

# Fabrication of Chitin Nanofiber-Reinforced Poly(lactic Acid) Nanocomposites by an Environmentally Friendly Process

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Poly(lactic acid) (PLA) reinforced with chitin nanofibers was produced from a mixture of a colloidal suspension of PLA particles with chitin nanofiber suspension. The dispersion medium was solely water, which was removed by filtration and drying. Nanocomposites were obtained by compression molding of the filtrates. Static tensile test and dynamic mechanical analysis were performed to evaluate the reinforcement as a function of nanofiber content. Chitin nanofibers delivered reinforcement similar to cellulose nanofibers, being especially effective at up to 70 wt% fiber load. The ultimate tensile modulus and strength reached 7.7 GPa and 110 MPa, respectively, at a nanofiber content of 70 wt%.

**Keywords:** Chitin, Nanofiber, Poly(lactic Acid), Nanocomposite.

## 1. INTRODUCTION

Chitin is one of the most abundant polysaccharides in nature, found in the form of nanofibers in the hard biocomposite material forming the protective shell of marine crustaceans, insects and in the cell walls of many filamentous fungi. The molecular structure of chitin is identical to that of cellulose, except for a hydroxyl group at every C-2 position of glucopyranose rings, which are replaced by an acetamido group as depicted in Figure 1. In natural circumstances, cellulose nanofibers are found in more strength demanding applications than chitin nanofibers. Cellulose makes up the framework of trees that have to resist stresses due to their own weight, height, and to the elements of weather, while crustaceans rely on chitin-based exoskeletons to support and protect their smaller bodies. Therefore, the extraction of chitin nanofibers is relatively easier compared to the extraction of cellulose nanofibers, even though both are embedded in matrix substances making complex composites.

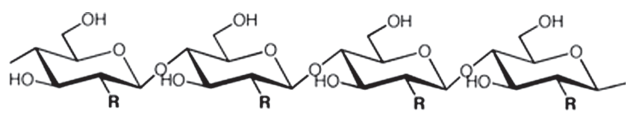
The hierarchical structure of chitin-based biocomposites consists of crystalline arrangements of 18–25 chitin

molecular chains wrapped by proteins, forming nanofibrils of about 2 to 5 nm in diameter and 300 nm in length. These chitin-protein fibrils are clustered in 50 to 300 nm fibers. These in turn form a planar woven branched network, in which the space between the fibers is filled with proteins and minerals, mostly CaCO<sub>3</sub> crystallites. The planes are stacked as a twisted plywood known as Bouligand pattern.<sup>1–4</sup> A mechanical process to extract chitin nanofibers was developed by Ifuku et al.<sup>5–8</sup> by dispersing purified chitin in water and passing the slurry through an ultra-fine friction grinder. The chitin slurry is passed through a tiny gap between a stator and rotor grindstones, where the material is subjected to shear forces and hydrostatic pressure that separates the bundles of fibrils into individual nanofibers. The pH of the slurry is adjusted to about 3 by addition of acetic acid, so that the cationization of the amino groups on the surface of chitin nanofibers would cause electrostatic repulsion and facilitate individualization, as described by Fan et al.<sup>9</sup> The grinded material after only a single pass forms a gel, due to the exposure of a greatly expanded surface area of individualized 10 to 20 nm in diameter nanofibers.

This highly versatile nanofiber extraction process has advantages in terms of transportation and storage since

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Cellulose: R = OH

Chitin: R = NHAc

**Fig. 1.** Structural formulas of cellulose and chitin.

weight and volume of semi-processed materials can be reduced by drying, and fibrillation can be accomplished after re-dispersion in water, which is not possible with cellulose. Because of the hydroxyl groups on the surface of the nanofibers, drying produces strong hydrogen bonds that impede proper nanofiber separation. But the electrostatic repulsive forces on the surface of chitin nanofibers in acidic medium overcomes this obstacle and even facilitates nanofibrillation, resulting in less intensive mechanical treatment that minimizes damage to the extracted nanofibers. These chitin nanofibers, among other applications, can be used as reinforcement of biopolymers to make environmentally friendly nanocomposites.

Poly(lactic acid) (PLA) is a bio-plastic produced from renewable resources, being the first commodity biopolymer available. It is a thermoplastic and can be processed in most polymer processing equipment to make films, fibers, or even injection molded parts, and is present in consumer products like disposable plates and cups, packages, and clothes. PLA is produced from lactic acid obtained by fermentation of glucose or starch, and can be made flexible or rigid, it is inherently clear, and can accept fillers. Given the right triggers, PLA easily degrades in the environment by hydrolysis, and eventually completely converts into harmless water and carbon dioxide, which is equivalent to the amount fixed by the growth of plant feedstock. Another very attractive feature of PLA is the possibility of chemical recycling. The polymer can be hydrolyzed with water to obtain the constituent monomer lactic acid, purified, and re-polymerized to make new PLA.

The major obstacle to reinforce thermoplastic matrixes with nanofibers has been the difficulty in attaining good dispersion of hydrophilic hydroxyl group-rich elements in a hydrophobic matrix. In particular, compounding with melt polymer has shown limited success, and is also known to inhibit the formation of a percolated network of nanofibers resulting in reduced reinforcement.<sup>10,11</sup> Among the few successes, Jonoobi et al.<sup>12</sup> produced cellulose nanofiber-reinforced PLA by extrusion of a pre-mixed master batch, obtaining well dispersed nanofibers that resulted in improvements in tensile modulus and strength. Another approach to achieve good nanofiber dispersion was proposed by Larsson et al.<sup>13</sup> by mixing cellulose nanofibers with PLA particles emulsified in water.

This study presents the fabrication of chitin nanofiber-reinforced PLA composites by mixing a PLA colloid with an aqueous suspension of chitin nanofibers. The use of

water as the dispersion medium ensured proper nanofiber dispersion in the matrix, with the additional benefit of reduced environmental harm. The reinforcing capability of chitin nanofibers showed potential analogous to cellulose nanofibers, indicating that chitin would be an additional source of nanofibers for eco-friendly materials.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

The chitin nanofibers were extracted from purified chitin powder (Nacalai Tesque) by a process described elsewhere.<sup>5</sup> The polylactic acid consisted of aqueous colloidal suspension of 2  $\mu\text{m}$  PLA particles (Landy PL-2000), produced by Miyoshi Oil and Fat Co., Ltd.

### 2.2. Composite Fabrication

A proper amount of chitin nanofiber slurry at 1 wt% nanofiber content was diluted with distilled water until attaining a volume of 300 ml and was stirred for 1 hour. Next, the PLA emulsion was added and stirring was maintained for another 2 hours. The total weight in dry basis of chitin nanofibers and PLA was set to be 1 g, and the nanofiber to PLA ratio was adjusted to deliver the desired nanofiber content to the final nanocomposites. The suspension was then vacuum filtered through a polytetrafluoroethylene membrane filter 90 mm in diameter (Millipore, pore size: 0.2  $\mu\text{m}$ ) and filtrates were dried at 110  $^{\circ}\text{C}$  in a convection oven for 5 hours. Dry sheets were additionally dried at 110  $^{\circ}\text{C}$  for 1 hour prior to compression molding to completely remove moisture. Finally the sheets were hot pressed at 180  $^{\circ}\text{C}$  and 2 MPa for 3 minutes to obtain the nanocomposites.

### 2.3. Scanning Electron Microscopy (SEM)

Chitin nanofiber/PLA filtrate was examined using a field emission scanning electron microscope, model JSM-6701F (JEOL Ltd.). The accelerating voltage was set to 3 kV, and samples were coated with platinum to avoid specimen charging. The thickness of the coating was approximately 2 nm.

### 2.4. Tensile Test

Samples were cut into rectangular pieces 10 mm wide and 50 mm long and subjected to tensile test in a universal material testing machine Shimadzu Autograph AGS-X at a strain rate of 1 mm/min. To prevent damage at the gripping points, the ends of each specimen were covered with aluminum and clasped with serrated chucks. The widths and thicknesses were measured at different points spaced 5 mm from each other along the specimens. Since the specimens were not hourglass-shaped but ribbon-shaped,

the cross-sectional areas corresponding to the actual fracture sites were considered to calculate the tensile modulus and strength. The specimen gage lengths were measured with a caliper for each sample upon gripping.

## 2.5. Dynamic Mechanical Analysis (DMA)

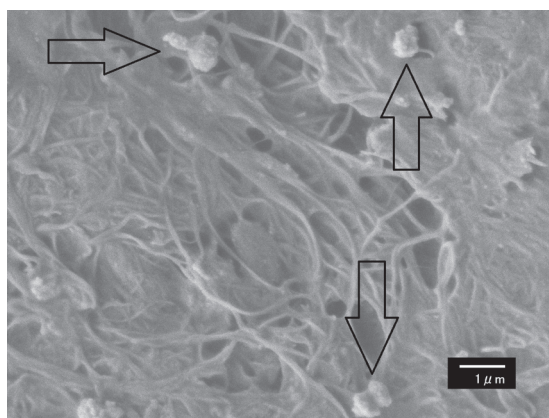
Dynamic mechanical properties were measured by a TA Instruments Q800 by the force vibration method in tensile mode. Samples about 0.15 mm thick were cut into approximately 6 mm by 40 mm rectangular pieces. Measurements were performed at a heating rate of 3 °C/min, with the gage length set to 25 mm, a preload of 0.01 N, and at a frequency of 1 Hz.

## 3. RESULTS AND DISCUSSION

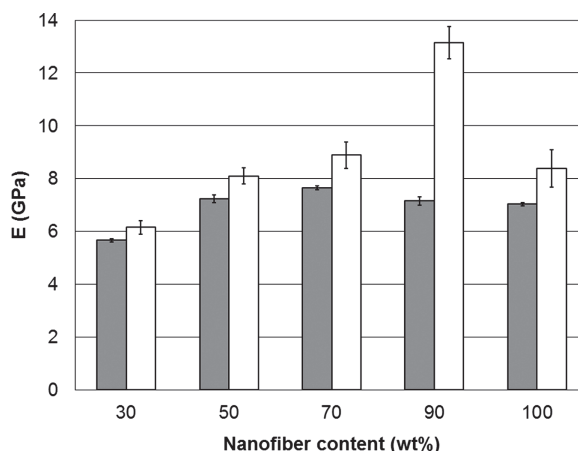
A typical SEM image on Figure 2 illustrates the state of dispersion of chitin nanofibers and PLA particles. The observation was performed in a dried sheet after filtration of the mixture of PLA colloid and nanofiber aqueous suspension. The chitin nanofibers are seen as tiny fibrils with widths below 100 nm, while the whitish grains correspond to PLA particles. Apparently the PLA particles are individualized as agglomerations were not observed.

The tensile modulus, strength, and strain at fracture of chitin nanofiber-reinforced PLA are shown in the form of bar graphs (gray bars) in Figures 3–5, respectively. For comparison purposes, the corresponding values of cellulose nanofiber-reinforced PLA from a previous study<sup>14</sup> are also shown (white bars). These cellulose nanofibers were mixed with PLA in the form of fibers, instead of PLA particles emulsion, but were similarly dispersed in water, filtered and hot pressed.

The tensile moduli plotted as a function of nanofiber content are depicted in Figure 3. There is an increase of modulus of chitin nanocomposites with nanofiber load up to 50 wt%, and from that point the values plateau at about 7 GPa. In the case of cellulose nanocomposites,<sup>14</sup> the trend

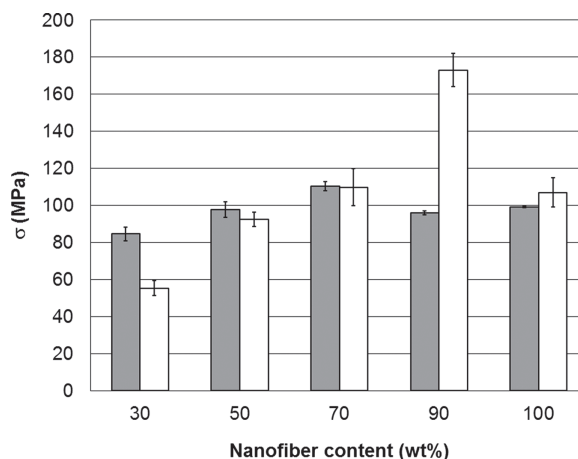


**Fig. 2.** Scanning electron micrograph of a chitin nanofiber/PLA filtrate. Arrows indicate PLA particles.

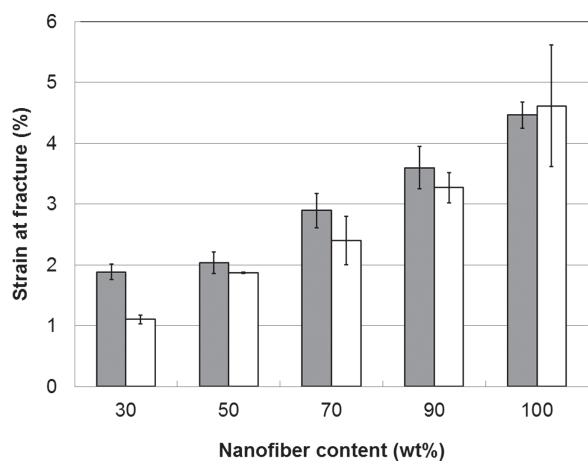


**Fig. 3.** Tensile modulus versus nanofiber content of chitin nanocomposites (gray bars) and cellulose nanocomposites (white bars).

was practically linear all the way up to a nanofiber content of 90 wt%, where the modulus raised to around 13 GPa. However, if compared in the range below 70 wt%, the values are very similar to those of chitin nanocomposites. This is intriguing considering that the modulus of the crystalline portions of chitin is reported to be 41 GPa,<sup>15</sup> almost a third of the 138 GPa measured for cellulose crystallites.<sup>16</sup> A possible explanation is that the less hydrophilic nature of chitin, containing fewer hydroxyl groups than cellulose, makes it more compatible with the hydrophobic PLA matrix. At the same time, lesser hydrogen bonds result in weaker interactions between the chitin nanofibers, producing less rigid percolated chitin nanofibers than cellulose nanofibers. For fibrous composites containing more nanofibers than resin, the percolation of nanofibers connected by hydrogen bonds plays a significant role in contributing to the stiffness of the composite, and it might be responsible for the lower modulus of chitin nanocomposites relative to cellulose counterparts at 90 wt% nanofiber content. One would object the direct comparison of the



**Fig. 4.** Tensile strength versus nanofiber content of chitin nanocomposites (gray bars) and cellulose nanocomposites (white bars).



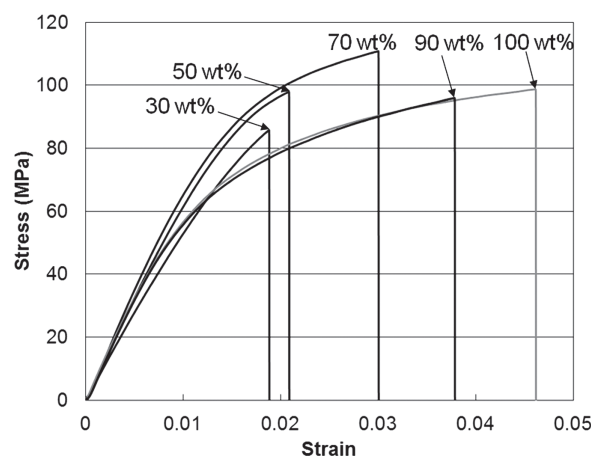
**Fig. 5.** Tensile strain versus nanofiber content of chitin nanocomposites (gray bars) and cellulose nanocomposites (white bars).

two composites since in the case of cellulose, nanofibers were mixed with pure PLA fibers prior to hot pressing, whereas chitin nanofibers were composed with PLA emulsion containing surfactants. However, a study describing cellulose nanofiber/PLA composites made from the same PLA emulsion (same manufacturer and product number) by Larsson et al.<sup>13</sup> delivered similar tensile modulus values at fiber contents below 50 wt%, suggesting that the role of the surfactant is not so relevant in this particular nanofiber load range.

A similar trend of leveling off above 50 wt% nanofiber load is observed for the tensile strength of chitin nanocomposites, as shown in Figure 4. Up to 70 wt% nanofiber content, chitin nanocomposites have similar strengths, if not higher than the cellulose-based ones. But again, at higher nanofiber contents, chitin delivered no further increase in strength as cellulose. Here, the less hydrophilic character seems to deliver better stress transfer between chitin nanofibers and PLA if compared to cellulose, especially at low nanofiber content (30 wt%), but at a high load of 90 wt%, chitin nanocomposite was no stronger than the 100 wt% nanofiber sheet, formed by a percolated structure attached exclusively by hydrogen bonds.

Nonetheless, the strain at fracture of chitin nanocomposites (Fig. 5) increased linearly with fiber content, showing slightly higher average values than cellulose nanocomposites at all nanofiber contents, except for the 100 wt% nanofiber sheet. The typical stress–strain curves of Figure 6 illustrate the tensile properties of composites at different chitin nanofiber loads.

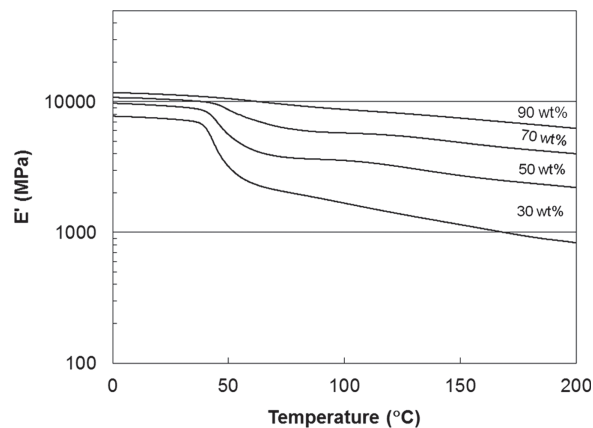
Apparently for chitin nanofibers, there is a compromise between the better compatibility with the matrix and the weaker interaction between nanofibers, both resulting from the lesser number of hydroxyl groups compared to cellulose. The former resulted in stronger nanocomposites than cellulose at low nanofiber load (30 wt%), where percolation is less predominant, whereas the latter resulted in weaker composites than the cellulose nanofiber



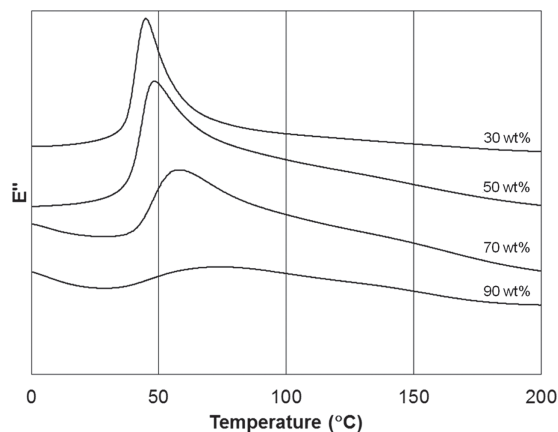
**Fig. 6.** Typical tensile stress–strain curves of chitin nanofiber-reinforced PLA. Percentages indicate nanofiber weight content.

counterparts at high nanofiber content (90 wt%). However, in between these values, the tensile properties were similar. Due to better compatibility with the matrix, chitin nanofibers show better reinforcing effects at lower nanofiber contents, while cellulose nanofibers exhibit better performance at higher nanofiber loads.

In addition to quasi-static tensile measurements, dynamic mechanical analysis (DMA) was performed. The storage moduli of chitin nanocomposites with different nanofiber contents as a function of temperature are shown in Figure 7. DMA confirms the increase in modulus from the tensile test, the dynamic modulus of the rubbery plateau also increases with chitin nanofiber content. The onset of modulus drop close to the glass transition temperature ( $T_g$ ), shifts towards higher temperatures as well. The loss modulus curves in Figure 8 show that the peak corresponding to  $T_g$  decreases in intensity, and is displaced to higher temperatures as the fiber content increases, from 44.2 °C at 30 wt%, to 70.4 °C at 90 wt% nanofiber load. This is an indication of a good interaction between the chitin nanofibers with the PLA matrix, reducing the



**Fig. 7.** Storage moduli as a function of temperature of chitin nanofiber-reinforced PLA. Percentages indicate nanofiber weight content.



**Fig. 8.** Loss moduli as a function of temperature of chitin nanofiber-reinforced PLA. Percentages indicate nanofiber weight content.

mobility of the PLA molecular chains. This phenomenon was not observed in the case of PLA reinforced with cellulose nanofibers,<sup>14</sup> but it is in accordance to DMA measurements of cellulose nanofiber-reinforced PLA reported by Larsson et al.<sup>13</sup> made from the same PLA colloidal suspension used in the present study. Jonoobi et al.<sup>12</sup> also detected the shift in  $T_g$  to higher temperatures in PLA reinforced with cellulose nanofibers at fiber contents of 5 wt% and lower.

#### 4. CONCLUSION

The present study described an environmentally benign method to homogeneously disperse chitin nanofibers in a PLA matrix by mixing aqueous suspensions of both phases. Tensile modulus and strength increased up to 70 wt% nanofiber content, topping at 7.7 GPa and 110 MPa, respectively, while strain at fracture increased all the way up to 90 wt% nanofiber load. Chitin nanofiber reinforcement is particularly effective at fiber contents below 50 wt% compared to cellulose nanofibers. The glass

transition temperature was shifted to higher temperatures as the fewer number of hydroxyl groups on the chitin nanofiber surface makes it less hydrophilic than cellulose, resulting in better compatibility with the hydrophobic PLA matrix. Chitin nanofibers have the potential to reinforce plastics as efficiently as cellulose nanofibers, with the advantages of being easier to extract and less hygroscopic. Chitin is an additional sustainable source of nanofibers with promising use in environmentally friendly materials.

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