

Reinforcing Natural Rubber with Cellulose Nanofibrils Extracted from Bleached Eucalyptus Kraft Pulp

Chunmei Zhang^{1,2}, Tianliang Zhai^{1,2}, Ronald Sabo³, Craig Clemons³,
Yi Dan^{1,*}, and Lih-Sheng Turng^{2,4,*}

¹ State Key Laboratory of Polymer Materials Engineering of China, Polymer Research Institute of Sichuan University, Chengdu 610065, China

² Wisconsin Institute for Discovery, University of Wisconsin–Madison, Madison, WI 53715, USA

³ Forest Products Laboratory, USDA Forest Service, Madison, WI 53726, USA

⁴ Department of Mechanical Engineering, Polymer Engineering Center, University of Wisconsin–Madison, Madison, WI 53706, USA

Reinforced natural rubber (NR) nanocomposites were prepared by solution mixing, casting, and evaporation of pre-vulcanized natural rubber latex and an aqueous suspension of cellulose nanofibrils (CNFs) extracted from bleached eucalyptus kraft pulp. Scanning electron microscopy (SEM) images showed that there were no micro-scaled aggregates observed in the nanocomposites. The addition of CNFs changed the mechanical behavior of the nanocomposites as observed in tensile tests. The tensile strength was significantly enhanced with CNFs, but the material became brittle at higher CNFs loading levels. Dynamic mechanical analysis (DMA) proved the strong reinforcing tendency of CNFs in the NR matrix as the storage modulus of the nanocomposites increased with CNFs content across the entire temperature range. Thermal gravimetric analysis (TGA) showed that CNFs had a slightly negative impact on the thermal stability of NR nanocomposites. There was no change in the glass transition temperature of the rubber matrix with the addition of cellulose nanofibrils, which was characterized by differential scanning calorimetry (DSC) measurements.

Keywords: Cellulose Nanofibrils, Natural Rubber, Nanocomposites, Mechanical Properties.

1. INTRODUCTION

The properties of polymeric materials can be tailored by adding fillers with varied surface chemistries and aggregate size/aspect ratios. In the rubber industry, carbon black, silica, and glass fibers are the most frequently used reinforcements.^{1–3} However, the high density and relatively high loading level of these fillers makes the density of filled rubber composites relatively high, thus reversing the outstanding light weight property of rubber materials.⁴ In addition, these fillers require long processing time during production and rely on the fossil fuels resources. Therefore, natural fibers such as bamboo, coir, and oil palm have also been developed to reinforce the rubber matrixes to improve or modify certain mechanical properties of the host matrix for specific applications.^{5–10}

There is currently a considerable interest in processing polymeric composites reinforced with nanosized

particles.¹¹ This class of materials known as nanocomposites is attracting the interest of both the scientific community and industry. Because of the nanoscale effect, these nanocomposites display some outstanding properties when compared to conventional composites prepared from the same source. As a result, many efforts have been made in recent years to obtain and use nanocrystals from polysaccharides such as cellulose.^{12–14} Cellulose is the most abundant renewable organic biomaterial on earth and is totally biodegradable. By extracting cellulose at the nanoscale level, the majority of defects associated with the hierarchical structure have been removed, and a new cellulose-based “building block” named cellulose nanoparticles (CNs) is now available for the next generation of cellulose-based composites. In the context of both biomass valorization and nanocomposite materials development, using CNs as the reinforcing constituent in rubber has received even greater attention.^{15–21} Cellulose nanoparticles typically have a strong axial elastic modulus, a relatively high aspect ratio, and a low density. They are easy

*Authors to whom correspondence should be addressed.
Emails: danyi@scu.edu.cn, turng@engr.wisc.edu

to process and cause little abrasion to equipment as reinforcing fillers in composites. Moreover, CNs is available as an aqueous suspension and hence latex blending provides a viable and convenient route to disperse the nano-reinforcements in the matrix.

Nanocomposites of natural rubber (NR) filled with CNs extracted from different sources and in different forms were reported by earlier researchers. Dufresne's group has extracted CNs from bleached sugar cane bagasse kraft pulp,²² sisal bleached pulp,²³ cassava bagasse,²⁴ and date palm trees.^{25,26} Visakh et al.²⁷⁻²⁹ used bamboo pulp as the source material. Abraham et al.³⁰ employed cellulose nanofibers obtained by the steam explosion of the banana fiber as the reinforcing filler for natural rubber. The CNs with different size/aspect ratios has different impacts on the properties of natural rubber composites. In the present study, we specifically used cellulose nanofibrils (CNFs) which were obtained by the tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation of bleached eucalyptus kraft pulp as the reinforcing filler for natural rubber latex. To the best of our knowledge, little work has been published so far on the isolation of CNFs from eucalyptus and its use in natural rubber composites. The natural rubber latex used in the study was a pre-vulcanized latex compound, which the crosslinking agent was already included and can be vulcanized either by time or heat. Vulcanization, a chemical process in which long chains of rubber molecules are crosslinked, transforms the soft, weak plastic-like material into a strong, elastic product with high and reversible deformability and good mechanical properties by strain-induced crystallization, low hysteresis, and excellent dynamic properties and fatigue resistance. After vulcanization, rubber loses its tackiness, becomes insoluble in solvent, and becomes more resistant to heat, light, and the aging processes.^{31,32} Crosslinking of the NR matrix by vulcanization might lead to green natural rubber-based nanocomposites with the mechanical properties and thermal stability required for practical applications. The nanocomposites were obtained by casting and water evaporation. The effects of filler content on structure, thermal stability, tensile properties, and dynamic mechanical properties of the composites were investigated.

2. EXPERIMENTAL DETAILS

2.1. Materials

The TEMPO-oxidized CNFs used in this study was prepared according to the procedure reported by Saito et al.³³ Commercially supplied bleached eucalyptus Kraft pulp (Aracruz Cellulose, Brazil) was received in dry form and used as the raw material. The pulp was first pre-treated with an acid wash by pulping the fibers and soaking them overnight at 2% solids, pH 2, and 2 wt% NaClO₂ (based on pulp weight). After filtering and washing the pre-treated fibers, they were then carboxylated using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), sodium chlorite,

and sodium hypochlorite as reactants at 60 °C for 3 days according to the procedure by Saito et al.³³ The TEMPO-oxidized pulp fibers were then washed thoroughly using reverse osmosis-purified (RO) water and homogenized in a disk refiner to break apart any fibril bundles. The fiber slurry was then diluted to facilitate separation of coarse and fine fractions by centrifugation at 12,000× g, and the coarse fractions were rejected. The nanofiber suspension was then concentrated to a solid content of approximately 0.6% using ultrafiltration. A final clarification step was performed, in which the nanofiber suspension was passed once through an M-110EH-30 Microfluidizer (Microfluidics, Newton, MA) with 200 μm and 87 μm chambers in series. The carboxylate content of the reacted pulp fibers was measured via titration based on TAPPI Test Method T237 cm-98 and found to be 0.65 mmol COONa per gram of pulp. The CNFs aqueous suspension with a weight concentration of 0.67% was obtained and used in this study.

Pre-vulcanized natural rubber latex with a 55% dry rubber content named HX-80 was purchased from Holden's Latex (New York, USA). The crosslinking process can be accomplished by either time or heat; that is, 3 days at room temperature or 4 hours at 50 °C.

2.2. Nanocomposite Films Processing

The CNFs aqueous suspension was mixed with the pre-vulcanized NR latex in fractions varying from 0 to 10 wt% (dry basis). The mixture was stirred using a magnetic stirrer for 4 h, cast in petri dishes, degassed to avoid the formation of irreversible bubbles during water evaporation, and then dried overnight at 60 °C. Further drying of the films was performed at 50 °C for 4 h to accomplish the crosslinking process. The dry films obtained were 0.4 to 0.6 mm thick depending on the filler content.

2.3. Characterization

2.3.1. Transmission Electron Microscopy (TEM)

For TEM imaging of the CNFs, the suspension was diluted and deposited on a glow-discharged copper grid with formvar and carbon film (400 meshes). The droplet was left on the grid for 2 min, and then rinsed thoroughly using a 2% aqueous uranyl acetate stain followed by blotting. Samples were imaged using a Philips CM-100 TEM (Philips/FEI Corporation, Eindhoven, Holland) which operated at 100 kV, spot 3200 μm condenser aperture, and 70 μm objective aperture. The images were captured and recorded using a SIA L3C 4-2M pixel CCD camera (Scientific Instruments and Application, Duluth, GA, USA).

2.3.2. Fourier Transform-Infrared Spectroscopy (FTIR)

Fourier transform-infrared spectroscopy (FTIR) spectra of NR, CNFs, and CNFs/NR composites were recorded by a Bruker Tensor 27 spectrophotometer at a resolution

of 2 cm^{-1} in the frequency range from 4000 cm^{-1} to 400 cm^{-1} . The attenuated total reflectance technique was employed.

2.3.3. Scanning Electron Microscopy (SEM)

The morphology of neat NR and CNFs/NR composites was examined with a LEO 1530 scanning electron microscope. Before the SEM observation, the composite films were submerged in liquid nitrogen and broken to expose the internal structure for SEM studies, and the fractured surface was sputter coated with gold.

2.3.4. Tensile Tests

The tensile behaviors of NR and the nanocomposite films were analyzed using an Instron 5967 Universal Testing Machine with a load cell of 30 kN. The experiments were performed at room temperature ($25\text{ }^{\circ}\text{C}$) and atmospheric conditions (relative humidity of $20\pm 5\%$), with a crosshead speed of 500 mm/min . The samples were prepared by cutting strips of the films 40 mm long and 10 mm wide. The distance between jaws was 20 mm , and the sample thickness was measured before each test. Five samples were tested for each material.

2.3.5. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis measurements were performed on a DMA Q800 (TA Instruments) using tensile mode. During the DMA test, the specimens were heated at a rate of $3\text{ }^{\circ}\text{C/min}$ from -80 to $40\text{ }^{\circ}\text{C}$ with a frequency of 1 Hz and amplitude of $50\text{ }\mu\text{m}$. The dimensions of the rectangular specimens were about 12 mm in length, 0.63 mm in width, and 0.4 to 0.6 mm in thickness, which were measured before each analysis.

2.3.6. Thermal Gravimetric Analysis (TGA)

The thermal stability of the materials was analyzed by a TGA Q50 (TA Instruments) from room temperature to $600\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C/min}$. Approximately 10 mg of neat NR and CNFs/NR nanocomposites of various NFC contents were used for each test. Samples were first dried at $60\text{ }^{\circ}\text{C}$ for 2 h prior to testing. The weight loss was recorded and normalized against the initial weight.

2.3.7. Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter Q20 (TA Instruments) was used to study the thermal properties of the nanocomposites. Prior to testing, the specimens were dried at $60\text{ }^{\circ}\text{C}$ for 2 h . Samples of 6 to 10 mg were placed in aluminum sample pans and cooled from room temperature to $-100\text{ }^{\circ}\text{C}$, then held at $-100\text{ }^{\circ}\text{C}$ for 3 min before heating to room temperature; the cooling and heating rates were both $10\text{ }^{\circ}\text{C/min}$. The glass transition temperatures of NR and CNFs/NR composites were obtained from the heating scans.

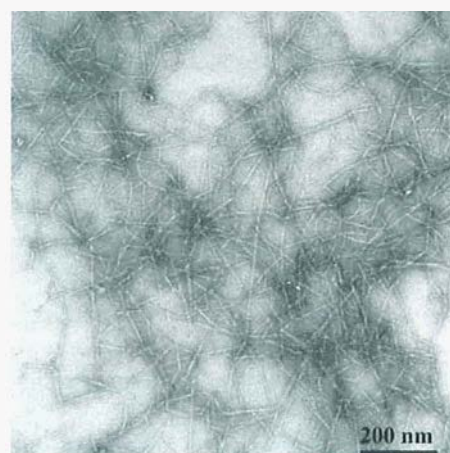


Fig. 1. TEM of TEMPO-oxidized cellulose nanofibrils.

3. RESULTS AND DISCUSSION

3.1. Morphology of CNFs

Morphological analysis of CNFs, which was extracted from bleached eucalyptus Kraft pulp by the TEMPO-mediated oxidation process, was conducted by TEM and is shown in Figure 1. It can be seen that CNFs have an interconnected web-like structure with fibrils having a diameter of 5 to 7 nm . The length was hard to estimate owing to difficulty in obtaining well-individualized nanofibrils in the TEM images, but may be considered to be on the micrometer scale.

3.2. Fourier Transform-Infrared (FTIR) Analysis

The FTIR spectra obtained for CNFs, NR, and their nanocomposites are shown in Figure 2. For CNFs dry film, the strong absorption peak centered at around 1058 cm^{-1} can be attributed to the C—O stretching vibration. This peak was not detected in NR or the 1% CNFs/NR nanocomposite, but there was a gradual increase in the intensity of this peak for the nanocomposites with an increase in

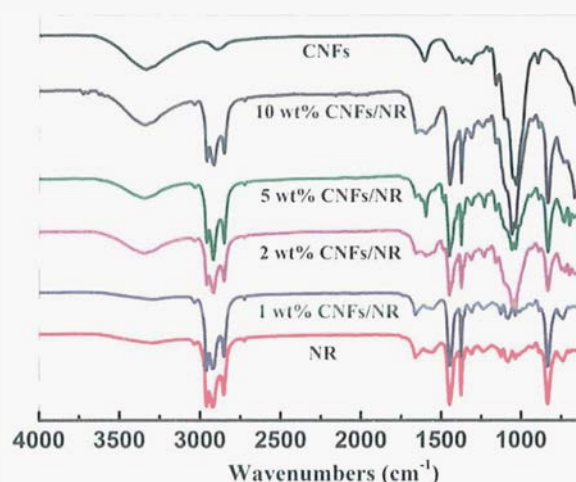


Fig. 2. FTIR spectra of CNFs, NR, and CNFs/NR nanocomposites.

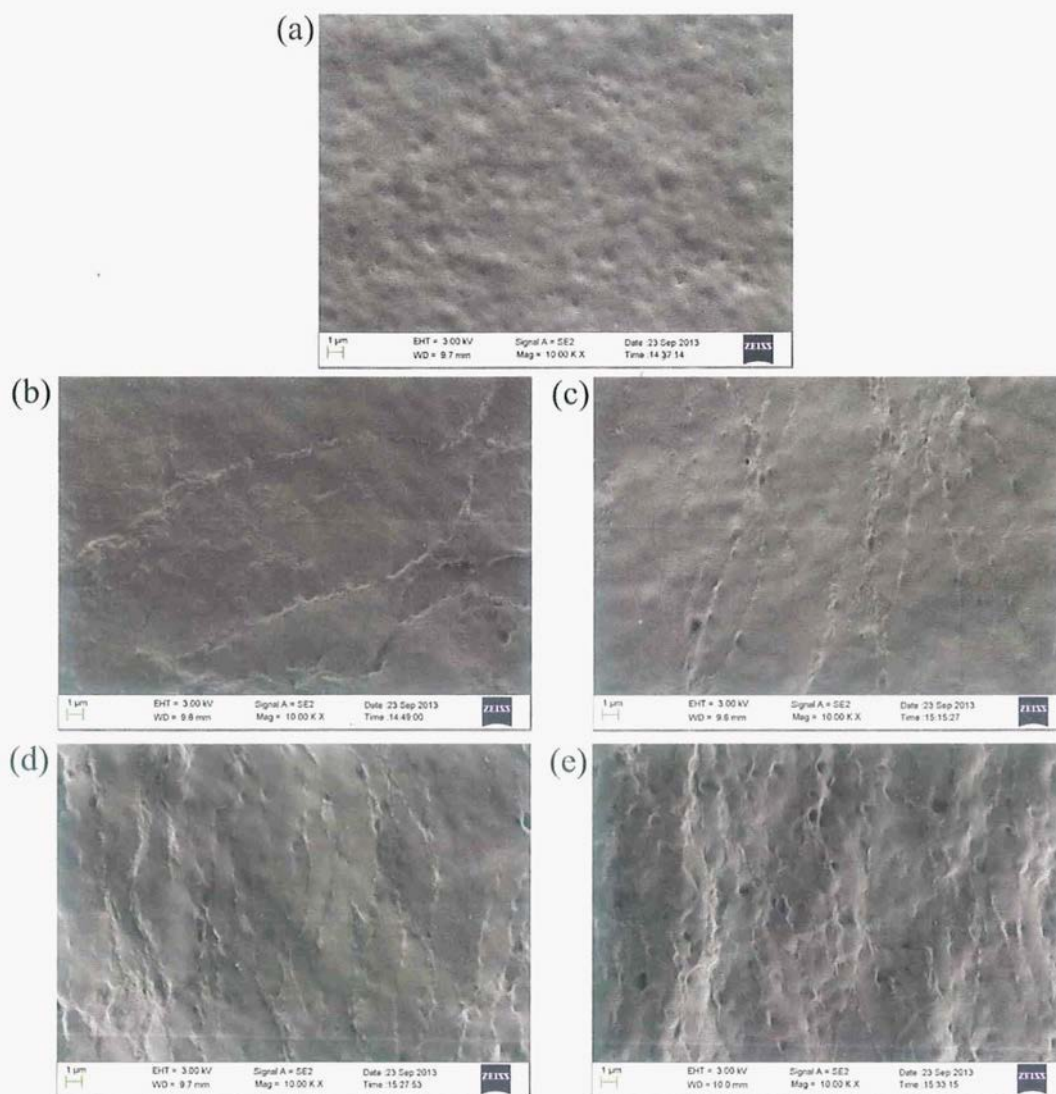


Fig. 3. SEM images of neat NR matrix (a) and nanocomposites with 1% (b), 2% (c), 5% (d) and 10% (e) CNFs content.

percentage of CNFs from 2% to 10%. In addition, the peak characteristic of the hydroxyl group at around 3340 cm^{-1} was also found in the nanocomposites with CNFs contents ranging from 2% to 10%. The presence of cellulose nanofibrils in the nanocomposites was confirmed. With low loading of CNFs, the spectra of NR and 1% CNFs/NR showed almost the same characteristic peaks.

3.3. Morphology of Nanocomposite Films

The morphological investigation of the cross-section of the prepared composite films was carried out using a scanning electron microscopy and was shown in Figure 3. The surface of unfilled NR displays a smooth and uniform morphology whereas the CNFs/NR nanocomposites give roughness morphology and even rougher when more CNFs were added. It is probably due to the brittle fracture of nanocomposites under liquid nitrogen. Though it is not possible to make conclusion that the threadlike wrinkles

are the alignment of nanofibrils on the fractured surface, the wrinkles evidence the existence of the nanofibrils. Nanoscale dispersion of cellulose nanofibrils cannot be evaluated at this magnification as the nanofibrils are hardly distinguishable, but it can be concluded that there are no micro-scaled aggregates in the nanocomposites, even at 5 and 10 wt% CNFs content. Cellulose nanofibrils seem to be homogeneously distributed in the rubber matrix, no particular sedimentation phenomenon of CNFs within the thickness of the films was observed during the composite preparation.

3.4. Tensile Properties of Nanocomposites

The tensile mechanical behaviors of the films of NR, as well as the nanocomposites reinforced with various contents of CNFs, were analyzed by tensile testing at room temperature. Figure 4 shows the typical stress-strain curves of five film materials. The increased initial slope

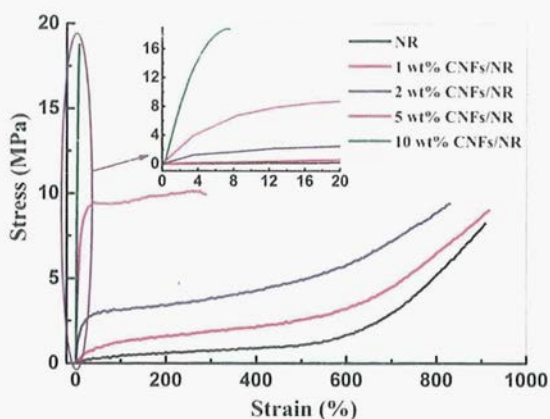


Fig. 4 Stress-strain curves of NR and CNFs/NR nanocomposites.

of the curves and the stress value clearly shows the significant reinforcing effect of CNFs on NR nanocomposite films. For neat NR and NR nanocomposites with 1 wt% CNFs, the stress continuously increased with the strain, which exhibited an elastic nonlinear behavior typical of amorphous polymers at temperatures over their glass transition temperatures. When the strain was over 600%, the stress rapidly increased until the films fractured. This sharp increase in stress was a typical behavior for vulcanized rubber, caused by the strain-induced crystallization at higher strain levels. With 2 wt% CNFs content, the mechanical behavior in the initial stretching region of the nanocomposite became a little different, that the stress significantly increased with the strain. This was analogous to a Hooke elastic deformation. The phenomenon was more pronounced in the case of nanocomposite with 5 wt% CNFs. However, the mechanical behavior of the NR nanocomposite with 10 wt% CNFs was much different. The sample exhibited brittle behavior with an elongation-at-break of only 7%. This was caused by the strong stiffness and brittle nature of CNFs. The mechanical properties derived from these tensile tests are reported in Table I. As can be seen, the tensile strength of neat NR was 8.3 MPa and increased to 10.0 MPa and 18.7 MPa with a CNFs content of 5 wt% and 10 wt%, respectively. However, the elongation-at-break decreased from 908% for neat NR to 288% for the 5 wt% CNFs/NR nanocomposite. The reduced elongation-at-break for the NR nanocomposite with high CNFs concentration may result from poor interfacial bonding between CNFs and NR. An increase in

the CNFs content increased the specific surface area of the filler in contact with the rubber matrix. The weakly bonded interface between CNFs and NR could act as defect leading to poor ductility. The tensile energy absorption (TEA) is the work necessary to break the specimen, which can be calculated from the area under the load-elongation curve. It can be seen that the TEA for pure NR was 18.1 J/m³. It increased with the addition of CNFs up to 40.8 J/m³ for NR nanocomposite with 2 wt% CNFs, which possessed the highest TEA, and then the TEA of the nanocomposites decreased with more CNFs to as low as 0.9 J/m³ for 10 wt% CNFs/NR composite. It can be concluded that while CNFs could increase the tensile strength and tensile modulus of the NR composites, only with less than 5 wt% content of CNFs can the extraordinary ductility of NR be retained.

3.5. Dynamic Mechanical Properties of Nanocomposite Films

Dynamic mechanical analyses of neat NR and of NR nanocomposites at different loading levels of CNFs were performed. Figure 5 shows plots of the storage modulus and tan δ (loss angle tangent) measured at 1 Hz as a function of temperature. At low temperatures, the storage modulus remained roughly constant. As noted in a publication by Nair et al.¹⁷ the storage modulus values for any glassy polymer were constant around 3×10^3 MPa, which was related to the fact that molecular motions are largely restricted to vibration and short-range rotational motions in the glassy state. It was also noted that the storage modulus of the nanocomposites increased with increasing content of cellulose nanofibrils, and the highest modulus was observed for the 10 wt% CNFs/NR nanocomposite.

From Figure 5(a) it can be seen that all samples displayed a significant modulus drop around -50°C ; i.e., in the glass-rubber transition zone. This modulus drop corresponded to the main relaxation phenomenon, which was associated with the anelastic manifestation of the glass transition. This resulted in a concomitant relaxation process where tan δ passed through a maximum (Fig. 5(b)). This relaxation process involved cooperative motions of long chain sequences. Above T_g in the rubbery plateau region, the modulus became almost constant again. The rubbery modulus was also greatly enhanced with an increase of CNFs in the NR matrix. For example, the relaxed modulus at 20°C of 1 wt% CNFs/NR nanocomposite was 5 times higher than that of neat NR. For the 10 wt% CNFs/NR nanocomposite, the rubbery modulus was more than 1170 times higher than that of NR. Visakh et al.²⁸ explained that the rubbery modulus depended on the degree of crystallinity of the material. In this study, the cellulose nanofibrils acted as physical crosslinks for the elastomer and increased the modulus substantially.

Figure 5(b) shows the evolution of tan δ as a function of temperature for NR and CNFs/NR nanocomposites. For neat NR, tan δ exhibited a maximum at around

Table I. Tensile property of NR and CNFs/NR nanocomposites.

Sample	Tensile strength (MPa)	Elongation-at-break (%)	Tensile energy absorption (J/m ³)
NR	8.3 ± 0.2	908 ± 13	18.1 ± 1.1
1 wt% CNFs/NR	9.0 ± 0.4	917 ± 20	29.6 ± 1.2
2 wt% CNFs/NR	9.4 ± 0.5	829 ± 10	40.8 ± 1.6
5 wt% CNFs/NR	10.0 ± 0.6	288 ± 8	27.3 ± 1.0
10 wt% CNFs/NR	18.7 ± 0.4	7 ± 0.7	0.9 ± 0.1

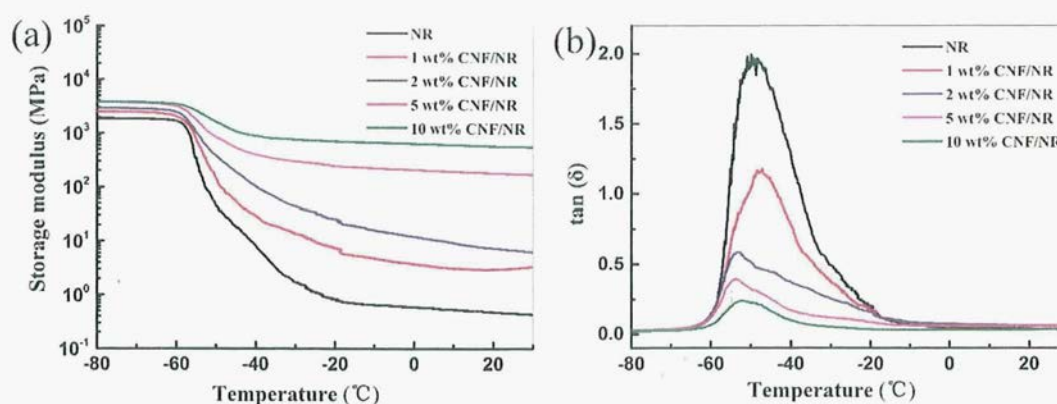


Fig. 5. (a) Storage modulus and (b) loss angle tangent of NR and CNFs/NR nanocomposites as a function of temperature.

−47°C. At CNFs contents above 1%, the $\tan \delta$ shifted to lower temperatures for the CNFs/NR nanocomposites. Similar results have been reported by Mele et al.³⁴ They explained that this shift was related to a phase inversion phenomenon occurring for a filler volume higher than the percolating threshold. Pasquini et al.²⁴ attributed this shift to the mechanical coupling effect. The intensity of the relaxation process for the nanocomposites was lower than that of neat NR. This can also be ascribed to a decrease in the amount of matrix material, which was responsible for the damping properties. Also, the molecular mobility of the NR chains in the vicinity of the nanofibrils was reduced as more CNFs were added.

3.6. Thermal Properties of Nanocomposites

Thermal degradation of cellulose materials or the reduction in mechanical properties at elevated temperatures is one of the major issues that limit their applications. So it is important to study the influence of cellulose nanofibrils on the thermal stability of natural rubber. The TGA and the derivative thermogravimetric analysis (DTG) curves for CNFs are shown in Figure 6(a). The initial weight loss at about 80 °C was a result of moisture loss upon heating since CNFs are very sensitive to water. Although it is not obvious in the TGA thermogram, it can be observed

in the DTG thermogram that the degradation of the cellulose nanofibrils involved two main degradation stages, with the maximum weight loss rates occurring at 255.8 and 302.3 °C, respectively. For cellulose, the degradation at lower temperatures is ascribed to the evolution of non-combustible gases such as carbon dioxide, carbon monoxide, formic acid, and acetic acid, while the second degradation stage is believed to be the pyrolysis and evolution of combustible gases.²⁷ The char residue at the end of heating was about 23%.

Figure 6(b) presents the TGA curves for neat NR and CNFs/NR nanocomposites. Unlike CNFs, all of the samples experienced only one weight loss peak (according to derivative TGA curves not shown here). A detailed view of the onset of degradation is shown in the inset figure. The onset of degradation for the nanocomposites shifted to lower temperatures with the addition of CNFs. The initial degradation temperature of neat NR was 350.0 °C, and it decreased slightly to 348.0 and 345.0 °C for nanocomposites with 2 wt% and 10 wt% CNFs, respectively. This is because of the lower onset degradation temperature of CNFs as compared to rubber.

In order to study the effect of the addition of cellulose nanofibrils on the glass transition temperature (T_g) of NR, differential scanning calorimetry (DSC) measurements

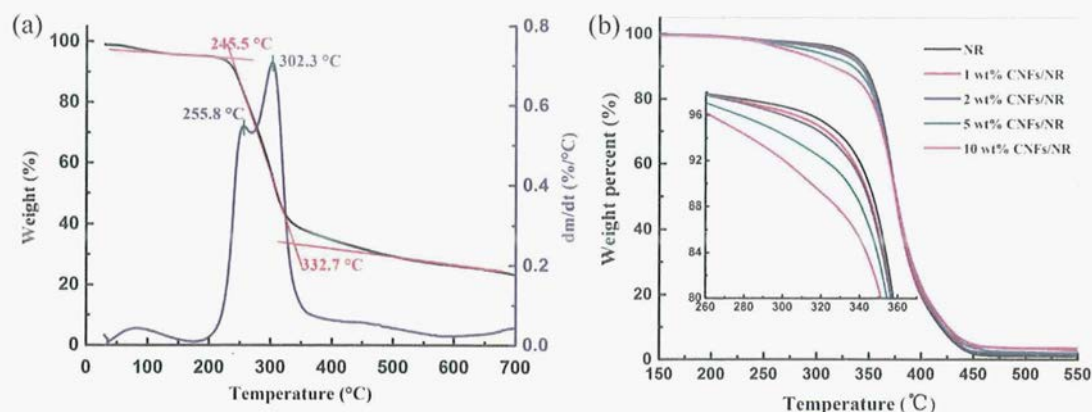


Fig. 6. TGA curves recorded for (a) CNFs and (b) CNFs/NR nanocomposites.

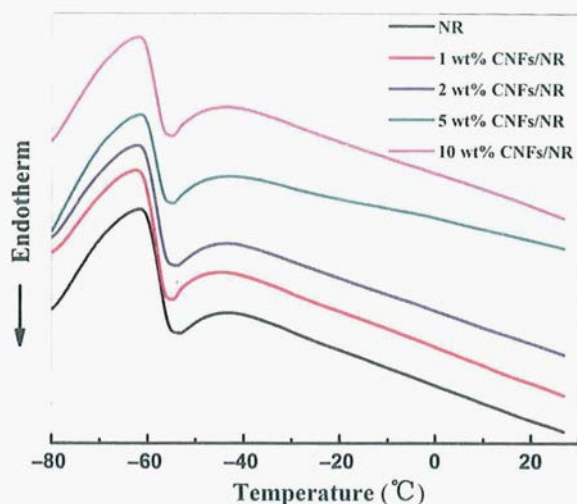


Fig. 7. DSC heating scans of NR and CNFs/NR nanocomposites.

were carried out for neat NR and CNFs/NR nanocomposites. The heat flow of the samples being heated from -100 °C to room temperature was recorded and is shown in Figure 7. All of the samples displayed a glass transition temperature of around -58 °C. Compared to neat NR, no significant variation of T_g upon addition of cellulose nanofibrils was observed for the nanocomposites. Similar results have also been reported by Bras et al.²² and Bendahou et al.²⁵ regardless of the cellulose nanoparticles used.

4. CONCLUSIONS

Cellulose nanofibrils were successfully extracted from bleached eucalyptus kraft pulp by a TEMPO-mediated oxidation process. The morphology, which was observed by TEM, featured an interconnected, web-like structure having a diameter of 5 to 7 nm and a length on the micrometer scale. The nanofibrils were used as the reinforcing agent in the NR matrix by casting a mixture of pre-vulcanized NR latex and CNFs aqueous suspension. The CNFs/NR nanocomposites displayed a strong peak centered at 1058 cm^{-1} in the FTIR spectra, which was attributed to the C—O stretching vibration of CNFs. Compared with the smooth fractured surface of neat NR matrix, CNFs/NR nanocomposites show more roughness morphology as observed by SEM and there are no micro-scaled aggregates presented in the nanocomposites. The addition of CNFs changed the mechanical behavior in the initial stretching region for the nanocomposites as observed in tensile tests. The tensile strength of the nanocomposites significantly increased with the addition of CNFs, accompanied by a moderate decrease in elongation-at-break when less than 5 wt% CNFs was added. However, the composites became brittle with higher CNFs content. Especially for the 10 wt% CNFs/NR nanocomposite, the tensile stress was as high as 18.7 MPa, but the elongation was only 7%. The DMA results showed that the storage modulus was

significantly enhanced with the addition of CNFs within the whole temperature scan, which served as good evidence of the strong reinforcing tendency of CNFs in NR. In addition, a slight negative shift in the $\tan \delta$ peak position was observed when more than 1 wt% CNFs was added to the matrix. The thermal stability of the nanocomposites decreased slightly with CNFs, which was ascribed to the lower onset degradation temperature of CNFs as opposed to rubber, as characterized by TGA measurements. The DSC results also showed that the addition of CNFs didn't impact the glass transition temperature of the rubber matrix. In order to retain the ductility of natural rubber when using cellulose nanofibrils as the reinforcing fillers, the interfacial bonding between CNFs and NR needs to be improved through chemical modification of CNFs.

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