

Biodegradable Composite Films based on κ -carrageenan Reinforced by Cellulose Nanocrystal from Kenaf Fibers

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Through alkali treatment, bleaching, and sulfuric acid hydrolysis, cellulose nanocrystals (CNCs) were prepared from kenaf fibers and were used as reinforcement materials in biocomposites based on κ -carrageenan. Biocomposites in the form of films were prepared by solution casting of a mixture of κ -carrageenan, glycerol, and various amounts of CNCs (0 to 8 wt%). Fourier transform infrared spectroscopy (FTIR) revealed that alkali treatment followed by bleaching totally removed lignin and hemicellulose from the kenaf. Morphological analysis of the fibers, cellulose, and κ -carrageenan of biocomposite films were carried out using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The effects of filler content on the mechanical and thermal stability of the κ -carrageenan biocomposite films were analyzed through tensile strength measurements and thermogravimetric analysis (TGA). At an optimum CNC content of 4%, the κ -carrageenan biocomposite films showed good dispersion, superior mechanical properties, and improved thermal stability.

Keyword: Kenaf; Cellulose nanocrystals; κ -carrageenan biocomposite films; Mechanical properties

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INTRODUCTION

The non-biodegradability of conventional plastic materials used for packing consumer goods, including food, is a growing environmental concern. This has led to a great deal of interest in biodegradable polymers as potential materials to replace petroleum-based packaging (Tharanathan 2003; Alves *et al.* 2006; 2011; Vieira *et al.* 2011).

Carrageenans are linear sulphated polysaccharides extracted from certain species of red seaweed of the *Rhodophyceae* class. The three most important carrageenans are the ι -, κ -, and λ -carrageenans. They differ in the number and position of ester sulfate groups per disaccharide unit. Carrageenans have been used in the pharmaceutical industry and in the food industry as thickening, gelling, and protein suspending agents. All carrageenan fractions are soluble in water and insoluble in organic solvents, oils, or fats. κ -carrageenan, which has one negative charge per disaccharide unit, forms strong gels and is a good film-forming material (Park *et al.* 2001; Lafargue *et al.* 2007; Sanchez-Garcia *et al.* 2010). However, these carrageenan films have been observed to be very brittle and difficult to remove from their supports without breaking. Because the brittleness can limit their potential applications, plasticizers are added to improve their flexibility (The *et al.* 2009).

Kenaf (*Hibiscus cannabinus*), which belongs to the genus *Hibiscus*, is a tropical plant and is a crop in several countries around the world, including Malaysia. Kenaf has shown potential for use as a fiber in composite products (Faruk *et al.* 2012). The simple

mixing and solution casting method are optimal for the fabrication of composites using kenaf as reinforcing filler. Cellulose contents of the kenaf fiber range between 30 to 63%, making kenaf a good source of cellulose (Kargarzadeh *et al.* 2012). There has been an increased interest in kenaf as an environmentally friendly and inexpensive reinforcing agent for use in composite materials (Farahani *et al.* 2012; Zainuddin *et al.* 2013).

Because of their high aspect ratio, good mechanical properties, and fully degradable and renewable characteristics, cellulose nanocrystals (CNCs) are increasingly being used as fillers for the development of new and inexpensive biodegradable materials. The high stiffness, low density, and eco-friendly nature of cellulose nanocrystals as reinforcing agents in nanocomposite materials with improved thermal and mechanical properties are some of the other benefits of nanocomposites (Soykeabkaew *et al.* 2012). A variety of biodegradable reinforcements such as flax, hemp, jute, rice husk, and pineapple leaf fiber have been used for the preparation of nanocomposites (Faruk *et al.* 2012). Nanocomposites have been successfully developed with uniform dispersion and significantly improved mechanical strength, even at very low reinforcement content, using such materials as fillers (Oksman *et al.* 2006).

Starch obtained from a variety of crops such as corn, wheat, rice, and potato is a source of biodegradable plastics. These starch sources are readily available at low cost when compared with most synthetic plastics. The addition of CNCs improves the thermomechanical properties and reduces the water sensitivity of starch-based nanocomposites. It has been reported that CNCs derived from rice husk increase the Young's modulus and tensile strength of thermoplastic starch films due to the strong interactions between the starch matrix and the high aspect ratio nanofibers (Abdul Khalil *et al.* 2012; Johar and Ahmad 2012). Khan *et al.* (2012), who investigated CNC-reinforced chitosan-based biodegradable films, found that the tensile strength of the nanocomposite films with 5% (w/w) CNC content was optimum and 26% higher than that of the control chitosan films. Furthermore, the incorporation of CNC significantly improved the barrier properties. Water vapor permeability of these chitosan/CNC films, which contained 5% (w/w) CNC, was lowered by 27%. Additionally, swelling studies revealed a reduction in water uptake of the CNC-reinforced chitosan films. Huq *et al.* (2012) prepared CNC-reinforced alginate-based nanocomposite film by incorporating small amounts of CNCs. The CNC-reinforced alginate-based composite film showed improved mechanical, thermal, and barrier properties.

The objective of this work was to develop fully renewable and biodegradable composite materials exhibiting improved thermal and mechanical properties that used cellulose nanocrystals from kenaf bast fibers as fillers. The effects of the CNCs as a reinforcing agent in composites were studied by varying the amount of the filler loaded in the materials.

EXPERIMENTAL

Materials

TA150 κ -carrageenan in powder form was supplied by Tacara Sdn. Bhd. (Tawau, Sabah, Malaysia). Kenaf fiber was supplied by Kenaf Industry Sdn. Bhd. (Malaysia). Sulfuric acid (98%), sodium hydroxide (99%), acetic acid (99.5%), and glycerol were purchased from System ChemAR (Malaysia). Sodium chlorite (80%) was purchased from Sigma-Aldrich (Germany).

Methods

Preparation of cellulose nanocrystals from kenaf fibers

Cellulose nanocrystals (CNCs) were prepared by treating kenaf fiber with alkali, followed by bleaching and hydrolysis using sulfuric acid (Sheltami *et al.* 2012). Kenaf fibers were cut into small pieces and stirred with a 4 wt% alkali solution at 80 °C for 3 h under mechanical stirring. The process was repeated three times. The alkali-treated kenaf fibers were then bleached three times with 1.7% sodium chlorite in an acetate buffer solution for 4 h at 80 °C. Following this, hydrolysis was performed at 45 °C under mechanical stirring using 65 wt% of sulfuric acid for 40 min. The hydrolyzed cellulose was then centrifuged several times at 10,000 rpm for 10 min at 10 °C. The suspension was dialyzed against deionized water until a constant pH (5 to 6) was reached. Following this, the suspension was neutralized using 1 wt% sodium hydroxide solution

Preparation of composite films

Biocomposite films based on κ -carrageenan were prepared by mixing carrageenan powder, filler (CNCs), and glycerol 50% (w/w) in distilled water then heating the mixture at 70 to 90 °C under continuous stirring until the suspension congealed. The amounts of filler used in the production of biocomposites were 2%, 4%, 6%, and 8%. Following this, the film-forming solution was spread over the casting plate using a casting knife to control the thickness, and it was allowed to dry at room temperature. The composite films were stored in a dry cabinet at 30% relative humidity for further characterization.

Fourier transform infrared spectroscopy (FTIR)

The changes in the functional groups and chemical characteristics of the kenaf fibers were examined by FTIR spectroscopy (Perkin-Elmer, USA). A thin sample was clamped against the vertical face of the crystal and analyzed in the transmittance mode. Infrared spectra of the samples between 4000 and 600 cm^{-1} were recorded at a resolution of 4 cm^{-1} .

Electron Microscopy

The morphology of the kenaf fibers after each treatment and of the composites was investigated using a (FESEM- Philips, XL3, Netherlands) field emission scanning electron microscope (FESEM). The composite films were frozen in liquid nitrogen and broken into small pieces. All samples, fibers, and matrix interfaces were attached to an aluminum stub by double-faced tape and coated with gold before analysis. The morphology of the CNCs was analyzed using a Philips CM30 transmission electron microscope (TEM). A droplet of a suspension was deposited on a copper grid and covered with thin carbon film. To enhance the contrast in TEM, the nanocrystals were negatively stained with 2% uranyl acetate solution in deionized water for 1 min and dried at room temperature.

Mechanical testing

Mechanical performance of the composite films was evaluated through tensile strength and Young's modulus measurements using a universal machine (Instron model 5560, USA) at room temperature. A crosshead speed of 5 mm/min, initial grip distance of 40 mm, and a load of 50 N were applied for the test. The thickness of each sample was measured at three different locations using a Mitotuyo micrometer, USA (± 0.01 mm). The average values from eight replicate measurements for each sample were calculated.

Thermogravimetric analysis

Thermal stability and degradation analyses of the composite films were carried out under an atmosphere of nitrogen using a Mettler Toledo thermogravimetric analyzer (TGA/SDTA 851-E, USA). Each composite film and other samples were heated from room temperature to 600 °C at a rate of 10 °C min⁻¹.

RESULTS AND DISCUSSION

FTIR Characterization

The FTIR spectra of raw kenaf fibers, alkali-treated kenaf, bleached kenaf, and that of cellulose nanocrystals are shown in Fig. 1. The peak in the range of 3400 to 3200 cm⁻¹ was assigned to the O-H stretching vibration of cellulose. The peak at ~2900 cm⁻¹ was assigned to C-H stretching vibrations (Brigida *et al.* 2010; Noranizan and Ahmad 2012; Safinas *et al.* 2013). The absorption at 1736 cm⁻¹ was assigned to the carbonyl group (C=O) stretching of the acetyl group or the ester linkage of the carboxylic group in the ferulic and *p*-coumeric acid moieties of lignin and/or hemicelluloses.

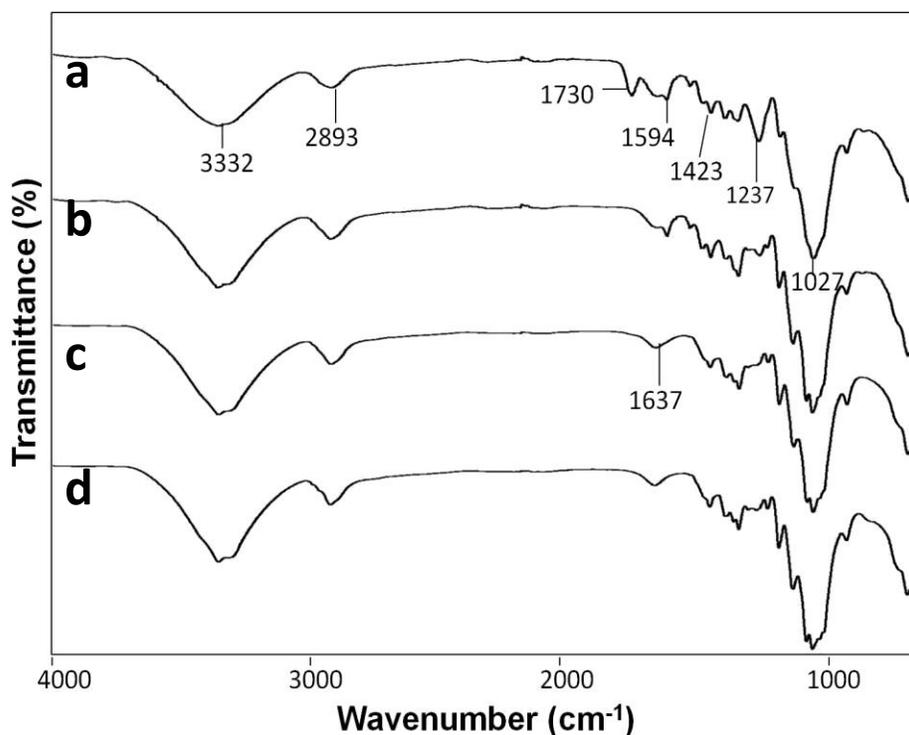


Fig. 1. FTIR spectra of (a) raw kenaf fiber, (b) alkali-treated fibers, (c) bleached fibers, and (d) cellulose nanocrystals

The loss of peak signal intensity at 1736 cm⁻¹ was attributed to the alkali treatment, which removed the hemicelluloses from the fiber surface. The peak at 1237 cm⁻¹ (Fig. 1a) was assigned to the C-O stretching of the aryl group of lignin and the loss of this peak in both fiber after alkali and bleaching treatment confirmed the removal of lignin by the chemical treatment. These two peaks were absent in the spectra of the alkali treated and bleached kenaf fibers, indicating that most of the hemicelluloses and lignin were removed by the pre-hydrolysis treatments (Troedec *et al.* 2008; Janobi *et al.* 2009; Kargarzadeh *et*

al. 2012; Sheltami *et al.* 2012). The peak at 1430 to 1420 cm^{-1} was assigned to the CH_2 symmetric bending, and the peak in the range of 1380 to 1320 cm^{-1} in all samples was assigned to the plane C-H bending and the C-O bending of the aromatic rings in the polysaccharides (Nacos *et al.* 2006; Adel *et al.* 2010). Finally, the peaks in the regions 1162 to 1125 cm^{-1} were assigned to the C-O-C asymmetric stretching mode of cellulose and hemicelluloses (Troedec *et al.* 2008; Safinas *et al.* 2013), while the peak at 1058 to 896 cm^{-1} was assigned to the C-O stretching and C-H rocking vibration of cellulose (Alemdar and Sain 2008).

Fiber Morphology

Figure 2 shows the surface morphologies of the kenaf fibers after various chemical treatments as revealed by FESEM. The micrographs reveal the morphological changes that occurred after treatment. The untreated kenaf fibers formed large bundles with rough surfaces (Fig. 2a). The presence of wax, oil, and surface impurities were clearly observed on the untreated kenaf fibers. The alkali-treated kenaf fiber (Fig. 2b) bundles had a smoother surface, likely due to the removal of certain amounts of hemicelluloses, lignin, wax, oils, and other impurities. Treatment with NaOH removed undesirable materials and separated fiber bundles into individual fibers (Aziz and Ansell 2004; Mohd Yuhazri *et al.* 2011; Shi *et al.* 2011; El-Shekeil *et al.* 2012). During alkalization at high temperature, hemicelluloses were hydrolyzed, and the lignin partially underwent depolymerization. Figure 2c shows the fiber surface after bleaching. The bleached fibers were the cleanest, and the bundles were finer than alkalized fiber due to the removal of lignin (Kargarzadeh *et al.* 2012).

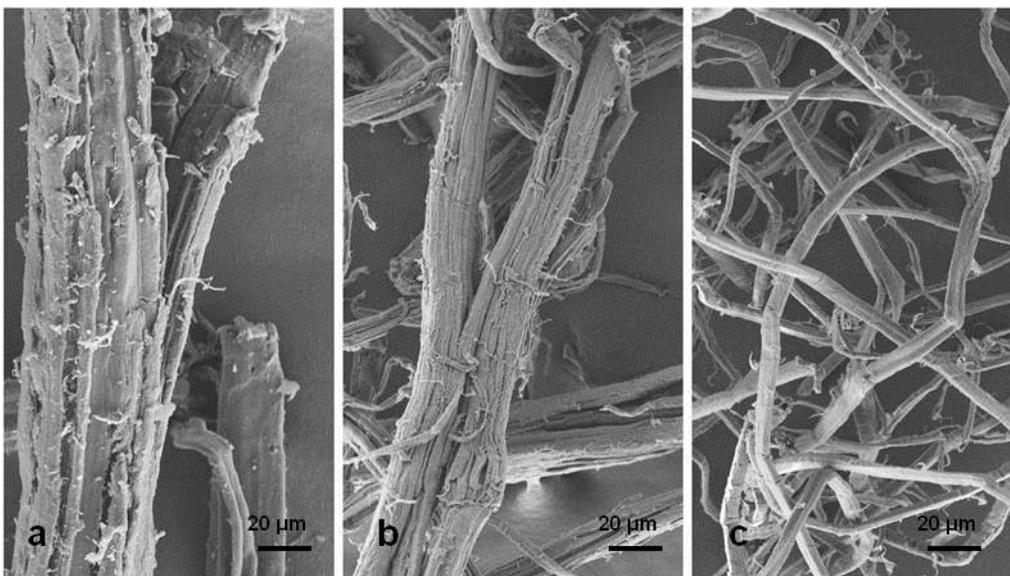


Fig. 2. FESEM micrographs of (a) raw kenaf fiber, (b) alkali-treated kenaf, and (c) bleached kenaf

Cellulose Nanocrystal Morphology

A transmission electron microscope (TEM) was used to analyze the cellulose nanocrystals from the kenaf fibers. Cellulose nanocrystals were obtained after hydrolysis with sulfuric acid was applied to the kenaf fibers. The cellulose nanocrystals of the kenaf fibers were approximately 12 to 15 nm in diameter and 101 to 260 nm in length. This size correlated with other TEM analysis results obtained from different fibers and treatment

methods. The hydrolyzed cellulose formed needle-shaped nanoparticles (Johar and Ahmad 2012). The CNCs have high aspect with the value in the range of 8 to 17. Some lateral agglomerations occurred among the nanofibrils, which were expected at high concentrations of the cellulose nanocrystals in suspension because of the self-association *via* hydrogen bonding of the fillers (Netoa *et al.* 2013).

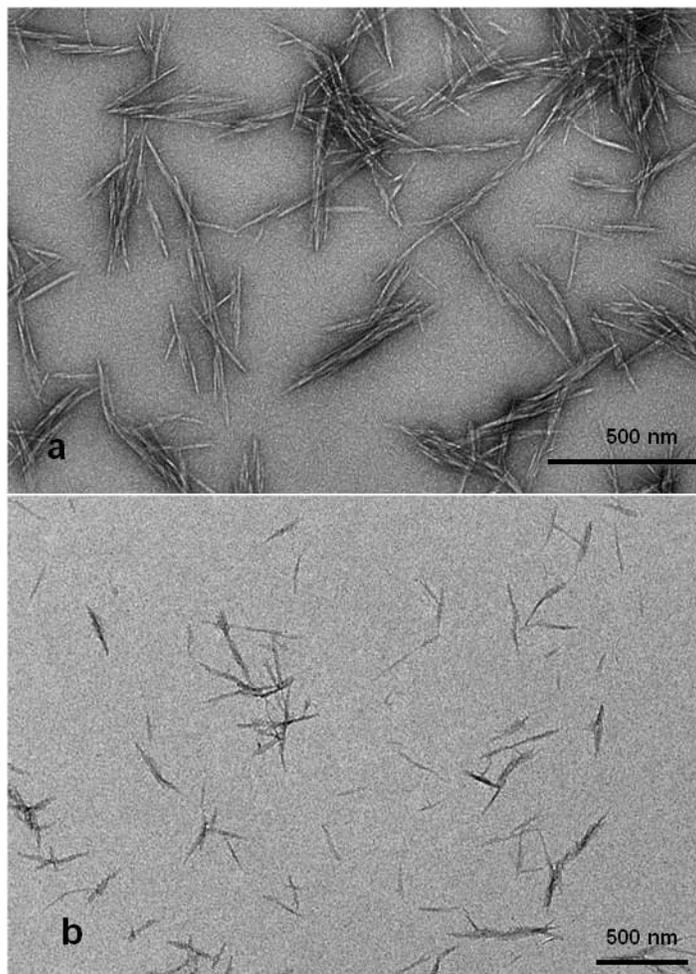


Fig. 3. TEM micrographs of CNCs from kenaf fibers. (a) high magnification and (b) low magnification

Morphological Characterization of Biocomposite Carrageenan

Figure 4 shows optical visual images of the biocomposite carrageenan films with 0% (a) and at the optimum 4% (b) CNCs content. Both images appear very similar, and the alphabet can be clearly seen through transparent biocomposite carrageenan films. The physical appearance of the film does not change much, and it can be considered to be the same as that of the matrix. This information can be of great importance due to most of the applications are using transparent and/or clear plastic.

On the other hand, field emission scanning electron microscopy was used to analyze the morphological structure of a cross-section of the CNC-reinforced film, particularly the homogeneity of the composite, the dispersion level of CNCs, and the presence of agglomerations within the continuous matrix.

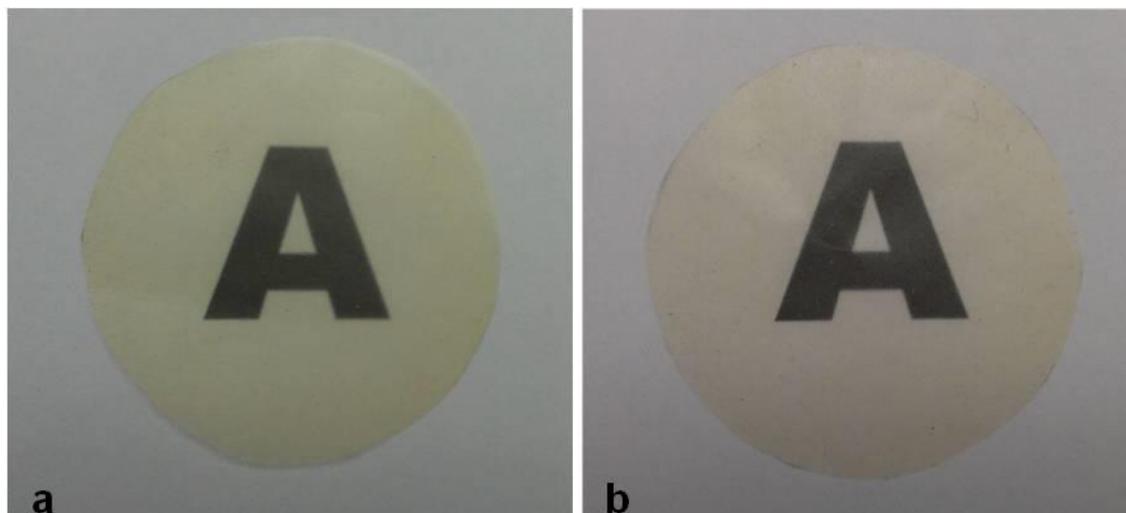


Fig. 4. Optical visual images of (a) matrix carrageenan film and (b) biocomposite carrageenan film with 4% CNCs loading

Figure 5 shows the cross-section surface of the carrageenan film (Fig. 5a), carrageenan film with 2% CNCs (Fig. 5b), carrageenan film with 4% CNCs (Fig. 5c), carrageenan film with 6% CNCs (Fig. 5d), and carrageenan film with 8% CNCs (Fig. 5e). The original matrix film showed a relatively smooth surface (Fig. 5a). The carrageenan composite film with 2% CNCs (Fig. 5b) showed a structure similar to that of the control, but became more structured when the CNC content reached 4%. However, the cross-section surface of the carrageenan films became rougher with increasing CNC content. The internal morphology changed substantially with the addition of 4% CNCs (Fig. 5c). The SEM images showed a smooth surface, which indicated strong interaction between CNCs and carrageenan.

The compact homogeneous carrageenan composite film with 4% CNCs showed good dispersion and distribution of CNCs within the polymer matrix. Chemical similarity between the carrageenan and CNCs ensured the compatibility of the nano-reinforcements and the structures were stabilized laterally by the formation of hydrogen bonds between hydroxyl groups (Oksman *et al.* 2006; Huq *et al.* 2012). However, in the composite film with 8% CNCs (Fig. 5e), the CNCs tended to agglomerate, which indicated that the filler was not dispersed well in the carrageenan-based film. Higher nanofiller content in the polymer matrix resulted in an increase in the amount of agglomeration due to the self-association of the fillers *via* hydrogen bonding (Sanchez-Garcia *et al.* 2010). Filler agglomeration reduced the interfacial contact between the fillers and the matrix, resulting in poor interfacial stress transfer.

Mechanical Properties

The mechanical properties of the carrageenan composite materials are shown in Fig. 6. With an increase in the amount of CNCs, the tensile strength and the Young's modulus of the composite continuously increased up to the optimum level. The neat matrix had the lowest tensile strength and Young's modulus, at 23.4 MPa and 773.1 MPa, respectively.

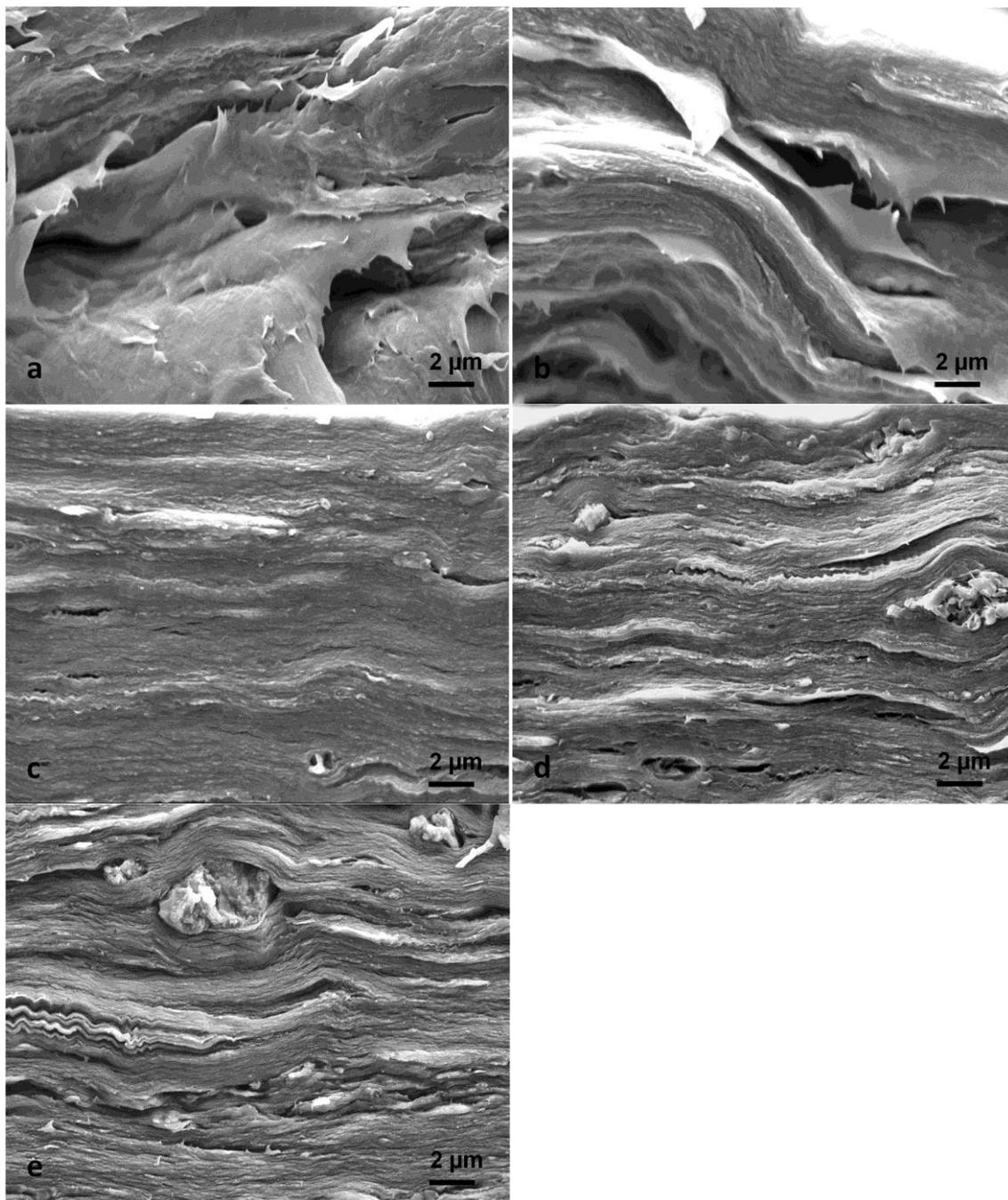


Fig. 5. FESEM micrographs of fractured surfaces of (a) carrageenan matrix, (b) carrageenan with 2% CNCs, (c) carrageenan with 4% CNCs, (d) carrageenan with 6% CNCs, and (e) carrageenan with 8% CNCs

The carrageenan matrix was reinforced by the addition of CNCs to the optimum amount of 4%. At this CNC content level, the tensile strength and Young's modulus were 36.8 MPa and 1339.9 MPa, respectively. The tensile strength and Young's modulus were found to be significantly higher in the composite materials with low CNC loading ($\leq 5\%$), which could be explained by the good dispersion of CNCs in the carrageenan matrix (Satyanarayana *et al.* 2009; Abdul Khalil *et al.* 2012).

The micrographs of the cross-section surface of the composite with 4% filler content (Fig. 5c) provide good evidence for the uniform dispersion of the fillers in the carrageenan matrix. Additionally, the improvement in the mechanical strength of the carrageenan-based composite films indicated an efficient load transfer at the CNC-polymer matrix interface, leading to a more uniform stress distribution. This can be attributed to the immense reinforcing potential of CNCs, which is due to good interfacial interaction or strong hydrogen bonding between the added fillers and the carrageenan matrix phase, because of their chemical similarity (Huq *et al.* 2012; Khan *et al.* 2012).

The superior Young's modulus values of the CNC-reinforced carrageenan films may be attributed to the increase in the stiffness of the films following the addition of CNCs. This enhancement was also related to the higher crystallinity (Liu *et al.* 2010). Cellulose nanocrystals also have high surface area to volume ratios (Eichhorn *et al.* 2010). Cellulose with highly crystallinity has a high surface area which enables increased surface interaction between the filler and the matrix, endowing the composite with superior mechanical properties (Zainuddin *et al.* 2013). Increasing the CNC content beyond the optimum levels had a negative impact on the mechanical properties of the composite materials.

The inferior performance of the composites at higher CNC loading is due to the aggregation and agglomeration caused by the presence of many fiber ends within the matrix. The agglomeration and aggregation of CNCs may occur while the fiber is in nano-phase, and the tendency to form large macroscopic fibers increases at higher filler loading. These phenomena resulted in inter-fiber interaction due to hydrogen bonding induced self-association (Fowler *et al.* 2006; Dorigato *et al.* 2013). These factors contributed to the lower tensile strength and Young's modulus of composites with 6% and 8% CNC content. However, the tensile strength and Young's modulus of the composites with high CNC content were still higher than that of the neat matrix. Thus, the CNCs acted as good reinforcing agents in the carrageenan films. For all biocomposite produced, elongation at break decreased with increasing filler content, except for 6% composition of CNCs. This is due to the increase in the tensile strength lead to decrease in the elongation at break point (Raj *et al.* 1990).

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out to investigate the thermal degradation of carrageenan matrices and carrageenan composites (Fig. 7). The decomposition data for all samples are summarized in Table 1. TGA thermograms showed that weight loss began from 50 to 150 °C for the carrageenan matrices and carrageenan composites. Initial weight loss corresponded to the evaporation of water trapped within the matrix, which existed in H-bonded form with the hydroxyl groups of the glucosyl units along the polymer chain and the hydroxyl groups of the plasticizer (Schlemmer and Sales 2010; Abdorreza *et al.* 2012).

The weight reductions at 125 to 230 °C and at 230 to 330 °C were attributed to the degradation of glycerol and polysaccharides. Similar results were also reported by Martin *et al.* (2012) with different matrices. The decomposition temperature increased due to the high glycerol content, suggesting that the plasticizer had stabilized the polymer to some extent. Additionally, the presence of glycerol promotes dispersion and leads to better interaction between fillers and the matrix (Ayuk *et al.* 2009; Li *et al.* 2009).

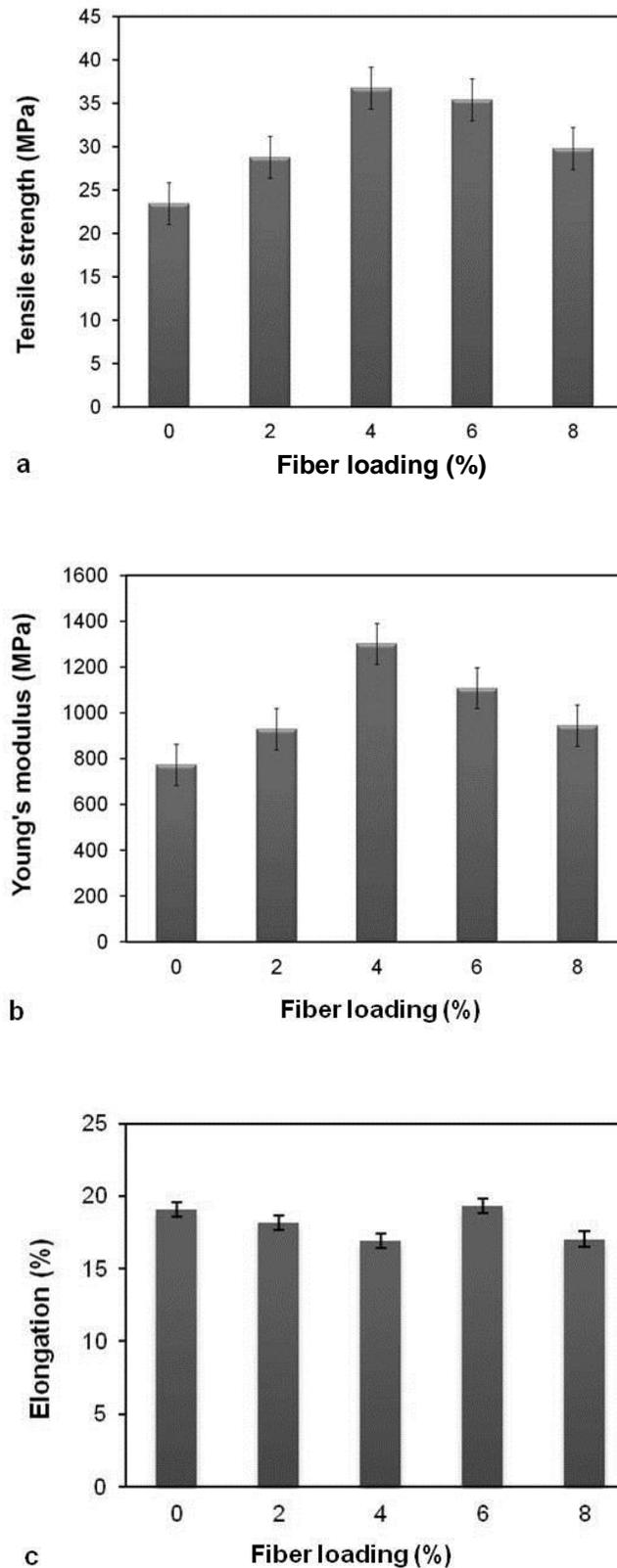


Fig. 6. Mechanical properties of carrageenan composites reinforced by CNCs. (a) tensile strength, (b) Young's modulus and (c) elongation at break

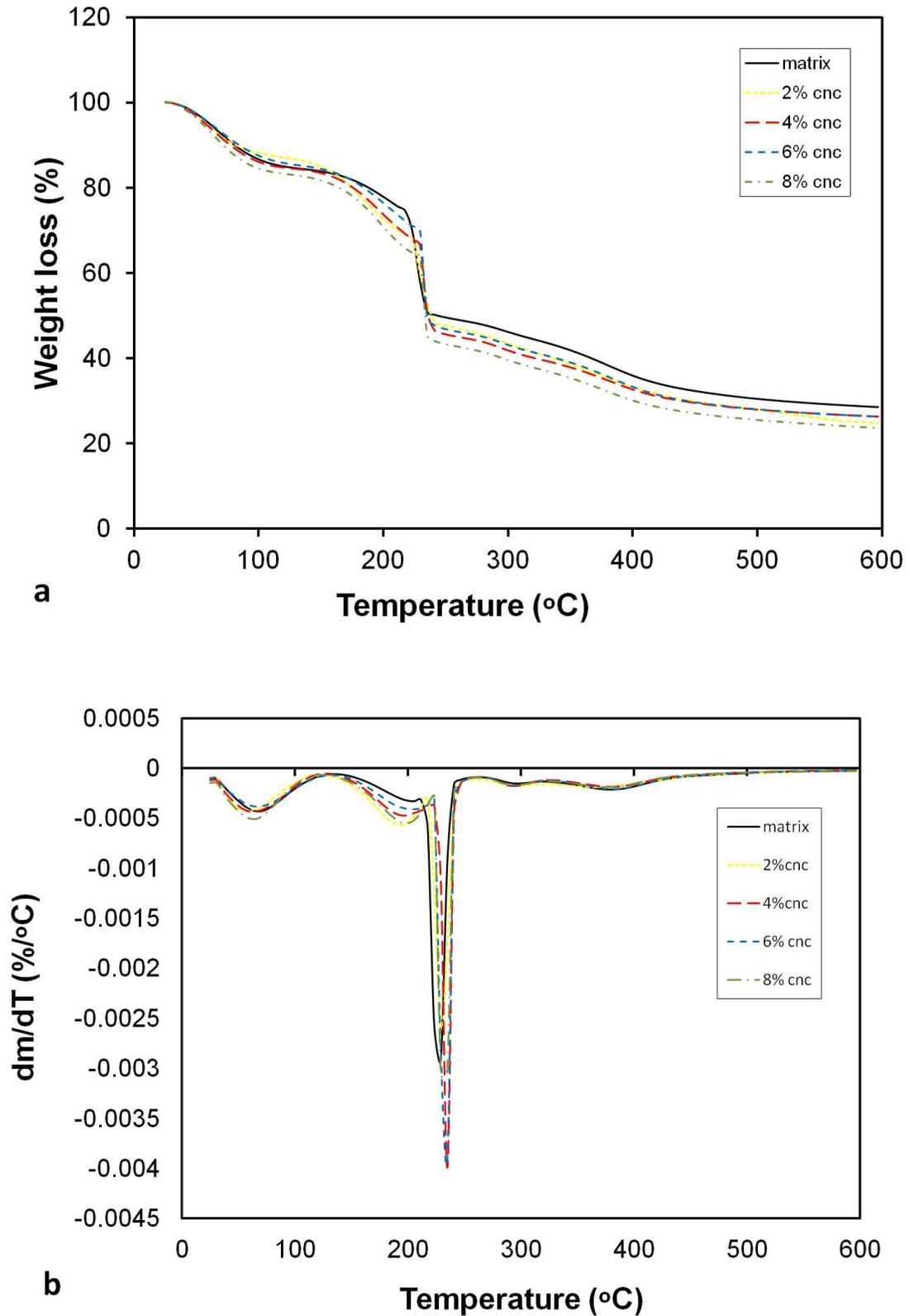


Fig. 7. (a) TGA and (b) DTG curves for carrageenan matrix and carrageenan composites filled with 2%, 4%, 6%, and 8% CNCs

In the case of composites, the second thermal degradation stage occurred between 227 and 242 °C. At 4% CNC content, the decomposition temperature was between 229 and 242 °C. The maximum degradation occurred at 236.5 °C. Higher thermal degradation resulted in better thermal stability of the composites. Incorporation of 2%, 6%, and 8% CNCs resulted in slightly reduced thermal stability. The higher thermal degradation temperature and better thermal stability of the composite with 4% CNC could be attributed to the strong interaction between the CNCs and the matrix phase, as well as to its superior mechanical properties (Fig. 6) (Li *et al.* 2009; Satyanarayana *et al.* 2009). When glycerol was added to biopolymer, it seems that the incorporation of CNCs had no significant effect on the thermal properties of the materials. The same trend also was reported by Averous and Boquillon 2004. Thus, addition of glycerol to plasticize the biopolymer was responsible for the observed decomposition temperature, whereas addition of the CNCs improved the thermal resistance of the biocomposites. The final remaining mass content for all samples accounted for nearly 30% of the initial mass. Hug *et al.* 2012 and Martins *et al.* 2012 also showed non-degraded material approximately around 20 to 40% at a degradation temperature of 500 to 600 °C.

Table 1. TGA Maximum, Derivative of Weight Loss (T_d), and Corresponding Peak Onset and Endset Values for the Composites

Sample	Onset (°C)	T_d (°C)	Endset (°C)
Carrageenan + glycerol	222.15	230.10	235.21
Carrageenan + 2% CNC + glycerol	227.32	233.36	240.13
Carrageenan + 4% CNC + glycerol	229.36	236.53	242.26
Carrageenan + 6% CNC + glycerol	227.54	234.97	240.62
Carrageenan + 8% CNC + glycerol	226.68	233.99	239.60

CONCLUSIONS

1. The properties κ -carrageenan biocomposite films were influenced by the presence of cellulose nanocrystals.
2. The TEM results showed that cellulose nanocrystals were successfully extracted from kenaf using sulfuric acid hydrolysis with length and cross-sections ranging from 101 to 260 nm and 12 to 15 nm, respectively.
3. κ -carrageenan/CNC biocomposite films were prepared via solution casting with glycerol as the plasticizer.
4. Thus, the thermal mechanical properties were investigated by different loading of CNC with the matrix.
5. It was found that the mechanical properties of the composites improved with the addition of CNC showing the highest tensile strength and Young's modulus at 4% CNC loading.
6. The incorporation of CNCs improved the thermal properties of the materials if compared to the neat matrix polymer.

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