Plasticized polylactic acid nanocomposite films with cellulose and chitin nanocrystals prepared using extrusion and compression molding with two cooling rates: effects on mechanical, thermal and optical properties

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Abstract

Triacetate citrate plasticized poly lactic acid and its nanocomposites based on cellulose nanocrystals (CNC) and chitin nanocrystals (ChNC) were prepared using a twin-screw extruder. The materials were compression molded to films using two different cooling rates. The cooling rates and the addition of nanocrystals (1 wt%) had an impact on the crystallinity as well as the optical, thermal and mechanical properties of the films. The fast cooling resulted in more amorphous materials, increased transparency and elongation to break, (approx. 300%) when compared with slow cooling. Chitin nanocomposites were more transparent than cellulose nanocomposites; however, microscopy study showed presence of agglomerations in both materials. The mechanical properties of the plasticized PLA were improved with the addition of a small amount of nanocrystals resulting in PLA nanocomposites, which will be further evaluated for film blowing and thus packaging applications.

Keywords: A. Nano-structures, B. Mechanical properties, B. Optical properties, E. Extrusion.

1. Introduction

Poly(lactic acid) (PLA) is one of the commercially available biodegradable polymers that has modulus and tensile strength comparable to petroleum-based polymers and can be produced from renewable sources. For this reason, PLA is a good alternative as a replacement for the conventional synthetic polymers in different applications, especially in packaging, where its high transparency is also an advantage. Nevertheless, PLA also has some drawbacks, such as its inherent brittleness, low thermal stability, low impact resistance and moderate gas barrier properties. PLA also presents a relatively low crystallization rate and is prone to aging at room temperature, aspects which are important from an industrial point of view [1,2]. Therefore, different efforts and approaches have been carried out in order to overcome the mentioned drawbacks and broaden its application areas.

Cellulose and chitin nanomaterials have attracted the attention of researches as additives in the green nanocomposites field because they are biodegradable, renewable and biocompatible polymers with good mechanical properties. Moreover, chitin has antibacterial properties, which can widen its use to the food packaging field. Cellulose nanomaterials have been extensively used as an additive to improve the thermal, mechanical and barrier properties of the PLA as well as to affect its crystallinity [3-7]. However, chitin in nanosize has been more often used in other polymeric matrix such as poly(caprolactone) [8,9], chitosan [10,11], natural rubber [12] and starch [13].

In the most of the studies, solvent casting is the most frequently used technique to prepare cellulose- and chitin-based nanocomposites and, in the case of chitin nanocompo-

sites, freeze-drying and electrospinning have been also tested. However, the melt-compounding technique is less common, especially in the case of chitin where only few studies have been found [9,13,14]. Extrusion is a conventional polymer-processing technique; therefore, there is growing interest in this technique for nanocomposite processing in industrial applications. The main challenges of this technique are the feeding of the nanomaterials into the extruder and obtaining well-dispersed and distributed nanocrystals in the polymer matrix. It is well known that materials in nanosize have a strong tendency to aggregate; in addition, cellulose and chitin form strong hydrogen bonds when dried and are also very difficult to redisperse. Therefore, drying prior the extrusion is not suitable, if the nanocrystals are not coated or chemically modified. We have shown in our previous studies [7,15,16] that liquid feeding of cellulose nanomaterials together with a suitable processing aid; such as plasticizer or water; is one way to avoid the drying process and to improve the dispersion of the nanomaterials in the matrix. However, when water or other solvents are used it is important to use a processing facility where the steam can be effectively removed during the processing, and this can be done using a co-rotating twin-screw extruder. When closed batch-wise processing is used the materials need to be dried since the moisture cannot be removed during the processing, also counter rotating twin-screw extruders are not suitable when liquids are used.

In the current study, plasticized PLA nanocomposites based on cellulose and chitin nanocrystals were prepared using liquid feeding of the nanomaterials together with a plasticizer into the extrusion process. The goal was to prepare PLA nanocomposites, which will be further evaluated for film blowing and packaging applications; therefore materials with high elongation to break and mechanical properties similar to those of PE

was targeted. The effect of two different nanocrystals and cooling rates of the films on the mechanical, thermal and optical properties of plasticized PLA were studied. In addition, it is believed that the addition of nanocrystals will improve the melt strength of the plasticized PLA, thus, enhance its processability during the film blowing.

Experimental

2.1. Materials

PLA in pellet form was used as matrix and supplied by FUTERRO (Escanaffles, Belgium). The used PLA had MFI 8 g/10 min (measured 190 °C/2.16 kg), tensile strength approx. 63 MPa, tensile modulus 3.8 GPa and elongation to break 2.3%. The PLA was plasticized using triethyl citrate (TEC) in liquid form ($\geq 99\%$ Alfa Aesar, Mw: 276.3 g/mol) purchased from WVR (Sweden). TEC is also used as a processing aid to facilitate dispersion of the nanocrystals and as liquid medium for their feeding. Ethanol (99.5%) was used as a solvent and was purchased from Solveco (Stockholm, Sweden). Cellulose nanocrystals (CNC 2013-FPL-CNC-049) 10.3 wt% in aqueous suspension and chitin nanocrystals (ChNC) 10.3 wt% concentration were used to reinforce the PLA-TEC polymer. The CNC, prepared by sulfuric acid hydrolysis, were kindly supplied by Forest Products Laboratory FPL, Madison, USA. Chitin powder from crustacean waste, was purified at Pontifical Catholic University of Chile and the ChNC were prepared using hydrochloric acid hydrolysis following the process reported elsewhere by Salaberria et al. [13].

2.2. Processing of nanocomposites

2.2.1. Preparation of suspensions for liquid feeding

The pumping suspensions of the CNC and ChNC (10.3 wt%) were first dispersed in ethanol with the ratio 1:1 water to ethanol (w:e) and then mixed with TEC. The suspen-

sions were magnetic stirred overnight and sonicated for 2 min in an ice bath prior the extrusion to enhance the dispersion. The final composition of the suspensions was 2.6 wt% nanocrystals, 52 wt% TEC, 22.7 wt% H₂O and 22.7 wt% ethanol. These mixtures were prepared according to a target composition for the final nanocomposites of 79 wt% PLA, 20 wt% TEC and 1 wt% nanocrystals. The chosen plasticizer content was based on our experience from the previous study [16] to have a pumpable suspension, cover the nanocrystals surfaces and taking into account that part of the plasticizer will evaporate during the processing. The suspensions were fed into the extruder at a specific pumping rate to reach the target composition of the nanocomposites. The plasticized PLA (PLA-TEC) was prepared in a similar way; the TEC was dissolved in the w:e mixture and then fed into the extruder. Parameters as composition and feeding rate of the suspension as well as the water and ethanol ratio need to be controlled. It is also very important that the water and ethanol content is kept as low as possible and retain the pumpability of the liquid. The pumping rate is also a crucial processing parameter; too high pumping rate will result in boiling and too fast evaporation of the liquid thus resulting in agglomerated nanocrystals.

2.2.2. Extrusion using liquid feeding

A co-rotating twin-screw extruder (ZSK-18 MEGALab, Coperion W&P, Stuttgart, Germany) with K-Tron gravimetric feeder (Niederlenz, Switzerland) for the neat PLA and a peristaltic pump (PD 5001 Heidolph, Schwabach, Germany) for the liquid feeding of nanocrystals and plasticizer were used. The extrusion was carried out at a screw speed of 300 rpm and with a temperature profile ranging from 170 °C at the feeding zone to 200 °C at the die. The standard screw configuration for the compounding of biocomposites was used, including melting, mixing and dispersing processing sections.

A schematic of similar screw is shown in our earlier publications with an extra mixing zone located in the middle [17]. The PLA as well as the prepared suspensions were fed in the main port of the extruder. The total material throughput was 3 kg/h, the feeding rate for the PLA was 2.3-2.4 kg/h and the pumping rate for the TEC solution, TEC/CNC and TEC/ChNC suspensions was 1.1 kg/h. Atmospheric venting at zone 2 and 4 and vacuum venting at the end of the extruder were used to evacuate the vapor generated during the process due to the evaporation of 22.7 wt% of ethanol and 22.7 wt% of water. The extruded strands were cooled in water bath, pelletized and dried at 55 °C overnight. The compositions of the prepared materials are shown in Table 1.

Films from of the compounded pellets (3.5 g) were compression molded using a LPC-300 Fontijne Grotnes press (Vlaardingen, Netherlands). Pellets were placed between metal plates with Mylar films and compression molded at 190 °C, first, using a contact pressure for 3.5 min, and then 4 MPa for 30 s. After the compression molding, the formed films were cooled either in air (from 190°C to RT in 5 min) to avoid crystallization or inside the metal plates (from 190°C to RT in 20 min) to allow crystallization. The films were denominated as “fast cooled (FC)” and “slow cooled (SC)”; these terms are used throughout this manuscript to identify the different materials. The thickness of the prepared films was ~100 µm and they were kept at room conditions for at least 1 day before testing.

2. Characterization

3.1. Microscopy

The starting aqueous suspension of nanocrystals and the prepared pumping suspensions were analyzed using an optical microscope, Eclipse MA200 Nikon (Tokyo, Japan). The dissolution of TEC into the water:ethanol mixture (1:1) and the dispersion of the nano-

crystals in the mixtures were analyzed. The prepared films were examined using polarizing optical microscope Eclipse LV100N POL Nikon (Shanghai, China) under polarized light.

The morphology of the used nanocrystals was studied using a Veeco Multimode Nanoscope V Atomic Force Microscope (AFM) (Santa Barbara, USA). A drop of highly diluted nanocrystal suspension was placed on a fresh mica plate and dried for the AFM study. All scans were performed in air and in tapping mode. The Nanoscope V software was used to measure the nanocrystal diameters from the height images.

The dispersion of the nanocrystals in the PLA matrix was evaluated on the cryogenic fracture surfaces of the prepared materials using a high-resolution Merlin SEM (Zeiss, Germany). A thin layer of gold was sputtered on the surfaces to avoid charging.

3.2. Thermogravimetric analysis

The thermal stability of both cellulose and chitin nanocrystals was studied using a TA instrument TGA-Q500 (NewCastle, USA) in air atmosphere. Nanocrystal films from the 10.3 wt% aqueous nanocrystal suspensions were prepared by casting and the tests were performed in ramp mode from 25 to 600 °C at 5 °C/min.

3.3. X-Ray diffraction

The crystallinity of the nanocrystal powders, as well as the crystallinity of both fast and slow cooled PLA-TEC and its nanocomposites films, were studied using a PANalytical Empyrean diffractometer (Almelo, The Netherlands) with CuK α radiation (wave length of 1.5405 Å). The range for 2 θ scan angles was from 5 to 40°, using steps of 0.03°. The measurements were conducted at an acceleration voltage of 45 kV and a current of 40 mA. The crystallinity index (CI) of the nanocrystals was estimated using equation 1 and

according to the peak high method (Segal et al., 1959) for cellulose [18] and its adaptation for chitosan (Struszczyk, 1987) [19].

$$CI = \frac{I_{maximum} - I_{am}}{I_{maximum}} \times 100 \quad (1)$$

Where $I_{maximum}$ is the height of the 200 peak intensity at $2\Theta \sim 22.4^\circ$ for cellulose and the height of the 110 peak intensity at $2\Theta \sim 19.5^\circ$ for chitin. I_{am} is the height of the amorphous diffraction peak in both cases, which is estimated as the minimum intensity between the 200 and 110 peaks ($2\Theta \sim 18^\circ$) for cellulose and the minimum intensity for chitin at $2\Theta \sim 16^\circ$ [18,19].

3.4. Differential scanning calorimetry

The thermal properties of the prepared materials were measured using a Mettler Toledo DSC822e differential scanning calorimeter (Schwerzenbach, Switzerland). Approximately 5 mg of each sample was placed in a hermetic aluminum pan and tested under N_2 atmosphere from 30 to 200 °C. The test was performed by a heating scan at 10 °C/min for both fast and slow cooled samples, followed by a cooling scan at 20 °C/min only for the fast cooled samples. Melting temperatures (T_m) as well as cold crystallization and melting enthalpies (ΔH_{cc} and ΔH_m) of the prepared materials were determined from the heating scans. The melt crystallization temperature and the melt crystallization enthalpy (T_{mc} and ΔH_{mc}) of the materials were determined from the cooling scan at 20 °C/min. The degree of crystallinity (X_c) of the prepared materials was calculated as [20]:

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^\circ} \times \frac{100}{w} \quad (2)$$

ΔH_m is the enthalpy for melting (pre-melt crystallization was subtracted from the melting enthalpy), ΔH_{cc} is the enthalpy for cold crystallization and ΔH_m° is the enthalpy

of melting for 100% crystalline PLA sample, which is assumed to be 93 J/g [20], and w is the weight fraction of PLA in the sample.

3.5. Optical properties

A Perkin Elmer UV/Vis Spectrometer Lambda 2S (Überlingen, Germany) was used to measure the light transmittance of fast and slow cooled PLA-TEC and its nanocomposites. The scans were carried out from 200 to 800 nm with a scan speed of 240 nm/min.

3.6. Tensile testing

The mechanical properties of both fast and slow cooled plasticized PLA and its nanocomposite films were measured using a conventional Shimadzu AG-X universal testing machine (Kyoto, Japan). A load cell of 1 kN, a gauge length of 30 mm and a crosshead speed of 3 mm/min were used. Samples were cut from the prepared films using a bone shape press mold following the ASTM D-638 standard. The tensile strength and the elongation to break were obtained directly from testing results, while the tensile modulus and toughness were calculated from the stress-strain curves. At least five test samples were measured and the values reported are an average of these tests.

3.7. Statistical analysis

One-way analysis of variance (ANOVA) followed by Tukey-HSD multiple comparison tests with a 0.05 significance level was used to analyze the results from mechanical testing.

3. Results and discussion

4.1. Preparation of suspensions for liquid feeding

Both cellulose and chitin nanocrystals were analyzed prior their preparation for the mixtures for liquid feeding. Fig. 1(a and c) shows the appearance and optical microscopy images of the initial aqueous nanocrystal suspensions. It is clear than the CNC suspen-

sion shows better isolation and dispersion than the chitin nanocrystals, which still contains some micro-sized particles from the raw material.

Fig. 1(b and d) shows the visual appearance of the pumping suspensions and their microstructures. It is seen that the addition of the ethanol and TEC is changing the consistency, especially of the CNC suspension, which is smooth in water suspension but show a different behavior with presence of TEC and ethanol. It is also visible that the chitin is less isolated than the cellulose nanocrystals in the final suspension (Fig. 1d).

4.2. Crystalline, morphological and thermal characteristics of the nanocrystals

Raw material morphology and sizes were studied with AFM. Fig. 2 shows height images of cellulose and chitin nanocrystals and Table 2 shows the measured diameter, length and aspect ratio. The measurements show that the maximum diameter and the maximum length of the ChNC were almost double that of the CNC. Also the aspect ratio of the ChNC is higher than that of the CNC. The reported values of nanocrystals length are for comparison purposes only.

Results from XRD study are shown in Fig. 2b. Cellulose nanocrystals present the typical peaks of cellulose I at 2θ values of 15° , 16° and 22.5° [21], and chitin nanocrystals show the typical α -chitin structure with two strong peaks at 2θ values of 9.2° and 19.2° and three weak peaks at 20.7° , 23.2° and 26.2° [13]. The measured crystalline index reported in Table 2 shows that the ChNC had higher crystallinity than the CNC.

The thermal properties in Fig. 2c show that the chitin crystals have higher thermal stability than the cellulose crystals, which show a typical two-step degradation of sulfuric acid hydrolyzed nanocrystals, and this lower thermal stability is due to the introduced sulfate groups on the CNC surface during the hydrolysis [22]. However, both nanocrystals are thermal stable at the processing temperature range, which was below 200°C .

4.3. X-Ray diffraction

Fig. 3 shows the diffraction patterns of fast and slow cooled PLA-TEC and its nanocomposites. Generally, the XRD of the plasticized PLA and the nanocomposites was very similar for both fast and slow cooling. It can be clearly seen that all samples that were fast cooled present an amorphous nature, since defined peaks were not seen, whereas all the samples that were slow cooled clearly show a significant peak. The slow cooled samples show typical peaks of PLA, being the most highly defined at $2\Theta = 16.6^\circ$ and 19.1° indicating crystalline PLA.

4.4. Thermal properties

DSC graphs for the fast and slow cooled plasticized PLA and their respective nanocomposites are shown in Fig. 4. It can be seen that FC samples (see Fig. 4a) show a melt peak and cold crystallization, whereas the SC samples (see Fig. 4b) only show the melt peak and higher crystalline materials. The T_g values were not detected in the DSC during the first heating scans, probably because this technique is not sensitive enough to detect the T_g transition [23]. The crystallinity of the slow cooled materials is for the cellulose nanocomposites (56%) compared to the plasticized PLA (51%) showing that the addition of CNC had a slightly increased the nucleation of spherulites. Although the chitin nanocomposite showed slightly higher melt crystallization temperature (Fig. 4c) its degree of crystallinity was slightly lower compared to that of the cellulose nanocomposite. This can be because the cellulose nanocomposite have a somewhat higher melt crystallization enthalpy (15 J/g), which indicates higher nucleation of the spherulites due to its higher surface area of CNC.

4.5 Optical transparency and visual appearance

UV/Vis spectroscopy was used to measure the light transmittance of the plasticized PLA films and their nanocomposites after fast and slow cooling. If the reinforcements are not on nanosize or if agglomeration occurs, the light scattering increases and the percentage of light transmittance decreases [24]. Therefore, the transparency of the nanocomposites can give an indication about the dispersion of the nanocrystals in the PLA matrix.

The UV/Vis spectroscopy results are shown in Fig. 5. It can be seen that fast cooling resulted in more transparent films compared to slow cooling, which resulted in haze films. Also the light transmittance of the fast cooled plasticized PLA at 550 nm (middle of the visible spectra) decreased by 12% with the addition of 1 wt% of ChNC and by 20% with the addition of 1 wt% CNC. The crystallization of PLA during the slow cooling process further increased these values by almost double.

Fig. 6 shows the visual appearance and the polarized optical microscopy images of the prepared films. The images of the slow cooled films (Fig. 6d, 6e and 6f) show the presence of spherulites, which are associated to the crystallization of the PLA. It can be seen that the spherulite size somewhat larger in slow cooled chitin nanocomposite film (Fig. 6f) if compared with the cellulose nanocomposite film (Fig. 6e). The slow cooled plasticized PLA (Fig. 6d) shows also some large spherulites, similar to those of the ChNC nanocomposite, but in lower amount.

4.5. Microstructures of fracture surfaces

Fig. 7 shows the cryogenic fractured surfaces of PLA-TEC and its slow cooled nanocomposites. It can be seen that the plasticized PLA surface looks smoother than the surface of the nanocomposites. The surfaces of both cellulose and chitin nanocomposites show some nanocrystals agglomerations (circles) and also either the presence of some

voids or evidence of crystals pull-out (arrows). Fast cooled materials were also studied in SEM but no big difference between the cryogenic fracture surfaces of the plasticized PLA and the cellulose nanocomposite was seen. In the case of the chitin nanocomposites, several micro-sized particles with a flake shape were seen, as expected. These results are in agreement with the result from the optical microscopy images of the prepared films, where nanocrystal agglomerations were seen in both materials.

4.6. Mechanical properties

Tensile properties of the fast and slow cooled PLA-TEC and their nanocomposites are shown in Table 3 and Fig. 8. It can be seen from the stress-strain curves that the fast and slow cooling resulted in completely different behavior. The FC materials showed yielding point, followed by strain softening and strain hardening, which is related to the necking phenomenon [25] and was clearly observed in the tensile tested samples (see Fig. 8b), indicating a ductile fracture [26]. Unlike the fast cooled materials, the slow cooled materials did not show necking but they showed stress whitening, which indicates crazing. From Fig. 8b it is possible to see that the whitening is stronger for the plasticized PLA and for cellulose nanocomposite than for the chitin nanocomposite. It seems that in these samples, some crazing was formed, resulting in a more brittle fracture in comparison with the fast cooled samples. Crazes involve local plastic deformation that results in a brittle fracture; however, massive crazing phenomena result in a ductile fracture [26], as observed in our previous study with plasticized PLA nanocomposite with cellulose nanofibers [16]. The yield strength and the Young's modulus of the fast cooled plasticized PLA were significantly increased with the addition of 1 wt% nanocrystals. These properties were improved by 316% (from 3.7 to 15.4 MPa) and by 267% (from 0.3 to 1.1 GPa), respectively, with the addition of CNC and by 478% (from

3.7 to 21.4 MPa) and by 300% (from 0.3 to 1.2 GPa), respectively, with the addition of ChNC. In addition, a trend to improve the work of fracture (toughness) is evident; however, the large standard deviation for the plasticized PLA affects the significant improvement. These materials showed an elongation to break of ~300% as a result of the ductile fracture. The addition of nanocrystals did not significantly affect the ultimate strength and the elongation to break of the fast cooled plasticized PLA.

In the case of the slow cooled plasticized PLA, the ultimate strength increased significantly based in the ANOVA test by 26% (from 15.8 to 19.9 MPa) with the addition of CNC and by 28% (from 15.8 to 20.3 MPa) with the addition of ChNC. The yield strength was increased by 9% (from 19.6 to 21.4 MPa) with the addition of CNC and it was not significant increased with the addition of the ChNC. However, the Young's modulus increased significantly by 67% (from 0.6 to 1.0 GPa) with the addition of ChNC while with the addition of CNC it was increased by 50% (from 0.6 to 0.9 GPa). The toughness and the elongation to break of the nanocomposites decreased in comparison with that of the plasticized PLA, probably due to their higher degree of the crystallinity, as shown in the DSC results.

Regarding the PLA crystallization, it is known that as a general tendency, the crystallization of semi-crystalline polymers results in an increase in the mechanical properties and in a drop on the elongation to break [4,27,28]. In this study, when comparing the fast cooled materials with the slow cooled materials, the PLA crystallization resulted in materials with lower elongation to break as expected, but no significant change of the modulus. An improvement of the yield and ultimate strength was seen only in the PLA-TEC and PLA-TEC-CNC samples. The PLA crystallization did not show any effect on the mechanical properties of the ChNC nanocomposites. Similar results were reported

by Li et al. [27], where the modulus and the tensile strength of crystalline PLA decreased in comparison with amorphous PLA at a specific plasticizer concentration. This behavior is likely due to the internal migration of the plasticizer from the crystalline to the amorphous regions, resulting in a local concentration of plasticizer in the amorphous phase [27,29]. In this study, this effect was more evident in the chitin nanocomposites, since they showed a tendency to be more amorphous materials.

4. Conclusions

We have demonstrated that compounding of PLA nanocomposite can be done using liquid feeding of aqueous suspension cellulose and chitin nanocrystals together with triethyl citrate as plasticizer and ethanol as solvent.

Results showed that the cooling rates significantly affected the crystallinity of the materials and, consequently, the transparency of the films and the elongation to break.

- Fast cooled films showed to be the most transparent materials and the highest elongation to break with values around 300%.
- The addition of 1 wt% of nanocrystals enhanced the mechanical properties of the plasticized PLA in both, fast and slow cooling, being more evident in the fast cooled materials.
- ChNC showed higher aspect ratio, higher crystallinity and presented an uncharged surface in comparison with the CNC, resulting in chitin nanocomposites with slightly higher mechanical properties and higher transparency.

We can conclude that fast cooling and the addition of a small amount of nanocrystals (1 wt%) resulted in nanocomposites with high elongation to break, and other mechanical properties similar to PE, which is very important for film blowing and potential use of the material in packaging applications.

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References

- [1] Lim LT, Auras R, Rubino M. Processing technologies for poly(lactic acid). *Prog Polym Sci* 2008;33:820-852.
- [2] Soulestin J, Prashantha K, Lacrampe MF, Krawczak P. Ch. 4. Bioplastics based nanocomposites for packaging applications. In: Pilla S, editor. *Handbook of bioplastics and biocomposites engineering applications, Part II*. New Jersey: Wiley Scrivener Publishing, 2011. p.77-120.
- [3] Jonoobi M, Harun J, Mathew AP, Oksman K. Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. *Compos Sci Technol* 2010;70:1742-1747.
- [4] Suryanegara L, Nakagaito AN, Yano H. The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites. *Compos Sci Technol* 2009;69:1187-1192.
- [5] Sanchez-Garcia MD, Lagaron JM. On the use of plant cellulose nanowhiskers to enhance the barrier properties of polylactic acid. *Cellulose* 2010;17:987-1004.

- [6] Pei A, Qi Zhou Q, Berglund LA. Functionalized cellulose nanocrystals as biobased nucleation agents in poly(L-lactide) (PLLA) – Crystallization and mechanical property effects. *Compos Sci Technol* 2010;70:815–821.
- [7] Oksman K, Mathew AP, Bondeson D, Kvien I. Manufacturing process of cellulose whiskers/polylactic acid nanocomposites. *Compos Sci Technol* 2006;66:2776-2784.
- [8] Morin A, Dufresne A. Nanocomposites of chitin whiskers from riftia tubes and poly(caprolactone). *Macromolecules* 2002;35:2190-2199.
- [9] Wu X, Torres FG, Vilaseca F, Peijs T. Influence of the processing conditions on the mechanical properties of chitin whisker reinforced poly(caprolactone) nanocomposites. *J Biobased Mater Bioenergy* 2007;1(3):341-350.
- [10] Mathew AP, Laborie MPG, Oksman K. Cross-linked chitosan/chitin crystal nanocomposites with improved permeation selectivity and pH stability. *Biomacromolecules* 2009;10:1627–1632.
- [11] Sriupayo J, Supaphol P, Blackwell J, Rujiravanit R. Preparation and characterization of α -chitin whisker-reinforced chitosan nanocomposite films with or without heat treatment. *Carbohydr Polym* 2005;62:130–136.
- [12] Nair KG, Dufresne A. Crab shell chitin whiskers reinforced natural rubber nanocomposites. 3. Effect of chemical modification of chitin whiskers. *Biomacromolecules* 2003;4:1835-1842.
- [13] Salaberria AM, Jalel Labidi J, Fernandes SCM. Chitin nanocrystals and nanofibers as nano-sized fillers into thermoplastic starch-based biocomposites processed. *Chem Eng J* 2014;256:356-364.

- [14] Rizvi R, Cochrane B, Naguib H, Lee PC. Fabrication and characterization of melt-blended polylactide-chitin composites and their foams. *J Cell Plast* 2011;47:283-300.
- [15] Bondeson D, Oksman K, Polylactic acid/cellulose whisker nanocomposites modified by polyvinyl alcohol. *Composites: Part A* 2007;38:2486–2492.
- [16] Herrera N, Mathew A.P, Oksman K. Plasticized polylactic acid/cellulose nanocomposites prepared using melt-extrusion and liquid feeding: Mechanical, thermal and optical properties. *Compos Sci Technol* 2015;106:149-155.
- [17] Hietala M, Samuelsson E, Niinimäki J, Oksman K. The effect of pre-softened wood chips on wood fibre aspect ratio and mechanical properties of wood polymer composites. *Composites: Part A* 2011;42:2110–2116.
- [18] Segal L, Creely J.J, Martin Jr A.E, Conrad C.M. An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Textile Research Journal* 1959;29:786-794.
- [19] Struszczyk H. Microcrystalline Chitosan. I. Preparation and Properties of Microcrystalline Chitosan. *J Appl Polym Sci* 1987;33:177-189
- [20] Mathew AP, Oksman K, Sain M. The effect of morphology and chemical characteristics of cellulose reinforcements on the crystallinity of polylactic acid. *J Appl Polym Sci* 2006;101:300-310.
- [21] Krässig HA. Cellulose: Structure, accessibility and reactivity. Second edition. Gordon and Breach Science, 1996.
- [22] Roman M, Winter TW. Effect of sulfate groups from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose. *Biomacromolecules* 2004;5:1671-1677.

- [23] Chartoff RP, Thermoplastic polymers. In. Turi EA, editor. Ch. 3. Thermal characterization of polymeric materials, Second Edition, Vol 1. San Diego, California: Academic Press, 1981. p.484-730.
- [24] Oksman K, Mathew AP. Ch. 5. Melt compounding process of cellulose nanocomposites. In: Oksman K, Mathew AP, Bismarck A, Rojas O and Mohini S, editors. Handbook of Green Materials, Vol. 2, Materials and Energy, Vol. 5. Singapore: World Scientific Publishing, 2014. p.53-68.
- [25] Li B, Dong F, Wang X, Yang J, Wang D, Wang Y. Organically modified rectorite toughened poly(lactic acid): Nanostructures, crystallization and mechanical properties. *Eur Polym J* 2009;45:2996-3003.
- [26] Galeski A. Strength and toughness of crystalline polymer systems. *Prog Polym Sci* 2003;28:1643–1699.
- [27] Li H, Huneault MA. Effect of nucleation and plasticization on the crystallization of poly(lactic acid). *Polymer* 2007;48:6855-6866.
- [28] Kowalczyk M, Piorkowska E, Kulpinski P, Pracella M. Mechanical and thermal properties of PLA composites with cellulose nanofibers and standard size fibers. *CompositesPart A* 2011;42:1509-1514.
- [29] Piorkowska E, Kulinski Z, Galeski A, Masirek R. Plasticization of semicrystalline poly(l-lactide) with poly(propylene glycol). *Polymer* 2006;47:7178-7188.

Figure Captions

Fig. 1. Visual appearance and optical microscopy images of a) aqueous CNC suspensions at 10.3 wt%, b) CNC pumping suspension, c) aqueous ChNC suspensions at 10.3 wt% and d) ChNC pumping suspension.

Fig. 2. a) AFM height images: CNC (left), size measurements (center) and ChNC (right) b) crystallinity of the nanocrystals and c) thermal stability of the nanocrystals.

Fig. 3. Crystallinity of FC and SC plasticized PLA and the nanocomposites a) PLA-TEC, b) PLA-TEC-CNC and c) PLA-TEC-ChNC.

Fig. 4. Thermal properties of plasticized PLA and its nanocomposites materials heating scans of a) FC materials, b) SC materials including the degree of crystallinity (X_c) and c) cooling scans of FC films including melt crystallization enthalpy values (ΔH_{mc}).

Fig. 5. UV/Vis transparency and the visual appearance of the prepared films a) fast cooling and b) slow cooling.

Fig. 6. Visual appearance and polarized optical microscopy images of: fast cooled a) plasticized PLA, b) cellulose nanocomposite and c) chitin nanocomposite. Slow cooled d) plasticized PLA, e) cellulose nanocomposite and f) chitin nanocomposite.

Fig. 7. HR-SEM micrographs of cryogenic fracture surfaces of slow cooled samples of a) PLA-TEC, b) PLA-TEC-CNC and c) PLA-TEC-ChNC, showing some agglomerations (circles). Micrographs at higher magnification of Fig. (b and c) are shown to the right, showing some voids (arrows).

Fig. 8. a) Typical stress-strain curves for FC and SC PLA-TEC and their nanocomposites and b) the specimens after the testing.

Tables

Table 1. Compositions of the compounded materials.

Materials	PLA (wt%)	Nano crystals (wt%)	TEC (wt%)
PLA-TEC	80	-	20 ^a
PLA-TEC-CNC	79	1 ^b	20 ^b
PLA-TEC-ChNC	79	1 ^b	20 ^b

^a Fed as liquid 0.6 kg solvent (water and ethanol) removed as vapor during the extrusion.

^b Fed as liquid, TEC and nanocrystal content in the suspensions were 52 wt% and 2.6 wt% respectively, and 0.5 kg/h solvent (water and ethanol) removed during the extrusion.

Table 2. Cellulose and chitin nanocrystal characteristics.

Nanocrystal type	Diameter (nm)	Length (nm)	Aspect ratio (l/d)	Onset temperature (°C)	Crystallinity (%)
CNC	5-13	185-568	35-45	219	80
ChNC	7-25	314-1571	47-63	280	91

Table 3. Mechanical properties of plasticized PLA and its nanocomposites

Cooling and material		Yield strength (MPa)	Ultimate strength (MPa)	Young's modulus (GPa)	Elongation to break (%)	Work of fracture (MJ/m ³)
FC	PLA-TEC	3.7 ^a ± 1.2	22.4 ^a ± 4.1	0.3 ^a ± 0.2	305 ^a ± 53	32.2 ^a ± 12.8
	PLA-TEC-CNC	15.4 ^b ± 1.7	24.2 ^a ± 0.9	1.1 ^b ± 0.4	309 ^a ± 34	45.5 ^a ± 7.8
	PLA-TEC-ChNC	21.4 ^c ± 3.9	21.0 ^a ± 2.0	1.2 ^b ± 0.4	262 ^a ± 24	36.9 ^a ± 4.4
SC	PLA-TEC	19.6 ^A ± 1.2	15.8 ^A ± 1.1	0.6 ^A ± 0.1	91 ^A ± 38	16.1 ^A ± 6.4
	PLA-TEC-CNC	21.4 ^B ± 0.2	19.9 ^B ± 0.4	0.9 ^{A,B} ± 0.1	30 ^B ± 9	5.6 ^B ± 1.8
	PLA-TEC-ChNC	20.9 ^{A,B} ± 0.5	20.3 ^B ± 0.5	1.0 ^B ± 0.3	16 ^B ± 4	2.9 ^C ± 0.8

Same superscript letters within the same column are not significantly different at 5% significance level based on the ANOVA and Tukey-HSD multiple comparison test.