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ORIGINAL ARTICLE

Effect of Curing Temperature on Cellulose Nanocrystal Reinforced Natural Rubber Latex

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ABSTRACT – Cellulose nanocrystal (CNC) was extracted from filter paper and isolated via sulphuric acid hydrolysis. This CNC was used as reinforcing elements in natural rubber latex (NRL) along with the cross-linking agents to prepare nanocomposite films. The effect of CNC loading on the mechanical properties, functional group presence and the glass transition temperature (T_g) of CNC/NRL nanocomposite at curing temperature of 70°C and 80°C were studied, respectively. CNC size and dimension was characterized using transmission electron microscope (TEM). Significant improvement of Young's modulus was observed as a result of the addition of CNC loading at 3 wt.% and the T_g only showed a small increase upon the addition of CNC. The best nanocomposite was found at a curing temperature of 80°C with a tensile strength of 144% improvement.

KEYWORDS
Natural Rubber Latex, Cellulose Nanocrystal, Nanocomposites

INTRODUCTION

Natural rubber latex (NRL) refers to the white sap that comes from *Hevea Brasilienis* tree. NRL in its original uncured form has low strength, softens in warm weather and brittle in cold weather and is almost limited in the use (Vandenplas & Raulf, 2017) . The properties of NRL, such as its elasticity and pliability, can fit into a plethora products (Ghani et al., 2019). Natural rubber sheet on its own can be cut and customized into multiple different products, such as a natural rubber gasket or seal which will ensure that mechanical parts are protected and working at full efficiency. NRL will undergo vulcanization, a chemical process where a long chains of rubber molecules are cross-linked, transforms the soft, weak plastic-like material into a strong elastic product with high and reversible deformability and good mechanical properties owing to strain-induced crystallization, low hysteresis, excellent dynamic properties and fatigue resistance (Visakh et al., 2012). These properties enabled it to be applied in many applications such as chemical, transportation, agriculture, and aerospace industries, among many more. The mechanical properties of NRL can be improved and tailored by cross-linking and addition of reinforcing fillers of varying chemistry and aggregate size/aspect ratio to suit the application concerned like cellulose nanocrystals (Gopalan Nair & Dufresne, 2003).

Cellulose nanocrystals (CNC) are highly crystalline rod-like nanomaterial that can be isolated from various bio sources, such as plants (e.g., cotton, wood, or straw etc.), marine animals (tunicate), and bacterial sources as well. The abundant availability, environmental friendliness, transparent characteristic, superior mechanical properties of CNC makes them desirable filler for NRL (Trache et al., 2017). Due to their advantages of having a high modulus, low density, and negligible thermal expansion, CNC have been widely used as reinforcement in various polymer matrices (Dufresne, 2017). Hence, these good properties are suitable as filler for NRL.

The first research using CNC as reinforcement filler was reported by Favier et al., 1995 (Favier et al., 1995) and found CNC improved the mechanical properties of the nanocomposite structure which is latex. Since then, there has been tremendous interest of using CNC as reinforcing filler in natural rubber. For NRL, curing temperature plays an important role in the interfacial elastomer-filler interactions and change in cross-link density of vulcanizates filled with CNC (Formela et al., 2015; H. Zhang et al., 2016). High curing temperature from 100℃-120℃ (Harahap et al., 2018) and 140℃-180℃ (H. Zhang et al., 2016) resulted in lower tensile strength value. If the curing temperature is too high, the crosslink formation will be interfered and an unstable crosslink bond will be produced. The curing temperature was choose based on Abraham et al., 2013.

Thus, in this study, the presence of CNC will be expected to improve the mechanical properties of NRL and the improvement was observed critically based on the effect of curing temperature.The CNC/NRL nanocomposite film was obtained by solution blending and casting. The CNC/NRL nanocompoite film were analysed using fourier transform infra red (FTIR), differential scanning calorimeter (DSC) and transmission electron microscope (TEM) as well.

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MATERIALS AND METHODS

Chemicals

High ammonia natural rubber was bought from Kinetic Chemicals (M) Sdn. Bhd. Malaysia while cellulose nanocrystals (CNC) was extracted from Whatman filter paper. 98% sulphuric acid (H_2SO_4) was purchased from Sigma Aldrich. The chemical for rubber compounding which are zinc oxide, zinc dithiocaramate (ZDC), zinc mercapto benzothiozole (ZMBT), potassium hydroxide (KOH) and sulphur was bought from Sigma Aldrich.

Isolation of CNC Via Sulphuric Acid Hydrolysis

CNC was prepared by H_2SO_4 hydrolysis, according to the procedure described in previous research (Mohd Amin et al., 2016) . 5g of filter paper was blended with deionised water. The solid to liquid ratio for this isolation process is 1:75 (g/ml). The H_2SO_4 was added slowly under vigorous stirring until the final solution reached an acid concentration of 32%. The ice bath was used to keep the temperature below 20°C while adding the acid. The mixture was heated for 3.5 hours at 50 °C. Then the cellulose suspension was dialysed against deionized water until the suspension reaches the neutral state (pH ~7). The cellulose suspension then was subjected to ultrasonic use of high intensity ultrasonic (QSonica ultrasonicator) for 30 minutes at an output of 500 W, a frequency of 20 kHz and amplitude of 20%. Finally, the suspension of cellulose was collected and stored in a chiller. Suspension was cool at room temperature and centrifuged at 4750rpm four to five times until turbid. The final nanocellulose suspension was kept as it is.

Preparation of Nanocomposites

The NRL was blended with other chemicals simultaneously as in Table 1. The compounding mixture was mixed using mechanical stirrer. The NRL mixture was casted on petri dish followed by drying at ambient temperature. Then the NRL films were cured at curing temperatures of 70°C and 80°C for 4 hours. The nanocomposite films were rested for at least 48 hours at room temperature before any further characterization (Hosseinmardi et al., 2017). The sample was labelled as X CNC/NRL where X represents the weight fraction of CNC.

Table 1. Formulation of the crosslinked CNC/NRL nanocomposite

	Weight % in nanocomposite				
CNC weight (%)	0	0.5	1	3	5
High Ammonia NRL	96.5	94.5	95.5	93.5	91.5
Potassium hydroxide solution	0.35	0.35	0.35	0.35	0.35
Sulphur	1.5	1.5	1.5	1.5	1.5
ZDC	0.75	0.75	0.75	0.75	0.75
ZMBT	0.6	0.6	0.6	0.6	0.6
ZnO	0.3	0.3	0.3	0.3	0.3

CHARACTERIZATION

Transmission electron microscopy (TEM) by Philips CM-100 which operated at 100kV, spot 3,200 μm condenser aperture, and 70 μm objective aperture and was employed to analyze the structure and the aspect ratio of the CNC. CNC were diluted in deionised water at a concentration of 0.08mg/ml and the suspension was sonicated for 1hour.

Fourier-Transform Infrared Spectroscopy (FTIR) spectra of the nanocrystals were recorded by Shimadzu IR-470IR spectrophotometer of range wavenumber 600cm^{-1} until 3,000cm^{-1}.

Differential scanning calorimeter (DSC) Model Q1000 from TA Instruments was used to determine the glass transition temperature (T_g) of CNC/NRL nanocomposite. All samples were analysed from -70°C to 0°C, at a heating rate of 10°C min^{-1} .

Mechanical testing was carried out using Instron Model 3367 Universal Testing Machine according to ASTM D-412. The rate of separation of power actuated grip was 50mm/min, which was maintained throughout the experiment. For each run, three strips of specimens were tested to evaluate the tensile properties.

RESULTS AND DISCUSSION

Morphology of CNC

Morphological of the CNC which was extracted from Whatmann filter paper is shown in Figure 1. Table 3 summarizes the length and aspect ratio of the nanocellulose based on the TEM images. The size of CNC was measured. Table 2 shows the overview of the dimension of CNC from different sources.

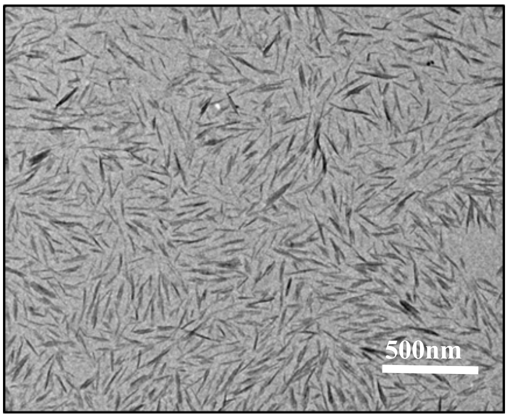

Figure 1. TEM image of CNC

Table 2. Overview of the isolation method and the dimension of CNC from different sources

Sources of Cellulose	Isolation Method	Length(nm)	Diameter(nm)	Aspect Ratio(L/D)	Production Yield(%)
Southern Pine	Sulphuric acid hydrolysis	77±21	9±2	8.5	(C. Zhang et al., 2014)
Cotton	Sulphuric acid hydrolysis	213±50	16±3	13	(Mohd Amin et al., 2016)
Pistachio shells	Sulphuric acid hydrolysis	187±42	12±1	16±3	(Marett et al., 2017)

Table 3. Dimensions and production yield of CNC isolated from Whatman filter paper

Sample	Length(nm)	Diameter(nm)	Aspect Ratio(L/D)	Production Yield(%)
CNC	344±111	34±11	11	96.7%

Based on Figure 1, it can be seen that CNC has needle-like shape. The aspect ratio from Table 3 is approximately within the range of the aspect ratio from the past research 8.5-13 (C. Zhang et al., 2014; Mohd Amin et al., 2016). This confirms the CNC has been successfully extracted from Whatman filter paper by using sulphuric acid hydrolysis isolation method with 96.7% production yield.

FTIR Analysis

The FTIR spectra of NRL and its nanocomposites are shown in Figure 2(a) and (b). The absorbance peaks for both curing temperature approximately between 3,328cm^{-1} until 3,400cm^{-1} are attributed to the stretching vibrations of –OH of CNC (Abraham et al., 2013). There is a gradual increase in the intensity peak on the nanocomposites with increasing of CNC content which is expected.

For FTIR spectra of both curing temperature, nanocomposites show peak between 2,850.60 cm^{-1} to 2,851.49cm^{-1}, 2,961cm^{-1} and 1,795cm^{-1} which are assigned to $–CH_3$, $–CH_2$ and C=C stretching, respectively, and there are peaks of –OH stretching between 3,362.31 cm^{-1} to 3,372.47cm^{-1} and C–O stretching between 1,409.64cm^{-1} to 1,432.34cm^{-1}. This shows the present of CNC and NRL in the nanocomposites. Similar results were found by Abraham et al., 2013.

Based on the FTIR peak at curing temperature of 70°C, neat NRL has the highest peak compared to neat NRL at curing temperature of 80°C. This might be during the compounding of NRL, there might have been some incomplete reaction in the formation of poly-isoprene due to the chemical reactions taking place between zinc metal and polyisoprene (Abraham et al., 2013). Meanwhile at curing temperature of 80°C, the most significant and highest absorbance peak around 1,409.64 cm^{-1} to 1,432.34cm^{-1} was found at 1 wt.% of CNC content.

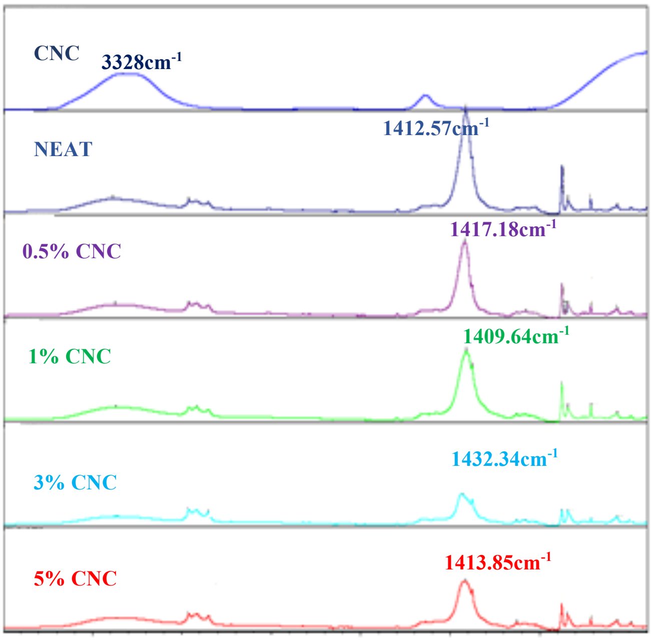

Figure 2a. FTIR spectra at 70°C

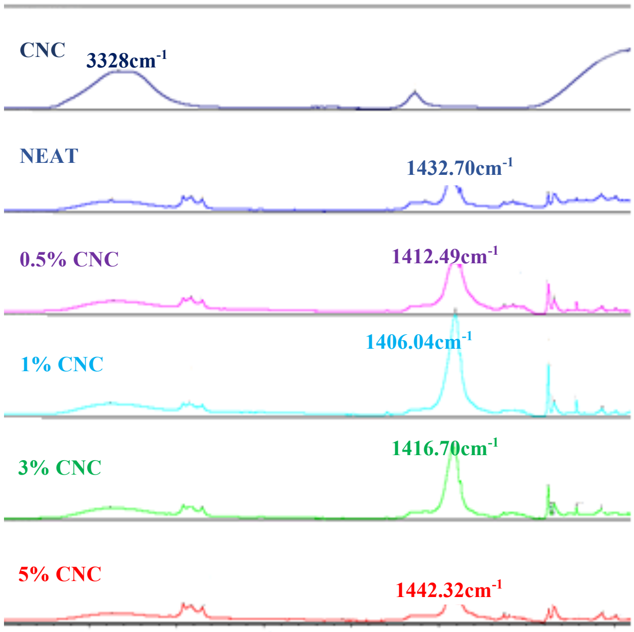

Figure 2b. FTIR spectra at 80°C

Differential Scanning Calorimeter Analysis

The glass transition temperature (T_g) of CNC/NRL nanocomposite was determined by differential scanning calorimetry (DSC). Figure 4 displays the curve of CNC/NRL nanocomposites at curing temperature of 70°C and 80°C.

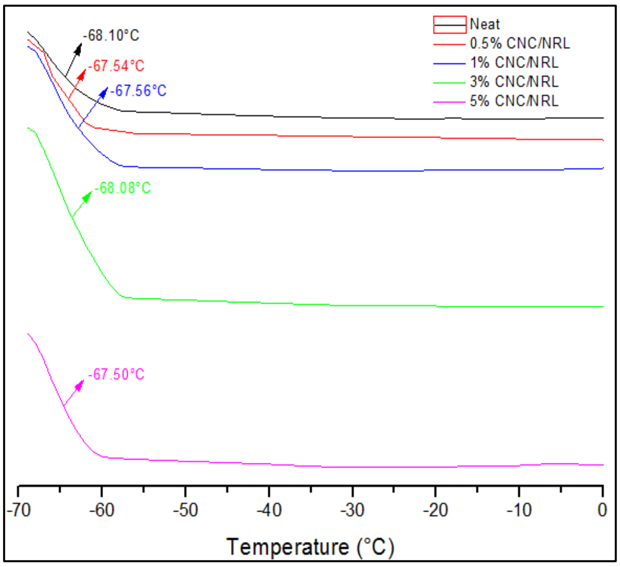

Figure 3a. T_g curve of CNC/NRL nanocomposites at 70°C

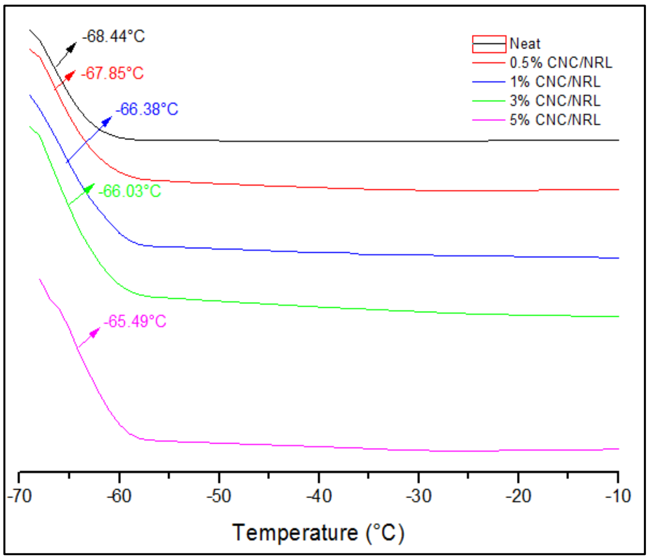

Figure 3b. T_g curve of CNC/NRL nanocomposites at 80°C

Based on Figure 3a and 3b, the T_g at curing temperature of 70°C was recorded from –68.10°C to –67.50°C whereas for 80°C was from –68.44°C to –65.49°C. The T_g of NRL/CNC nanocomposite at 70°C and 80°C showed a small increase with the increasing of CNC content. This also was proved by Bendahou et al., 2010 and Bras et al., 2010 which reported that no significant variation of T_g upon increasing content of CNC. Hence, the results might clarified that there is no significant chemical bonding formed and the original structure of NRL is remained.

Mechanical properties

Mechanical properties of CNC/NRL nanocomposites at two different curing temperatures are reported in Table 4, where the addition of CNC has a significant impact on the mechanical performance. Figure 4a and 4b shows the stress-strain curves for the composites at curing temperature of 70°C and 80°C, respectively.

Table 4. Tensile properties of Neat NRL and CNC/NRL nanocomposites

Temperature (°C)	Sample	Tensile Strength (MPa)	Elongation Break (%)	Young Modulus,E (kPa)
70	Neat NRL	33.30±2.61	823±28.25	10.06
	0.5% CNC/NRL	36.68±9.89	789±78.52	12.32
	1% CNC/NRL	43.61±2.87	825±78.04	13.09
	3% CNC/NRL	77.50±11.64	939±105.63	19.30
	5% CNC/NRL	68.22±4.55	879±102.88	23.64
80	Neat NRL	34.64±14.0	903±137.52	9.40
	0.5% CNC/NRL	52.79±3.56	848±50.02	17.40
	1% CNC/NRL	60.48±6.20	892±73.80	19.31
	3% CNC/NRL	84.73±0.91	943±73.94	25.44
	5% CNC/NRL	75.51±11.32	977±138.23	24.50

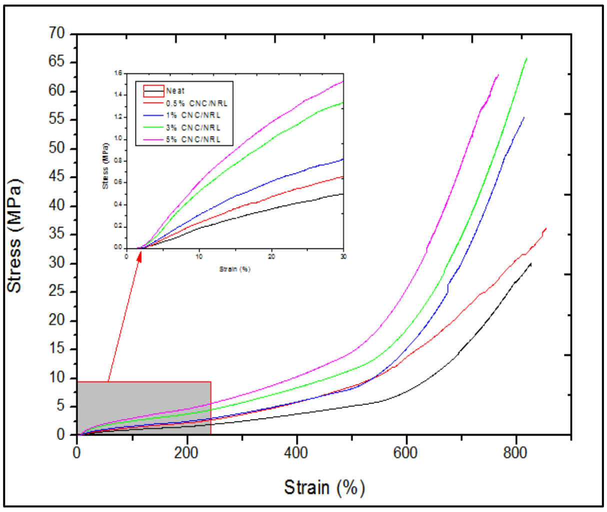

Figure 4a. Stress-strain curves at 70°C

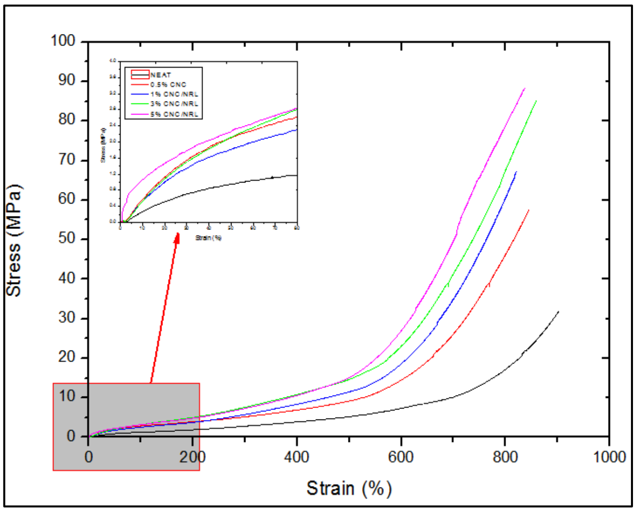

Figure 4b. Stress-strain curves at 80°C

At both curing temperature, tensile strength and modulus increased upon CNC addition to the NRL meanwhile slightly decreased in elongation at break. At 70°C, the maximum increase of tensile strength and modulus was achieved for nanocomposites at 3wt.% of CNC, which are 131% and 92% of improvement, respectively. Meanwhile for samples at curing teperature of 80°C, the best tensile strength and modulus was achieved for nanocomposites also with 3 wt.% of CNC, with 144% and 171% of improvement, respectively. These results are due to the reinforcing effect of the CNC and its interaction with NRL on the molecular chain which provide higher strength than the NRL matrix. According to Kargarzadeh et al., 2015, CNC addition formed percolation network within the polymer matrix and the interfacial interaction between matrix and CNCs. Thus, the CNC-CNC and NRL-CNC reactions are both responsible to the mechanical enhancement of the resulting nanocomposites. Notably, for both curing temperature, 5% CNC addition decreased the tensile strength by approximately 11% and 12%, respectively. These results can be attributed to the possible restriction of polymer chain mobility in the vicinity of nanocrystals(C. Zhang et al., 2014).

Hence, the better nanocomposites film is 3% CNC/NRL at 80°C of curing temperature with 84.73MPa (tensile strength) and 25.44kPa (young modulus) than 3% CNC/NRL at 70°C due to its lower value of tensile strength (77.50MPa) and tensile modulus (19.30kPa).

CONCLUSION

CNC with an average length of 344±111nm and diameter of 34±11 nm were successfully extracted from filter paper via acid hydrolysis and was used as reinforcing filler in high ammonia NRL. CNC/NRL nanocomposite films were prepared by casting of a mixture of CNC aqueous suspension and high ammonia NRL. The morphology of CNC was observed by TEM, which resulted a needle-like shape. The T_g for both curing temperature samples has insignificant increase from approximately –68°C until –65°C upon CNC addition. At 3 wt.% of CNC loading at 80°C of curing temperature shows best mechanical properties with an average tensile strength (84.73±0.91 MPa) and tensile strain (943±73.94 %). The addition of CNC increased the tensile strength and modulus of the nanocomposites and slightly decreased the ductility, as obtained from tensile test results. Hence, the addition of CNC and curing temperature also affect the properties of NRL.

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