

Thermal and Mechanical Properties of Natural Rubber Composites Reinforced with Cellulose Nanocrystals from Southern Pine

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ABSTRACT: There is currently a considerable interest in developing bio-based and green nanocomposites in industrial and technological areas owing to their biodegradability, biocompatibility, and environmental friendliness. In this study, a bio-based nanosized material, cellulose nanocrystals (CNC), extracted from southern pine pulp was employed as a reinforcing agent in a natural rubber (NR) matrix. NR/CNC nanocomposites were prepared by a solution mixing and casting method. The morphology, thermal, and mechanical properties of the nanocomposites were investigated using scanning electron microscopy, Fourier transform-infrared spectroscopy, tensile tests, dynamic mechanical analysis, thermal gravimetric analysis, and differential scanning calorimetry. The CNC displayed a gradient dispersion in the nanocomposites, and no microscaled aggregates were observed. Both the tensile strength and modulus of the nanocomposites increased with the addition of CNC, accompanied by a slight decrease in elongation at break. The storage modulus also improved with the addition of CNC, which served as good evidence of the reinforcing tendency of CNC in the NR matrix. The thermal stability of the nanocomposites showed an insignificant decrease in CNC addition. The glass transition temperature of the nanocomposites was not influenced by CNC. © 2014 Wiley Periodicals, Inc. *Adv Polym Technol* 2014, 33, 21448; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.21448

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Introduction

Natural rubber (NR) is the oldest known rubber with a high molecular weight polymer of isoprene (2-methyl 1,3-

butadiene).^{1,2} It is one of the most attractive and important elastomers widely used in industrial and technological areas. It is naturally available in the form of a stable colloidal dispersion of rubber particles, known as NR latex. The properties of NR can be tailored by the addition of fillers of various surface chemistries and aggregate size/aspect ratios to suit the desired application. Carbon black and silica are the most frequently used reinforcing fillers in the rubber industry.^{3–5} However, the processing of these fillers leads to high energy consumption and environment pollution. Moreover, the high density of these fillers makes the

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final filled rubber composites have a high density as well, which reverses the outstanding light weight property of rubber materials. Therefore, the need to develop bio-based fillers that are light weight, biodegradable, nonpetroleum-based, carbon neutral, and have a low environmental impact has been increasing in demand. Currently, there is also a growing interest in preparing nanocomposites filled with nanosized rigid particles.^{6–8} The concept of using nanocomposites originates from both the point of view of fundamental property determination and the development of new materials to meet a variety of applications. Owing to the nanoscale building blocks of a nanocomposite, there are many more interfaces between the two intermixed phases compared to a conventional composite with microscale fillers, and these interfacial interactions will create a noticeable reinforcing impact.

Cellulose nanoparticles (CNs) are extracted from cellulose at the nanoscale. They are ideal materials on which to base the new biopolymer nanocomposites industry.^{9,10} Crystalline CNs possess high axial elastic modulus, and their mechanical properties are within the range of other reinforcement materials.¹¹ The preparation of reinforced polymer materials with CNs has seen rapid advances and considerable interest in the past decade owing to their renewable nature, high mechanical properties, and low density, as well as their availability and the diversity of their sources. CNs are also available as aqueous suspensions; hence, solution blending with NR latex provides a viable route of dispersing the CNs in the NR matrix. There are six types of cellulose particles—i.e., microfibrillated cellulose, nanofibrillated cellulose, cellulose nanocrystals (CNC), tunicate cellulose nanocrystals, algae cellulose particles, and bacterial cellulose particles—that describe the main cellulose-based nanoparticles, which typically differ from each other based on the cellulose source materials and particle extraction methods. Each particle type is distinct, having a characteristic size, aspect ratio, morphology, crystallinity, crystal structure, and properties. Among these CNs, CNC have attracted much more attention due to their high aspect ratio (3–5 nm wide, 50–500 nm in length) and high crystallinity (54–88%). CNC are the rod-like or whisker-shaped particles that remain after the acid hydrolysis of other cellulose fibers.

NR-based nanocomposites with CNC, extracted from bagasse,^{12,13} syngonanthus nitens,¹⁴ sisal,¹⁵ palm tree,^{16,17} bamboo,^{18–20} banana fiber,²¹ etc., can be found in the literature. Most of these studies used latex-blending techniques, whereas very few reports developed vulcanized NR nanocomposites. CNC obtained from different sources is different in size/aspect ratios and has different impacts on the properties of NR composites. Southern pines are principal sources of softwood products in the United States. To the best of our knowledge, little work has been published on the isolation of CNC from southern pine or their use in NR composites. In this study, we prepared CNC by sulfuric acid hydrolysis of southern pine pulp. The morphology was observed by transmission electron microscopy (TEM). The NR latex used in this study was a prevulcanized latex compound. The cross-linking of the NR matrix by vulcanization could lead to NR-based green nanocomposites with the mechanical properties and thermal stability required for practical applications. This work aims to evaluate the use of this specific nanomaterial as a reinforcing agent in a NR matrix in the form of latex. The nanocomposites were obtained by solu-

tion blending, casting, and water evaporation, and the effects of CNC on the structure, as well as the thermal and mechanical properties, was studied.

Experimental Setup

MATERIALS

Commercially available dissolving pulp dry lap made from southern pine was used as the starting material for producing CNC. Strips of the dissolving pulp were reacted with 64% sulfuric acid at 45°C for approximately 1.5 h under a nitrogen blanket with constant stirring. The hydrolysis reaction was terminated by diluting with water to approximately a 10-fold volume of the initial suspension. The CNC were neutralized by adding an aqueous sodium hydroxide solution of about 5% concentration. At this point, the CNC were not colloidal and settled due to the high salt concentration. Continued dilution and decanting were carried out until the sodium sulfate concentration was about 1%. The sodium sulfate and other salts were removed by ultrafiltration in a tubular ultrafiltration unit. Fresh water was added to the suspension during ultrafiltration to keep the CNC concentration at approximately 1%. After essentially all of the salt was removed, the CNC suspension was concentrated in the same ultrafiltration unit. The final concentration of the CNC was approximately 10% by weight.

Prevulcanized NR latex with a 58% dry rubber content was kindly supplied by Chemionics Corporation (Tallmadge, OH). The NR latex was precompounded with cross-linking components, and, at the recommended curing temperature of 100°C, it will be fully cured in 15 min.

NANOCOMPOSITE FILMS PROCESSING

The CNC aqueous suspension was mixed with the prevulcanized NR latex in fractions varying from 0 to 5 wt% (dry basis). The mixture was stirred using a magnetic stirrer for 4 h, casted 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 100°C for 15 min to accomplish the cross-linking process. The dry films obtained were 0.4–0.6 mm thick depending on the filler content.

CHARACTERIZATION

Transmission Electron Microscopy

For TEM imaging of the CNC obtained, the suspension was diluted and deposited on a glow-discharged copper grid with formvar and carbon film (400 meshes). The droplet was maintained 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, Eindhoven, The Netherlands), 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 4–2 M pixel CCD camera (Scientific Instruments and Application, Duluth, GA).

Fourier Transform-Infrared Spectroscopy

Fourier transform-infrared spectroscopy (FTIR) spectra of NR, CNC, and NR/CNC nanocomposites were recorded by a Bruker Tensor 27 spectrophotometer at a resolution of 2 cm^{-1} in the frequency range from 4000 to 400 cm^{-1} . The attenuated total reflectance technique was employed.

Scanning Electron Microscopy

The morphology of NR and NR/CNC composites was examined with a LEO 1530 scanning electron microscope. Before the scanning electron microscopy (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.

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°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 film 40 mm long by 10 mm wide. The distance between the jaws was 20 mm , whereas the thickness was measured before each measurement was taken. Five samples were tested for each material, and the average values and standard deviations were reported.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) measurements were performed on a DMA Q800 (TA Instruments) in tensile mode. During the DMA test, the specimens were heated at a rate of 3°C/min from -80 to 40°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.

Thermal Gravimetric Analysis

Specimens used for thermal gravimetric analysis (TGA) were first dried at 60°C for 2 h prior to testing. TGA was performed using a TGA Q50 (TA Instruments) from room temperature to 600°C at a heating rate of 10°C/min . Approximately 10 mg of neat NR and NR/CNC nanocomposites of various CNC contents were used for each test. The weight loss was recorded and normalized against the initial weight.

Differential Scanning Calorimetry

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°C for 2 h . Samples

of $6\text{--}10\text{ mg}$ were placed in aluminum sample pans and cooled from room temperature to -100°C , then held at -100°C for 3 min before heating to room temperature; the cooling and heating rates were both 10°C/min . The glass transition temperatures of NR and NR/CNC nanocomposites were obtained from the heating scans.

Results and Discussion

MORPHOLOGY OF CNC AND THE NANOCOMPOSITE FILMS

The TEM image in Fig. 1 shows the size and size distribution of a dilute suspension of CNC extracted from southern pine pulp. From the image, it can be seen that the CNC were well separated with no aggregation. The CNC displayed slender rods and had a broad distribution in length ranging from 30 to 100 nm , as obtained using digital image analysis. The diameters fell between 6 and 10 nm . The average length and width were estimated to be 77 ± 21 and $9 \pm 2\text{ nm}$, respectively. Therefore, the average aspect ratio (L/D) of the CNC was around 8.5 .

An examination of the cross section of the prepared nanocomposite films was carried out using a scanning electron microscope and the images are shown in Fig. 2. The longitudinal direction displays the thickness of the composite film. The surface of unfilled NR gives a smooth and uniform morphology, whereas the NR/CNC nanocomposites show nonuniform dispersion with a lower CNC rich layer and upper NR rich layer structure, especially at 5% CNC content; the nanocomposite shows a gradient of CNC concentration between the upper and lower faces of the films. It is concluded that the CNC tended to precipitate to the bottom of the film by the casting and evaporation method. Nanoscale dispersion of cellulose nanofibrils cannot be evaluated at this magnification, but it can be seen that there are no microscaled aggregates in the nanocomposites, even at 5% CNC content.

FTIR ANALYSIS

As mentioned above, the NR/CNC nanocomposite films prepared by the casting and evaporation technique in this study formed an internal, nonuniform dispersion with a CNC-rich layer and NR-rich layer structure. When the samples were subject to FTIR spectroscopy for characterization, both the lower (which was adhesive to the bottom of the Petri dish during evaporation) and upper surfaces of the films were tested. The spectra obtained are presented in Fig. 3. From the figure, it can be seen that the spectrum of the upper surface for all nanocomposite films showed the same characteristic peak as that of NR. However, the lower surfaces of the nanocomposites exhibit a much different spectrum. The strong peak characteristic of C–O stretching vibration of CNC, which was centered at around 1056 cm^{-1} , was also found in the lower surfaces of the NR/CNC nanocomposite films. The intensity of this peak gradually increased with the content of CNC in the nanocomposites. In addition, only the lower surfaces of the nanocomposite films displayed a broad absorption peak at around 3336 cm^{-1} , which

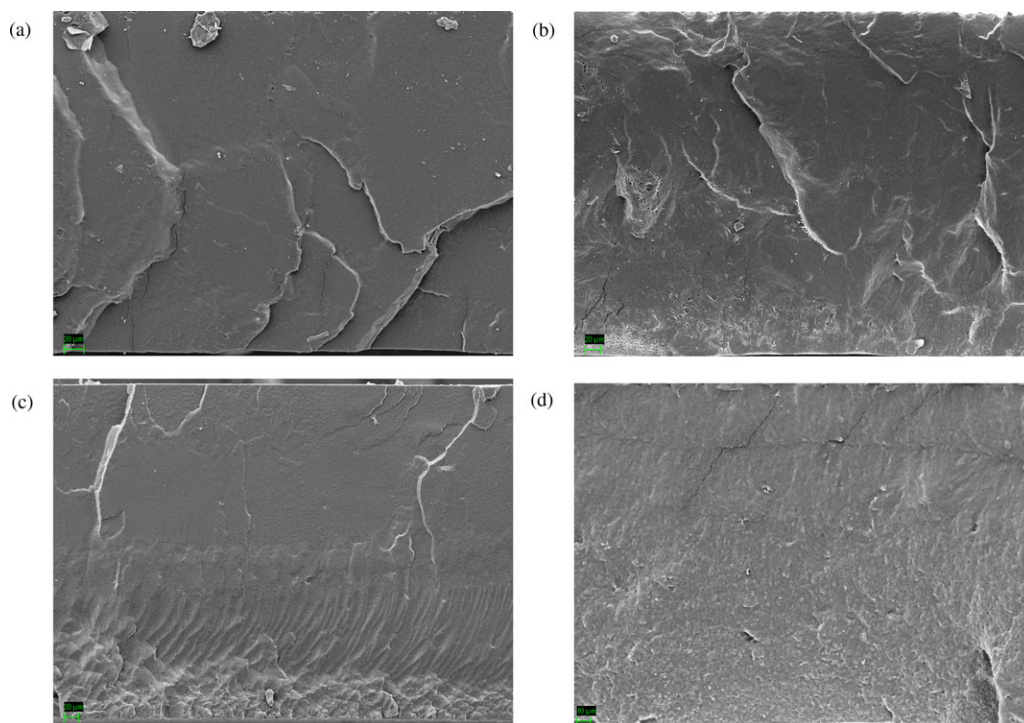


FIGURE 1. TEM image of CNC.

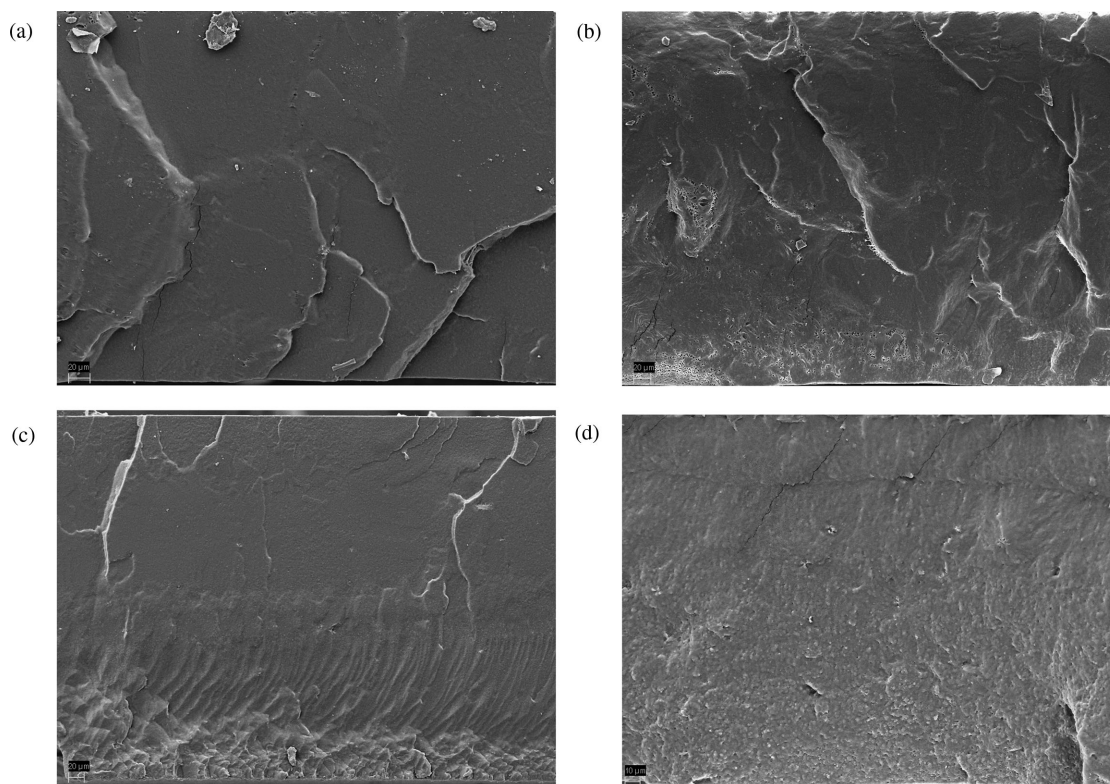


FIGURE 2. SEM images of NR matrix (a) and nanocomposites with 1% (b), 2% (c), and 5% (d) CNC content. The scale bars are 20 μm in (a)–(c) and 10 μm in (d).

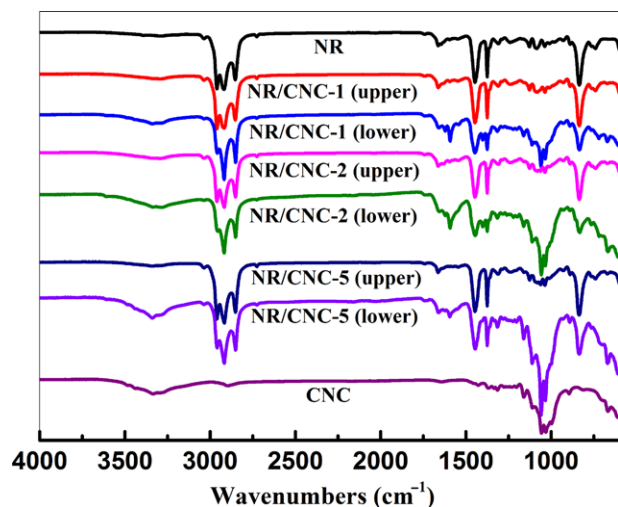


FIGURE 3. FTIR spectra of CNC, NR, and NR/CNC nanocomposites.

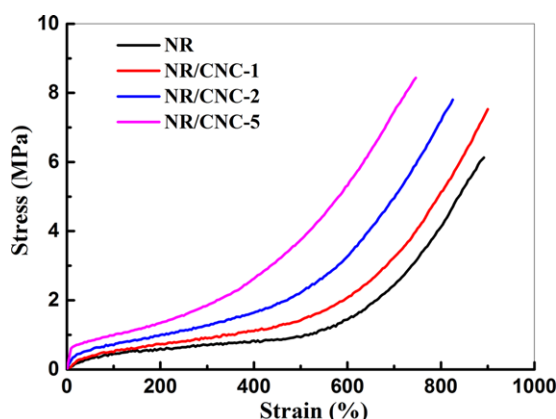


FIGURE 4. Stress-strain curves of NR and NR/CNC nanocomposites.

was attributed to the hydroxyl groups of CNC. The results are in agreement with the SEM observation that the NR/CNC composite films obtained by the casting and evaporation process in Petri dishes resulted in films with a CNC-rich layer at the bottom and an NR-rich layer at the top; where the interactions between CNC and NR were too weak to prevent from this happening.

MECHANICAL PROPERTIES OF NANOCOMPOSITES

The tensile mechanical behaviors of the NR/CNC nanocomposites, as well as the pure NR films, were characterized at room temperature. Typical stress versus strain curves for these materials are shown in Fig. 4. Pure NR exhibited an elastic nonlinear behavior typical of amorphous polymers at a temperature below their glass transition temperature, where the stress continuously increased with the strain. When the strain was over 600%, the stress rapidly increased up to fracture. This sharp increase in stress was caused by strain-induced crystallization during the rapid stretching phase. The initial slopes of the curves increased with the addition of CNC, which clearly showed the reinforcing effect of CNC on NR nanocomposite films. When conducting

TABLE I
Tensile Properties of NR and NR/CNC Nanocomposites

Sample	Tensile Strength (MPa)	Elongation at Break (%)	Conventional Modulus at 200% (KPa)
NR	6.1 ± 0.2	892 ± 30	108 ± 5
NR/CNC-1	7.5 ± 1.1	900 ± 20	177 ± 6
NR/CNC-2	7.8 ± 0.7	825 ± 15	266 ± 6
NR/CNC-5	8.4 ± 1.0	746 ± 27	423 ± 10

the experiments, samples with higher amounts of CNC were also produced and tested. However, the nanocomposite films fractured with a thin layer separated from the surface of the matrix, which obviously was the CNC-rich layer precipitated at the bottom during the evaporation process. Therefore, only the properties of nanocomposite films with CNC content up to 5% were presented in this paper. Table I lists the corresponding data deduced from the curves; i.e., the tensile strength, conventional modulus at 200% strain, and the elongation at break.

Both the tensile strength and modulus increased upon CNC addition to the rubber, resulting in a slightly decreased elongation at break. The increased tensile strength and modulus observed with increasing CNC content was attributed to the possible restriction of polymer chain mobility in the vicinity of nanocrystals. The maximum increase of tensile stress and modulus was achieved for nanocomposites with 5% CNC, which was 38% and 433%, respectively, and was accompanied by a 16% drop in elongation at break. The group of Siqueira^{14,15} and Abraham²¹ reported a significant drop in the elongation at break with the addition of CNs, whereas the elongation at break was not significantly affected by the CNC in the current study. Furthermore, the addition of CNC did not change the tensile behavior of the nanocomposites despite the improved tensile strength and modulus. All of these results suggest that the vulcanization or cross-linking of the NR phase, rather than the presence of CNC, predominate the tensile behavior. Previous studies on cross-linked NR reinforced with cellulose nanofibers¹⁸ and cellulose nanowhiskers¹⁹ reported similar behavior.

DYNAMIC MECHANICAL PROPERTIES OF NANOCOMPOSITES

Dynamic mechanical analyses of pure NR and nanocomposites with different concentrations of CNC were performed. Figure 5 shows the curves of the storage modulus (Fig. 5a) and $\tan \delta$ (tangent of loss angle, Fig. 5b) versus the temperature at a frequency of 1 Hz. At low temperatures, NR was in the glassy state and its storage modulus remained roughly constant at 1.7 GPa. This was due to the fact that in the glassy state, the molecular motions were largely restricted to vibration and short-range rotational motions. The glassy modulus improved to 1.9 and 2.8 GPa with the addition of 1% and 2% CNC, respectively. And the highest modulus was observed for the nanocomposite containing 5% CNC, which was 3.2 GPa. The enhanced modulus even below the glass transition temperature was good evidence of the reinforcing tendency of CNC in the NR matrix. Furthermore, all of the samples experienced a sharp decrease in storage modulus around -50°C , corresponding to the main energy dissipation phenomenon at around the glass transition temperature.

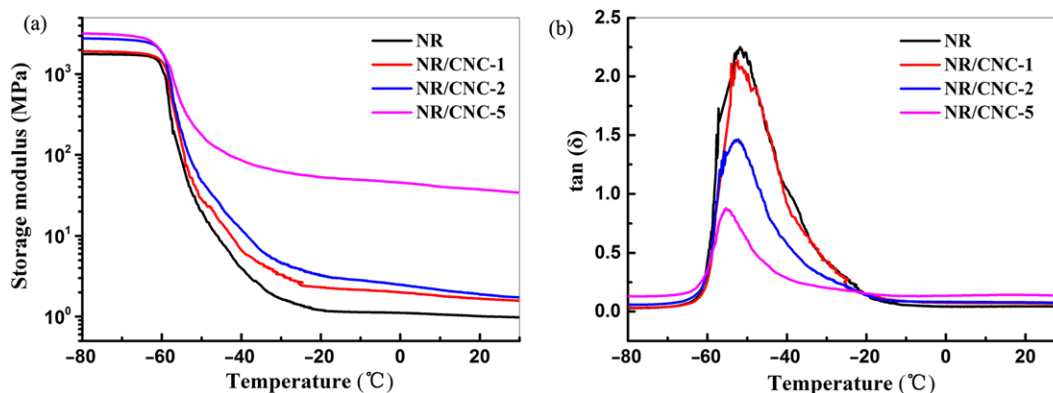


FIGURE 5. (a) Storage modulus and (b) loss angle tangent of NR and NR/CNC nanocomposites as a function of temperature.

This involved the cooperative motions of long-chain sequences, which led to a concomitant maximum in the loss angle (Fig. 5b). Finally, the modulus reached a plateau, corresponding to the rubbery state. The storage modulus above the glass transition temperature is known as the rubbery modulus, which is dependent on the degree of crystallinity of the material. The crystalline CNC particles acted as physical cross-links for the elastomer and increased the modulus substantially. Above the glass transition temperature, a much more significant reinforcing effect of the nanoparticles with filler percentages was observed. The storage modulus for NR fell to the region of 1 MPa at room temperature (25°C). In the case of the nanocomposites, the storage modulus increased by 63% with a 1% CNC addition (1.6 MPa at 25°C), especially for the 5% CNC-filled nanocomposites (35 MPa at 25°C) where the rubbery modulus was more than 34 times higher than that of the unfilled matrix.

The evolution of the tangent of the loss angle as a function of temperature for NR- and CNC-reinforced NR films is presented in Fig. 5b). An insignificant decrease was observed when increasing the cellulose nanocrystal content. $\tan \delta$ exhibited a maximum of around -51°C for pure NR and shifted to -52 , -53 , and -55°C for NR/CNC nanocomposite with CNC contents of 1%, 2%, and 5%, respectively. Similar results have been reported by Pasquini et al.¹³ who attributed this shift to the mechanical coupling effect. Mele et al.²² explained that this shift was related to a phase inversion phenomenon occurring for a filler volume higher than the percolating threshold. Generally, the $\tan \delta$ peak shows the amount of matrix material capable of relaxation, which depends on the concentration of the matrix phase and the restriction of chain mobility at the interface between the matrix and the reinforcement material. In the current study, the intensity of the relaxation process was also evidenced by a decrease with increasing CNC content. This was directly linked to a drop in the elastic tensile modulus that was ascribed to a decrease of matrix material, which was responsible for the damping properties.

THERMAL PROPERTIES OF NANOCOMPOSITES

The thermal stability of NR/CNC nanocomposites was studied by TGA. Figure 6 shows the TGA curves of CNC, NR, and the nanocomposites having a CNC content of 1%, 2%, and 5%. The initial weight loss at about 80°C for CNC was a result of

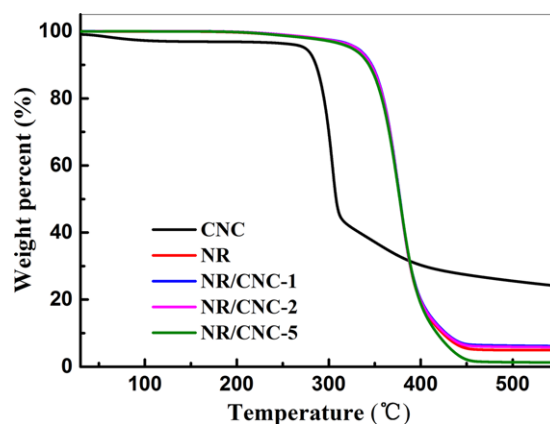


FIGURE 6. TGA curves recorded for CNC, NR, and NR/CNC nanocomposites.

moisture evaporation upon heating since CNC was very sensitive to water. Thermal decomposition of CNC in a nitrogen atmosphere started at about 288.1°C , followed by a major loss of weight during pyrolysis. Char residue took up about 25% of the material that was left at the end of heating. NR showed an onset of degradation at 352.1°C , with this temperature being evidenced by a slight decrease to 351.6 , 351.5 , and 350.1°C for nanocomposites with 1%, 2%, and 5% CNC content, respectively. The insignificant lower onset degradation in the case of NR/CNC nanocomposites was due to the lower onset degradation temperature of CNC as compared to NR, but both the rubber and the nanocomposites followed almost the same thermal degradation behavior. DSC measurements were performed for NR and NR/CNC nanocomposites to study the influence of CNC on the glass transition temperature of the NR matrix. All of the samples were first cooled to -100°C and then heated to room temperature. Figure 7 displays the DSC traces corresponding to the heating scans of all materials. In the literature, Bras et al.¹² and Bendahou et al.¹⁶ reported that no significant variation of T_g upon addition of CNs was observed for the nanocomposites. In the current study, similar results were also found in that both the NR and NR/CNC nanocomposites displayed a glass transition temperature of around -60°C .

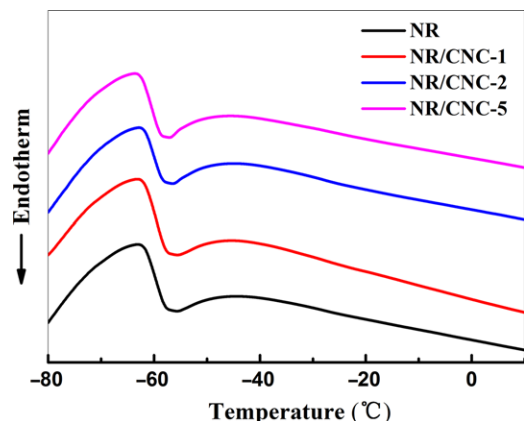


FIGURE 7. DSC heating scans of NR and NR/CNC nanocomposites.

Conclusions

CNC with an average length of 77 ± 21 and width of 9 ± 2 nm were successfully extracted from southern pine pulp by acid hydrolysis and were used as reinforcing agents in vulcanized NR. NR/CNC nanocomposite films were prepared by casting/evaporation of a mixture of CNC aqueous suspension and prevulcanized NR latex. Sedimentation phenomenon of CNC in the nanocomposites was observed by SEM, which resulted with a lower CNC-rich layer and upper NR-rich layer structure, and it was further proved by FTIR spectra. There were no microscaled aggregates presented in the nanocomposites. The addition of CNC increased the tensile strength and modulus of the nanocomposites and slightly decreased the ductility, as obtained from tensile test results. DMA results showed that both the glassy and rubbery modulus was improved upon CNC addition, which verified the reinforcing tendencies of CNC in an NR matrix. Moreover, the addition of CNC also led to a peak of $\tan \delta$, which was insignificantly shifted to a lower temperature. NR and NR/CNC nanocomposites followed the same thermal degradation behavior as the TGA results. The onset decomposition temperature of the nanocomposites was reduced slightly

with more CNC, which was due to the lower stability of CNC compared to that of NR. Both NR and NR/CNC nanocomposites displayed a glass transition temperature of around -60°C during the DSC heating scan.

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