

Poly lactide Latex/Nanofibrillated Cellulose Bionanocomposites of High Nanofibrillated Cellulose Content and Nanopaper Network Structure Prepared by a Papermaking Route

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Received 14 August 2011; accepted 25 October 2011

DOI 10.1002/app.36413

Published online 26 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Previous attempts to use polylactide (PLA) latex particles and nanofibrillated cellulose (NFC) in papermaking processing have been limited to low NFC content. In the present study, a bionanocomposite material was successfully produced using a PLA latex and NFC. The components were mixed using a wet mixing method and bionanocomposite films were made by filtration followed by hot pressing. In composite materials, the dispersion of the reinforcing component in the matrix is critical for the material properties. Biopolymers such as PLA are non-polar and soluble only in organic solvents; NFC is, however, highly hydrophilic. By utilizing latex, i.e., an aqueous dispersion of biopolymer micro-particles, wet mixing is possible and the problem of aggregation of the hydrophilic

nanocellulose in organic solvent is avoided. The properties of the resulting NFC/PLA latex bionanocomposite films were analyzed. Thorough blending resulted in good dispersion of the reinforcing component within the matrix. Adding increasing amounts of NFC improved the Young's modulus, tensile strength, and strain at break of the bionanocomposite material. The increase in the tensile properties was linear with increasing NFC content as a result of the good dispersion. The NFC also improved the thermal stability of the bionanocomposite material. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2460–2466, 2012

Key words: biopolymers; mechanical properties; nanocellulose; nanocomposites; polylactide latex

INTRODUCTION

Considerable attention has in recent years been devoted to the development of new types of nanocomposite materials that utilize nanocellulose as reinforcement.^{1–5} Nanocellulose is a natural material with excellent strength properties⁶ and since cellulose is both biodegradable and renewable, combining nanocellulose with a biopolymer matrix such as polylactide (PLA) produces a “green” environmentally friendly bionanocomposite material.

Cellulose is a linear polymer made of D-glucose units. In the fiber cell wall, the cellulose chains are bundled together into microfibrils containing both crystalline and amorphous segments. The microfibrils are in turn arranged into larger microfibril aggregates with a width between 10 and 30 nm.⁷ Nanocellulose, i.e., cellulose materials with at least one dimension in the nanometer range, is normally produced by disintegration of cellulosic fibers,

resulting in two different cellulose nanoparticles with different properties: nanocellulose whiskers and nanofibrillated cellulose (NFC). Whiskers are stiff, crystalline rods produced by hydrolysis of cellulose down to the leveling off degree of polymerization (DP). Whiskers have the lowest aspect ratio of the nanocellulosics with a width of about 5 nm and length of 200 nm.³ NFC, on the other hand, consists of longer and more flexible microfibrils with a width of about 15–20 nm and a length of several micrometer.¹ NFC is produced as an aqueous dispersion. In dispersion, the long microfibrils form an entangled network and the result is a translucent gel-like substance with high viscosity.

NFC is normally produced by mechanical disintegration of wood fibers using a high pressure homogenizer. This process was first developed by Turbak et al.⁸ in the early 1980s but due to the high energy requirements involved, the process was not further developed. Recently, various methods have been developed in this lab in order to decrease the energy consumption and to facilitate the fibrillation process. These methods include different pre-treatments of the wood pulp.^{9–11} One pre-treatment introduces charges in the fibers by carboxymethylation of the pulp. The increased charge density causes repulsion

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between fibrils in the fiber wall and thus facilitates the fibrillation.¹⁰ Another pre-treatment utilizes a combination of refining and mild enzymatic hydrolysis.^{9,11} The enzymes selectively hydrolyses amorphous parts of the cellulose but compared to the strong acid hydrolysis utilized to produce cellulose whiskers, this comparatively mild enzymatic treatment has only limited effect on the DP of the cellulose.⁹ The importance of a high DP for the mechanical properties of NFC films has previously been studied.⁶

For nanocomposite materials, good dispersion of the reinforcing component in the matrix is crucial for the material properties.^{3,12} In the manufacturing of bionanocomposite material, the mixing is therefore critical to be able to fully utilize the reinforcing potential of the NFC. Biopolymers such as PLA are non-polar and thus not soluble in water, which complicates the use of hydrophilic NFC as reinforcement. Latices are dispersions of polymer particles in aqueous media, using the matrix in latex form enables direct wet mixing of the biopolymer with the NFC in its dispersed state, thus preventing aggregation from occurring on drying.

The reinforcing effect of nanocellulose in a synthetic latex material has been investigated in previous studies.^{13–19} Whisker reinforced nanocomposite materials were made by solvent casting the synthetic latex reinforced with varying amounts of tunicate cellulose whiskers. These studies showed that the tensile properties increased with increasing whisker content. A strong increase in tensile properties above T_g was noted due to the formation of a strong whisker network at whisker concentrations above the percolation threshold, which was as low as a 6%.^{13–16} The strength of the network is due to the strong hydrogen bonds between the cellulose whiskers. The effect of whiskers and NFC in thermoplastic composite materials has been compared. In comparison with whiskers, NFC usually results in a stronger material with higher modulus and lower elongation at break due to the possibility of NFC to form entanglements.^{19,20}

PLA latex has previously been used in a three-component system consisting of the latex, commercial NFC, and bamboo fibers. In this system, the nanocellulose improved both modulus and bending strength.^{21,22} A low amount of NFC leads to improved tensile properties. However, adding larger amounts of NFC to a thermoplastic biopolymer matrix tends to affect the mechanical properties negatively due to NFC aggregation if the NFC is not able to be thoroughly dispersed in the matrix.²³ However, Leitner et al.²⁴ made a high content nanocellulose composite material using water soluble polyvinyl alcohol as matrix. The tensile strength increased linearly as the nanocellulose content was increased, showing that the composite strength comes from the cellulose reinforcement. Nakagaito et al.²⁵ made a

PLA fiber/NFC material using a papermaking-like method and achieved good dispersion again resulting in a linear improvement in all tensile properties with increasing nanocellulose content.

This article deals with the properties of NFC/PLA latex bionanocomposites. The latex was a commercial PLA latex. NFC with high aspect ratio was produced by homogenization of enzymatically pre-treated wood pulp. A wet mixing technique was used to prepare a bionanocomposite material with good dispersion of the reinforcing component in the PLA matrix. While previous attempts to use NFC with PLA latex were limited to low NFC content,^{21,22} the present study successfully produced high NFC content nanocomposites with nanopaper network reinforcement structure and strongly improved mechanical properties. Bionanocomposites with NFC content spanning the whole range from 0 to 100% were made and the properties of the materials analyzed.

MATERIALS AND METHODS

Materials

The latex was a commercial PLA latex (Landy PL-2000, Miyoshi Oil & Fat Co., Ltd., Japan) with a mean particle size of 2 μm and a minimum film forming temperature (MFFT) of 90°C. The solids content of the latex was 41 wt %. The pulp was a never dried, bleached, two-stage softwood sulfite pulp with high hemicellulose content (approximate 14%) (Domsjö Eco Bright, Domsjö Fabriker AB, Sweden). The pulp was pre-treated according to a method described previously,⁹ involving refining and mild enzymatic hydrolysis. The treated pulp was fibrillated by homogenization using a Microfluidizer (Microfluidizer M-110EH, Microfluidics Corp., Newton, Massachusetts, USA). The pulp was passed three times through a pair of Z-shaped chambers connected in series with inner diameter of 400 μm and 200 μm followed by five passes through a chamber pair with inner diameter of 200 μm and 100 μm . The solid content of the resulting NFC was 2% by weight. PLA in pellet form was utilized for the reference films (Ingeo 2002D, NatureWorks LLC, Minnetonka, Minnesota, USA), chloroform (p.a.) and NaHCO_3 were used as received.

Preparation of bionanocomposites

The NFC was diluted from 2 wt % to a concentration of 0.2 wt % and dispersed by one passage through the Microfluidizer equipped with a Z-shaped chamber pair with inner diameters 200 μm and 100 μm . Bionanocomposites of varying NFC and latex contents were made by blending NFC and latex with a solid content of 41 wt % to a final total

concentration of 0.2 wt %. Buffer solution, NaHCO_3 was added to the suspensions to a final concentration of 10^{-3}M . The NFC and latex were thoroughly blended by one passage in the Microfluidizer at a pressure of about 1200 bar. Deionized water was used in all dilutions. The final suspensions were degassed under vacuum for at least 30 min with magnetic stirring. Films were made by vacuum filtration of the 0.2 wt % suspension on a filter membrane (0.65 μm DVPP, Millipore, Billerica, Massachusetts, USA).⁶ The NFC content in the films was varied from 0 to 100 wt %. Free standing films were made with a NFC content of 25 wt % or more. Films containing less than 25 wt % NFC were fragile and were thus left on the filter membrane and analyses of these films were made on films still on the filter membrane. The films were placed between metal wires under a pressure of a 10 kg weight and dried at 55°C for around 48 h. All films were then hot pressed at 150°C for 4 min at 4.9 MPa. Prior to hot pressing the films were dried at 50°C overnight. The films had a final diameter of around 75 mm and a grammage of around 80 g m^{-2} .

Pure latex was mixed with buffer and then dewatered using the same filtration setup as for the composites films. The dewatered latex material was removed and oven dried at 55°C. Dried latex was then hot pressed as described above. The resulting latex films were utilized for determining the crystallinity and thermal degradation of pure latex films.

To compare the mechanical properties of the bionanocomposites, films of a commercial PLA was made. Films from NatureWorks PLA Ingeo 2002D were made by solvent casting. The pellets were dissolved in chloroform under slow magnetic stirring. The dissolved PLA solution was poured into glass petri dishes covered with Teflon foil and dried at room temperature (RT) under a glass cover. The resulting films were dried overnight at 55°C and then hot pressed at 150°C for 4 min at 4.9 MPa.

Characterization

Tensile test of the bionanocomposite films were performed using a MTS tensile tester with a Teststar II S controller (MTS Systems Corp., Eden Prairie, Minnesota, USA). The tensile tester was equipped with a 500 N load cell. The relative humidity during testing was 50% and the temperature 23°C. The films were conditioned for at least 48 h prior to testing. The gap distance was 30 mm and the strain rate was 10% min^{-1} . The film thickness was calculated from an average of at least ten measurements using a micrometer. Specimens from the films were made by punching strips with a length of 40 mm using a sharp puncher. The average width of the specimen was determined using a caliper. The average width

was 6.2 mm. The STFI FractureTester software (Innventia AB, Sweden) was used to determine the tensile properties of the bionanocomposites. This software follows ISO 1924-3 (Paper and board—Determination of tensile properties—Part 3) when calculating the tensile properties. The tensile properties were calculated using the applied load and actual initial cross-sectional area.

The tensile properties of samples with an introduced defect were analyzed using the same setup as for the tensile tests. These samples had a length of 40 mm, and a width of 20 mm with an 8 mm center notch. The samples and notches were all cut using a laser beam to avoid damages at the edges of the notch. The strength properties of the notched samples were calculated from the applied load and the actual initial cross-sectional area across the notch.

Dynamic mechanical thermal analysis (DMTA) was performed on a Perkin-Elmer DMA7 (Perkin-Elmer, Waltham, Massachusetts, USA) operating in tension mode. The samples were mounted in a closed chamber and the measurements were done in a helium atmosphere. The samples were about 3 mm wide. The gap distance was 10.5 ± 0.4 mm. The measurements were performed at a frequency of 1 Hz, and constant amplitude of 2 μm . A conditioning step was first performed; samples were heated from 30°C to 80°C, held for 30 min at 80°C and then cooled. The DMTA was performed by heating the samples from 30°C to 250°C at a heating rate of 2 °C min^{-1} . The measurements were performed under dry conditions, 0% RH. The mean values of two to five measurements were calculated.

The mass loss during heating was determined by thermogravimetric analysis (TGA) using a PerkinElmer TGA7 instrument (PerkinElmer, USA). Samples were dried at 105°C for 15 min and then heated from 105°C to 600°C at a heating rate of 10 °C min^{-1} . The balance purge gas was N_2 at a flow rate of 40 mL min^{-1} . As sample purge gas, helium was used at a flow rate of 26 mL min^{-1} .

Field emission-scanning electron microscopy (FE-SEM) images were taken on fracture surfaces with a Hitachi S-4800 (Hitachi High-Technologies Inc., Canada). The operating voltage was 1 kV. Samples were mounted on a split mount holder and then coated with 1.5 nm carbon (Cressington 108carbon/A coater, Cressington, UK) followed by 5 nm Au/Pd (Cressington 208HR sputter coater equipped with a MTM-20 high resolution thickness controller).

RESULTS AND DISCUSSION

To be able to fully utilize the reinforcing properties of NFC the dispersion of the NFC within the matrix is critical. Bionanocomposite films with varying NFC contents were successfully produced using PLA

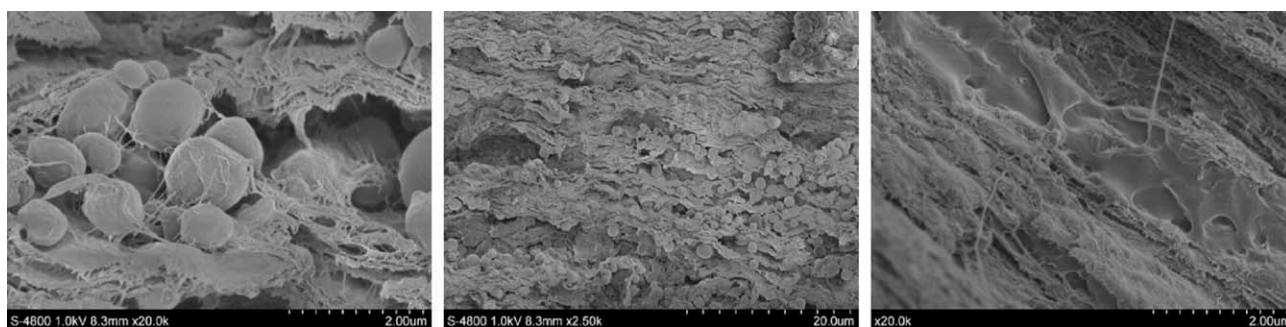


Figure 1 FE-SEM images of a freely dried in RT (left, center) and oven dried and hot pressed (right) films with 60 wt% NFC. In the center image the layered structure of the composite can be seen.

latex and a wet mixing technique. The resulting films were hot pressed and their properties analyzed.

Figure 1 shows the FE-SEM images of fracture surfaces of two films both containing 60 wt % NFC. The fracture surface of the film that has been freely dried at room temperature (RT) shows the latex particles dispersed within the NFC network. After hot pressing, the latex particles have melted into the NFC network. As shown in a previous study,²⁶ the preparation method (filtration) used in this study leads to the arrangement of NFC in the films in a layered structure. It was also noted that there seem to be a latex concentration gradient in the film. The influence of this was considered not to influence the properties but this was not further studied.

Mechanical properties

The tensile properties of bionanocomposite films and of pure PLA after hot pressing were analyzed. The Young's modulus, strength, and strain at break as a function of the NFC content are plotted in Figures 2–4. In Figure 2, the Young's modulus versus the NFC content is plotted. The pure NFC film has a high Young's modulus of 13 GPa, similar to

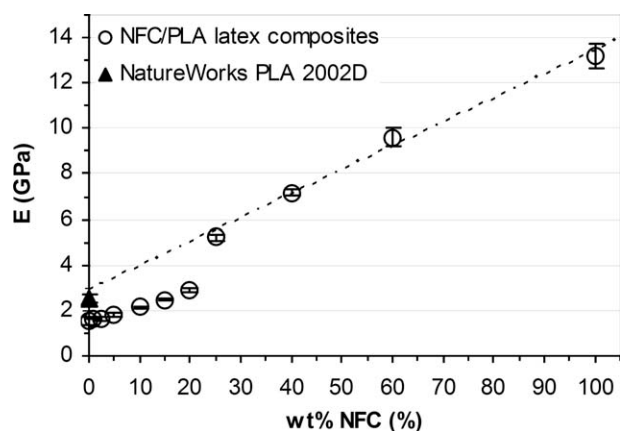


Figure 2 The Young's modulus as a function of NFC content, the error bars are the standard deviations.

the result previously obtained by Henriksson et al.^{6,26} for the same type of NFC films. For the composites, there is a clear linear increase in the modulus with increasing NFC content. The modulus of the bionanocomposites reinforced with less than 25 wt % NFC shows the same linear trend but on a lower level, probably due to the fact that these bionanocomposite films are still supported by the filter membrane that dampens the effect somewhat.

The tensile strength (Fig. 3) follows the same linear trend with increasing NFC content as does the evolution of the strain at break (Fig. 4). It seems that at high contents of NFC, strain at break is controlled by the NFC nanopaper network structure with favorable effects. Adding NFC directly to a PLA solution can lead to aggregation of the NFC and reduced mechanical properties at higher NFC contents.²³ The trend of a progressive increase in the tensile properties with increasing nanocellulose content observed in this study has also been noted in a previous study by Nakagaito et al.²⁵ They developed a papermaking-like method for producing a biocomposite material. A commercial NFC was mixed with PLA fibers in water, thin sheets were prepared and a composite material was made by stacking and hot

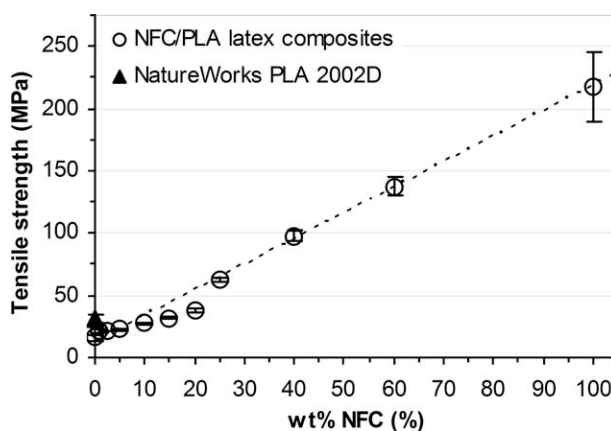


Figure 3 Ultimate tensile strength of bionanocomposite as a function of NFC content (for reference PLA the yield strength is plotted), the error bars are the standard deviations.

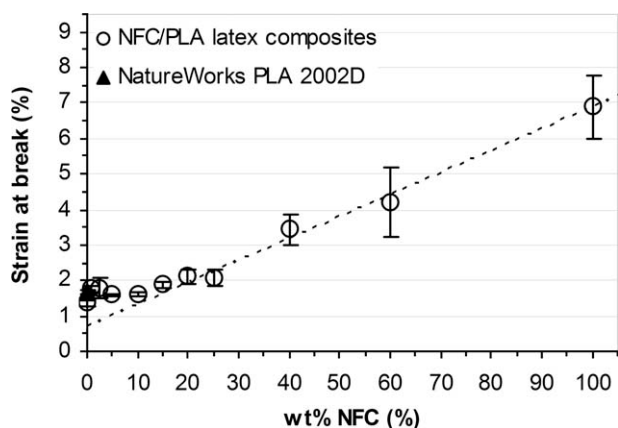


Figure 4 Strain at break (strain at yield for reference PLA), the error bars are the standard deviations.

pressing the sheets. Modulus, strength, and strain at fracture all increased with NFC content in a linear fashion, as an example the modulus was increased from 5 to 9 GPa and the tensile strength from about 35–110 MPa going from 10 to 70 wt % NFC. The linear increase in tensile properties proved that a good dispersion of the NFC was obtained even at high levels of reinforcement. As a comparison, the modulus in this study was increased from 5 to about 10 GPa and the strength from 60 to 137 MPa going from 25 to 60 wt % NFC reinforcement. Compared to the reference commercial PLA film, reinforcing the PLA latex with less than 10 wt % NFC gives similar properties and the good dispersion of the NFC within the matrix resulted in increasingly improved mechanical properties. Typical stress–strain curves showing the continuous increase in the tensile properties are presented in Figure 5.

Small flaws and defects are easily introduced in the manufacturing process of composite materials. Defects in a material drastically reduce the strength properties, the ability of a material to resist crack propagation around a defect is therefore interesting to characterize. Compared to tensile test where the

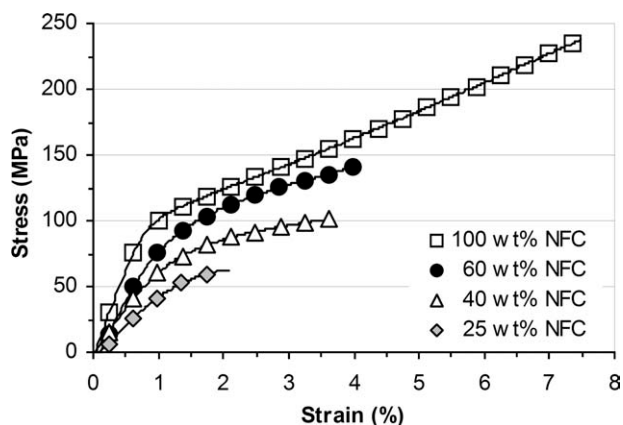


Figure 5 Typical stress–strain curves for bionanocomposites.

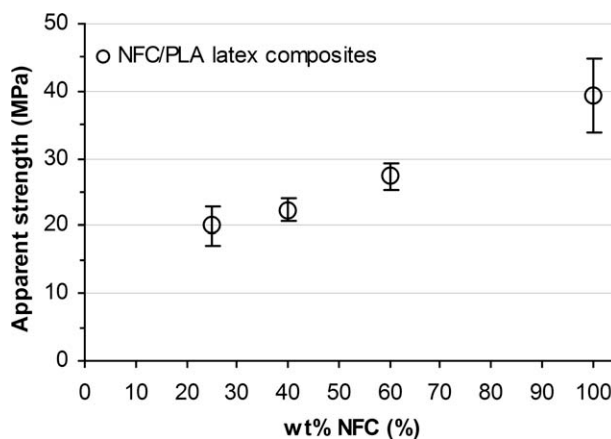


Figure 6 Apparent ultimate strength of notched samples with varying NFC content.

applied stress is distributed uniformly in the sample, introducing a sharp defect, a notch, in the sample leads to severe stress concentrations at the edge of the notch when the sample is strained. The fracture toughness of the material can then be evaluated, provided specimen dimensions meet the requirements for valid fracture toughness data. Samples with a centered notch were made and strained to break using the same setup as in the tensile test. The strength and strain at break of notched samples, here referred to as the apparent strength and apparent strain at break was estimated.

The apparent strength of notched samples is plotted in Figure 6, and follows the same trend as the tensile strength for the composites. The increase is linear going from 25 wt % reinforced NFC reinforced bionanocomposite films to pure NFC films. The apparent strength is, however, drastically reduced compared to the tensile strength. The apparent strength is related to fracture toughness, and the data mean that increasing NFC content has a positive effect on this property. The apparent strain

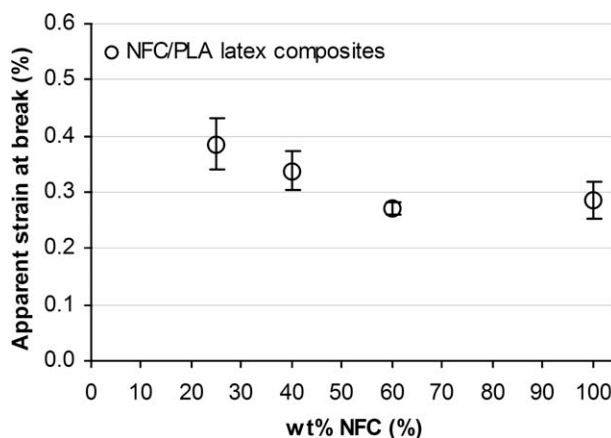


Figure 7 Apparent strain at break for notched samples with varying NFC content.

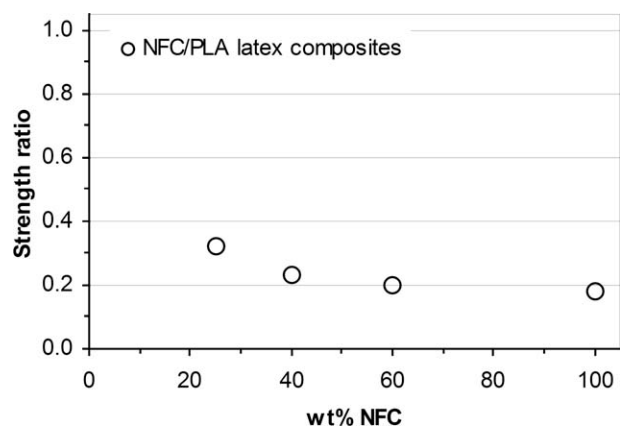


Figure 8 The ratio of the apparent strength of notched samples to the tensile strength of un-notched samples.

at break shows a different behavior compared to the tensile strain at break (Fig. 7). It seems that increasing the NFC content will cause the bionanocomposites to display a more brittle fracture behavior. The ratio of the apparent strength to the tensile strength is plotted in Figure 8 against the NFC content. From this data it can be seen that although the strength is still improved by increasing the NFC content, the bionanocomposite material seems to become relatively more sensitive to defects.

Thermal properties

The thermal properties of the NFC/PLA latex composites were analyzed with DMTA and TGA.

The storage modulus in the linear range was determined with DMTA and the relative change in storage modulus is plotted in Figure 9. As the matrix changes from a glassy to a rubbery state a drop in the storage modulus is seen. The onset of the drop in storage modulus is about 35°C and slightly shifted towards higher temperatures with increasing NFC content. The magnitude of the drop in storage modulus in the rubbery region at temperatures

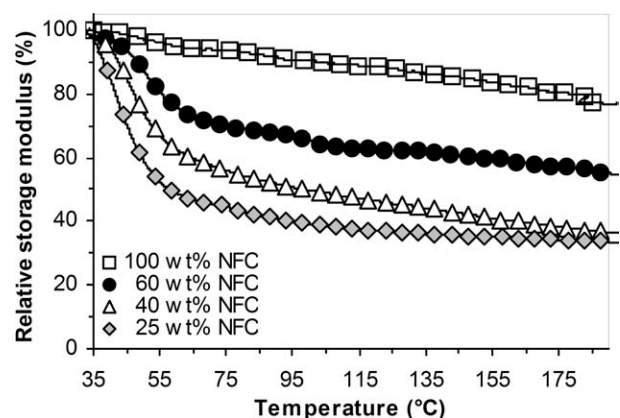


Figure 9 Storage modulus of freestanding films.

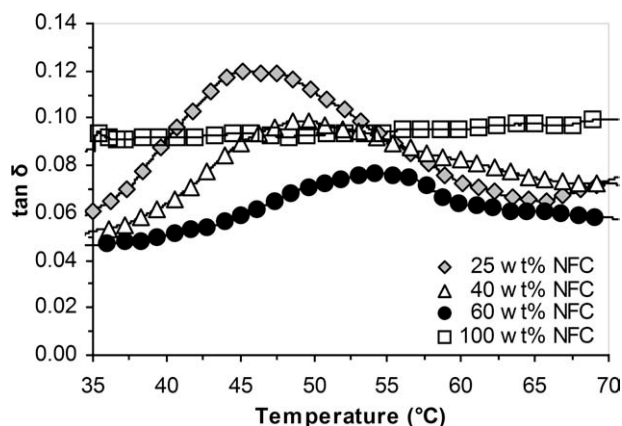


Figure 10 $\tan \delta$ of freestanding films with different NFC content.

above the glass transition temperature is decreased with increasing NFC content.

The melting temperature, T_m , of PLA is typically between 130°C and 160°C.²⁷ Above the T_m , the PLA softens and the modulus is lost. In the study by Nakagaito et al.,²⁵ previously mentioned, the storage modulus of nanocomposites with a NFC content of 70 wt % and higher was preserved above 150°C, the melting temperature of the PLA matrix. It was suggested that at 70 wt % nanocellulose reinforcement and higher, the percolated nanocellulose network preserved the modulus of the composite after the melting of the matrix. In this study, the modulus of the composites is maintained at high temperatures even at a lower NFC content, 25 wt %, indicating that the NFC is well dispersed and forms an entangled network even at lower levels of reinforcement.

The temperature corresponding to the peak in the $\tan \delta$ data is approximated as the T_g of the matrix (Fig. 10). The magnitude of the peak decreases with increasing NFC content due to the lower relative amount of amorphous polymer in the bionanocomposite material with increasing NFC content. The T_g peak is slightly shifted toward higher temperatures with increasing NFC content (Table I). A shift in the $\tan \delta$ peak indicates that the motion of the matrix polymer chains has been physically restricted, possibly due to the interaction with the reinforcing network.²⁸ The shift of the $\tan \delta$ peak toward higher temperature and the preserved storage modulus at high temperatures means that the thermal stability

TABLE I
Temperature of the $\tan \delta_{\max}$

NFC content (wt %)	$T_{\tan \delta, \max}$ (°C)
25	47.1
40	49.1
60	54.4

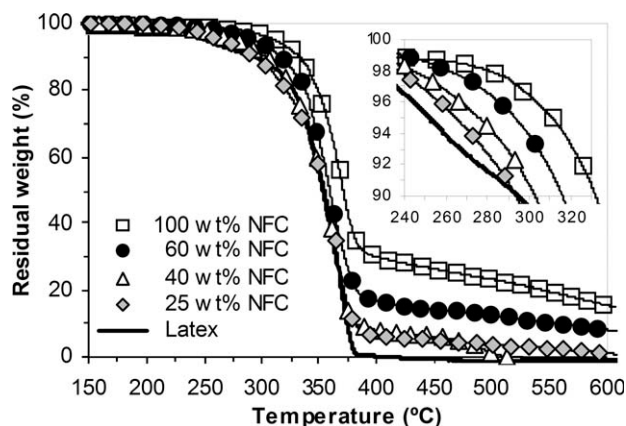


Figure 11 Typical curves from the TGA of the bionanocomposites.

of the composite material is improved with increasing NFC content.

The thermal stability of the bionanocomposite samples was also studied with TGA. With increasing NFC content in the bionanocomposites the onset point of degradation was continually shifted toward higher temperatures again confirming that the addition of NFC improves the thermal stability of the NFC/PLA bionanocomposite material (Fig. 11).

CONCLUSIONS

Utilizing a matrix in latex form enabled the production of a bionanocomposite material using a straightforward wet mixing method similar to papermaking. Thorough blending was achieved by using a homogenizer. Good dispersion of the components was obtained in the resulting bionanocomposite material resulting in improved mechanical properties even at a high NFC content. These high strength and stiffness values have not been reached previously with latex-based NFC/PLA composites. Tensile strength, Young's modulus, and strain at break were all linearly increased with increasing NFC reinforcement. Analysis of the fracture behavior of notched samples showed that as the NFC content increased, so did the fracture toughness, expressed as apparent strength for a given crack size. An increasing volume fraction of NFC at the crack tip does apparently have restricting effects on crack growth. Although the material became stronger with increasing NFC content, the material also became relatively more sensitive to defects. The NFC in the bionanocomposite material also gave improved thermal stability, probably due to the formation of a strong NFC network within the matrix.

We thank Lennart Salmén and Anne-Mari Olsson, Innventia AB, for their help with the DMTA. The SustainComp project,

a part of the EU 7th framework program and the financing parties in Innventia's "Applied and Exploratory Paper Chemistry" Research Cluster are gratefully acknowledged for financial support.

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