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Polyester-Grafted Cellulose Nanowhiskers: A New Approach for Tuning the Microstructure of Immiscible Polyester Blends

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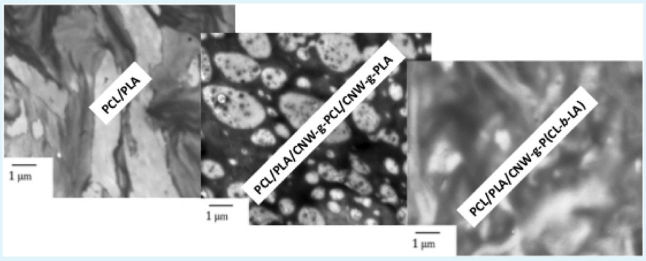

ABSTRACT: Cellulose nanowhiskers (CNW), extracted from ramie fibers by sulfuric acid hydrolysis, were used as substrates to compatibilize binary polyester blends containing 50/50 (w/w) polycaprolactone (PCL) and polylactide (PLA). To tailor their interfacial energy and fine-tune their adhesion with the components of the blend, CNW were subjected to different surface polyester grafting by the means of ring-opening polymerization. PCL and PLA homopolyesters as well as P(CL-*b*-LA) diblock copolymers were successfully grafted on the surface of CNW and the resulting substrates were loaded into the PCL/PLA blend by melt-blending. Morphological and rheological analyses were conducted in order to evaluate the ability of these nanoparticles to enhance the compatibility of PCL/PLA blends. Our results showed that unmodified CNW as well as (co)polyester-grafted CNW improved, at different levels, the compatibility of PCL/PLA blends by preventing from coalescence the dispersed domains. (co)polyester-grafted CNW also enhance the mechanical properties of the blend, which can be explained by the formation of cocontinuous phase morphology at the interface. Our findings suggest that (co)polyester-grafted CNW, especially CNW-g-P(CL-*b*-LA) diblock copolymers, can serve as a suitable nanofiller to tune the compatibility of PCL/PLA blends and their related microstructures.

KEYWORDS: *cellulose nanocrystals, polymer compatibilization, polyester, polylactide, nanocomposite*

INTRODUCTION

In recent years, environmental concerns and the expected shortage in the fossil reserves have stimulated further development of biomaterials for advanced applications. Polymers derived from renewable resources are the frontrunner of the advances realized in this trend. Nowadays, PLA is considered the most popular and important biodegradable polymer derived from renewable resources through bioconversion and polymerization.[1] In addition to being biodegradable and biocompatible, PLA possess some potential properties such as good processability, excellent tensile strength and stiffness equivalent to some commercial petroleum-based polymers. These properties make PLA a versatile material in commodity and engineering applications such automotive, medical, and packaging. However, one major disadvantage of PLA is its brittleness, which restricts its use in many fields. One of the most practical strategies for tuning the properties of polymers is blending with another polymer allowing tailoring the overall properties of the final material through a synergistic combination of the desirable properties of each component in one system. Thus, to improve the brittleness of PLA, blending with a ductile biodegradable polymer such as polycaprolacone (PCL) has been widely used. However, PLA/PCL blend, as most polymeric blends, are proven to be thermodynamically immiscible, leading to poorly compatible heterogeneous blends having multiphase morphology with poor interfacial adhesion, subsequently impacting the final mechanical properties of the blend.[2−4] To improve the compatibility of such systems, we have reported different strategies. Although chemical modification of one or both components of the blend has been reported to provide better results than simple physical blending, a good knowledge on the engaged reaction and its control during the processing are prerequisite.[5] Hence, polymer blending is considered as more practical alternative as it is mainly governed by the composition and rheological properties of the blend. On the basis of the relationship between rheological properties and the morphology of PLA/PCL blends, numerous studies were dedicated at kinetically improving the phase structure of the blend by optimizing processing conditions during the melt-blending.[4,6,7] Alternatively, more studies were devoted on using a third component, acting as compatibilizer, in order to modify both the interfacial energy and the adhesion between immiscible polymers. Such agents are known to limit the coalescence of the immiscible domains, therefore allowing the compatibilization of the polymer phases. Diblock or multiblock copolymers were reported, among various compatibilizers that have been studied so far, to be efficient in improving the compatibility in the case PLA/PCL blends.[8−11]

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Table 1. Synthesis Conditions of CNW-g-polyesters, Recovery Yields, and Final Content in CNW within the Nanohybrids

nanohybrid	m_{monomer} (g)	m_{CNW} (g)	T (°C)	t (h)	$m_{\text{CNW-g-Polyester}}$ (g)	yield (%)[a]	% CNW
CNW-g-PLA	10	1.4	80	24	10	83	14
CNW-g-PCL	10	1.4	95	24	9.8	85	14
CNW-g-P(CL-*b*-LA)	10	1	80	48	9.3	83	11

[a] Determined by gravimetry (see Experimental Section).

More recent studies have evidenced that nanofillers can also be good candidates to replace conventional polymeric compatibilizers. Indeed, nanofillers can modify the interfacial properties of the immiscible blend in accordance with two possible mechanisms: (i) dynamic compatibility, obtained when the polarity or viscosity of each polymer component is strongly different; consequently, the nanofiller tends to be localized preferentially within the more polar or the less viscous phase. During the processing, such a mechanism can prevent the coalescence of the domains, leading to the so-called "kinetic compatibilization"; (ii) thermodynamic compatibility, resulting when the nanofillers are miscible or at least compatible with the two polymers, leading to a thermodynamic enhancement of the compatibility between the immiscible partners. Mainly organo-clays have been considered in improving the miscibility of PLA/PCL blend[12,13] and many other polymer blends.[14−21] Carbon nanotubes are also evolved as compatibilizers for immiscible polymeric blends,[22−25] and were successfully employed recently in the case of PLA/PCL blend.[26] Moreover, the combination of both clays and carbon nanotubes was also reported of being effective in enhancing the compatibility of polycarbonate/polypropylene immiscible blends.[27]

Cellulose nanocrystals (CNC) or nanowhiskers (CNW) are rodlike defect free crystalline nanoparticles obtained after the acid hydrolysis of cellulose fibers. Recently, CNW warrant tremendous level of attention not only because of their inherent renewability and sustainability in addition to their abundance but also because of their unsurpassed quintessential physical and chemical properties. They have been widely studied as reinforcing agents in nanocomposites because of their low cost, availability, renewability, lightweight, nanoscale dimension, and unique morphology.[28−30] We have reported their successful incorporation, after surface chemical modification, in both PLA[31] and PCL.[32,33] The strategy consisted of grafting polymer chains, similar to the used matrix, at the surface of the CNW through "grafting from" approach and then melt-blending the resulting nanohybrid in the respective matrix. It has been evidenced that the grafted polymeric chains form with unbounded polymeric chains from the matrix a cocontinuous phase at the interface through physical entanglement or cocrystallization. Consequently, the physical performances of final nanocomposites were greatly enhanced upon the incorporation of CNW-based nanoparticles.

In light of these advances, one can expect that the use of such anisotropic fillers can provide both reinforcement and compatibilization effects. It appears that CNW have never been reported as compatibilizers in immiscible polymer blends; therefore, we explore in the present work the feasibility of using CNW, chemically grafted or not, as compatibilization agents to tune the microstructure (and related properties) of immiscible PLA/PCL blends. CNW were subjected to different surface chemical modification including the grafting of PLA and PCL homopolyesters as well as P(LA-*b*-CL) diblock copolymers. The resulting substrates were incorporated in a PLA/PCL blend having equivalent weight ratio of both components where extreme immiscibility is expected. The morphology as well as thermomechanical and rheological properties of the obtained materials were systematically investigated to shed light on the effect of the CNW-based nanoparticles on the compatibilization of the immiscible blend.

EXPERIMENTAL SECTION

Materials. Pure ramie fibers were obtained from Stucken Melchers GmbH & Co. (Germany). Sulfuric acid (95%), acetone (99%), toluene (anhydrous, 99.8%) and dichloromethane (99.5%), were all obtained from Sigma-Aldrich. ε-Caprolactone (ε-CL, 99%) was dried 48 h over calcium hydride, distilled under reduced pressure prior to use and stored under nitrogen atmosphere. L-Lactide (L-LA) (99%, Galactic) was recrystallized in toluene at 0 °C and dried under a vacuum at ambient temperature. Tin(II) ethylhexanoate ($Sn(Oct)_2$) (95%, Aldrich) was used as received without further purification. Commercial grade of PCL (CAPA6500, $M_n \approx 50\,000$ g/mol) was supplied by Solvay. PLA was supplied by NatureWorks, and has the following characteristics: number-average molecular weight of 130,000 g/mol (PS standards), a polydispersity (M_w/M_n) of 1.9 and a D-isomer content estimated to 4.4 wt %.

Cellulose Nanowhisker Preparation. Cellulose nanowhiskers (CNW) were extracted from purified ramie fibers as previously described in the literature.[33] Briefly, pure ramie fibers were cut into small pieces and submitted to acid-hydrolysis with a 65% (w/w) H_2SO_4 solution at 55 °C for 30 min and with continuous mechanical stirring. The resulting suspension was washed with water until neutrality by multiple centrifugation steps and dialyzed against deionized water. The obtained suspension was homogenized using an Ultra Turrax T25 homogenizer for 5 min at 13 500 rpm, filtered through a glass sinter (no. 1) in order to remove unhydrolyzed fibers. The suspension was then concentrated, providing the stock suspension.

Surface Grafting of PCL and PLA Polyesters. The grafting of PLA, PCL, or P(CL-*b*-LA) copolymers on the surface of CNW was realized through ring-opening polymerization initiated from the hydroxyl groups available at the surface of CNW as already described in our previous works.[31,32] Prior to the reaction, an aqueous suspension of CNW was solvent-exchanged with acetone and then with dried toluene by several successive centrifugation and redispersion operations (realized under ultrasonication). The CNW in toluene suspension were introduced into a two-neck flask equipped with a three-way stopcock and a magnetic stirring bar under nitrogen flow. Two toluene distillation steps were carried out in order to remove any residual water. The flask was then immersed in an oil bath and heated up to desired temperature (95 °C in the case of PCL grafting and 80 °C in the case of PLA and P(CL-*b*-LA) copolymers). For the PCL grafting, ε-CL and a catalytic amount of $Sn(Oct)_2$ (2 wt % with respect to the monomer) were added, with the required volume of toluene, to the reaction flask using flame-dried syringes. The polymerization was allowed to proceed for 24 h and was stopped by adding a few drops of diluted aqueous hydrochloric acid solution (1 M). CNW-g-PCL were recovered by precipitation with heptane, filtered and purified by multiple dissolution−precipitation and thorough washings before being dried until constant weight at 40 °C under vacuum. For CNW-g-PLA preparation, a determined amount of purified L-LA previously dissolved in hot dry toluene and a catalytic amount of $Sn(Oct)_2$ (2 wt % with respect to the monomer) were added to CNW-toluene suspension. The polymerization was allowed to proceed at 80 °C before the addition of a few drops of

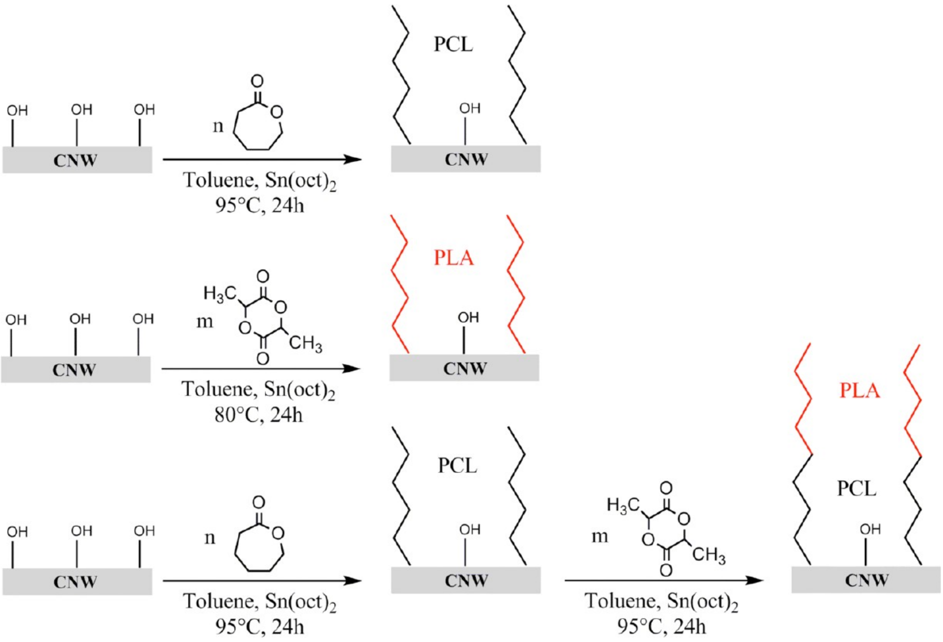

Figure 1. Sketch of the synthesis of the different CNW-g-polyesters as initiated from the CNW surface.

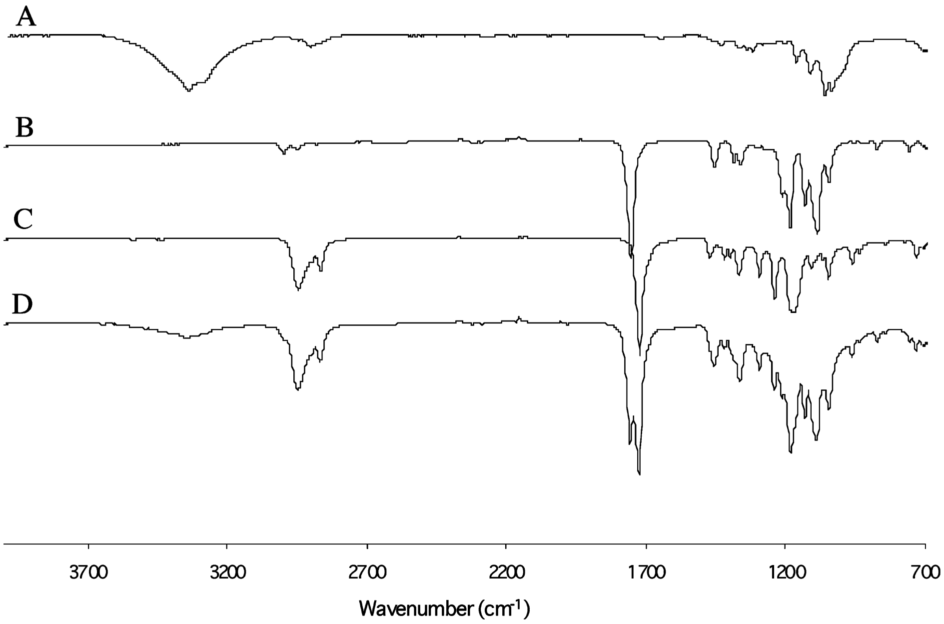

Figure 2. FTIR spectra of (A) unmodified CNW, (B) CNW-g-PCL, (C) CNW-g-PLA, and (D) CNW-g-P(CL-*b*-LA) nanohybrids.

diluted hydrochloric acid (0.1 M) and further purification and drying as described above.

A procedure similar to that for PLA grafting was followed in the case of CNW-g-P(CL-*b*-LA) synthesis, by adding L-LA to the mixture containing CNW-g-PCL before allowing the copolymerization to proceed for additional 24 h. The different synthesis conditions and the corresponding recovery yields are gathered in the Table 1.

Preparation of the PCL/PLA Blends. Blends based on 50/50 (w/w) of PCL/PLA as a matrix and 2% (wt/wt CNW content) polyester-grafted CNW or neat CNW as nanofillers were prepared by melt-blending in a ThermoHaake MiniLab Rheomex CTW5 mini-extruder (processing temperature, 165 °C; speed, 100 rpm; time, 5 min). Then, rectangular samples (35 mm × 12 mm × 3 mm) to be used for dynamical mechanical thermal analysis (DMTA) or thin cylinder (25 mm × 1.5 mm) to be used for rheology measurements were prepared by injection-molding at 190 °C.

Characterizations. Fourier transform infrared (FTIR) spectra were recorded using a BIO-RAD Excalibur spectrometer equipped with an ATR Harrick Split Pea. Pellets of dried unmodified CNW or CNW-g-polyester samples were made with KBr, and the spectra were recorded using a spectral width ranging from 700 to 4000 cm^{-1} with 4 cm^{-1} resolution and an accumulation of 16 scans.

The morphology of the blends was analyzed by scanning electron miscroscopy (SEM) and transmission electron microscopy (TEM). For SEM analyses, the samples were cryo-fractured coated with gold/palladium and observed using an ABT-55 microscope at an applied tension of 10 kV. For TEM observations, cross sections of the samples were catted under cryogenic conditions using an Ultracut FC4E microtome from Reichert-Jung. The analyses were performed with a Philips CM200 electron microscope, using an accelerator of 120 kV on the same samples.

Thermal characterizations using differential scanning calorimetry (DSC) were performed using a TA Instruments Q200 apparatus. A heat/cool/heat procedure was applied screening a temperature range from −80 to 200 °C with a rate of 10 °C/min. Thermal characteristics were determined from the second heating scan.

Rheological analyses were performed on an ARES rheometer at 160 °C. The measurements were carried out in an oscillatory shear mode using a parallel plate geometry of 25 mm. Samples were placed between plates and melted for 5 min before analyses. First of all, strain sweep measurements were carried out to determine the linear viscoelastic region at a frequency of 1 Hz. Once this strain value fixed, frequency sweeps in range of 0.01 to 100 Hz were conducted.

RESULTS AND DISCUSSION

Cellulose nanowhiskers (CNW) surface-grafted by polyester chains, either PCL or PLA, have been shown to finely disperse in respective polyester matrix. Moreover, the mechanical properties of the resulting nanocomposites were greatly improved and this enhancement is believed to originate from the cocontinuous phase created between the grafted polyester chains, on the surface of CNW, and the matrix.[31−33] Accordingly and by tuning the interfacial composition of these nanofillers, one could expect some potential compatibilization by using polyester-grafted CNW in PCL/PLA immiscible blends. For this purpose, different polyester-grafted CNW substrates were synthesized by the means of “grafting from” approach through surface-initiated ring-opening polymerization as sketched in Figure 1. CNW were grafted by in situ grown PCL, PLA, and P(CL-*b*-LA) diblock copolymer chains, coined as (CNW-g-PCL), (CNW-g-PLA), and CNW-g-P(CL-*b*-LA), respectively.

The synthesis conditions for PCL and PLA grafting were similar to those already reported in our previous work,[31,32] and they were adapted to the grafting of P(CL-*b*-LA) copolyesters. These conditions and the respective results are collected in Table 1. After 24 h (for PCL or PLA) or 48 h (for P(LA-*b*-CL)) of reaction time, the substrate was recovered by precipitation and purified by multiple dissolution−precipitation and thorough washings to remove any residual monomers and unattached polymer chains. In all cases, the overall yields exceeded 80% as determined by gravimetry. The content of CNW within the final nanohybrids was of about 14% in the case of CNW-g-PCL and CNW-g-PLA and 11% for CNW-g-P(CL-*b*-LA).

The success of the grafting of different polyester chains on the surface of CNW was confirmed by FTIR analysis. Figure 2 attests to the presence of each polyester chain onto the corresponding substrate by the appearance of their characteristic absorption bands assigned to the carbonyl functions at 1728 cm^{-1} for PCL segments and 1748 cm^{-1} for PLA segments. It is worth noting that both peaks were present in the spectrum of CNW-g-P(CL-*b*-LA) confirming the success of the successive copolymerization of both CL and LA monomers onto the CNW surface.

CNW-grafted polyesters were further characterized by DSC. As already reported, CNW grafted with either PCL or PLA showed the corresponding melting peaks of the respective grafted polyester.[31,32] In the case of CNW-g-P(CL-*b*-LA) nanohybrid, two melting endotherms attributed to each polyester block were clearly observed. On one hand, a crystallization exotherm is observed at 72 °C followed by the melting endotherm at 157 °C typical of the PLA segment. On the other hand, the melting endotherm of the PCL block is observed at 56 °C. These observations show clearly that both blocks were able to crystallize, suggesting that the reached degree of polymerization and the grafting density were high enough to induce a crystallization of polyester segments.

FTIR and DSC indicate the successful synthesis and grafting of the different polyesters onto CNW surface. Yet, the covalent grafting was further evidenced by a suspension test in chloroform as already described in the case of CNW-PLA and CNW-PCL.[31,33] Similarly to the strategy followed in the previous works, three compositions were dispersed in chloroform: (1) unmodified CNW, (2) CNW simply mixed with PCL and PLA (in the same composition as for the nanohybrid); and (3) a CNW-g-P(CL-*b*-LA) nanohybrid. Figure 3A shows pictures of the dispersed states of the different samples immediately after stopping the stirring agitation. As expected, the CNW-g-P(CL-*b*-LA) nanohybrid shows much better stability than the unmodified CNW and physically blended mixtures as attested for by the permanent homogeneous white colored suspension (even after 5 months, see Figure 3B). The dispersion of the CNW in chloroform could be indirectly attributed to the covalent polymer grafting onto the cellulose nanocrystal surface.

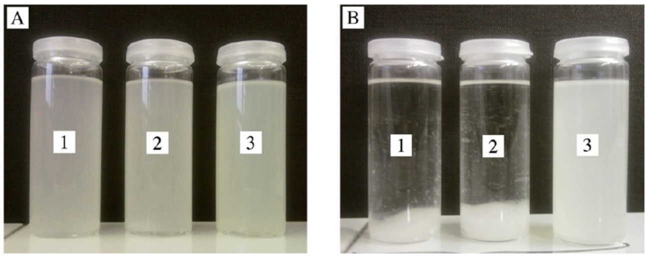

Figure 3. (1) Unmodified CNW, (2) physical mixture of unmodified CNW/PLA/PCL, and (3) CNW-g-P(CL-*b*-LA) nanohybrid in chloroform suspension; pictures recorded (A) immediately after stopping the stirring agitation and (B) 5 months later.

PCL/PLA/CNW BLENDS. PCL/PLA binary blend and different ternary blends based of equivalent weight ratio of PCL and PLA and 2% of CNW nanofiller either grafted or not by (co)polyester chains were prepared by melt-blending in a mini-extruder at 165 °C for 5 min at 100 rpm, and then injection-molded at 190 °C for the preparation of DMA and rheology specimens. Table 2 gathers the list of prepared materials.

Table 2. List of the Different Blends Prepared by Melt-Blending

polyester matrix	fillers	composition PCL/PLA/filler
PCL/PLA		50/50
PCL/PLA	unmodified CNW	49/49/2
PCL/PLA	CNW-g-PCL/CNW-g-PLA	49/49/1/1
PCL/PLA	CNW-g-P(CL-*b*-LA)	49/49/2

Neck eyes observation of the injection-molded samples of the PCL/PLA binary blend, different PCL/PLA blends filled with unmodified or polyester-grafted CNW provided a first macroscopic evaluation about the effect of CNW on a PCL/PLA immiscible blend. Binary PCL/PLA blend presents a very rough surface. At the opposite of the unfilled PCL/PLA immiscible blend, all ternary blends containing CNW appear compact with a more regular and homogeneous macrostructure. These first observations need to be correlated with other microscopic characterizations.

SEM micrographs of the freeze fracture surfaces of the different blends are shown in Figure 4. A typical two-phase structure where one polymeric phase is dispersed in the other one can be observed in Figure 4A. Because of the contrast limitation between the two aliphatic polyesters presence (both able to crystallize), it is difficult to associate a phase to given polyester. The morphology does not change significantly the morphology of the blend with the loading of CNW-g-PCL and CNW-g-PLA as shown in Figure 4C. This observation may be explained by the tendency of each polyester-grafted CNW to locate in the corresponding polyester phase, which does not impact the microstructure of the blend. A reduced gap between the phases, compared to neat PCL-PLA blend, could be observed from high-magnification micrographs (not shown here). Although CNW were not evidenced on the SEM images of the ternary blends even at high magnification because of the lack of contrast, the probable localization of these modified CNW at the interface is suspected, and it might be the origin of the reduction of the interphase gap between the two phases.

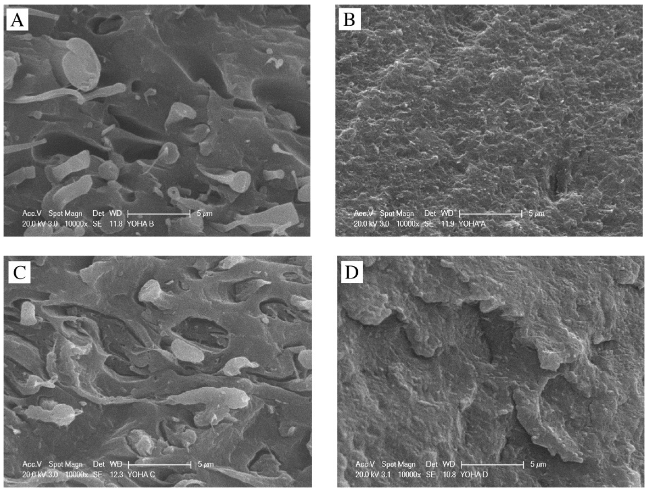

Figure 4. SEM images for the samples of (A) binary PCL/PLA blend, and different ternary blends (B) PCL/PLA/unmodified CNW, (C) PCL/PLA/CNW-g-PCL/CNW-g-PLA, and (D) PCL/PLA/CNW-g-P(CL-*b*-LA).

Surprisingly, the morphologies of the blends filled with unmodified CNW and CNW surface-grafted with P(CL-*b*-LA) copolymer shown in images B and D Figure 4, respectively, are very different, as they are homogeneous. The loading on these cellulosic substrates induced a fine miscibility of the blend giving rise to this homogeneous microstructure. If the presence of such morphology with modified CNW could be explained by the enhanced compatibility between CNW and the polymers; the obtaining of similar microstructure when loading unmodified CNW is still quiet surprising because the interfacial incompatibility between both polymers and CNW. These observations were confirmed with in-depth TEM analyses.

Figure 5 displays TEM images recorded for cryo-microtomed binary and ternary blends. Again, a typical two-phase structure can be observed in Figure 5A and it is also impossible to associate a phase with given polyester.

As observed in Figures 5B to D, the morphologies are very different and depend on the nature of the ternary blend. Cellulose nanoparticles were not evidenced on the TEM images of the ternary blends even at high magnification because of the lack of contrast. Nevertheless, regarding the low viscosity of PCL and its low hydrophobicity as compared to PLA, CNW are most likely to be localized in PCL and at the interface. Surprisingly, one can observe that the loading of unmodified CNW (Figure 5 B) induces a large reduction of the size of the PLA/PCL domains, which results probably from the fine dispersion of one polymer in another in an emulsionlike system. This dispersion is maintained through the melt-blending by the presence of CNW that have been reported to possess the ability to act as emulsion stabilizers.[34,35] Interestingly, almost the same morphology and homogeneous microstructure are observed for the PCL/PLA blends filled with the CNW surface-grafted by the P(CL-*b*-LA) block copolyester (Figure 5D). Choi et al.[11] studied the compatibilization of PCL/PLA blend with P(LA-*b*-CL) copolymer and have shown that this copolymer was located at the interface of the PLA matrix and the dispersed PCL domains enabling a good stabilization of these domains in the matrix. The presence of similar copolymer, e.g., P(CL-*b*-LA) at the surface of CNW, confirms the existence of strong interfacial compatibilization between PLA and PCL thanks to the CNW-based nanohybrid.

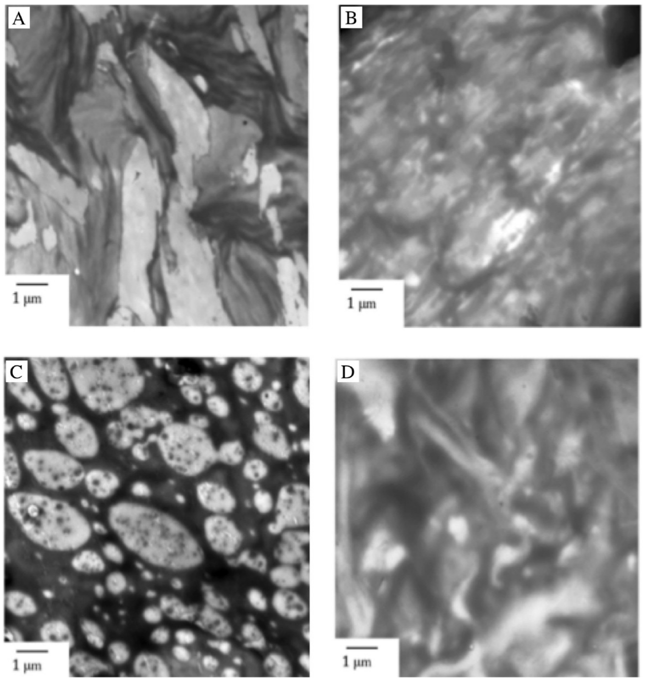

Figure 5. TEM images for the samples of (A) binary PCL/PLA blend, and different ternary blends (B) PCL/PLA/unmodified CNW, (C) PCL/PLA/CNW-g-PCL/CNW-g-PLA, and (D) PCL/PLA/CNW-g-P(CL-*b*-LA).

Moreover, the TEM image of the PCL/PLA/CNW-g-PCL/CNW-g-PLA blend, depicted at Figure 5 C, shows a completely different morphology where white domains are surrounded by a more continuous black matrix. Similar distribution was observed for melt-mixed immiscible blends having a cocontinuous morphology, specially when the observation was realized at the cross-section taken perpendicularly to the direction of the extrusion.[7] Wu et al.[26] reported also similar morphology obtained with PC/PLA blends loaded with anisotropic nanofillers, e.g. multiwalled carbon nanotubes (MWCNT). Authors were able to localize MWCNT at the interface and within the PCL part as these fillers have more affinity with PCL. In the present work, a clear localization of CNW was not successful even at high magnification. But regarding the nature of each nanohybrid, both are most likely to be present at the interface with a tendency for CNW-g-PCL to diffuse into PCL as attested by TEM analysis (at high magnification, not shown here) where small black nano-objects were observed.

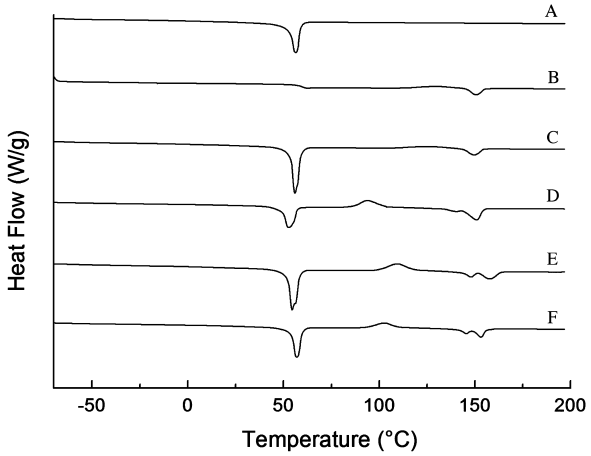

Figure 6. DSC curves of (A) neat PCL, (B) neat PLA, (C) binary PCL/PLA blend, and different ternary blends (D) PCL/PLA/unmodified CNW, (E) PCL/PLA/CNW-g-PCL/CNW-g-PLA, and (F) PCL/PLA/CNW-g-P(CL-*b*-LA).

The thermal properties of the blend were probed using DSC. In Figure 6, thermographs taken from the second heat for pure PLA, pure PCL, and the different blends are shown. The melting temperature of PCL is estimated to be 56.4 °C and the glass transition and melting temperatures of PLA are 60 and 150 °C, all consistent with literature values. In the immiscible blend PCL-PLA, the current temperature peaks remain unchanged and should be that of the homopolymers. It was difficult to determine exactly the transition temperatures of the blends because the peaks overlap. Differences in DSC scans were clearly observed upon the loading of unmodified and polyester-grafted CNW, attesting that the systems have distinctive and complicated behaviors. Although slight changes of the melting crystallization as well as the corresponding melting enthalpies of the PCL part were observed, noticeable variability in the DSC traces was observed around the PLA crystallization and melting. These observations clearly indicate that CNW in blends acts as a kind of heterophase crystal nucleation agent as already reported. This behavior is particularly surprising in the case of unmodified CNW. In fact, the alteration of the crystallinity of PLA upon the addition of CNW attest that they or part of them are locate at the PLA phase at the opposite of what one could expect. First, one can observe the appearance of a new crystallization peak at 94 °C with the incorporation of unmodified CNW that shifted to 102 and 110 °C when CNW-g-P(CL-b-LA) and CNW-g-PCL/CNW-g-PLA were added, respectively. Furthermore, all ternary blends showed two melting peaks located between 140.7/150.9 °C for unmodified CNW, at 145.3/153.3 °C for CNW-g-P(CL-b-LA) and at much higher values e.g. 147.9/158.2 °C for CNW-g-PCL/CNW-g-PLA. The presence of such double melting peak in the case of PLA is a well-known phenomenon caused by the modification of the PLA crystal growth. This phenomenon is often ascribed to the coexistence of two crystalline structures: less perfect crystals (α'-form crystals), which have enough time to melt and to reorganize into crystals with higher structural perfection (α-form crystals), before they remelt at higher temperature.[36,37] The areas under these melting peaks are directly related to the crystal perfection. Qualitatively, this crystal growth is affected by the type of CNW substrates added to the blend, as the PLA melting points changed for the three formulations. Quantitatively, the nature of CNW substrates induced a change of the relative content in α-crystals and consequently the crystals perfection as well as the amount of the crystalline phase of PLA. Indeed, the crystallinity of PLA has significantly increased upon the incorporation of unmodified CNW because the total melting enthalpy increased from 7.3 J/g in neat PLA or 9 J/g in PCL-PLA blend to almost 20 J/g in blend loaded with unmodified CNW. The amount of α'-form crystals was however important in the case of PCL-PLA blend filled with CNW-g-PCL/CNW-g-PLA. All these revealed observations regarding the crystalline structure may affect the phase behavior and consequently the miscibility of the different blends as already reported on the relationship linking the crystalline structure to the interfacial adhesion and miscibility of polymeric blends. The importance of interfacial adhesion affecting the properties of immiscible blends was studied by LeClair and Favis,[38] who suggested that interfacial behavior is driven by the crystallinity of the blend components. Accordingly, the crystallization induced upon the loading of CNW most probably at the interface of the phases may be the origin of this enhanced adhesion and homogeneous microstructure. This fact was clearly observed in the case of unmodified CNW and CNW-g-P(CL-LA) nanoparticles that have almost equivalent affinity to both components. In the opposite, CNW-g-PCL and CNW-g-PLA are most likely to be in the respective polymer altering its crystalline structure but with limited effect on the interfacial adhesion and hence giving rise to heterogeneous blend according to SEM and TEM analyses.

The presence of these polyester-grafted nanoparticles is expected to affect also the rheological properties of the ternary nanocomposites. In order to appreciate the miscibility of the components in the different blends, the measurements were realized at molten state. Figure 7 presents the evolution of the

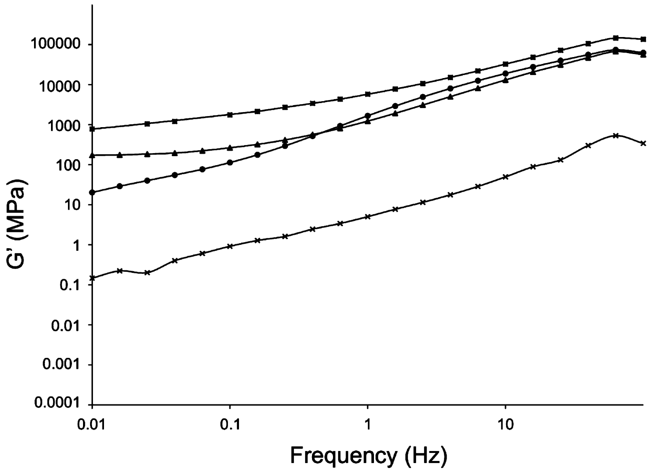

Figure 7. Dynamic storage modulus versus frequency as recorded for (□) PCL/PLA binary and different ternary blends: (●) PCL/PLA/unmodified CNW, (■) PCL/PLA/CNW-g-PCL/CNW-g-PLA, and (▲) PCL/PLA/CNW-g-P(CL-*b*-LA).

storage modulus (G') as a function of frequency sweep and Figure 8 pictures of the blends at the end of the analyses for the binary and ternary PCL/PLA-based blends. Despite the low temperature at which the measurements were performed, e.g. 160 °C, a low G' modulus was measured for the PCL/PLA binary blend consequential of a very low viscosity (see Figure 7A) which make the analyses poorly reproducible. Remarkably, the addition of unmodified CNW or their modified counterparts in a quantity as tiny as 2 wt % significantly modifies the rheological behavior because the modulus of the polymer blend largely increases in the entire frequency range. Such effect finds its explanation in the previously suggested interfacial compatibilization. Interestingly, the addition of CNW-grafted polyesters further enhances the low-frequency modulus. Indeed, when the CNW are grafted by either homopolyester (PCL or PLA) or by the P(CL-*b*-LA) diblock copolymer, the G' values recorded at low-frequency increases by about one to 2 orders of magnitude with respect to the PCL/PLA blend loaded with unmodified CNW. This "solidlike" behavior can be accredited to the appearance of strong interactions between grafted polyester chains and the components of the blend, inducing a strong adhesion between them. This effect is even more pronounced for the PCL/PLA/CNW-g-PCL/CNW-g-PLA nanocomposite. The rheological effect of the polyesters-grafted CNW is also clearly proven on Figure 8C, D. After analysis, the samples present a typical viscoelastic behavior of high viscosity. No degradation was observed during the analysis whatever the temperature.

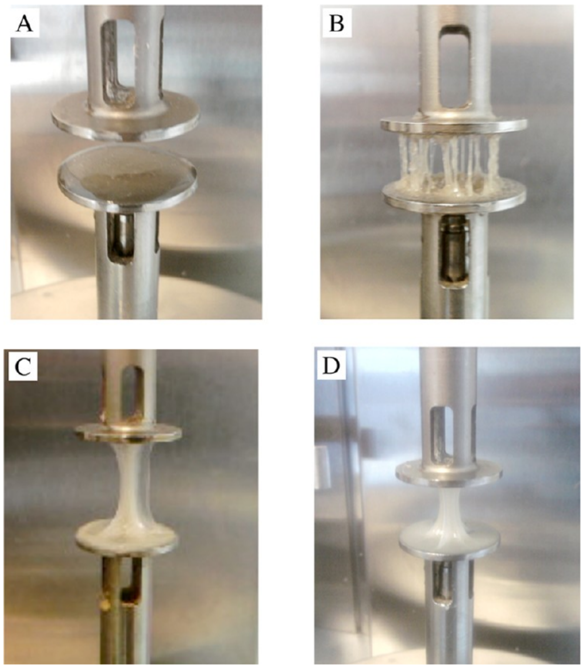

Figure 8. Comparative pictures of (A) PCL/PLA binary and (B–D) different ternary blends: (B) PCL/PLA/unmodified CNW, (C) PCL/PLA/CNW-g-PCL/CNW-g-PLA, and (D) PCL/PLA/CNW-g-P(CL-*b*-LA).

CONCLUSION

Cellulose nanowhiskers, extracted from natural fibers, were used as nanofillers to enhance the compatibility of immiscible polymeric blends. Biodegradable polymers, polycaprolactone and polylactide, were chosen in this study for their biomedical and industrial applications. Prior to the loading, CNW were subjected to different chemical modifications allowing the grafting of PCL, PLA, or P(CL-*b*-LA) (co)polymers at their surface. The study revealed that the compatibilization of the PCL/PLA blend was strongly affected by the addition of CNW substrates prompting the creation of cocontinuous microstructure. Better interfacial adhesion, however, was obtained by the incorporation of polyester-grafted CNW, arising probably from the cocrystallization between the grafted polyester chains and the respective phase. The large affinity between the different CNW substrates and the blend components determined their localization. Though, the reinforcing effect together with the improved compatibility is believed to result from interfacial localization of CNW nanofillers. To better understand the origin of such morphological and rheological observations, a more detailed study is certainly needed to complete these preliminary observations.

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Notes

The authors declare no competing financial interest.

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