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Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion

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Abstract

The aim of this study was to develop cellulose nanofiber (CNF) reinforced polylactic acid (PLA) by twin screw extrusion. Nanocomposites were prepared by premixing a master batch with high concentration of CNFs in PLA and diluting to final concentrations (1, 3, 5 wt%) during the extrusion. Morphology, mechanical and dynamic mechanical properties (DMA) were studied theoretically and experimentally to see how different CNF concentrations affected the composites' properties. The tensile modulus and strength increased from 2.9 GPa to 3.6 GPa and from 58 MPa to 71 MPa, respectively, for nanocomposites with 5 wt% CNF. The DMA results were also positive; the storage modulus increased for all nanocomposites compared to PLA; being more significant in the high temperature region (70°C). The addition of nanofibers shifted the tan delta peak towards higher temperatures. The tan delta peak of the PLA shifted from 70°C to 76°C for composites with 5 wt% CNF.

Key words: A. Nanocomposites, Cellulose; B. Mechanical properties; C. Modeling; D. Dynamic mechanical thermal analysis, E. Extrusion.

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1. Introduction

Poly(lactic acid) (PLA) is a biodegradable, thermoplastic, aliphatic polyester which can be derived from renewable resources such as starch and is a sustainable alternative to petrochemical-derived products. PLA has been found to have good stiffness and strength and is being used in several applications, such as food packaging, water and milk bottles, degradable plastic bags as well as in automotive applications. The products made from PLA are bio-degradable and are found to fully disappear in less than 30 days in ideal conditions [1-3].

Cellulose nanofibers (CNFs) and nanowhiskers (CNWs) derived from renewable biomass have attracted much interest as an alternative to micro-sized reinforcements in composite materials [4-26]. One challenge when using nanocelluloses is that, due to their polar surfaces, it is difficult to disperse them uniformly in a non-polar medium. This might be the reason why the processing of cellulose nanocomposites was first limited to solvent casting, where water soluble or dispersive polymers were the most common matrices [4-13]. However, the development of other, more flexible and industrially viable processing techniques is necessary to promote commercialization of these materials. Therefore, several interesting processing methods have recently been reported for these materials [14-26].

One of the developed processing methods has been melt compounding [14-21]. The melt compounding of cellulose nanocomposites presents several challenges [14]. The major difficulties are to feed the nanocelluloses into the extruder and achieve uniform dispersion in the polymer's matrix. The nanocelluloses have a very high surface area and have a tendency to aggregate when dried. That can be avoided by first mixing them in a suitable medium, either in a liquid, which is then fed into the extruder, or first dried and then extruded [14-22].

Extensive studies of nanocelluloses as reinforcement in PLA have been carried out and the nanocomposites have been prepared by solvent casting as well as melt compounding [14-17]. In the first study, a slurry of plasticizer and CNWs was pumped into the melt PLA during extrusion to solve the feeding problem and improve the dispersion of CNWs in PLA [14]. The results showed that the CNWs improved the mechanical properties of the PLA, but the used additives had a negative impact. In the next study, cellulose microfibrils (CMFs) were used and compared to CNWs [15]. The results showed limited improvements in the mechanical properties and agglomerated CMFs in PLA. In the next study, PLA nanocomposites were successfully processed by extrusion using a surfactant, which facilitated the dispersion of nanowhiskers in PLA matrix [16]. In this case, both liquid feeding and dry feeding of CNWs into the polymer melt were attempted [16]. Later on, polyvinyl alcohol was tested as a carrier polymer for CNWs and compounded with PLA during extrusion [17]. In this case, PVA formed CNW-rich domains in the continuous PLA matrix [17], which led to relatively small improvements in mechanical properties.

Okubo and co-workers [19] have also studied the process and properties of PLA nanocomposites, where the PLA water slurry was premixed with microfibrillated cellulose (MFC) and processed using a roller mixer followed by drying and injection molding. They reported that the addition of 1 and 2 wt% of MFC had a positive impact on the modulus as well as on composites' fracture energy, but the strength did not show any improvements. The well-dispersed fibrils with lower concentration improved the composites' modulus by 31% and the fracture energy by almost 200% [19].

Yano and co-workers [20, 21] have also studied PLA nanocomposite reinforced with cellulose microfibrils and have reported promising results. The microfibrils were mixed with PLA in an organic solvent, and then roller-mixed to attain uniform dispersion of the cellulose fibrils. The Young's modulus and tensile strength of PLA increased using the microfibrils as

reinforcements, being highest at 10 wt%, when the modulus and strength increased by 40% and 25%, respectively.

In the current study, nanofibers separated from kenaf pulp were used as reinforcing phase for PLA matrix. Nanocomposites were prepared using a two-step process: master batch preparation using a solvent mixture followed by extrusion process and injection molding. The effect of nanofiber content (1, 3, 5 wt%) on the composites' mechanical properties and thermal stability was evaluated theoretically and experimentally. Microscopic analysis was used to study of nanofibers' morphology and surface fracture of nanocomposites.

2. Experimental

2.1 Materials

Matrix: Poly (lactic acid) (PLA), ESUN™, extrusion grade was supplied by Shenzhen Bright China Industrial Co., China. The used PLA has a density of 1.24 g/cm³ and the melt flow index (MFI) of 20 g/10 min at 190°C/ 2.16 kg, reported by the material supplier.

Reinforcement: Cellulose nanofibers were isolated from kenaf pulp. The details of the pulping process have been reported earlier by us [27]. The kenaf pulp was immersed in distilled water for 8 h. Diluted suspension: fiber concentration of 0.5% was distributed in the water using high shear mixing, Silverson L4RT (England), at 4000 rpm for 20 min. The suspension was grinded using a ultra-fine grinder, MKCA 6-3 from Masuko (Japan) at 3500 rpm in contact mode for approx. 15 min. to obtain cellulose nanofibers. Figure 1 shows the AFM images of the isolated nanofibers, indicating that the fibrillation process was successful and the pulp was isolated to an entangled network of nanofibers. The diameters of the fibers were measured using Nanoscope V software, showing that the diameters ranged from 40 to 70 nm, and the length was estimated to be several micrometers, from the AFM images .

Chemicals: Chloroform and acetone were purchased from Merck (Darmstadt, Germany).

Both of the chemicals were used in master batch preparation in order to dissolve PLA.

2.2 Processing of nanocomposites

Nanocomposites were prepared using a two-step process: master batch preparation using a solvent mixture followed by extrusion process.

2.2.1 Preparation of the master batch

Adequate amount of PLA (refer to Table 1) for each material was weighed and completely dissolved in a solvent mixture of acetone and chloroform in the ratio of 9:1 by stirring at 55°C. The nanofibers in aqueous medium were solvent-exchanged to acetone by a series of centrifuging and re-dispersing steps. After that, different mixtures of PLA and nanofibers were prepared by mixing the acetone-based nanofiber suspensions with dissolved PLA (see Table 1). Then, the mixture was casted in Petri-dishes and allowed to evaporate at room temperature overnight followed by oven vacuum-drying at 55°C for 8 h. The composite films obtained from the casting were crushed using a kitchen blender until a particulate material was obtained.

2.2.2 Extrusion process and sample preparation

Nanocomposites were manufactured using a twin screw extruder, Coperion W&P ZSK 18 MEGALab (Stuttgart, Germany), with a screw speed of 120 rpm and the temperature profile was varied from 165°C at the feeding zone to 200°C at the die. The crushed master batch was dry-mixed with PLA, diluting it to 1, 3 and 5 wt% nanofiber contents. The mixtures were vacuum-dried at 55°C for 8 h prior to the process whereby the PLA and its nanocomposites were compounded, followed by the pelletizing step. The formulations of prepared materials are presented in Table 1.

The extruded pellets were dried at 55°C for 6 h prior to injection molding (Haake MiniJet II) of the test specimens according to ASTM, D638 type 5, testing method. The barrel

temperature of the injection molding machine was set at 200°C. The injection pressure was kept constant at 400 bar and the mold temperature was 70°C. The injection-molded specimens were used for evaluation of the mechanical and thermal properties.

2.3 Characterization

2.3.1 Microscopy

The microstructures of nanocomposites were investigated using scanning electron microscopy (SEM). Fractured surfaces from tensile testing were analyzed in a Jeol, JSM-6460 (Japan). The acceleration voltage was 5 kV and samples were sputter-coated with gold to avoid charging.

2.3.2 Tensile testing

The tensile tests were performed using a universal testing machine, Hounsfield H25KS, (United Kingdom), with a load cell of 10 kN and with a crosshead speed of 3 mm/min. The injection-molded specimens (ASTM, D638 type 5) were used for tensile testing and the gauge length was 30 mm. The elastic modulus was calculated from the initial part of the slope from stress–strain curves. At least five test samples were tested for each material and the average values are presented.

2.3.3 Dynamic mechanical properties (DMA)

The dynamic mechanical properties of the nanocomposites were carried out using the dynamic mechanical analyzer, DMA Q800 TA Instruments (New Jersey, USA), in tensile mode. The measurements were performed at a constant frequency of 1 Hz with a temperature range from 25°C to 110°C at a heating rate of 3°C/ min. The test specimen dimensions were approx. 2.0 x 5.0 x 30.0 mm (thickness x width x length). The presented data is based on three measurements.

3. Results and discussion

3.1 Nanocomposite morphology

SEM micrographs of fractured surfaces of the PLA and its nanocomposites are presented in Figure 2. The aim was to investigate if any CNF aggregates were visible in the fractured surfaces. Compared to pure PLA, the surface of the PLA-CNF1 and PLA-CNF3 nanocomposites showed no significant differences, but the nanocomposite with 5 wt% CNF (PLA-CNF5), had a rougher surface compared to those with lower nanofiber contents (Fig 2d). A more detailed micrograph of this composite is shown in Figure 3. The image shows small areas which are attributed to small aggregates of CNFs. Generally, a relatively good dispersion was achieved in composites with low fiber contents (1 and 3 wt%).

3.2 Mechanical properties

Figure 4 shows typical stress–strain curves of neat PLA and PLA-CNF composites with different fiber contents and Table 2 shows the average values and standard deviations of the mechanical properties. The tensile properties indicated that the strength and modulus were improved with increased nanofiber contents. The modulus of the PLA was increased from 2.9 GPa to 3.6 GPa with the addition of 5 wt% nanofibers, which corresponds to a 24% increase. Similarly, a 21% increase in tensile strength was observed for PLA-CNF5 composites compared to pure PLA. Table 2 shows that the average value of maximum strain was reduced by increased nanofiber contents. The positive impact of the nanofibers especially in the composite strength indicated that the used nanofibers have good mechanical properties and that there is interaction between the PLA and the CNFs. However the large standard deviations especially on the modulus and strain values indicated that the nanofibers were not homogeneously distributed.

Yano and co-workers reported similar improvements for PLA-nanocomposites with 5 wt% fiber content [20, 21].

In order to see the reinforcing potential of CNFs, common theoretical models developed by Halpin-Tsai and Krenchel were used and compared to experimental data.

The theoretical modulus for the composites (E_{comp}) based on the Halpin-Tsai equation given below, see Eq (1) - Eq (3) [28].

$$E_{comp} = E_m (1 + \zeta \eta \phi) / (1 - \eta \phi) \quad (1)$$

$$\eta = (E_r / E_m - 1) / (E_r / E_m + \zeta) \quad (2)$$

E_m is the modulus of the matrix, E_r is the modulus of the reinforcements and ϕ is the volume fraction. The Halpin-Tsai equation is usually used for aligned fiber composites, but it has also been used before to predict the modulus of nanocomposites [4, 26].

$$\zeta = (2 \times l) / d \quad (3)$$

ζ is a shape parameter, depending on the geometry and aspect ratio of the reinforcement. The length of the nanofibers was predicted to be 10 μm and the diameter to be 100 nm. The diameter value is based on our microscopy study (AFM) where the measured diameters were below 100 nm while the length is estimated from the AFM study considering that nanofibers are several micrometers in length though the exact measurement of the length is not possible because of the entangled structure.

The modulus prediction by Krenchel [29] might be a more reasonable model for the CNF composites prepared by compounding and injection molding because we do not expect aligned nanofibers after the injection molding, but rather that they are randomly distributed in plane. In this case the modulus is predicted by following Eq (4) [29], which have also been used for carbon nanotube composites [30].

$$E_{comp} = E_m (1 - \phi) + \eta_l \eta_o E_r \phi \quad (4)$$

η_l is the length correction factor and η_o orientation factor, being 3/8 when the fibers are oriented randomly in plane. The η_l is calculated from the following expression Eq (5, 6),

$$\eta_l = 1 - ((\tanh(\beta l / 2)) / (\beta l / 2)) \quad (5)$$

$$\beta = 1 / r (E_m / 2 E_r \ln(R / r))^{1/2} \quad (6)$$

where the l is the fiber length and r is the radius. R/r is predicted to be $(K_r/\phi)^{1/2}$, where K_r depends on the fiber geometrical packing, and it is chosen to be $\pi/4$, considering the square packing.

The volume fractions of nanoreinforcements were calculated using the Eq (7),

$$\phi = (w_r/\rho_r) / ((w_r/\rho_r) + (1 - w_r)/\rho_m) \quad (7)$$

where, w_r is weight % of reinforcements, ρ_r represent the density of the fibers and ρ_m is the density of the matrix polymer. The following values for the matrix and the cellulose nanofibers were used for theoretical calculations: $E_m = 2.9$ GPa, $E_r = 138$ GPa [31], $\rho_m = 1.25$ g/cm³, and $\rho_r = 1.58$ g/cm³ [32], the length of the nanofibers was predicted to be 10 μ m and the diameter was chosen to be 100 nm. The volume fractions of nanofibers were determined to be 0.8%, 2.4%, and 4%, respectively.

The comparison between the experimental data and predictions by the Halpin-Tsai and Krenchel are presented in Figure 5. When comparing the results one has to keep in mind that the theoretical calculations by Halpin-Tsai are based on systems where the reinforcements are fully dispersed and aligned in the longitudinal direction and have perfect interfacial adhesion to the matrix, or where the reinforcing phase is randomly distributed in the matrix (Krenchel).

Figure 5 show that CNFs have a potential as reinforcement in polymers, especially if the fibers are aligned as seen in the model by Halpin-Tsai. The composites' experimental values are more near the prediction based on the Krenchel's model, as expected because the fibers might be randomly orientated in the PLA. The lower experimental values might be caused by fiber aggregation, especially with higher loading and suggest possibilities for further improvement in properties.

3.3 Dynamic mechanical properties

Figure 6 shows the storage modulus and tan delta as a function of temperature of the prepared materials. Generally, it is possible to see that the PLA has a transition around 60°C. The storage modulus of PLA is increased with increased nanofiber content, in glassy as well as in rubbery state. The storage modulus of PLA has a significant drop on the transition region, whereas the drop is relatively less for the nanocomposites. Above the transition region, around 60°C, the modulus of the PLA nanocomposite was remarkably higher than PLA and the improvement is most significant at 5 wt% of nanofibers, indicating entangled nanofibers. Table 3 shows the storage modulus of the composites at two different temperatures. The storage modulus of the CNF composites was higher in the glassy and rubbery regions compared to pure PLA. The storage modulus data of PLA and the nanocomposites at 25°C support the data obtained from tensile testing and the trend as well as the values are found to be comparable. The improvement is most obvious at 70°C, where the modulus was 2.5 GPa for PLA-CNF5 compared to 100 MPa for pure PLA. The large modulus improvement after the relaxation, forming a “plateau” indicates entangled nanofibers and this is most obvious for the composites with highest nanofiber content; similar tangling behavior for nanofibers have been reported by Dufresne et al [33].

Figure 6b shows how the addition of different content of nanofibers influenced the tan delta peak position of PLA. As can be seen from Figure 6b, the tan delta peak is shifted to higher temperature with increased nanofiber contents. The tan delta peak temperatures are given in Table 3. The peak position for PLA was at 70°C and increased to 76°C for the composites with 5% CNF. Additionally, Figure 6b shows that the intensity of the tan delta peak decreased with the concentration of nanofiber content compared to neat PLA. This indicates that fewer polymer chains are participating in this transition. The increase in modulus, together with positive shift in tan delta peak position, can be attributed to physical interaction between the polymer and reinforcements that restrict the segmental mobility of the

polymer chains in the vicinity of the nanoreinforcements [18]. It may also be noted that results from the viscoelastic behavior of the composites agree with the mechanical properties, suggesting that the reinforcing effect of nanofibers in PLA led to restriction of molecular chain mobility.

3.4 Film transparency

The visual study of the transparency of PLA and the PLA-CNF nanocomposites with different nanofiber contents is presented in Figure 7. Generally, the transparency of the PLA-CNF nanocomposites was good but as seen in the Figure 7 some white spots are visible in the PLA-CNF5 composite. These spots are expected to be CNF aggregates in the PLA matrix.

4. Conclusions

Cellulose nanocomposite processing via a master batch with high content of nanofibers in PLA was attempted. The master batch and the bulk PLA were premixed and compounded during extrusion to obtain nanocomposites with different fiber compositions.

The morphology studies of PLA and its nanocomposites showed that a relatively good dispersion was achieved as no CNF aggregates were visible in the fracture surfaces of the PLA-CNF1 and PLA-CNF3 nanocomposites. The PLA-CNF5 however shows small aggregates, indicating that the nanofibers were not as well dispersed in this composite.

The visual characterization of the prepared materials showed small white spots, especially in composites with 5 wt% CNF, which further indicated that nanofibers were aggregated in that composite.

The evaluation of the mechanical properties of the PLA and its nanocomposite showed a trend that the tensile strength and modulus were improved with increased nanofiber content. The modulus of the PLA was increased from 2.9 GPa to 3.6 GPa with the addition of 5 wt% nanofibers, and a 21% increase of tensile strength was observed.

It was also found that the experimental modulus of the nanocomposites was lower than the theoretical predictions based on Halpin-Tsai and Krenchel. The comparison between the theoretical and experimental results showed that CNF has good potential as a reinforcement, especially if the nanofibers can be aligned but also that it might be possible to improve the properties even for randomly oriented nanofibers if the dispersion can be improved.

The DMA study indicated that the increased modulus, together with positive shift in tan delta peak position, is attributed to physical interaction between the polymer and nanofibers that restrict the segmental mobility of the polymer chains in the vicinity of the CNFs. Furthermore, storage modulus showed a plateau after the relaxation, especially when the nanofibers content was 5 wt% indicating entangled nanofibers.

This study shows that the melt compounding process using the master batch is a very promising method to reach good processability of cellulose nanocomposites and achieve improved mechanical and thermal properties for PLA. However, further work is needed to improve the dispersion of the nanofibers in the PLA.

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References

1. Meinander K, Niemi M, Hakola JS, Selin J-F. Polylactide-degradable polymers for fibres and films. *Macromolecules Symp* 1997; 123: 147–54.
2. Oksman K, Skrifvars M, Selin J-F. Natural Fibres as Reinforcement in Polylactic Acid (PLA) Composites, *Comp Sci Technol*, 63 (2003) 1317-1324.

3. Mathew AP, Oksman K, Sain M. Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC). *J Appl Polym Sci* 2005; 97: 2014-2025.
4. Helbert W, Cavaille JY, Dufresne A. Thermoplastic Nanocomposites Filled with Wheat Straw Cellulose Whiskers. *Pol Comp* 17, 1996: 604-611.
5. Heux L, Chauve G, Bonini C. Nonflocculating and chiralnematic self-ordering of cellulose microcrystals suspensions in nonpolar solvents. *Langmuir* 2000;16:8210
6. Mathew AP, Dufresne A, Morphological investigation of nanocomposites from sorbitol plasticized starch and tunicin whiskers. *Biomacromolecules* 2002; 3: 609-617.
7. Morin A, Dufresne A. Nanocomposites of chitin nanofibrils from *Riftia* tubes and poly(caprolactone). *Macromol* 2002;35:2190
8. Gousse C, Chanzy H, Excoffier G, Soubeyrand L, Fleur. E. Stable suspensions of partially silylated cellulose whiskers dispersed in organic solvents. *Polymer* 2002;43:2645
9. Samir MASA, Alloin F, Sanchez J-Y, Kissi NE, Dufresne A, Crosslinked nanocomposite polymer electrolytes reinforced with cellulose whiskers. *Macromol* 2004;37:1386
10. Samir MASA, Alloin F, Dufresne A. Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules* 2005; 6: 612-626
11. Kvien I, Oksman K. Orientation of Cellulose Nanowhiskers in Polyvinyl Alcohol (PVA), *Appl Phys A*, 87, (2007), 641-643.
12. Petersson L, Kvien I, Oksman K. Structure and thermal properties of polylactic acid/cellulose whiskers nanocomposite materials. *Comp Sci Technol* 2007; 67: 2535-2544.

13. Chakraborty A, Sain M, Kortschot M. Reinforcing potential of wood pulp-derived microfibrils in a PVA matrix. *Holzforschung* 2006; 60: 53-58.
14. Oksman K, Mathew AP, Bondeson D, Kvien I. Manufacturing process of cellulose whiskers/ polylactic acid nanocomposites. *Comp Sci Technol* 2006; 66: 2766-2784.
15. Mathew AP, Chakraborty A, Oksman K, Sain M. The structure and mechanical properties of cellulose nanocomposites prepared by twin screw extrusion. In *Cellulose nanocomposites: Processing, Characterization and Properties*. Eds Oksman K and Sain M, ACS Symposium Series, 938, Oxford University Press, USA, 2006.
16. Bondeson D, Oksman K. Dispersion and characteristics of surfactant modified cellulose whiskers nanocomposites. *Compos Interfac* 2007; 14: 617-630.
17. Bondeson D, Oksman K. Polylactic acid/cellulose whisker nanocomposites modified by polyvinyl alcohol. *Comp Part A* 2007; 38: 2486-2492.
18. Bondeson D, Syre P, Oksman Niska K. All Cellulose Nanocomposites Produced by Extrusion, *J Biomat Bioenergy*, 2007; 1: 367-371.
19. Okubo K, Fujii T, Thostenson ET. Multi-scale hybrid biocomposite: Processing and mechanical characterization of bamboo fiber reinforced PLA with microfibrillated cellulose *Comp Part A*:2009;40: 469-475
20. Iwatake A, Nogi M, Yano H. Cellulose nanofiber-reinforced polylactic acid. *Comp Sci Technol* 2008; 68: 2103-2106.
21. Suryanegara L, Nakagaito AN, Yano H. The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites. *Comp Sci Technol* 2009; 69: 1187-1192.

22. Wang B, Sain M. Dispersion of soybean stock-based nanofiber in a plastic matrix. *Polym Int* 2007; 56: 538-546.
23. Seydibeyoğlu MÖ, Oksman K. Novel nanocomposites based on polyurethane and microfibrillated cellulose. *Comp Sci Technol* 2008; 68: 908-914.
24. Nakagaito AN, Yano H, The effect of morphological changes from pulp fiber towards nano-scale fibrillated cellulose on the mechanical properties of high-strength plant fiber based composites. *Appl Phys A* 2004; 78: 547-552.
25. Nakagaito AN, Fujimura A, Sakai T, Hama Y, Yano H. Production of microfibrillated cellulose (MFC)-reinforced polylactic acid (PLA) nanocomposites from sheets obtained by a papermaking-like process. *Comp Sci Technol* 2009; 69: 1293-1297
26. Petersson L, Oksman K. Biopolymer based nanocomposites: Comparing layered silicates and microcrystalline cellulose as nanoreinforcements. *Comp Sci Technol* 2006; 66: 2187-2196.
27. Jonoobi M, Harun J, Shakeri A, Misra M, Oksman K. Chemical composition, crystallinity and thermal degradation of bleached and unbleached kenaf bast (*Hibiscus cannabinus*) pulp and nanofibers. *Bioresources* 2009; 4: 626-639
28. Agarwal BD, Broutman LJ. Analysis and performance of fibre composites. Second ed. USA: John Wiley & Sons, Inc; 1990; 129.Composites
29. Krenchel H. Fibre reinforcement, Akademisk Forlag, Copenhagen, Denmark, 1964.
30. Gómez-del Río T. Poza P, Rodríguez J, García-Gutiérrez MC, Hernández JJ, Ezquerro T.A. Influence of single-walled carbon nanotubes on the effective elastic constants of poly(ethylene terephthalate), *Comp Sci Technol* 2010; 70: 284–290.

31. Nishino T, Takano K, Nakamae K. Elastic modulus of the crystalline regions of cellulose polymorphs. *J. Polym Sci B: Polymer Phys* 1995; 33: 1647-1651.
32. Ganster J, Fink H-P. Physical constants of cellulose. In: Brandrup J, Immergut EH, Grulke EA, editors. *Polymer handbook*, Fourth ed., Vol 1. John Wiley & Sons, Inc.; USA 1999.
33. Samir MASA, Alloin F, Paillet M, Dufresne A. Tangling effect in fibrillated cellulose reinforced nanocomposites, *Macromol*, 2004, 37, 4313-4316.

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Table captions

Table 1. Material formulations in the processing and in the final compositions

Table 2. Mechanical properties of the PLA and its nanocomposites with different compositions

Table 3. Storage modulus and tan delta peak temperatures of the PLA and its nanocomposites

Figure captions

Figure 1. AFM images of isolated nanofibers after grinding process, a) height image with measured fiber dimensions, b) fiber diameter measurements and c) amplitude image.

Figure 2. Fractured surfaces of neat PLA and its nanocomposites with different CNF contents: a) PLA, b) PLA-CNF 1, c) PLA-CNF 3 and d) PLA-CNF 5

Figure 3. Detailed view of the fractured surface of PLA-CNF5 nanocomposite showing CNF aggregates.

Figure 4. Tensile stress–strain curves of PLA and PLA nanocomposite based on cellulose nanofibers

Figure 5. Experimentally measured tensile modulus for nanocomposites compared to theoretical estimations by Halpin-Tsai and Krenchel.

Figure 6. DMA analysis of PLA and PLA nanocomposites; a) storage modulus; b) tan δ curves

Figure 7. Visual comparison of the transparency of PLA and its nanocomposites

Table 1. Material formulations in the processing and in the final compositions

Materials	Master batch			Bulk PLA (g)	Final composition (%)
	PLA (g)	CNF (g)	Solvent mixture (g)*		
PLA	15	-	300	85	PLA (100)
PLA-CNF1	14	1	300	85	PLA-CNF (99\1)
PLA-CNF3	12	3	300	85	PLA-CNF (97\3)
PLA-CNF5	10	5	300	85	PLA-CNF (95\5)

*: Solvents were evaporated during drying of the master batch

Table 2. Mechanical properties of the PLA and its nanocomposites with different compositions

Materials	Tensile modulus (GPa)	Tensile strength (MPa)	Max strain (%)
PLA	2.9 ± 0.6	58.9 ± 0.5	3.4 ± 0.4
PLA-CNF1	3.3 ± 0.4	63.1 ± 0.9	2.8 ± 0.3
PLA-CNF3	3.4 ± 0.1	65.1 ± 0.6	2.7 ± 0.2
PLA-CNF5	3.6 ± 0.7	71.2 ± 0.6	2.7 ± 0.1

Table 3. Storage modulus and tan delta peak temperatures of the PLA and its nanocomposites

Materials	E' at 25°C (MPa)	E' at 70°C (MPa)	Tan δ peak (°C)
PLA	2600 ± 100	100 ± 00	70 ± 0
PLA-CNF1	2800 ± 100	170 ± 30	71 ± 1
PLA-CNF3	3100 ± 200	340 ± 10	73 ± 1
PLA-CNF5	4400 ± 400	2500 ± 300	76 ± 0













