk polymerization and 26% for in suspension process.

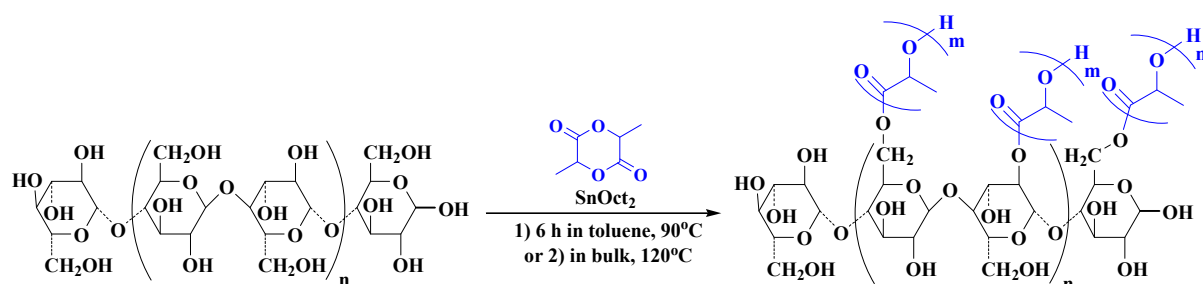


Figure 1. Scheme of PLLA grafting from NCC.

The successful modification of NCC with PLLA was proved by solid state FTIR spectroscopy (Fig. 2). For comparison, pure PLLA sample was synthesized by ring-opening polymerization. The synthesis was carried out in bulk at 130 °C for 24 h using the ratios: $[L\text{-lactide}]:[methanol] = 10000$, $[methanol]:[Sn(Oct)_2] = 2$. The polymer yield was equal to 83%. The obtained PLLA had following characteristics (size-exclusion chromatography in THF at 40 °C): $M_w = 99000$, $\bar{D} = 1.26$. FTIR spectra were registered for both in suspension and in bulk obtained modification products. In the spectra of NCC modified by PLLA a band at 1755 cm^{-1} corresponding to the C=O bond stretching in PLLA was detected. This band was absent in the spectra of unmodified NCC.

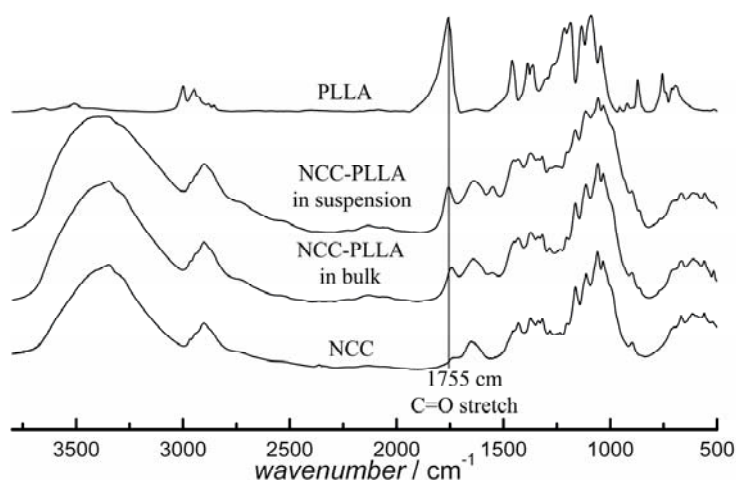


Figure 2. FTIR spectra of registered for pure NCC and PLLA as well as for NCC modified with PLLA.

Taking into account that chemical modification of polymers changes their thermal stability, the modified NCC was subjected to thermogravimetric analysis (TGA). The analysis was performed in air atmosphere at temperatures from 25 to 600 °C and heating rate 5 °C/min. The obtained TGA and differential thermal gravimetry (DTG) curves are presented in Fig. 3. Pure PLLA demonstrated the sharp loss of weight due to destruction, while NCC and NCC-PLLA samples demonstrated an initial mass loss (about 3.5%) from 40 °C to 120 °C. At this step, the loss of the hydrated and coordinated water molecules from the cellulose environment takes place. After this the smooth weight loss occurs until 400 °C.

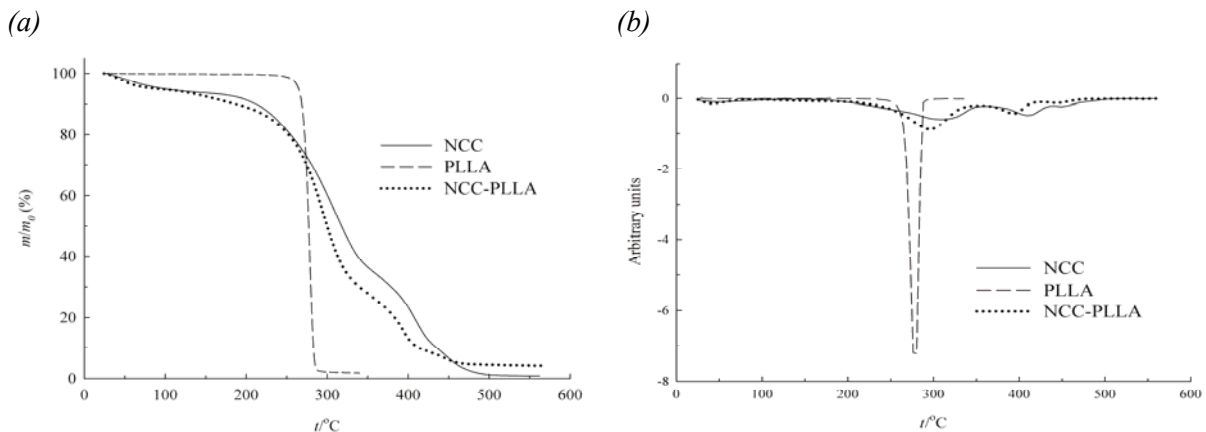


Figure 3. TGA (a) and DTG (b) curves for pure NCC and PLLA as well as NCC modified with PLLA.

Table 1 summarizes the temperatures of polymer decomposition for 5 (τ_5) and 10% (τ_{10}) mass loss. The highest thermal stability was detected for pure PLLA, whereas the lowest one was observed for pure NCC. As it was expected, the thermal stability of NCC-PLLA sample was between those demonstrated by parental polymers.

Table 1. Thermal characteristics for modified and native polymers.

Samples	$\tau_5/^\circ\text{C}$	$\tau_{10}/^\circ\text{C}$
NCC	220	241
PLLA	265	269
NCC-PLLA*	228	249

*Sample prepared in solution

Additionally, the samples of unmodified and modified NCC were analyzed by dynamic light scattering to monitor the changes in characteristics such as hydrodynamic size (D_H), polydispersity index (PDI) and ξ -potential of different NCC samples (Table 2). As it can be seen from the data presented, the lyophilization and following redispersion of commercially available NCC led to the increase of D_H and PDI of cellulose nanoparticles. In its turn, the NCC surface grafting with water insoluble PLLA chains resulted in additional increase of hydrodynamic diameter. Such effect was a result of hydrophobic interactions between PLLA chains in water that caused the partial NCC aggregation. As to ξ -potential of NCC, the absolute value was decreased after modification with PLLA. That also indirectly testifies the changes in surface chemistry.

Table 2. Hydrodynamic diameter (D_H), polydispersity index (PDI) and ξ -potential of pure and modified NCC (DLS in water).

Samples		D_H , nm	PDI	ξ -potential, mV
NCC native	commercial suspension	128	0.28	-23.0 ± 1.7
NCC native	liophylized + redispersed	264	0.58	-25.0 ± 0.5
NCC-PLLA	liophylized + redispersed	460	0.23	-19.6 ± 0.5

2.2. Preparation of PCL-NCC-PLLA composite films

The obtained NCC-PLLA was used as filler for PCL matrix. With aim to prepare the PCL films the matrix polymer was synthesized by ring-opening polymerization in bulk at 130 °C for 24 h. The polymerization mixture was composed in the following manner: $[\varepsilon\text{-caprolactone}]:[\text{methanol}] = 2500$, $[\text{methanol}]:[\text{Sn}(\text{Oct})_2] = 2$. PCL yield was equal to 81%. The molecular weight characteristics of PCL were determined by size-exclusion chromatography in THF at 40 °C. The calibration curve built for polystyrene standards was used for this purpose. M_w and $\bar{D}$ were found to be 155000 and 1.53, respectively. The PCL films were prepared *via* casting of the polymer solution with or without NCC onto the flexible cellophane substrate and followed with solvent evaporation [11].

The prepared films made of native PCL and PCL filled with 5 wt% of NCC and NCC-PLLA were analyzed by polarized light microscopy (Fig. 4). The film without fillers presents the phase relief due to existence of crystalline and amorphous regions. The addition of both NCC and NCC-PLLA affects the organization of macromolecules in the material – less crystalline areas of PCL were observed by this method. The NCC particles tend to form aggregates (Fig. 4b and c). The average sizes of aggregates was estimated using Fiji ImageJ free software and were equal to 1.91 and 1.01 μm for unmodified NCC and NCC-PLLA, correspondingly.

**Figure 4.** Images obtained by polarized light microscopy for films based on native PCL (a) and PCL filled with NCC (b) and NCC-PLLA (c).

2.3. Mechanical properties of biocomposites

Mechanical characteristics of the films were determined under conditions of uniaxial extension using band-like samples of 2 mm $\times$ 20 mm. Experiments were carried out at the extension speed of 10 mm/min. The Young's modules (E), tensile strengths (σ_b) and elongation at break (ε_b) were determined for three kinds of films: pure PCL, PCL filled with unmodified NCC and PCL filled with NCC-PLLA (Table 3). The characteristics of the initial PCL film were in agreement with data published elsewhere [12]. An introduction of 5 wt% pure NCC into PCL film did not influence the value of Young's modulus but led to the drastic decrease of elongation at break and tensile strength. The filling of PCL with NCC-PLLA provides the better compatibility of the nanofiller with hydrophobic polymer matrix. Comparatively to the material filled with unmodified NCC, the

modification of NCC allowed for the increase of Young's modulus, σ_b and ε_b by approximately 1.5, 1.7 and 1.3 times.

Table 3. Mechanical properties of pure PCL and composite films.

Film	E , MPa	σ_b , MPa	ε_b , %
PCL	324±16	25.0±3.2	830± 58
PCL+5 wt% NCC	352±28	7.9 ±0.6	19±5
PCL+5 wt% NCC-PLLA	512 ±11	13.2±0.8	25±5

2.4. Biological evaluation of biocomposites

The effect of NCC and NCC-PLLA application on cells adhesion on the surface of PCL-based films was evaluated using bone marrow mesenchymal stem cells (MSC). The films pieces were placed into 96 well plate and MSC (5×10^3 cells per well) were seeded. After 24 hours of incubation the non-attached dead cells were washed out and the amount of attached cells was evaluated using MTT-test. Fig. 5 illustrates the dependence of formazan optical density on material composition. The optical density is proportional to the number of cells adhered to the surface of the films. In all cases, the measured parameter was at the same level. That indicates the comparable cell adhesion. Thus, the introduction of NCC into PCL as well as modification of NCC did not make materials toxic for the cells. It allows the suggestion of further surface modification of NCC with cells instructive peptides to permit the direct cell-material interactions.

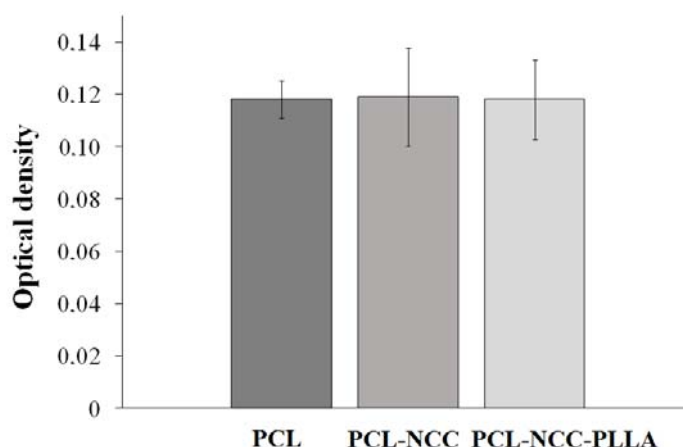


Figure 5. Adhesion of the cells (MSC) on the surface of native and composite films.

3. Conclusions

In order to enhance the compatibility of biodegradable PCL with nanocrystalline cellulose and mechanical properties of composite material, PLLA was covalently grafted onto the NCC surface *via* "grafting from" approach. The obtained composite PCL-NCC-PLLA films demonstrated significant improvement of Young's modulus comparatively to initial PCL and PCL-NCC materials. Taking into account the biocompatibility of the prepared PCL-NCC-PLLA films, the composite materials are seemed to be perspective in the field of nanobiomaterials.

Acknowledgements

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