

Preparation and Characterization of Electrospun PLA/Nanocrystalline Cellulose-Based Composites

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ABSTRACT: Biodegradable nanocomposites of Nanocrystalline Cellulose (NCC) and electrospun poly-(lactic acid) were prepared via a new mixing technique. Dispersion of hydrophilic NCC in hydrophobic PLA was improved through aqueous mixing and freeze drying of perfectly suspended NCC with PLA nanofibers. Freeze drying produced aerogels with good mechanical integrity. The aerogels were further processed via hot pressing. Resulting composites displayed an improvement in mechanical properties, which was greatest at temperatures below the glass transition temperature of PLA. The optimum compositions were found to be in the 0.5–3% NCC (by weight) range. Experiments performed also showed that due to electrospinning, the crystallinity of the PLA slightly increased and this is accompanied by a decrease in its glass transition temperature. Furthermore, adding NCC to the electrospun PLA matrix did not alter the crystallinity of the final composite. The composites investigated proved their potential to be used in packaging and tissue engineering applications. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3345–3354, 2013

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INTRODUCTION

Cellulose is the most abundant polymer on earth and is obtained from renewable resources. The cellulose macromolecule is the principal structural element of the cell wall of many plants.¹ Cellulose, like most polymers, consists of crystalline and amorphous regions. As a result of subjecting cellulose fibers to acid hydrolysis, perfect cellulose nanocrystals are obtained which are rod-like in shape.² This product is known as cellulose nanocrystals and has high strength due to its dense and orderly crystalline structure. The value of Young's Modulus for a perfect crystal of native cellulose, as obtained from various literature, has been calculated to be between 130 and 250 GPa, while the tensile strength of the same is estimated to lie between 0.8 and 10 GPa.³ This therefore makes it an ideal material to reinforce polymers. What is more, working on the nanoscale provides many benefits, especially where composites are concerned, since the large aspect ratio of the nanocrystalline cellulose (NCC) ensures a large interfacial area between the fiber and matrix constituents. For example, the NCC of tunicate has an aspect ratio of 65.⁴

Poly-(lactic acid) (PLA) is obtained completely from renewable resources such as corn and sugar beets,⁵ and not from oil-based materials unlike other polymers. Among the aliphatic polyesters, it is considered to be a material with much potential due to its outstanding biodegradability, high tensile strength, and good

compatibility.⁶ However, despite all these advantages, PLA has the drawbacks of having a low toughness and therefore cannot be processed as extensively as would be required for various applications.⁷ Since PLA is such an eco-friendly material, it is important from the perspective of sustainability that efforts be made to use it in a host of applications, many of which would have high mechanical strength requirements. Such efforts include producing nanocomposites where, for example, nanoclay or NCC is used to reinforce the PLA and thus improve its properties.

This article addresses the development of a material, consisting of electrospun PLA and NCC, that may potentially be used as a renewable alternative in both tissue engineering and packaging. This material must therefore be obtained from renewable sources and be biodegradable and biocompatible, and must have good mechanical and barrier properties and porosity/density. The first three characteristics are already inherent in the constituent materials being considered in this case, and the mechanical properties will be investigated as part of this article.

Electrospinning is an electrostatic technique employed in the production of fibers with large aspect ratios.⁸ It has the possibility of being used in everything from protective clothing to optical electronics,⁸ though current research focuses on using it in the areas of healthcare and biotechnology. Electrospinning depends on many parameters which determine the morphology

and diameter of the final electrospun fibers. Examples of such parameters are the applied voltage, the type of collector, and the concentration and viscosity of the solution of the polymer from which the fibers are being made.

Composites which use NCC as the reinforcement phase are typically prepared by either melt compounding or solution casting.⁹ Various studies have investigated the properties of such nanocomposites prepared by melt compounding^{10–13} or solution casting.^{13–17} Composites consisting of NCC and PLA are known to have poor dispersion of the filler in the matrix, as will be discussed later in this article, and therefore various studies have addressed how the dispersion of the NCC in the PLA can be improved by different strategies such as by treating the surface of the NCC before mixing it with the PLA^{18,19} or by adding a further component to the composites.²⁰

Potential application areas for the composites addressed in this article, in addition to packaging and tissue engineering, include agricultural equipment, marine structures, and even applications in the automotive industry.²¹ Moreover, the composites may be used in the fabrication of textiles. Other potential industrial and medical applications in which the composites could be used are in structural applications (as construction materials) and as an excipient for drug delivery.²²

MATERIALS AND METHODS

Materials

Filter paper purchased from Whatman® was grinded and used as source of cotton cellulose (CC). Sulfuric Acid (H₂SO₄), 95–97%, Reagent Grade, was purchased from Scharlau. Acetone was purchased from Sigma-Aldrich and the PLA was Nature-Works Ingeo 4060D Sealant Grade PLA. PLA 4060D has about 11–13% D-lactide content and a density of 1.24 g/cc.²³ Not only is it easy to process but it is also amorphous in nature. This is beneficial since in composites made of this type of PLA and cellulose, assessment of the reinforcing performance of the NCC need not consider the changed crystalline structure of the polymer. This would not be true for semi-crystalline polymers, whose crystallization behavior may change due to the addition of nanofillers.²⁴

Nanocrystalline Cellulose (NCC) Preparation

The following procedure used in the production of NCC is employed as a result of previous studies performed by the authors which indicated that such values for the experimental parameters were optimum for NCC production.²⁵ 10 g of CC was mixed with 91 mL of 66% (w/w) H₂SO₄ using the Varian Dissolution System (VK7010) at 25°C with 250 rpm agitation. After 180 minutes, 187 mL of 50% H₂SO₄ was added. Then the cellulose centrifugation was done, which was a two stage process. In the first stage, immediately following the hydrolysis, the cellulose suspension was centrifuged one time at 23°C using the Allegra™ 25R Centrifuge. The duration and speed of the centrifugation were ten minutes and 4700 rpm, respectively. After this, two layers were obtained as a product of the centrifugation: the NCC and the recovered cellulose layers. The NCC layer was diluted with chilled water to approximately four times its original volume. It was then covered with

parafilm and left to settle for about 24 hours so that a top liquid portion and a bottom solid portion were obtained. Much of the top portion liquid was then decanted which was followed by the second stage of the centrifugation. The centrifugation conditions were identical to those used in the first stage of centrifugation with the exception that the centrifugation was performed three times. The solid NCC material was collected at the end of the centrifugation runs and was dialyzed for three days until the pH was neutralized. The resultant suspension was weighed and then sonicated using the Hieschler Ultrasonic Processor UP400S for up to 7 minutes. After dialysis, the yield was calculated by withdrawing a known, small amount of the sample and obtaining its oven-dried weight with the help of the New Brunswick Scientific Innova 40 Incubator Shaker. The yield was calculated based on the solid product weight after drying, compared to the starting weight. The sample was also freeze-dried using the VirTis Wizard 2.0 Freeze Drier.

PLA Micro- and Nanofibers Preparation

10% (wt/v %) solution of PLA in Acetone was prepared by dissolving 100 g of PLA in 1000 mL of Acetone under continuous stirring at 45°C. The solution was electrospun to prepare the PLA micro- and nanofibers using the MECC (Mechanics Electronics Computer Corporation) NANON-01A electrospinning machine. The solution was contained in a 10 mL syringe whose needle tip (inner diameter = 0.84 mm) was 15.0 cm from the surface of a rotating drum (outer diameter = 20 cm and width = 22 cm), which was used as a collector (rotational speed = 50 rpm). The applied electrical potential was 25 kV. The feed rate was controlled at 2 mL/hour.

Preparation of PLA-NCC Composite Material

A specific amount of NCC solution, of 1.73% (wt %), was mixed with 10 g of electrospun PLA material to prepare various weight percentages of NCC (0%, 0.5%, 1%, 2%, 3%, and 5%). This was done by first cutting 10 g of the electrospun PLA sheet [the microstructure of which is shown in Figure 1(B)] into small pieces and then mixing these pieces with 125 mL of water. The resulting mixture was then grinded some more and then 75 mL of water was added to it along with the required amount of NCC solution, as per the NCC percentage composition being prepared. Next, the resulting mixture was mechanically homogenized for 15 minutes using the IKAT25 mechanical homogenizer, after which it was put for freeze drying in the VirTis Wizard 2.0 Freeze Drier. Freeze drying produced aerogels with good mechanical integrity.

In order to transform the composites into a form that could be tested for its mechanical properties, these aerogels were further processed via hot pressing. They were hot pressed with a force of 57 ± 4 N using a 1600W Black & Decker iron for about 15 seconds. The samples were sandwiched in between aluminum foil as the pressure was applied through the hand-held iron. The temperature of the iron was $145 \pm 3^\circ\text{C}$ as measured by a thermocouple, also sandwiched between the aluminum foil layers. Thus rigid films of the composites were obtained and these were cut into tensile test specimens (using the Ray-Ran

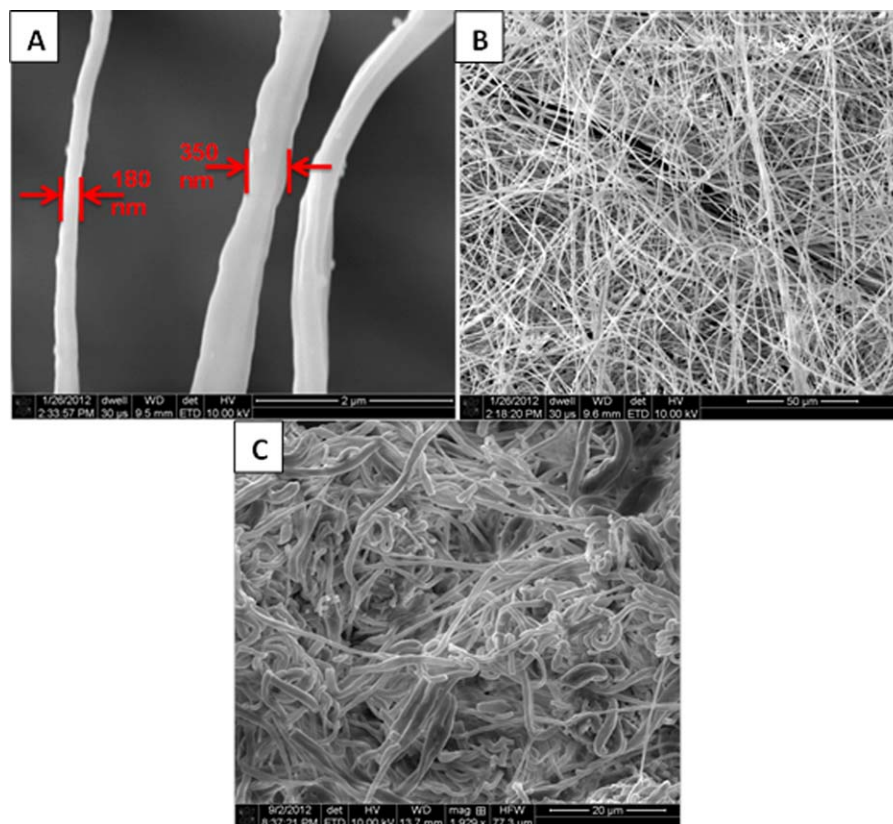


Figure 1. SEM images of (A) individual electrospun PLA fibers; (B) a network of electrospun PLA fibers; (C) 0% NCC electrospun PLA/NCC composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Hand Operated Test Sample Cutting Press) and manually cut into Dynamic Mechanical Analysis (DMA) bars.

In addition, for the sake of this paper, when the term “electrospun PLA/NCC composites” is used, it refers to all the samples experimented with, including those which had 0% NCC, and thus only PLA, but were processed in the same way that the other samples were. They are different from the “Neat PLA” referred to in the paper which is plain PLA that has not been electrospun and is the starting material used in the preparation of the electrospun PLA.

SEM Characterization of Electrospun PLA and PLA/NCC Composites

Various samples were mounted on a carbon tape. Their microstructure was imaged at low-vacuum mode using Quanta™ FEG 250 Scanning Electron Microscope by FEI.

Tensile Testing of Electrospun PLA/NCC Composites

Mechanical properties of the hot-pressed composites were determined from the stress–strain curves that were generated from the tensile tests. Five samples were tested at each composition of the prepared composites. During this testing, the material was subjected to a static load and pulled until it reached the fracture point and broke. The Instron 5966 machine was used for performing the tensile test at room temperature and 50% humidity and with a crosshead speed of 0.1 mm/min. The tensile test dumbbell-bar specimens used in this investigation have

9.80 mm gauge length, 3.30 mm width, and their thickness lies in the range of 1.00–1.20 mm for all samples.

Dynamic Mechanical Analysis of Electrospun PLA/NCC Composites

The mechanical characteristics of the hot-pressed composites were studied using a dynamic mechanical analyzer (DMA8000 from Perkin Elmer). Five samples were tested at each composition of the prepared composites. The DMA bars were clamped between the movable and stationary fixtures using the single cantilever setup, and then enclosed in a thermal chamber. The analyzer applied oscillations to the test sample while slowly moving through a temperature range of room temperature to 100°C.

Differential Scanning Calorimetry of Electrospun PLA/NCC Composites

The thermal characteristics of samples of the neat PLA and freeze-dried 0%, 1%, 3%, and 5% NCC electrospun PLA/NCC composites were studied using a differential scanning calorimeter (DSC4000 from Perkin Elmer). Three samples were tested at each of these compositions. 6–10 mg of the sample was heated from 20 to 200°C at a rate of 2°C/min in a nitrogen stream (20 mL/min).

Microstructure Analysis

X-ray diffractograms (XRD) data of the hot-pressed samples of the 0%, 1%, 3%, and 5% NCC electrospun PLA/NCC composites were obtained with an X-ray diffractometer (PANalytical,

X'Pert Pro). The XRD graphs thus acquired were used to compare the crystallinity of the composites.

RESULTS AND DISCUSSION

Characterization of Electrospun PLA Fibers

The microstructure of the electrospun PLA fibers was imaged using a SEM. The fibers had a diameter ranging from approximately 150–400 nm, as shown in Figure 1(A). Even smaller fiber sizes can be prepared using lower concentrations of the polymer solution. Figure 1(B) shows a network of these PLA fibers and shows their disorientations.

Structure Analysis of Electrospun PLA/NCC Composites

The technique used to develop the PLA/NCC composites of this research is novel due to the fact that the PLA used in it is electrospun as well as due to the fact that during the mixing procedure of the composite constituents, homogenization is used. Figure 1(B) shows a Scanning Electron Microscope (SEM) image of the electrospun PLA used as a starting material in the preparation of these composites. Figure 1(C) shows an SEM image of the electrospun PLA once it has been homogenized i.e. the hot-pressed 0% NCC composite sample. Due to this homogenization, the PLA is not completely dissolved i.e. it still retains the unique characteristics of the electrospun material even within the composite. As a result of this novel technique, the final composite obtained also has much structural integrity, as will be discussed in this paper. The electrospun PLA has the advantage of having a high porosity, as is clear from the SEM image of Figure 1(B), making it ideal for tissue engineering applications.²⁶ In fact, many studies have been done on electrospun PLA, particularly as a constituent of composite materials. These studies include Dong et al., Gui-Bo et al., Vicens, and the studies mentioned in Huang et al.^{27–30} This proves the great potential of electrospun PLA to be used in a large array of commercial applications.⁵

When fabricating composites, the dispersion of one constituent in the other is a matter of much importance as this has a significant impact on the determination of the overall mechanical properties of the composite material. Significant increases in the mechanical characteristics are possible if uniform dispersion of the reinforcement in the matrix is achieved along with good interfacial adhesion. One of the greatest challenges of developing nanofibers of cellulose for further applications as advanced materials is their tendency to form aggregates due to their hydrogen bonding.³¹ This non-uniform dispersion of the particles would cause stress concentration in the composite, making the composite material weaker and more susceptible to failure.¹³

Chemical compatibility between the filler and the matrix materials plays a critical role in the determination of the dispersion of the filler within the matrix and in the adhesion between both of these phases.³² Thus, when speaking about PLA and cellulose in particular, it must be considered how PLA is hydrophobic in nature.³³ In contrast, cellulose nanocrystals are hydrophilic due to the large number of hydroxyl groups³⁴ on their surface and this limits their dispersion in polymer matrices and hydrophobic solvents.³⁵ In other words, PLA is not soluble in water, while the cellulose nanocrystals, as a result of their strong hydrogen

bonding, cannot easily be used in systems that are not water based.¹⁶ Weak filler–matrix interactions are therefore present in PLA/cellulose composites since there is low interfacial compatibility between the non-polar matrix and the highly polar surface of the cellulose fibers.³² The difficulty of obtaining well-dispersed NCC in a PLA matrix is thus clear.³⁶

With respect to the composites developed as part of this research, NCC forms a perfect suspension in water due to surface sulfation induced through the hydrolysis process. Electrospinning is therefore employed in this research to enable the NCC used to reach its full potential, since by electrospinning there is an improvement in the dispersion of the NCC in the PLA matrix and in the alignment of these nanofibers within this matrix.³⁷ Though PLA does not dissolve in water, if it is scattered in water in the form of colloids which have sizes comparable to those of the cellulose nanofiber reinforcement,³⁴ good mixing of the two components can be achieved. The advantage of electrospinning the PLA is thus evident, since it reduces the PLA to nanodimensions. This is clear from Figure 2(A), which schematically compares between the microstructure of PLA/NCC composites and electrospun PLA/NCC composites. This schematic diagram is supported by SEM images: Figure 2(B) shows a 5% PLA/NCC composite (solution cast and without electrospinning of the PLA). The agglomerated NCC particles are evident. Figure 2(C) shows the hot-pressed 5% NCC composite sample studied as part of this research. In the SEM image, the electrospun PLA can be distinguished along with the NCC particles in a more homogeneous mixture, relative to Figure 2(B). Moreover, on comparison with the SEM image of Figure 1(C), the presence of NCC in the 5% NCC composite sample and not in the 0% NCC composite sample can be understood since Figure 2(C) shows the PLA fibers and the dispersed NCC. As a result of all these images, the improved dispersion interaction of the electrospun PLA with the NCC has been proved.

Figure 3 shows the freeze dried composite samples of two different NCC concentrations. The one on the left has 0% NCC while the one on the right has 1% NCC. It is apparent how adding the NCC has improved the structural integrity of the material, proving its potential application in tissue engineering. In fact, as the NCC percentage increased the freeze-dried samples became more rigid. Not only is this clear from Figure 3 but this was also observed during the physical examination of the composite samples and it will also be proven in the case of the hot-pressed composite samples (Figure 5).

Mechanical Analysis of Electrospun PLA/NCC Composites

Tensile Testing of Electrospun PLA/NCC Composites

Multiple samples of each composition of the composites were tested for their tensile properties, and the curves shown in Figure 4 were obtained as a result. The curves in the figure are each for single samples that have been chosen as they best represent the trend found at that particular composition. The corresponding average values for the Young's Modulus, tensile strength, and percentage elongation at fracture are also mentioned in Table I. The standard deviation in results obtained was $\pm 5\%$.

As is clear from the curves, the increase in NCC content of the composites has led to an increase in their elastic modulus

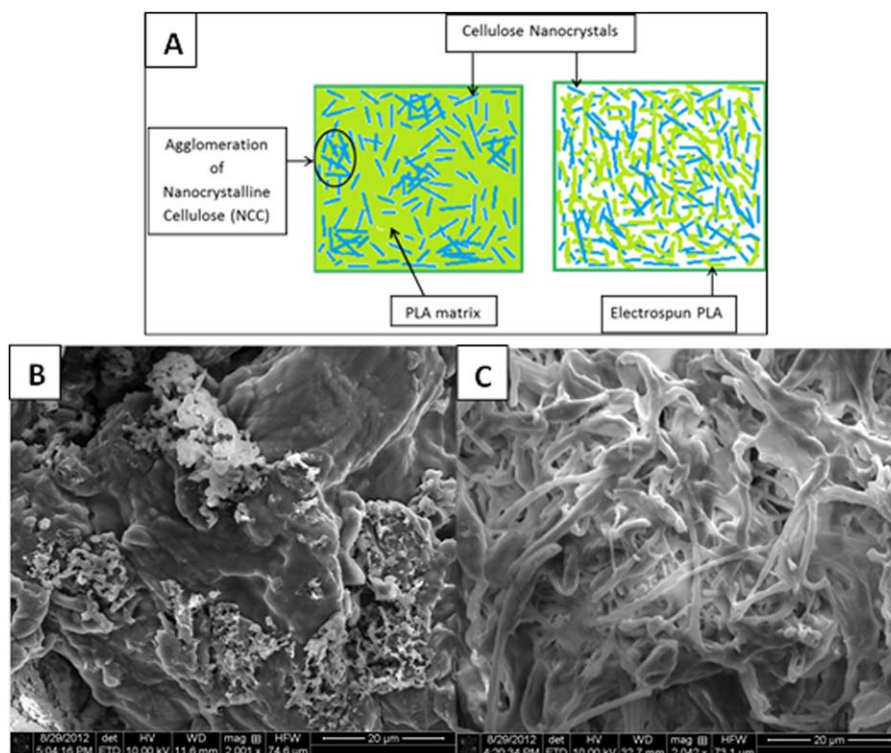


Figure 2. (A) A schematic diagram showing the improved dispersion of NCC as a result of electrospinning PLA; (B) an SEM image of a 5% PLA/NCC composite; (C) an SEM image of the 5% NCC electrospun PLA/NCC composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

values, with all the composite samples performing better than the 0% NCC sample. All of the composite samples with NCC have similar modulus values except for the 1% NCC sample which has a notably higher value than the rest. In addition, the curves do not show any significant evidence of the necking phenomenon and this shows the good dispersion of the NCC in the electrospun PLA matrix, as similarly discussed in Cao et al.³⁸

In terms of ultimate tensile strength, after the 0% NCC sample, the value of this parameter increases until it reaches its maximum value for the 1% NCC sample. After that, it decreases,



Figure 3. Photos of freeze dried 0% NCC electrospun PLA/NCC composite sample (left) and freeze dried 1% NCC electrospun PLA/NCC composite sample (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

but the 2% and 3% NCC samples still perform better than the sample without any NCC; this is not valid for the 5% NCC sample. In addition, it is important to note that especially for the 0.5% and 1% NCC composition, adding the NCC also helped to make the material tougher since the toughness of the material is represented by the area under the curve. In addition, the 0.5% NCC sample was one of the most ductile samples, and in general, for the compositions after the 1% NCC sample, the

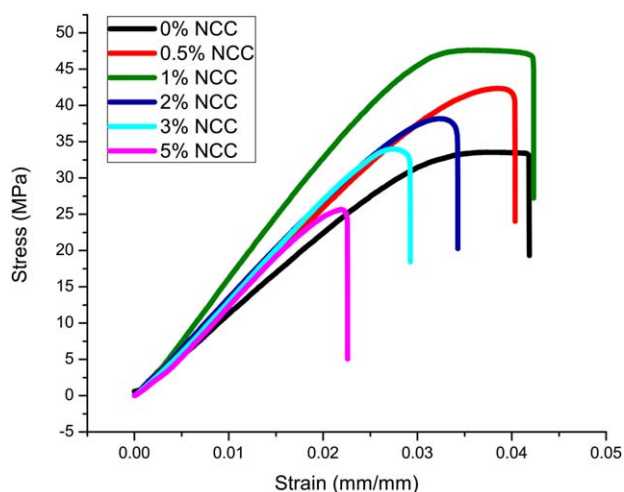


Figure 4. Stress–strain curves of the electrospun PLA/NCC composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Electrospun PLA/NCC Composites' Results Obtained by Tensile Testing

Parameter	0% NCC	0.5% NCC	1% NCC	2% NCC	3% NCC	5% NCC
Young's modulus (GPa)	1.11	1.31	1.67	1.34	1.41	1.38
Tensile strength (MPa)	33.56	42.36	47.63	38.19	34.01	25.67
% Elongation (@ fracture)	4.19	4.04	4.23	3.43	2.92	2.43

brittleness of the material increased as the NCC content increased. Not only is this also obvious from Figure 5 which shows a 0.5% NCC composition sample on the right and a 5% NCC sample on the left, but it can also be deduced from both Figure 4 and Table I. Figure 4 clearly shows how the 0.5% NCC sample is more ductile than the 5% NCC sample since it has undergone a considerably greater amount of plastic strain at fracture, while Table I specifies a percentage elongation for the 0.5% NCC sample which is almost double that of the 5% NCC sample. Oka mentions in his work how such a trend of increasing rigidity with increasing NCC concentration is due to the NCC particles causing the increased restraining of the PLA molecular chains which causes a reduction in the mobility of the PLA fibers, making the material stiffer overall. This restraining is the result of the fibrous microstructure of the NCC developed during the hydrolysis process.¹³

These trends deduced from the stress–strain curves are due to the fact that till the threshold composition of 1% NCC, the composite material is reinforced by the filler which forms a “percolating network structure above the percolation threshold” as a consequence of the hydrogen bonding between the NCC nanoparticles.³⁹ However, after 1%, as the NCC concentration is increased, there is a decrease in the mechanical strength due to the fact that the percolating network structure has become more rigid due to self-aggregation of the NCC and this has also contributed to the increasing brittleness of the samples.⁴⁰

Dynamic Mechanical Analysis of Electrospun PLA/NCC Composites

The samples were tested for their dynamic mechanical properties, and the storage modulus values shown in Figure 6 were obtained. As in the tensile testing, multiple samples of each composition of the composites were tested, and the curves in the figure are each for single samples that have been chosen as they best represent the trend found at that particular composition.

The sample with no NCC had the minimum strength and the maximum storage modulus values were found at the loading



Figure 5. The increasing brittleness of the electrospun PLA/NCC composites with increasing NCC content [Left: 5% NCC; Right: 0.5% NCC]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

level of 3% NCC. After this, the strength of the composites decreased, so that the 5% sample had modulus values very close to that of the 2% composite, although they were still greater than those of the 0% NCC sample. In addition, from Figure 6 it can be seen that the trend followed by the curves for all the samples is more or less the same, regardless of the amount of NCC which the sample contained.

Table II shows the storage modulus values for the composites at different temperatures along with the corresponding percentage difference in values relative to the values at 0% NCC. The increase in modulus was most pronounced at lower temperatures below the glass transition temperature of PLA. In contrast, above the glass transition temperature such a trend was not found, with the samples actually experiencing a decrease in the modulus values at 70°C. This is because at lower temperatures when the components of the composites are solid in nature, there is better bonding at the interface and therefore more uniform stress transfer⁴¹ between the PLA matrix and reinforcing NCC. This leads to an increase in the composites' strength. In contrast, at higher temperatures, the PLA softens and there is a “thermal expansion mismatch” between the PLA and cellulose fibers.¹⁰ This leads to an overall decrease in the composites' strength. Other studies have found that the greatest improvement of the composite's properties were at higher temperatures near the glass transition temperature of PLA.¹⁶ The fact that this research does not corroborate with such studies is advantageous since it means that the composites being studied are strongest at lower temperatures, which is ideal as a result of the fact that most of the applications in which these composites

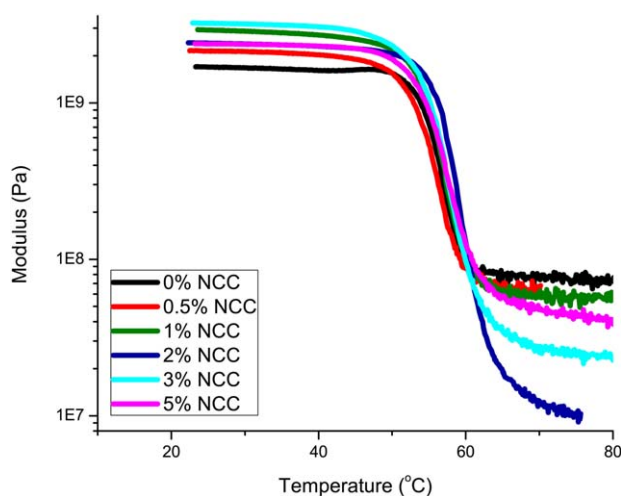


Figure 6. Modulus–temperature curves of the electrospun PLA/NCC composites obtained by DMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Electrospun PLA/NCC Composites' Storage Modulus Values Obtained by DMA

Composite sample	Storage modulus values (GPa)			% Change in modulus (relative to the 0% NCC sample)		
	at 25°C	at 40°C	at 70°C	at 25°C	at 40°C	at 70°C
0% NCC	1.694	1.611	0.075			
0.5% NCC	2.148	2.028	0.064	26.800	25.909	-14.667
1% NCC	2.490	2.364	0.058	46.989	46.724	-22.667
2% NCC	2.411	2.302	0.012	42.326	42.893	-84.000
3% NCC	3.230	3.067	0.025	90.673	90.400	-66.667
5% NCC	2.380	2.308	0.048	40.496	43.265	-36.000

could potentially be employed would take place at room temperature or body temperature, both of which are below the glass transition temperature of PLA.

Therefore the optimum composition for the electrospun PLA/NCC composites from the perspective of tensile testing is different from the optimum composition with respect to DMA. This is because the DMA technique measures the storage moduli of a material and shows how the mechanical properties of a material vary with temperature changes. It is consequently a measure of dynamic properties as opposed to the elastic modulus, measured by tensile testing, which is a measure of the strength of the material in static conditions. Consequently, the storage modulus and Young's modulus have different values for a single material, generally speaking,⁴² and similarly a certain composite composition may not be ideal in all circumstances.

Thus, it can be concluded that in terms of mechanical properties, the composite samples in the 0.5% NCC to the 3% NCC range were found to be ideal. This corroborates with the findings of Dong et al. who studied composites made of electrospun PLA with clay and found the compositions in the 0.5–3% clay range to have the most enhanced dispersion,²⁷ and it is well known that improved dispersion of the filler in the matrix helps improve the composite's mechanical properties.

Crystallinity of Electrospun PLA/NCC Composites and their Components

Many studies have been done on the effect that electrospinning has on the crystallinity of polymers. Some studies reported a decrease in crystallinity and that the fibers possessed poor crystallinity.^{43–45} Others reported an increase in crystallinity of the electrospun fibers.⁴⁶ The decrease in crystallinity may be attributed to the fact that the rapid solidification of the polymer solution during electrospinning results in the formation of small crystallites with imperfections such as defects which in turn leads to lower crystallinity values.⁴⁷ The increase in crystallinity, on the other hand, may be attributed to the fact that as the polymer solution emerges through the nozzle during the electrospinning process, there is a partial ordering effect and so highly oriented fibers are obtained.⁴⁸

It must be realized that whether there is an increase or decrease in the crystallinity of the polymer, as well as the extent of this change, depends on many factors such as the concentration of

the polymer solution,⁴⁹ electrospinning parameters such as the feed rate,⁵⁰ the type of polymer and the type of solvent used,⁵¹ whether any surfactants are used,⁵² etc. In fact, the crystallinity of the fibers mainly depends on the degree of ordering caused by the time taken for crystallization "during the flight of the jet" as well as the effect of the electrostatic field.⁵³ Yet others argue that alignment does not affect the crystallinity of the electrospun fibers since the alignment is due to the stretching of the material caused by electrospinning while the lack of crystallization is due to the insufficient time given to the polymer to crystallize during the process.⁵⁴

DSC Scans of the Materials

Figure 7 shows the DSC curves of the 0%, 1%, 3%, and 5% NCC electrospun PLA/NCC composites relative to that of neat PLA. All the curves experience a significant dip near 60°C due to the glass transition temperature of PLA. It is also evident that the trend followed by all the samples is very similar. However, comparing the top curve with the rest of the curves shows how electrospinning the PLA has had an effect on its

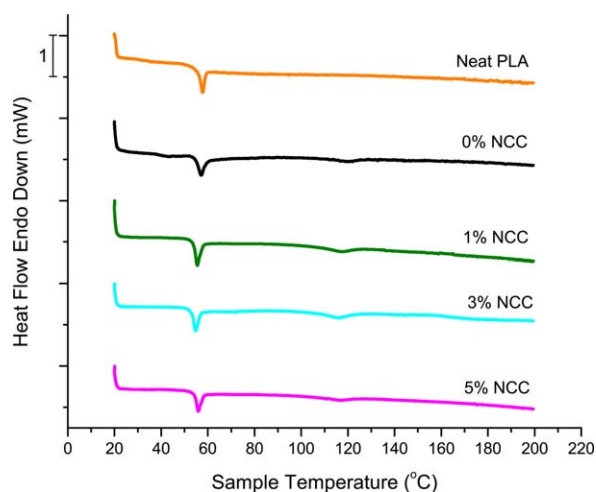


Figure 7. DSC curves obtained for the different electrospun PLA/NCC composite samples and neat PLA. Neat PLA is the PLA starting material while 0%NCC represents the material which has been processed like the rest of the composite samples but does not contain any NCC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

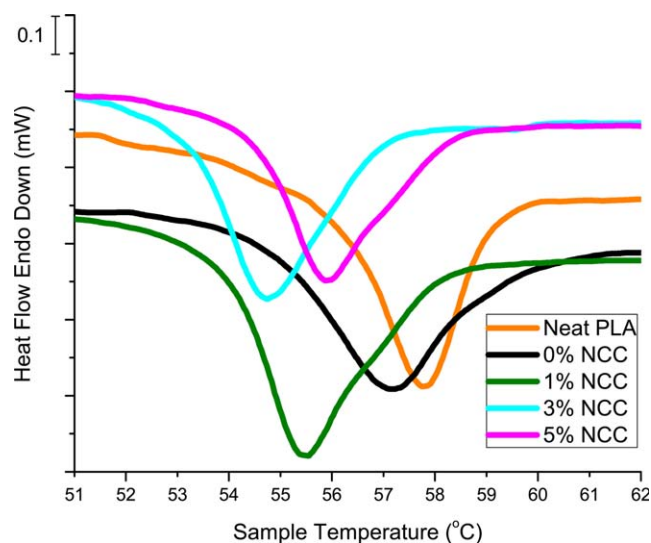


Figure 8. DSC curves obtained for the different electrospun PLA/NCC composite samples and neat PLA – Magnified in the T_g region. Neat PLA is the PLA starting material while 0%NCC represents the material which has been processed like the rest of the composite samples but does not contain any NCC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crystallinity. On careful examination, a slight endothermic peak may be seen at approximately 120°C for the composite samples. This peak is not present in the curve of neat PLA and may be defined as the melting point of the crystalline region, and this would only be possible if the crystallinity of the material has increased due to the electrospinning, so that it is no longer only the amorphous PLA starting material.

Yet another explanation for this endothermic peak could be that it is cold crystallization due to the rearrangement of the amorphous portions of the polymer into a crystalline phase.⁵⁵ However, this would indicate that the material is becoming more crystalline during the DSC process while the material is being heated, and this has been reported to cause improved mechanical properties for the material.⁵⁵ It must be remembered that the samples tested with the DSC were the freeze-dried samples of the composites which had not been hot pressed. Thus this cold crystallization peak proves how subjecting the freeze-dried composites to heat would increase their strength, as well as how this characteristic may be used to obtain better composites since as the crystallization temperature increases, there is a sharp rise in the rate of cold crystallization.⁵⁵ The hot pressing done to prepare the composite samples tested as part of this research would therefore be a reflection of this phenomenon.

T_g Variation of Electrospun PLA/NCC Composites and their Components

Figure 8 shows how electrospinning the PLA has caused a slight decrease in its T_g , which is given by the lowest point of the curves. This is because, generally speaking, the transformation of a polymer into electrospun fibers results in a reduction in the material's glass transition temperature and melting temperature as a consequence of the rapid solidification and high elongation rate during electrospinning.⁵⁶

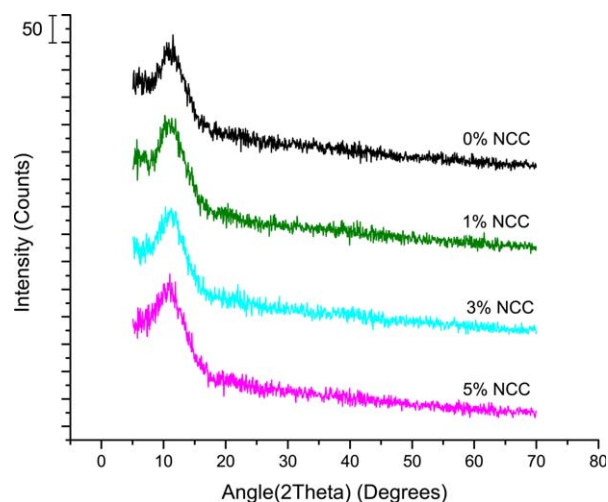


Figure 9. The XRD patterns obtained for the different electrospun PLA/NCC composite samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In addition, the addition of NCC to the PLA has led to a further decrease in the T_g . This is true for all the composite samples investigated, which all have T_g values less than that of the 0% NCC composite. This trend was similar to that found by Dong et al. for some of their electrospun PLA/clay composite samples.²⁷ This may be ascribed to the fact that the NCC has been able to interact with the supramolecular structure of amorphous phase of the PLA and affect its hydrogen bonding.⁵⁷ This has enabled the increase in mobility of the macromolecules to happen at an earlier temperature, therefore decreasing the material's T_g .

The overall trend in glass transition temperature and crystallinity for these electrospun PLA/NCC composites is similar to the trend found for hemp fiber-reinforced PLA composites.⁵⁸

XRD Scans of the Materials

XRD scans of the 0%, 1%, 3%, and 5% NCC composites are shown in Figure 9. It is clear that all the curves are almost identical, and so the addition of NCC has not had any significant effect on the crystallinity of the samples. This corroborates with what was learned about the composites from their DSC curves (Figure 7), where the composite samples also had almost identical curves.

CONCLUSIONS

A novel material with improved mechanical properties is prepared by mixing electrospun PLA fibers, of nanodimensions, with isolated NCC. Dispersion of NCC in PLA is therefore improved to a certain extent and a more homogeneous composite material is produced. Electrospun PLA/NCC composites with NCC concentrations of 0.5–3% are found to be the optimum compositions with improved mechanical properties (both tensile and dynamic properties). Furthermore, adding NCC to the electrospun PLA matrix did not alter the crystallinity of the final composite, but it did cause the glass transition temperature to decrease.

The freeze dried electrospun PLA/NCC nanocomposites exhibited the promising characteristics of structural integrity and

porosity, reaffirming their potential to be used in scaffolds for tissue engineering. On the other hand, possible applications for the hot pressed composites studied as part of this research are as biodegradable packaging material, construction materials and in the textile and automotive industries.

REFERENCES

1. Dumitriu, S.; Perez, S.; Mazeau, K. *Polysaccharides: Structural Diversity and Functional Versatility* (Chapter 2: Conformations, Structures, and Morphologies of Celluloses), 2nd ed. New York: CRC Press, **2005**.
2. Habibi, Y.; Lucia, L. A.; Rojas, O. J. *Chem. Rev.* **2010**, *110*, 3479.
3. Zimmermann, T.; Pöhler, E.; Geiger, T. *Adv. Eng. Mater.* **2004**, *6*, 754.
4. Garcia de Rodriguez, N. L.; Thielemans, W.; Dufresne, A. *Cellulose* **2006**, *13*, 261.
5. Xiang, C.; Frey, M. W. *Fiber Science and Apparel Design*. Cornell University, "Nanocomposite fibers electrospun from biodegradable polymers," New Orleans, LA, USA, **2008**.
6. Yang, K.; Wang, X.; Wang, Y. *J. Ind. Eng. Chem-Seoul* **2007**, *13*, 485.
7. Pilla, S.; Kramschuster, A.; Lee, J.; Clemons, C.; Gong, S.; Turng, L.-S. *J. Mater. Sci.* **2010**, *45*, 2732.
8. Bhardwaj, N.; Kundu, S. C. *Biotechnol. Adv.* **2010**; *28*, 325.
9. Oksman, K.; Mathew, A. Processing and Properties of Nanocomposites Based on Cellulose Whiskers, in 9th International Conference on Wood and Biofiber Plastic Composites, Madison, WI, USA, 22 May 2007.
10. Huda, M. S.; Mohanty, A. K.; Drzal, L. T.; Schut, E.; Misra, M. *J. Mater. Sci.* **2005**, *40*, 4221.
11. Jonoobi, M.; Harun, J.; Mathew, A. P.; Oksman, K. *Comp. Sci. Technol.* **2010**, *70*, 1742.
12. Shumigin, D.; Tarasova, E.; Krumme, A.; Meier, P. *Mater. Sci. (MEDŽIAGOTYRA)* **2011**, *17*, 32.
13. Oka, M. A. *PLA and Cellulose based Degradable Polymer Composites*; Georgia Institute of Technology: USA, **2010**.
14. Nakagaito, A. N.; Fujimura, A.; Sakai, T.; Hama, Y.; Yano, H. *Comp. Sci. Technol.* **2009**, *69*, 1293.
15. Suryanegara, L.; Nakagaito, A. N.; Yano, H. *Cellulose* **2010**, *17*, 771.
16. Petersson, L.; Kvien, I.; Oksman, K. *Comp. Sci. Technol.* **2007**, *67*, 2535.
17. Kowalczyk, M.; Piorkowska, E.; Kulpinski, P.; Pracella, M. *Comp. Part A: Appl. Sci. Manufact.* **2011**, *42*, 1509.
18. Lin, N.; Chen, G.; Huang, J.; Dufresne, A.; Chang, P. R. *J. Appl. Polym. Sci.* **2009**, *13*, 3417.
19. Lin, N.; Huang, J.; Chang, P. R.; Feng, J.; Yu, J. *Carbohydr. Polym.* **2011**, *83*, 1834.
20. Bondeson, D.; Oksman, K. *Comp. Part A: Appl. Sci. Manufact.* **2007**, *38*, 2486.
21. Takahashi, Y. *Cellulose Nanoparticles: A Route from Renewable Resources to Biodegradable Nanocomposites*, Ph.D., State University of New York College of Environmental Science and Forestry, United States: New York, **2007**.
22. Hamad, W. Y.; Miao, C. "Nanocomposite Biomaterials of Nanocrystalline Cellulose (NCC) And Polylactic Acid (PLA)," U.S. Patent 2011019609411-Aug-2011.
23. MatWeb: Material Property Data, "NatureWorks® Ingeo™ 4060D Sealant Grade PLA," **2011**. [Online]. Available: <http://www.matweb.com/search/datasheettext.aspx?matguid=46b73a0a9abe4e63aa37cfa6bb785644>. [Accessed: 28-Dec-2011].
24. Wang, B. *Dispersion of Cellulose Nanofibers in Biopolymer Based Nanocomposites*, Ph.D., University of Toronto (Canada): Canada, **2010**.
25. Pirani, S.; Hashaikeh, R. *Carbohydr. Polym.*, **2013**, *93*, 357.
26. Sill, T. J.; von Recum, H. A. *Biomaterials* **2008**, *29*, 1989.
27. Dong, Y.; Chaudhary, D.; Haroosh, H.; Bickford, T. *J. Mater. Sci.* **2011**, *46*, 6148.
28. Gui-Bo, Y.; You-Zhu, Z.; Shu-Dong, W.; De-Bing, S.; Zhi-Hui, D.; Wei-Guo, F. *J. Biomed. Mater. Res. A* **2010**, *93*, 158.
29. Huang, Z.-M.; Zhang, Y.-Z.; Kotaki, M.; Ramakrishna, S. *Comp. Sci. Technol.* **2003**, *63*, 2223.
30. Vicéns, M. A. R. *Cellulose Nanocrystals Reinforced Electrospun Poly(lactic acid) Fibers as Potential Scaffold for Bone Tissue Engineering*; MSc, Forest Biomaterials, North Carolina State University, Raleigh: North Carolina, **2010**.
31. Lu, P.; Hsieh, Y.-L. *Carbohydr. Polym.* **2010**, *82*, 329.
32. de Azeredo, H. M. C. *Food Res. Inter.* **2009**, *42*, 1240.
33. Chouwatat, P.; Polsana, P.; Noknoi, P.; Siralermukul, K.; Srikulkit, K. *J. Metals Mater. Min.* **2010**, *20*, 41.
34. Wang, T. *Cellulose Nanowhiskers and Nanofibers from Biomass for Composite Applications*; Ph.D., Chemical Engineering, Michigan State University, United States, Michigan, **2011**.
35. Kloser, E.; Gray, D. G. *Langmuir* **2010**, *26*, 13450.
36. Pei, A.; Zhou, Q.; Berglund, L. A. *Comp. Sci. Technol.* **2010**, *70*, 815.
37. Petersson, L.; Oksman, K. *Comp. Sci. Technol.* **2006**, *66*, 2187.
38. Cao, X.; Chen, Y.; Chang, P. R.; Muir, A. D.; Falk, G. *eXPRESS Polym. Lett.* **2008**, *2*, 502.
39. Siqueira, G.; Bras, J.; Dufresne, A. *Polymers* **2010**, *2*, 728.
40. Krishnamachari, P.; Zhang, J.; Lou, J.; Yan, J.; Uitenham, L. *Inter. J. Polym. Anal. Character.* **2009**, *14*, 336.
41. Lovely, M. *Short Isora Fibre Reinforced Natural Rubber Composites*; Ph.D., Cochín University of Science and Technology, Kerala, India, **2006**.
42. PerkinElmer. *Introduction to dynamic mechanical analysis (DMA): A Beginner's guide*, **2008**.
43. Deitzel, J.; Kleinmeyer, J.; Harris, D.; Beck Tan, N. *Polymer* **2001**, *42*, 261.
44. Lee, K. H.; Kim, H. Y.; Khil, M. S.; Ra, Y. M.; Lee, D. R. *Polymer* **2003**, *44*, 1287.
45. Zeng, J.; Chen, X.; Liang, Q.; Xu, X.; Jing, X. *Macromol. Biosci.* **2004**, *4*, 1118.

46. Costa, L. M. M.; Bretas, R. E. S.; Gregorio, R. *Mater. Sci. Appl.* **2010**, *1*, 246.
47. Dhanalakshmi, M. *eXPRESS Polym. Lett.* **2008**, *2*, 540.
48. Veluru, J. B.; Satheesh, K.; Trivedi, D.; Ramakrishna, M. V.; Srinivasan, N. T. *J. Eng. Fibers Fab.*, **2007**, *2*, 25.
49. Zong, X.; Ran, S.; Fang, D.; Hsiao, B. S.; Chu, B. *Polymer* **2003**, *44*, 4959.
50. Zhang, S. Mechanical and Physical Properties of Electrospun Nanofibers; MSc, Textile Chemistry, North Carolina State University, Raleigh, North Carolina, **2009**.
51. Kim, C.-W.; Kim, D.-S.; Kang, S.-Y.; Marquez, M.; Joo, Y. L. *Polymer* **2006**, *47*, 5097.
52. Talwar, S.; Krishnan, A. S.; Hinestroza, J. P.; Pourdeyhimi, B.; Khan, S. A. *Macromolecules* **2010**, *43*, 7650.
53. Zhao, S.; Wu, X.; Wang, L.; Huang, Y. *J. Appl. Polym. Sci.* **2004**, *91*, 242.
54. Shi, Q.; Wan, K.-T.; Wong, S.-C.; Chen, P.; Blackledge, T. A. *Langmuir* **2010**, *26*, 14188.
55. Wellen, R. M. R.; Rabello, M. S. *J. Mater. Sci.* **2005**, *40*, 6099.
56. Mohammad, F. *Speciality Polymers: Materials and Applications*. Anshan Ltd.: Tonbridge Wells, **2007**.
57. Frone, A. N.; Panaitescu, D. M.; Donescu, D.; Spataru, C. I.; Radovici, C.; Trusca, R.; Somoghi, R. *BioResources* **2011**, *6*, 487.
58. Auras, R.; Lim, L.-T.; Selke, S. E. M.; Tsuji, H. *Poly(lactic acid) Synthesis, Structures, Properties, Processing, and Applications*. Hoboken, N.J.: Wiley, **2010**, p 303.