



Article

Polylactic Acid Reinforced with Mixed Cellulose and Chitin Nanofibers—Effect of Mixture Ratio on the Mechanical Properties of Composites

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Abstract: The development of all-bio-based composites is one of the relevant aspects of pursuing a carbon-neutral economy. This study aims to explore the possibility to reinforce polylactic acid by the combination of cellulose and chitin nanofibers instead of a single reinforcement phase. Polylactic acid colloidal suspension, cellulose and chitin nanofiber suspensions were mixed using only water as mixing medium and subsequently dewatered to form paper-like sheets. Sheets were hot pressed to melt the polylactic acid and form nanocomposites. The combination of cellulose and chitin nanofiber composites delivered higher tensile properties than its counterparts reinforced with cellulose or chitin nanofibers alone. Cellulose and chitin appear to complement each other from the aspect of the formation of a rigid cellulose nanofiber percolated network, and chitin acting as a compatibilizer between hydrophobic polylactic acid and hydrophilic cellulose.

Keywords: cellulose; chitin; nanofiber; polylactic acid; paper; compression molding

1. Introduction

Due to pressing ecological issues of modern civilization, the need to find new substitute materials that minimize environmental footprint is becoming ever more urgent. A substantial part of materials used in everyday life consist of polymers because they are lightweight, versatile, low cost, and easy to manufacture. However, polymers and derived composites mostly aim at long term durability to the detriment of easy disposability. They are generally made from fossil-based synthetic materials, but polymers are also produced by plants and animals through biochemical reactions. These naturally synthesized polymers are known as biopolymers. Among these biomass-derived polymers, cellulose is the most abundant polysaccharide comprising 40% of the organic matter on earth [1]. Cellulose is mostly found in the cell wall of plant fibers, as the structural reinforcement that provides the mechanical rigidity to support the plants' bodies. This framework is comprised of tiny semi-crystalline fibrous elements known as cellulose nanofibers, possessing mechanical properties similar to those of aramid fibers. The Young's modulus of the crystalline portions were measured to be 138 GPa [2], whereas the estimated tensile strength along the length of the nanofiber is in the range of 1.6 to 3 GPa [3].

Chitin is another highly plentiful polysaccharide available in nature, also found in the form of nanofibers in the exoskeleton of marine crustaceans, insects and in various filamentous fungi. The molecular structure of chitin is identical to that of cellulose, apart from the fact that a hydroxyl group of every glucose ring is replaced by an acetamido group [1]. The reduced number of hydroxyl groups makes chitin less hydrophilic than cellulose.

Poly(lactic acid) is the first commodity large-volume biopolymer available. It is a polyester synthesized by condensation polymerization of lactic acid, a naturally occurring organic compound that can be obtained by fermentation of sugar or starch-derived feedstocks. Poly(lactic acid), from here on abbreviated as PLA, is a versatile thermoplastic that can be processed in conventional polymer processing equipment into films, fibers, and injection-molded parts. Besides, under appropriate composting conditions PLA can be easily decomposed into carbon dioxide and water.

Numerous composites of PLA reinforced with either cellulose or chitin nanofibers have been developed by various methods like film casting, melt compounding, and papermaking. Casting is the easiest way to obtain small samples in laboratory, through slow evaporation of water from aqueous suspensions of latex resin and nanofibers. Among the more industrially-oriented processes, the melt compounding method has been extensively studied by Oksman and coworkers. They started using microcrystalline cellulose, and after finding out that separation into whiskers did not occur during compounding [4], N,N-dimethylacetamide and lithium chloride mixture was used to swell the microcrystalline cellulose. Subsequent disintegration into whiskers while compounding with PLA in a twin screw extruder was accomplished with addition of polyethylene glycol to lower the viscosity of the compound [5]. However, the mechanical properties of composites were not improved over the neat PLA due to thermal degradation of cellulose and residual swelling agents and the presence of polyethylene glycol. Other processing aids like glycerol triacetate to disperse cellulose nanofibers [6], triethyl citrate to disperse chitin and/or cellulose nanofibers [7,8] produced composites with better mechanical properties compared to the PLA-plasticizer mixture, but still worse than the neat PLA. Kiziltas et al. tried poly hydroxyl butyrate as a disperser of cellulose nanofibers with similarly limited results [9]. Iwatake et al. came up with a different approach by dissolving PLA in an organic solvent and mixing it with cellulose nanofibers previously suspended in the same solvent before melt compounding [10], and the study was continued by Suryanegara et al. with promising results [11]. Oksman and colleagues, in turn, prepared high-cellulose nanofiber content master batch following a similar protocol and further diluting it with additional PLA by compounding in a twin-screw extruder [12]. The tensile modulus and strength were increased by over 20% relative to neat PLA at 5 wt % nanofiber load. Acetylation to hydrophobize cellulose nanofibers and subsequent melt compounding from master batch did not show significant difference from non-treated nanofibers though [13]. A similar study was reported by Li et al. [14] who used polyethylene glycol and polyethylene oxide to enhance dispersion of chitin nanofibers with PLA powder in aqueous suspension, and freeze-drying prior to melt compounding. However, the aqueous mixture of only nanofibers and PLA gave the best mechanical properties, confirming the negative effect of adding other substances. In effect, the tensile stress increased with nanofiber content up to 30 wt % [15]. Another of their studies proposed the use of sodium ionomer to enhance flowability of the molten compound as viscosity increases with nanofiber content [16]. Flexural properties more than tripled over neat PLA at a nanofiber load of 40 wt %. Impact toughness was increased by about 300% as well. Even though melt compounding is an established industrial process, the mechanical properties are limited due to difficulties in nanofiber dispersion especially at high contents, and to the lack of the formation of a stiff percolated network of nanofibers linked by hydrogen bonds [17–20]. The percolation phenomenon has been long recognized as the reason ordinary papers are made by cellulosic pulp fibers mutually adhered by hydrogen bonds, without the need for adhesives. The importance of percolation on nano-scale cellulose reinforcements was first noticed by Favier et al. [21,22] in 1995. Nanocomposites made by film casting of cellulose whiskers and latex resin showed shear modulus at rubbery state staying constant up to the temperature of cellulose decomposition while the modulus of the pure matrix resin had a decreasing slope. The phenomenon was attributed to a percolation effect of the cellulose whiskers, forming a stiff framework connected by hydrogen bonds. Studies using chitin whiskers showed varied results, in some cases producing partial formation of percolated networks [23] and in others the formation of a rigid network [24]. Later, the use of cellulose nanofibers also confirmed the occurrence of percolation [25]. Following studies however, identified an important difference

in the sense that whiskers formed networks linked solely by hydrogen bonds whereas nanofibers formed networks by hydrogen bonds and mechanical entanglements due to their flexible nature as opposed to stiff whiskers [26–30]. Due to its high hydrophilicity, the most effective way to achieve good dispersion of cellulose nanofibers in hydrophobic PLA is by mixing them in aqueous medium. Although PLA is insoluble in water, aqueous suspensions can be obtained by using PLA short fibers or particles, that can be easily mixed with cellulose nanofibers in water suspension. After dewatering, the mixture forms paper-like sheets that can be laminated and compression molded. Previous attempts by the paper-making method were effective in reinforcing PLA with cellulose nanofibers [31–33] and chitin nanofibers [34]. Our previous studies concerning nanocomposites of PLA with cellulose compared to those with chitin nanofibers showed that both nanofiber types can reinforce the matrix up to high nanofiber contents. Cellulose delivered higher reinforcement at high nanofiber loads whereas chitin showed better reinforcement at lower nanofiber loads. In composites containing less reinforcing nanofibers, the percolated network of microfibrillated cellulose (MFC) would be weaker while the chitin nanofiber (ChNF)-PLA interaction would deliver the mechanical strength, favoring the ChNF-rich composites. Composites with higher contents of nanofibers are expected to be stronger at MFC-rich compositions as the MFC percolation is predominant. Therefore, the natural following step would be to evaluate the effect of both nanofibers acting together as the reinforcing phase. However, studies on the combination of both cellulose and chitin nanofibers as reinforcements have been scarce, or even unavailable especially when the matrix is PLA. The aim of this study was to explore the possibility of joint reinforcement by cellulose and chitin nanofibers of PLA matrix, and confirm the validity of this approach. The experiments demonstrated that it is possible to produce cellulose-chitin hybrid nanocomposites with mechanical properties superior to those of nanocomposites reinforced solely with cellulose or chitin alone. The combination of cellulose and chitin nanofibers as reinforcing phase opens the opportunity to develop nanocomposites with better mechanical performances and perhaps helps to lower the cost of raw materials. Chitin nanofibers demand less energy intensive nanofibrillation treatments to be produced than cellulose nanofibers [35].

2. Materials and Methods

2.1. Materials

The polylactic acid used as matrix phase comprised of the aqueous colloidal suspension types Landy PL-1000, Landy PL-2000, and Landy PL-3000 produced by Miyoshi Oil and Fat Co., Ltd., Tokyo, Japan. All varieties have weak anionic character and consist of 40 wt % PLA particles suspended in dispersing agents. Average particle sizes are 5, 2, and 1 μm for Landy PL-1000, PL-2000, and PL3000, respectively. The original industrial applications were as highly heat-resistant adhesive (PL-1000), coating and thermal adhesive (PL-2000), and coating (PL-3000). Cellulose nanofibers consisted of a commercially available microfibrillated cellulose (MFC) morphology of tradename Celish KY-100G provided by Daicel Corporation, Tokyo, Japan. The chitin nanofiber (ChNF) was extracted from purified chitin powder from crab shells (Nacalai Tesque, Inc., Kyoto, Japan) by grinding, following a previously reported protocol [34] that delivered fibrils with diameters below 100 nm. First, 30 g of chitin powder was suspended in 2 L of distilled water in which 30 g of acetic acid was added and stirred for 16 h. The acidic medium protonates the amino portion of the acetoamido groups of chitin, producing electrostatic repulsion that facilitates individualization of nanofibers. Subsequently, the powder aqueous suspension was passed through an ultra-fine friction grinder Supermasscolloider MKCA6-2 (Masuko Sangyo Co., Ltd., Saitama, Japan). With the grindstone aperture adjusted to a point when the stones slightly touch each other at a rotational speed of 1500 rpm, the suspension was poured into the grinder and the aperture was immediately closed by 0.15 mm. A tiny aperture is maintained by the hydrodynamic pressure created by the wet spinning grindstone. The suspension was passed twice through the grinder while 1 L of distilled water was gradually added to avoid evaporation and drying up of the grindstone aperture that would stop rotation. The obtained suspension after fibrillation therefore totaled 3 L, with a ChNF concentration of 1 wt %.

2.2. Nanocomposite Fabrication

Thin nanocomposites with the same reinforcing phase content of 50 wt % but varying ChNF to MFC ratios of 1:0, 4:1, 3:2, 1:1, 2:3, 1:4, and 0:1 were fabricated. The necessary amount (0–1.5 g) of MFC was diluted in 300 g of distilled water and stirred for one hour. Next, the ChNF aqueous suspension was slowly added by a dropper to the suspension so that the amount of added ChNF (0–1.5 g) with MFC totaled 3 g. The ChNF-MFC suspension was diluted by adding distilled water up to 600 g and the stirring was continued for another hour. The PLA Landy PL-2000 weighing 3 g (colloidal suspension containing 40 wt % PLA particles) was diluted in 200 g of distilled water and stirred for 30 minutes. This PLA suspension was slowly dripped to the ChNF-MFC suspension and further stirred for three hours. Finally, the suspension was stirred under reduced pressure for at least one hour, in order to eliminate entrapped air bubbles. The obtained suspensions were vacuum filtered through Buchner funnel and filter paper 110 mm in diameter Advantec 101 (Toyo Roshi Kaisha, Ltd., Tokyo, Japan). Retentates were peeled off from the filter papers, sandwiched in between filter papers Advantec 2 (Toyo Roshi Kaisha, Ltd., Tokyo, Japan) and perforated metal plates and oven-dried at 50 °C for 48 h. Dried sheets were further dried at 105 °C for one hour to completely remove moisture, and compression molded at 180 °C and 10 MPa for five minutes.

The same protocol was adopted to produce nanocomposites with the same ChNF to MFC ratios, but with amounts of reinforcing and matrix phases adjusted to achieve total reinforcement contents of 25 wt % and 75 wt %. For these composites, the matrix consisted of a mixture of Landy PL-1000 and Landy PL-3000 in a 1:1 ratio, since the variety Landy PL-2000 production was halted during the course of this study.

Additional thicker specimens were fabricated for Izod impact strength test and heat deflection temperature measurement. Nanocomposites with reinforcing phase content of 50 wt % with different ChNF to MFC ratios of 4:1, 3:2, 1:1, 2:3, 1:4, and 0:1 were prepared. The ChNF-MFC-PLA aqueous suspensions were prepared following the already described method and using Landy PL-1000 and Landy PL-3000 1:1 mixture. Suspensions were vacuum filtered through Buchner funnel and filter paper Advantec 101 (Toyo Roshi Kaisha, Ltd.) with 270 mm in diameter. Since the retentates were too thin, an additional step was necessary to mold thicker pieces. The retentates were released from the filter paper and put inside a circular form 115 mm in diameter with a meshed bottom covered with filter paper and molded by placing a 3.5 kg weight on top of it for one hour. Next the molded cake was oven dried at 70 °C for 48 h and at 105 °C for another 24 h. Dried cakes were cut into 10 mm by 80 mm pieces, further dried at 105 °C for one hour and compression molded at 190 °C and 10 MPa for 20 min.

2.3. Tensile Test

Specimens with dimensions of 10 mm by 80 mm were subjected to tensile test using an Instron 5567 (Instron Corp., Norwood, MA, USA) universal materials testing machine equipped with a 5 kN load cell, at a strain rate of 1 mm/min and the gage length set to 30 mm. To prevent damage at the gripping points, the ends of each specimen had carton paper tabs glued at both sides and clasped with serrated chucks. As the specimens were ribbon shaped and the failure would occur at different places, the widths and thicknesses were measured at equally spaced points along the length. The resulting cross sectional areas corresponding to the actual fracture sites measured before fracture were considered to calculate the tensile modulus and strength.

2.4. Heat Deflection Temperature (HDT)

The deflection temperature of nanocomposites was measured following the Japanese Industrial Standards JIS K7191-3 under a load of 0.45 MPa (Method B) and 1.8 MPa (Method A). Specimen dimensions were 80 mm in length, 10 mm in width, and 4 mm in thickness.

2.5. Izod Impact Strength Test

Impact resistance of nanocomposites was measured by an Izod impact tester (No. 158, Yasuda Seiki Seisakusho, Ltd., Hyogo, Japan). Notched specimens 80 ± 2 mm long, 4.0 ± 0.2 mm thick, 10.0 ± 0.2 mm wide with remaining width of 8.0 ± 0.2 mm at the notch, were tested according to the Japanese Industrial Standards JIS K7110.

2.6. X-ray Computed Tomography

The 3D imaging of samples were obtained by a high resolution desk-top micro-CT SKY Scan 1172 (Bruker-Micro CT, Kontich, Belgium).

3. Results and Discussion

The results of tensile test of the thin ChNF-MFC-PLA nanocomposites are shown in Figure 1. It depicts nanocomposites containing 50 wt % nanofibers but with differing ChNF to MFC ratios. Among the nanocomposites with varying ChNF to MFC compositions, there is a clear predominance of the ChNF-MFC mixed nanocomposites over those reinforced solely either with ChNF or MFC. In this 50 wt % nanofiber load case, the equal amounts of chitin and cellulose (ChNF to MFC ratio of 1:1) produced the best tensile property results. Although it seems counterintuitive, the phenomenon might be explained in terms of the number of hydroxyl groups present in chitin and cellulose. Cellulose molecule has three hydroxyl groups attached to each glucose ring, whereas chitin retains only two as the C-2 position is occupied by an acetamido group, making chitin less hydrophilic than cellulose. At the higher MFC content end of the ChNF-MFC composition spectrum, the percolation of cellulose nanofibers forms a stiff network interconnected by hydrogen bonds that confers much of the strength to the composites. On the other extreme containing more chitin, the more hydrophobic character relative to cellulose makes chitin more compatible with the hydrophobic PLA, with the percolated network playing a lesser role on strength. However, when chitin and cellulose were combined, both percolation of cellulose and better affinity of chitin with the PLA matrix seem to have worked in concert to enhance the mechanical properties of the composites. This hypothesis is based on the results of a previous study [34] in which ChNF-PLA composites were stronger than MFC-PLA composites at lower nanofiber contents, while MFC-PLA composites were stronger at higher nanofiber loadings. In order to verify this assumption, nanocomposites with different reinforcing nanofiber contents were later produced and tested. For lesser reinforcing nanofiber containing composites, the percolated network of MFC would be weaker while the ChNF-PLA interaction would be dominant, resulting in a shift of the mechanical property peak to the ChNF-rich side of composites. On the other hand, composites containing higher amounts of nanofibers would have the peak shifted towards the MFC-rich composites due to the MFC percolation controlling the mechanical properties.

At the time of fabrication of a new batch of composites, the production of the colloidal suspension type Landy PL-2000 had been discontinued by the manufacturer. Unable to purchase the same product, other two varieties Landy PL-1000 and Landy PL-3000 still in production were purchased and mixed in a 1 to 1 ratio, to replace PL-2000. The mixture was not intended to serve as an equivalent substitute for Landy PL-2000, as the mechanical properties of the composites with the new PLA matrix decreased relative to the previous one. However, the measurements are still valid for comparative purposes concerning variations in ChNF to MFC ratio. The results of tensile test are presented in Figure 2. As predicted, the composites containing 75 wt % nanofibers had the peak of strength (ChNF to MFC ratio of 2:3) shifted towards higher MFC content. This means that at higher nanofiber content, the contribution of MFC to the mechanical properties of composites is dominant, by the formation of a percolated network that promotes stiffness and strength. Looking at the composites with low nanofiber content of 25 wt % in Figure 3, even though it is subtle, the highest strength is displaced to the side with higher ChNF content. In this case, the percolated framework of MFC becomes less relevant to the strength of composites, and the affinity of ChNF with PLA matrix becomes determinant to the

properties of the composite. Once again, the combination of ChNF and MFC reinforcing nanofibers delivered higher strength than ChNF or MFC reinforcements alone. The data depicted in Figures 1–3 are summarized in Figure 4.

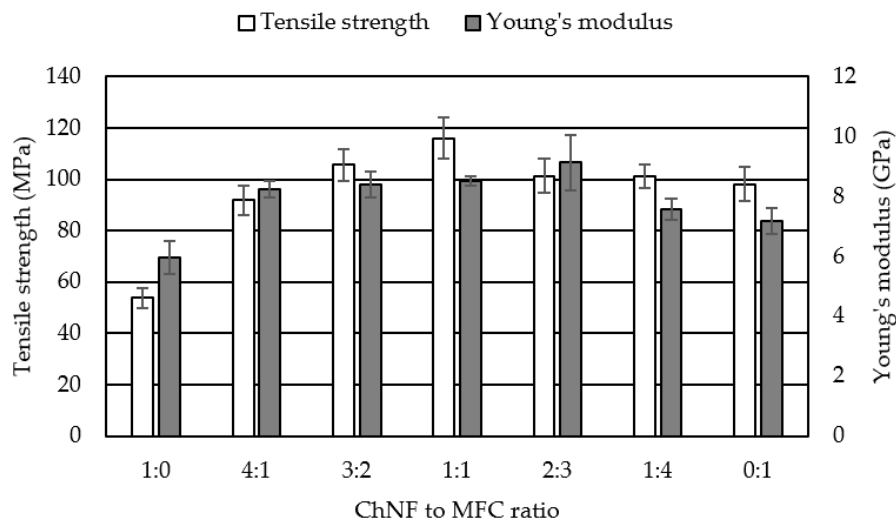


Figure 1. Tensile strength and Young’s modulus of nanocomposites with 50 wt % reinforcing phase with varying chitin nanofiber (ChNF) to microfibrillated cellulose (MFC) ratios.

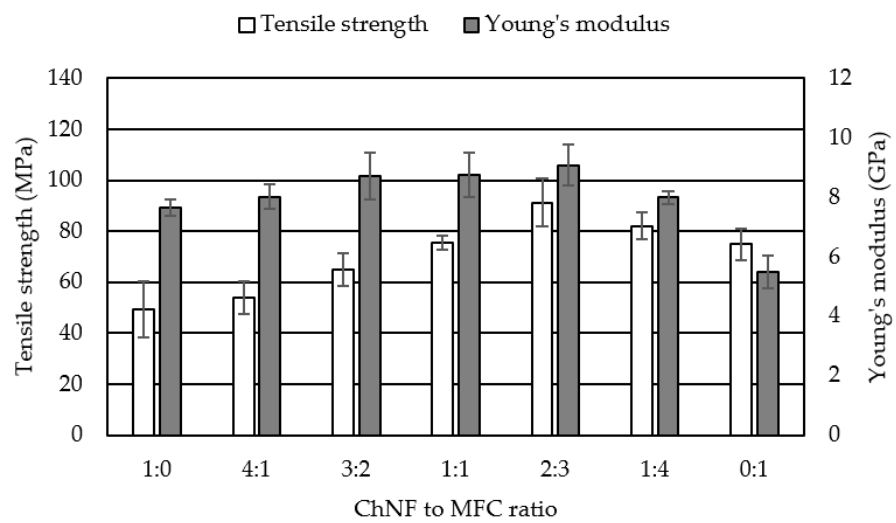


Figure 2. Tensile strength and Young’s modulus of nanocomposites with 75 wt % reinforcing phase with varying chitin nanofiber (ChNF) to microfibrillated cellulose (MFC) ratios.

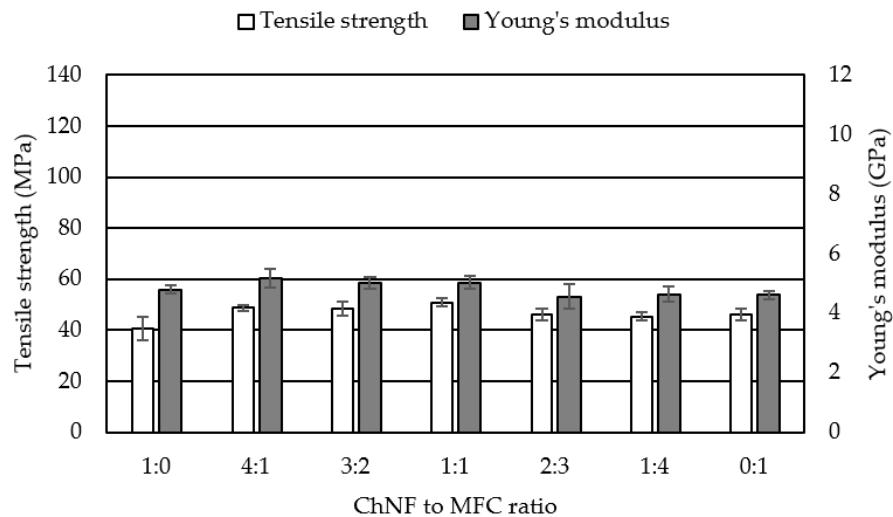


Figure 3. Tensile strength and Young’s modulus of nanocomposites with 25 wt % reinforcing phase with varying chitin nanofiber (ChNF) to microfibrillated cellulose (MFC) ratios.

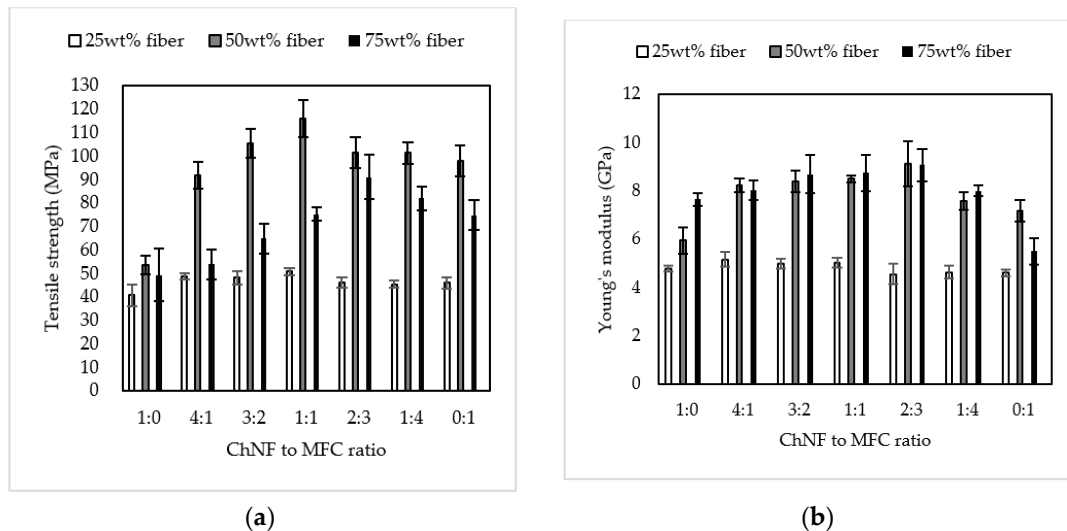


Figure 4. Plots summarizing the data of all composites (reinforcement fraction of 25 wt %, 50 wt %, and 75 wt %) as a function of varying chitin nanofiber (ChNF) to microfibrillated cellulose (MFC) ratios: (a) tensile strength; (b) tensile modulus.

To evaluate the mechanical properties of composites at higher temperatures, the heat deflection temperature (HDT) was measured. As shown in Figure 5, by Method B of HDT measurement, all nanocomposites warped in the direction opposite to the application of the load of 0.45 MPa as the temperature was increased. This phenomenon was likely caused by a ChNF-MFC distribution gradient along the thickness of the specimens. Due to the fabrication process, reinforcing fibrils tend to concentrate on the bottom side of the specimens during dewatering, effectively restraining the thermal expansion of the PLA matrix at one side of the composite. As the temperature approached 200 °C, the only nanocomposite to deflect by 0.34 mm was PLA containing solely MFC, with an HDT of 191 °C. As the remaining nanocomposites did not show any deflection up to 200 °C, they were subjected to a higher load of 1.8 MPa following Method A of measurement, and the results are depicted in Figure 6. The HDT for nanocomposites containing ChNF to MFC ratios of 1:4, 1:1, and 4:1 were 60, 75, and 96 °C respectively, increasing with increments in ChNF content. This is attributed to the intermediate hydrophilic ChNF that delivered a better bond between the hydrophobic PLA and hydrophilic MFC, delivering good stress transfer even at high temperature.

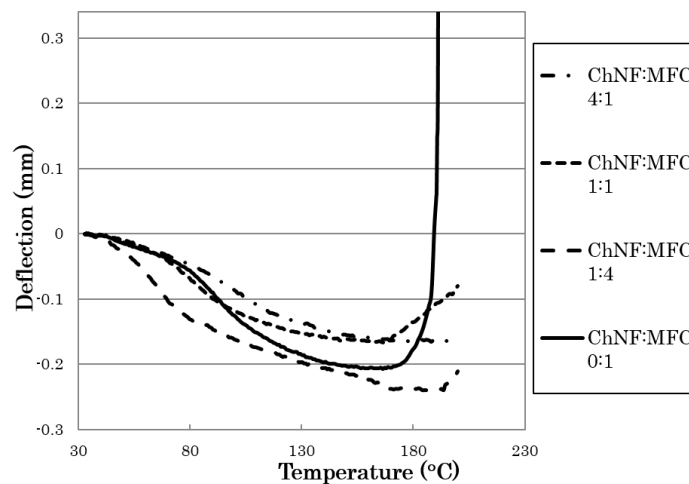


Figure 5. Heat deflection temperature (HDT) curves by the Method B (load of 0.45 MPa) of nanocomposites with 50 wt % reinforcing phase with varying chitin nanofiber (ChNF) to microfibrillated cellulose (MFC) ratios.

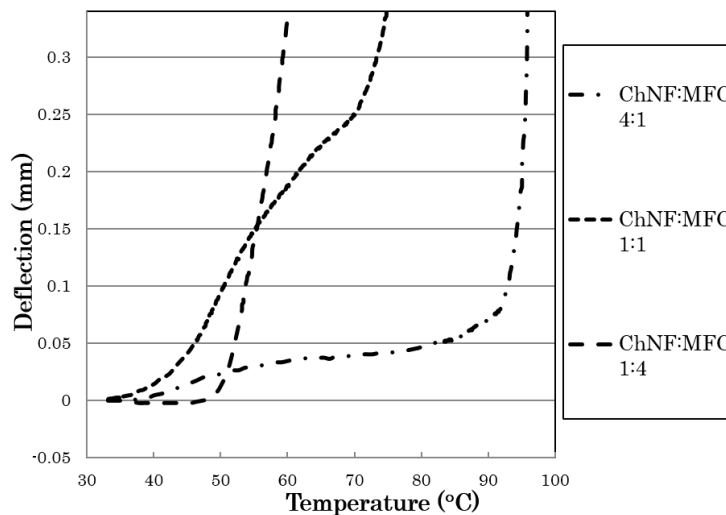


Figure 6. Heat deflection temperature (HDT) curves by the Method A (load of 1.8 MPa) of nanocomposites with 50 wt % reinforcing phase with varying chitin nanofiber (ChNF) to microfibrillated cellulose (MFC) ratios.

Izod impact test results are shown in Figure 7. The ChNF-MFC nanocomposites containing 50 wt % nanofibers delivered impact resistance higher than neat PLA and similar to that of MFC-reinforced composite, with the ChNF to MFC ratio 3:2 composite showing slightly higher mean impact strength. However, considering the whole series of measured values and the size of the error intervals, there were no significant differences in impact resistance when chitin and cellulose were combined. Although a clear change was not observed when reinforced with ChNF-MFC mixture or MFC only, it is an indication that the combination of cellulose and chitin nanofibers had no negative effect on the impact resistance of composites, corroborating the results of enhanced impact strength obtained in chitin nanofiber-reinforced PLA reported by Li et al. [14]. According to their reasoning, the impact strength is obtained owing to uniformly dispersed nanofibers forming a network that absorbs large amounts of energy during the fracture. The state of nanofibers dispersion of the composites in the present study is shown by X-ray tomography images in Figure 8. It is difficult to state that dispersion was achieved at nano-scale since the resolution is limited to a few micrometers, but agglomerations at micro-scale can be observed. There are apparent differences in dispersion

depending on the ChNF to MFC ratio, but they did not significantly affect the impact resistance of the nanocomposites.

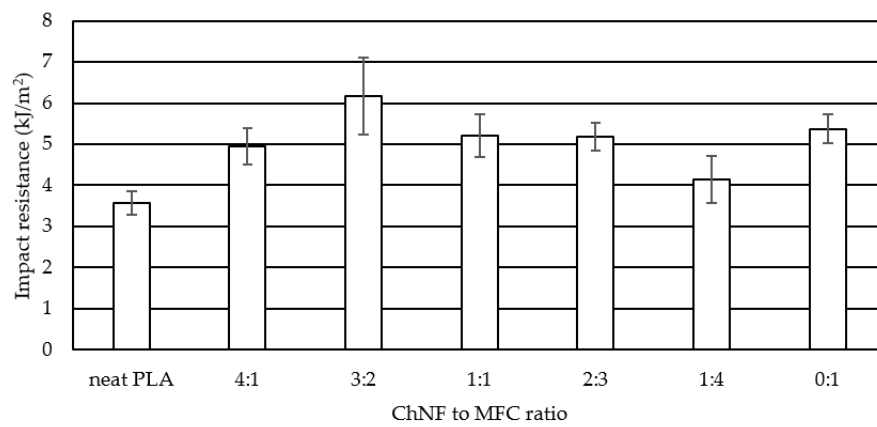


Figure 7. Notched impact resistance of nanocomposites with 50 wt % reinforcing phase with varying chitin nanofiber (ChNF) to microfibrillated cellulose (MFC) ratios.

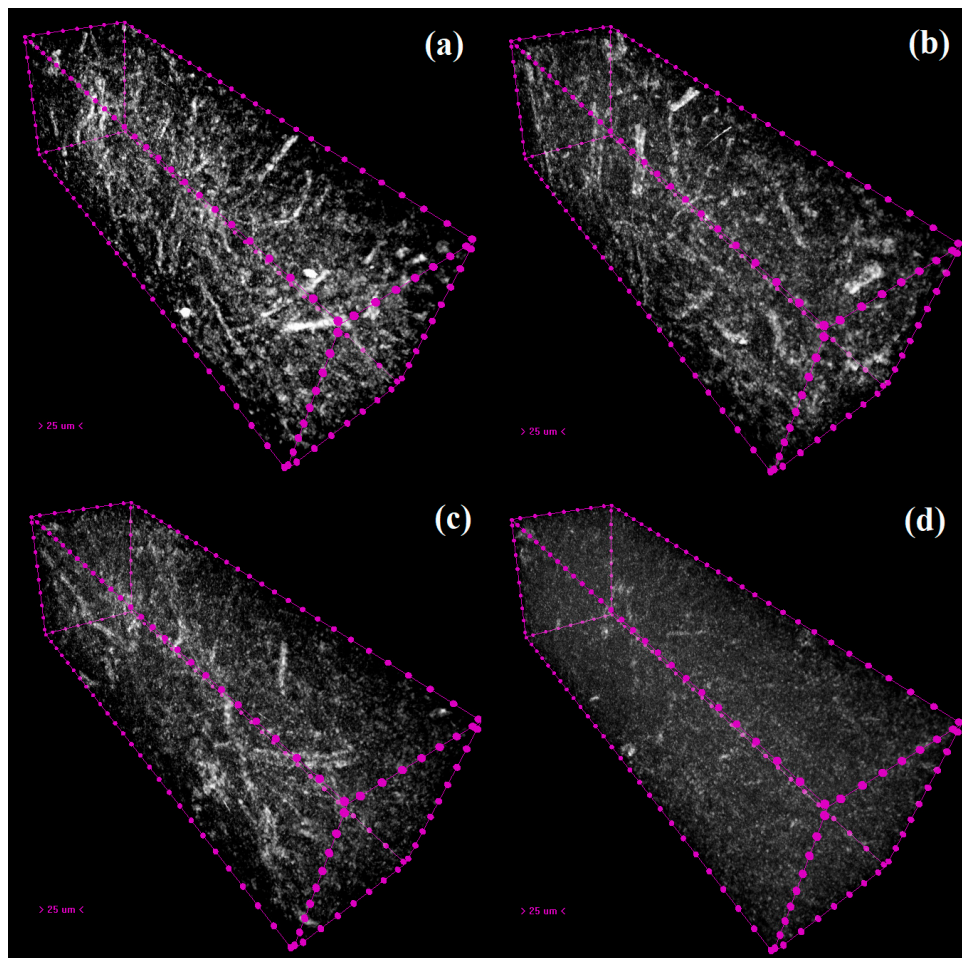


Figure 8. X-ray computed tomography of nanocomposites with 50 wt % reinforcing phase with varying chitin nanofiber (ChNF) to microfibrillated cellulose (MFC) ratios: (a) 4:1; (b) 1:1; (c) 1:4; (d) 0:1 (all MFC-reinforced). Due to the resolution limitation, the ChNF comprised of sub-micrometer diameter elements is not observable, whereas the portion of MFC larger than a few micrometers is seen as white spots.

Considering all the mechanical properties evaluated for the nanocomposites, it was revealed that the combination of ChNF and MFC to reinforce PLA produces higher mechanical performance than PLA reinforced with ChNF or MFC separately. Even though each type of reinforcing nanofiber provides significant reinforcement to PLA, there is some kind of synergistic effect that enhances the reinforcement when mixed. The combination of hydrophilic MFC, less hydrophilic ChNF and hydrophobic PLA composite resembles the composition of plant fibers. The cell wall of plant fibers is a biocomposite made of a framework of cellulose embedded in hydrophobic lignin matrix, in addition to compounds called hemicelluloses. Hemicelluloses have a hydrophilic character in between cellulose and lignin, working as a compatibilizer to hydrophilic cellulose and hydrophobic lignin. In that sense, the ChNF-MFC-PLA can be seen as a biomimetic nanocomposite system. This study revealed that not only is it possible to reinforce hydrophobic resins with either cellulose or chitin nanofibers, but the combination of these nanofibers can further improve the reinforcing effect. Even though the extraction of cellulose nanofibers is difficult and costly, the extraction of chitin nanofibers is relatively easier and therefore less costly [35]. The proper combination of these two nanofibers may bring a method of reducing the production cost of cellulose-based nanocomposites while enhancing their mechanical properties.

4. Conclusions

This study assessed the effect of the combination of chitin and cellulose nanofibers on the reinforcement of polylactic acid composites fabricated by a papermaking process. The following conclusions can be summarized.

1. The tensile strength, tensile modulus, and heat deflection temperature of chitin-cellulose nanocomposites were increased relative to their counterparts reinforced only by chitin nanofibers or only by cellulose nanofibers;
2. The reinforcing mechanism of chitin-cellulose nanofibers is presently not fully understood and requires additional studies;
3. The chitin-cellulose reinforcement increases the impact resistance of PLA with values on a par with cellulose nanofiber-reinforced PLA;
4. The overall cost of nanocomposites could potentially be reduced by addition of chitin nanofibers as they are easier to extract than cellulose nanofibers.

Author Contributions: A.N.N. and H.T. conceived and designed the experiments; S.K. performed the experiments; A.N.N., S.K., and H.T. analyzed the data; A.N.N. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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