Journal of Polymer Science and Technology 4(1) 2019:22-32
ISSN: 2550-1917

APPLICATION OF CELLULOSE NANOCRYSTALS (CNC) AS REINFORCING MATERIALS IN BIO-NANOCOMPOSITES

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ABSTRACT

Cellulose nanocrystals (CNC) is a promising renewable biomaterial as reinforcing filler in many different applications. CNC from different types of Malaysian resources natural fibres such as mengkuang leaf, kenaf, coconut fibres, and rice husk have been used as reinforcing material in biocomposite. Starch biocomposites reinforced by CNC through solution casting technique were successfully fabricated. The starch biocomposite films reinforced with nanocrystals from kenaf and rice husk showed an improvement in tensile strength and modulus. It was found that kenaf CNC biocomposite shows better mechanical and morphological properties compared to rice husk CNC biocomposite. Poly(acrylic acid) hydrogels reinforced with CNC from both natural fibres were also prepared. CNC hydrogels have better performace compared to PAA hydrogels without CNC. The hydrogels reinforced kenaf CNC showed higher storage modulus compared to rice husk CNC hydrogel. The finding has shown the ability of the CNC hydrogels to respond to different pH values along with its high mechanical stability suggested that CNC hydrogels are promising candidates as drug carriers. This paper provides the potential application of CNC with improving properties.

Keywords: Biocomposite; hydrogel; natural fibres; nanocomposite; starch

INTRODUCTION

It is noteworthy that in Malaysia, lignocellulosic biomass which is the main resource in the production of CNC can be obtained abundantly from different sources. CNC has many unusual and unique properties whose physical and chemical properties are very different from the properties of cellulose at the macro scale, in addition to having all the biodegradable attributes associated with its plant-based source. Research focusing on the use of natural fibress as nano-materials has been carried out in the Universiti Kebangsaan Malaysia (UKM) since eight years ago using different sources such as mengkuang leaf, kenaf, coconut fibres, rice husk, etc. as shown in Figure 1 [1-4].

Generally, natural fibres can be grouped into four main groups depending on the source i.e. leaf fibres, bast fibres, fruit fibres, and seed fibres. Natural fibres are being used as potential reinforcing materials because of so many advantages such as abundant availablility, low weight, biodegradable, cheap, renewable, low abrasive nature, and exhibit good mechanical properties [5]. On the other hand, natural fibres also have some disadvantages such as moisture absorption,

quality variation, low thermal stability, and poor compatibility with the hydrophobic polymer matrix [6]. To overcome these problems, modification on the fibres needs to be done.

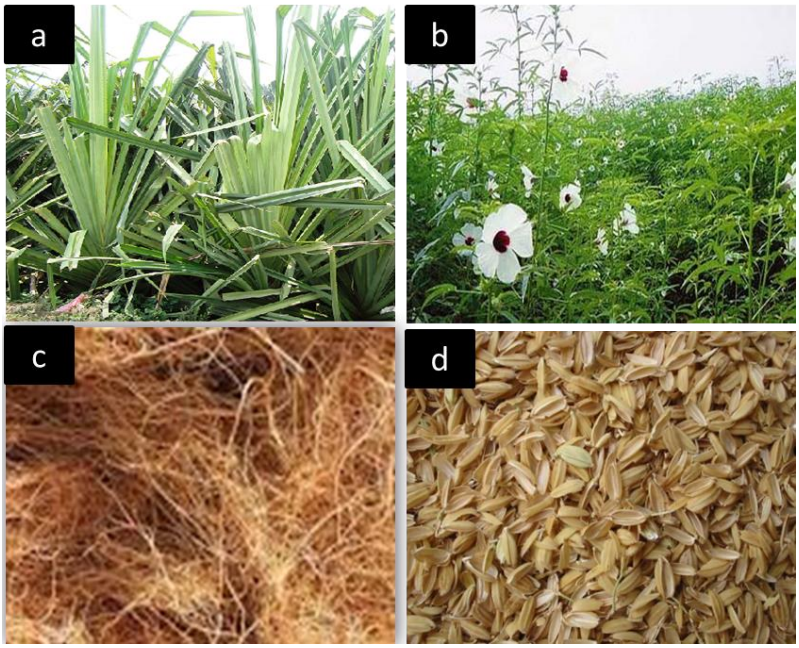

Fig. 1 Natural sources of fibres from (a) mengkuang leaves, (b) kenaf, (c) coconut, and (d) rice husk.

Nanotechnology involves developing the ability to control the shape, size, and chemical composition of the cellulose structures in the 1-100 nanometers scale (10^{-9} meter; one ten-thousandth of a millimeter). In the crystalline regions, cellulose chains are closely packed together by a strong and highly intricate intra- and intermolecular hydrogen-bond network while the amorphous domains are regularly distributed along the microfibrils [7]. The crystalline region provides higher crystallinity which leads to the improvement of mechanical strength and stiffness of the fibres. Removing the amorphous region affects the structure and crystallinity of the fibress. Furthermore, the thermal stability and the surface morphology of the fibress are affected by the removal of the amorphous parts. Recent researches have shown improvement in the crystallinity, the thermal stability during the cellulose extraction [1-4]. This will give a major contribution to the improvement of the mechanical and thermal properties of the bio-composites and proved that CNC can be used as reinforcing fillers in bio-nanocomposite materials. The results in significant modification of CNC can radically change the process/product configuration and ultimately the final product. The development of CNC has made it possible to manipulate and create novel materials and structures at the nanoscale.

This review paper focuses on efforts, to use CNC in the biocomposite application. In this case, CNC is usually extracted from natural fibres such as mengkuang leaf, kenaf, empty fruit bunch, coconut fibres, rice husk, etc. to examine their potential for use as reinforcement fillers in the biocomposite application. The use of CNC from potential Malaysian resources has shown not only to improve the modulus but also the strength, thermal and morphological properties due to direct filler-matrix interaction and the uniform dispersion of fillers in the matrix.

EXPERIMENTAL

Preparation of cellulose nanocrystals from natural fibress

Cellulose nanocrystals (CNCs) from natural fibress i.e. mengkuang leaves, kenaf bast fibres, rice husk, and coconut fibres were prepared by acid hydrolysis of the cellulose obtained as described elsewhere [1-4]. Briefly, natural fibres were vigorously stirred in a 4% alkali solution at 80 °C for 3 h. This process was repeated three times. Afterward, bleaching was performed three times with 1.7% sodium chlorite solution and acetic acid buffer solution for 4 h at 80 °C. Hydrolysis was conducted at 45 °C with 65% sulfuric acid (H_2SO_4). The time for hydrolysis in this research was fixed at 40 min, which was found previously to be optimum [1-4]. The process was terminated by placing the reaction flask into an ice bath. The excess sulfuric acid was then removed by repeated centrifugation at 11200g for 10 min. Following this, the resulting suspension was dialyzed against distilled water using a cellulose membrane for two weeks. The final suspension had a pH of 6.

Preparation of biocomposite films

For comparison study CNC from two different sources which is from kenaf bast fibres and rice husk, was used as reinforcing filler in starch biocomposite films [8-9]. Fabrication of CNC-reinforced thermoplastic cassava starch (TPCS) biocomposite films based on solution casting was carried out according to the previous study with modifications [10]. Cassava starch (CS) was first mixed with sorbitol and glycerol (50:50) in distilled water and heated at ~71 °C under continuous stirring until the mixture had gelatinized. After this, composites with different fibre loading (2%, 4%, 6%, 8%, and 10%; dry starch basis) were prepared by the addition of aqueous suspension. The final water content was adjusted to 20 wt% (water + suspension on a dry starch basis) for all of the samples. Each mixture was cast into a Petri dish and left overnight in an oven before being kept at room temperature in a conditioning desiccator at 30% relative humidity prior to testing. The thicknesses of the processed samples were fixed to produce 250 to 300 μm thick plates.

Preparation of poly(acrylic acid)-CNC hydrogels

For comparison study, CNC from two different sources i.e. from kenaf bast fibres and rice husk were used as reinforcing filler in poly(acrylic acid) (PAA) hydrogels [11]. The hydrogels were prepared by crosslinking AA monomer in CNC suspension using APS as initiator and MBA as a crosslinker. A mixture of water (10 mL), AA, and CNC was prepared and then homogenized to ensure the CNC dispersed homogeneously. The mixture was then heated and stirred on a hot plate after adding 10 mL of a 3% MBA solution. At 50 °C, 5 mL of 2% APS solution was added into the mixture and allowed to mix homogenously until 60 °C. The mixture is then cast onto a preheated petri dish. The hydrogels obtained were then immersed in distilled water for 24 h in order to leech out any unreacted chemical. The hydrogel is then dried in an oven at 70 °C for two days.

Characterization of CNC

Transmission electron microscopy (TEM) was conducted using a Philips CM30 microscope to investigate the morphology of the cellulose nanocrystals. A droplet of a diluted suspension was deposited on a Cu grid covered with a thin carbon film. To enhance the contrast, the nanocrystals were negatively stained with 2 wt% uranyl acetate solution (an organometallic complex) in deionized water for 1 min and then dried at room temperature.

Characterization of starch-CNC biocomposites

The mechanical performance of the films was evaluated in terms of tensile strength and tensile modulus using a universal testing machine (Instron model 5566, USA) at room temperature according to ASTM D882. A crosshead speed of 50 mm/min, an initial grip distance of 40 mm, and a load cell of 50 N were used for this test. The film thickness was determined at five points. The samples were cut into a dumbbell shape and the average value of seven replicates for each sample was taken.

The morphology of the composite films was investigated using a Zeiss Supra 55VP field emission scanning electron microscopy (FESEM). The biocomposite films were frozen in liquid nitrogen and broken into small pieces. All the samples were mounted on the aluminum stub. Before observation, the samples were coated with gold using a Sputter Coater model BioRAD to prevent charging. The samples were observed using an applied tension of 10 kV.

Characterization of PAA-CNC hydrogels

A swelling test at different pH values was performed to study the effect of pH on the swelling behavior of the hydrogels. In this study, three different buffer solutions were prepared at pH 3, 7, and 11. Before the swelling tests were performed, the hydrogel samples were cut into disk shapes. The disk-shaped hydrogels were then weighed before immersing into the buffer solutions. Readings of the weight of the hydrogels after immersion were recorded at predetermined time intervals over a 48-h period. Before weighing, the excess buffer solution on the surface of the hydrogels was removed using filter paper. The swelling ratio of the hydrogel was calculated using Eq. (1).

$$\text{Swelling ratio } (\%) = \frac{W_t - W_0}{W_0} \times 100\% \quad (1)$$

where W_t is the weight of swollen hydrogel and W_0 is the initial weight of the hydrogel.

Rheological behaviors of swollen hydrogel were studied using Anton Paar rheometer model Physica MCR 301 in parallel plates. Strain sweep test was first carried out in order to determine the linear viscoelastic range of the hydrogel where storage modulus was independent of the strain amplitude. A frequency sweep test was then done to study the viscoelastic behavior of the hydrogel. The storage modulus as the function of angular frequency (ω) from 0.1rad/s to 100 rad/s at constant strain and temperature.

RESULTS AND DISCUSSION

TEM analysis

Figure 2 shows TEM micrographs obtained for CNC resulting from H_2SO_4 hydrolysis of purified (a) mengkuang leaves, (b) kenaf bast fibres, (c) coconut fibres, and (d) rice husk fibress. To produce CNC, cellulose generally has to be treated with H_2SO_4. The acid hydrolysis will help to disintegrate and facilitates the defibrillation of the fibres at a nanoscale level. The acid hydrolysis treatment was expected to cleave the amorphous region of cellulosic microfibrils transversely keeping the ordered crystalline domains intact. The treatment subsequently reduces the size of the fibress from the micro to the nanometer scale [12].

The rod-like or needle-shaped CNC was characterized by their length, diameter, and aspect ratio. The range dimensions of the CNC and the aspect ratios obtained from the various sources of fibres are listed in Table 1. The dimensions of CNC for all fibres are different as this range depends on the source of the cellulose [13]. As can be seen in the table, the diameter is in the range of 5 to 25 nm whereas the length in the range of 50 to 400 nm.

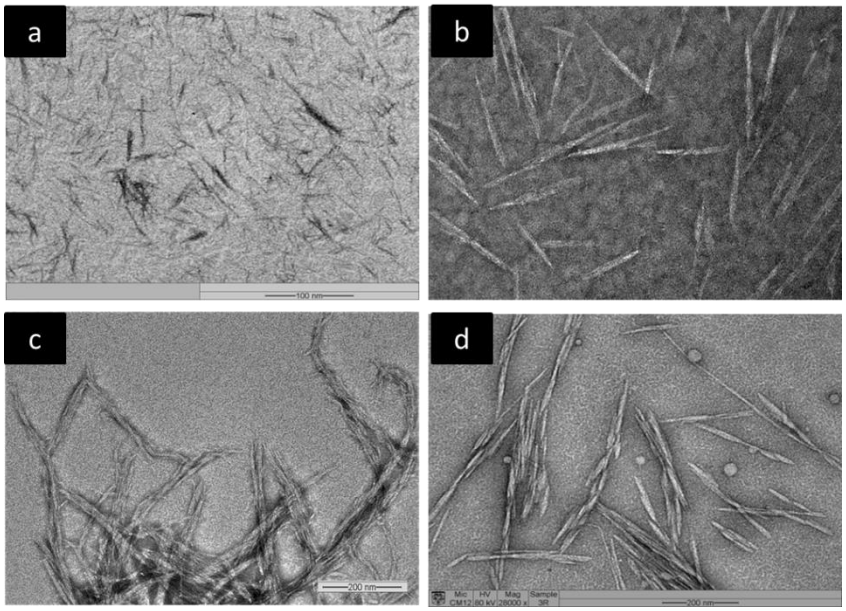

Fig. 2 TEM micrographs from a diluted suspension of CNC extracted from (a) mengkuang leaves, (b) kenaf, (c) coconut, and (d) rice husk [1-4].

Table 1 Data of diameter distribution and aspect ratio of CNC extracted from various sources

Sources of CNC	Diameter, d (nm)	Length, l (nm)	Aspect ratio (l/d)	References
Mengkuang leaves	5–25	50–400	10–20	[1]
Kenaf bast fibre	9–15	95–222	13.2	[2]
Coconut fibre	9–24	73–226	8–25	[3]
Rice husk	15–20	150–300	10–15	[4]

Mechanical properties of starch-CNC biocomposites

Previous studies by Zainuddin et al. (2013) and Johar et al. (2012) have found that the tensile strength of starch biocomposite increased with the addition of kenaf CNC (CNCk) and rice husk CNC (CNCr), respectively [8-9]. The improvement of tensile strength in % of two different starch biocomposites films is plotted in Figure 3. As can be seen in Figure 3, the addition of kenaf CNC in starch resulted in a higher improvement of tensile strength than that of biocomposite with the addition of rice husk CNC. This is due to the lower aspect ratio of rice husk compared to kenaf fibres.

The TPCS biocomposite with 6 wt% CNCk showed the highest improvement of tensile strength among the biocomposites with an enhancement of 134% in terms of tensile strength compared to control film. This significant improvement for TPCS-CNCk was mainly due to the high specific area and high L/D ratio, which provided better reinforcement capability. This also reflected the strong interfacial interaction that occurred between starch and cellulose. The ability of the nanofibress to restrict matrix mobility also contributed to this improvement. This improvement was due to the strong interfacial interaction between starch and fibress, which brings about good stress transfer. On the other hand, the slight decrease for the composites at certain loadings was mainly due to the entanglement of the fibress inside the matrix phase [8].

Meanwhile, the addition of CNCr to the starch matrix also improved the tensile strength even though it is not that significant compared to CNCk biocomposite. The 6% TPCS-CNCr showed the highest improvement of tensile strength with 52% enhancement. This insignificant improvement for the TPCS-CNCr compared to kenaf CNC biocomposite was mainly due to the low aspect ratio of the CNCr. However, the tensile strength with the CNCr biocomposite was still higher than that of the starch matrix alone. This also reflected the good interfacial interaction that occurred between the starch and the CNCr [9]. The formation of a rigid network of CNCs due to the interaction among the CNCs by intra- and intermolecular hydrogen bonds and/or the mutual entanglement between the CNCs and the starch matrix could be additional reasons for the higher tensile strength [9, 14].

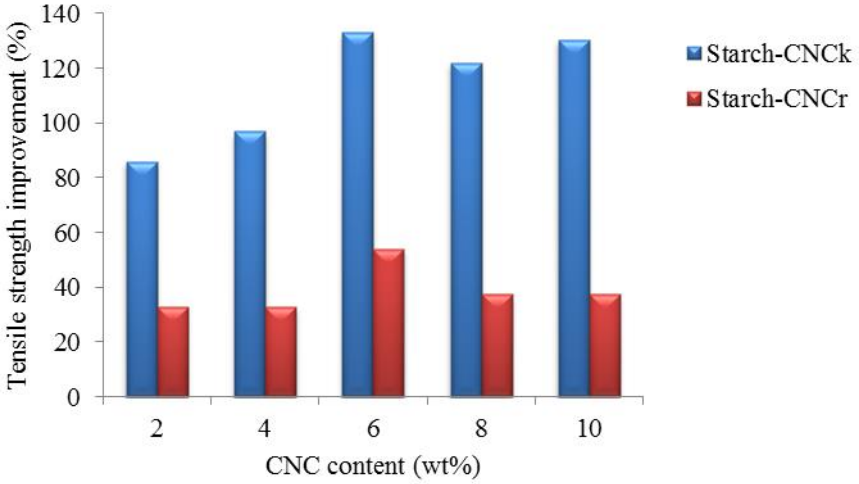

Fig. 3 Effect of CNC from various sources on tensile strength [8-9].

Previous studies also have found that the tensile modulus of starch biocomposite increased with the addition of CNCk and CNCr [8-9]. The improvement of tensile modulus in % of two different starch biocomposites films are presented in Figure 4. As can be seen in Figure 4, the addition of CNCk in starch resulted in a higher improvement of tensile modulus than that of biocomposite with the addition of CNCr. This is due to the lower crystallinity index of CNCr (59%) compared to CNCk (82%) [4, 8]. Figure 4 shows a clear tendency of increasing stiffness for all of the composites with increasing CNC content. For TPCS-CNCk, the improvement in the tensile modulus may be related to the increased stiffness due to the addition of CNC [15]. The high crystallinity of the CNCk led to more rigid materials in the case of TPCS-CNCk and hence its high modulus. The high surface area displayed by this highly crystalline nanocellulose, therefore, increased the surface interaction between the filler and the matrix and led to a mechanical improvement in terms of its modulus.

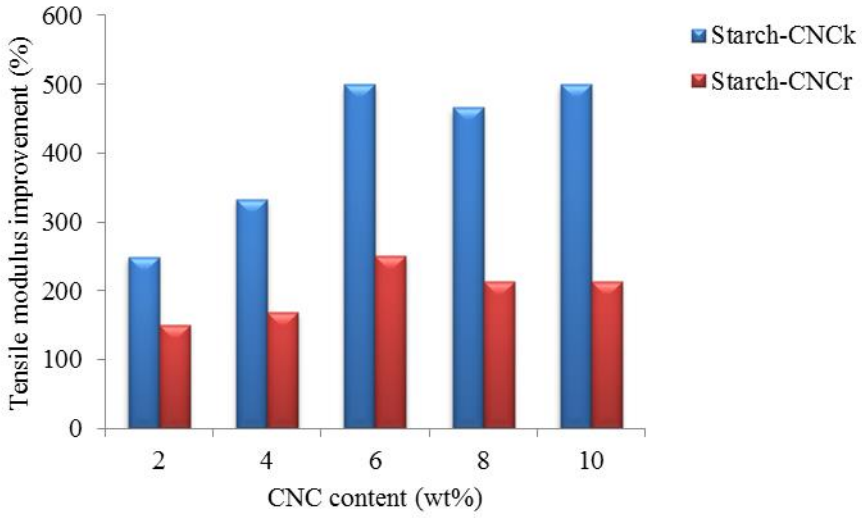

Fig. 4 Effect of CNC from various sources on tensile modulus [8-9].

Morphological properties of starch-CNC biocomposites

The FESEM micrographs of TPCS-CNCk and TPCS-CNCr films are shown in Figure 5. TPCS-CNCk displays a relatively smoother surface compared to the composites reinforced with CNCr The smooth surface observed for TPCS-CNCk compared to CNCr composite film indicates that CNCk, are probably homogenously dispersed within TPCS since no aggregates can be seen. This fine dispersion of CNCk within the polymer matrix would results in an improvement in the mechanical properties of the nanocomposite compared to the TPCS-CNCr.

The strong interaction between the CNCs and starch can also be seen as the CNCs were completely covered by the matrix. This is attributed to not only the good CNCs dispersion in the matrix but also the strong nanofiller–matrix adhesion by hydrogen bonding interactions [16-18].

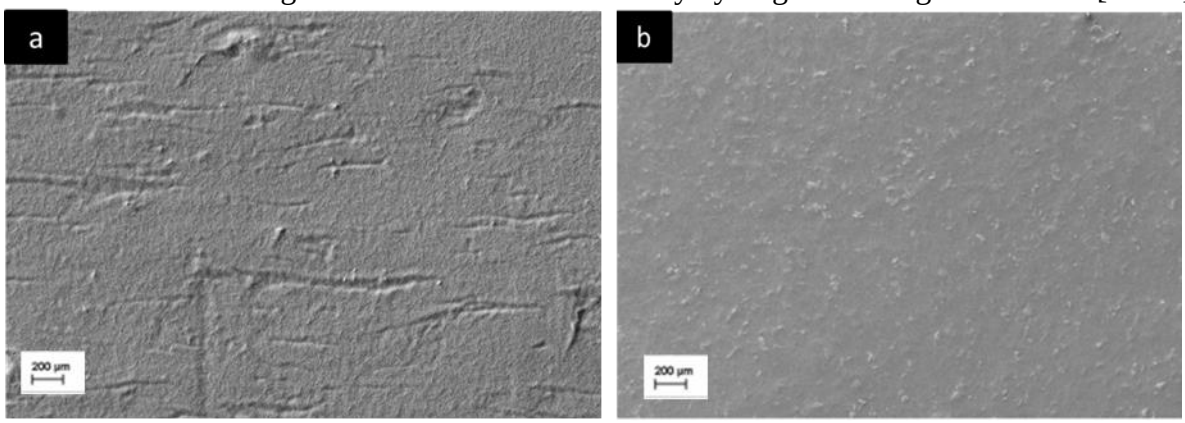

Fig. 5 SEM micrographs of (a) starch-CNCk and (b) starch-CNCr biocomposites [8-9].

Swelling properties of PAA-CNC biocomposites

The equilibrium swelling ratio of hydrogel with different CNC sources was illustrated in Fig 6. For all the pH tested, 10% of CNCk hydrogel displays the highest equilibrium swelling ratio. CNC is hydrophilic in nature due to the presence of –OH group. Therefore, the increase in equilibrium

swelling ratio observed on both CNC/PAA hydrogel is due to the increase in hydrophilic groups which facilitate water sorption into the hydrogel.

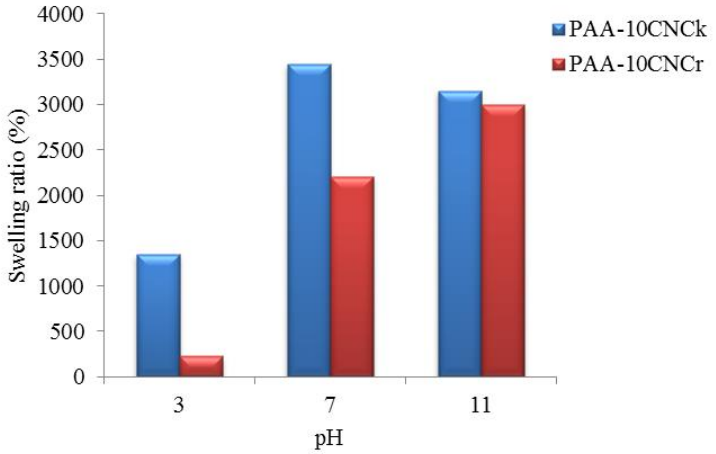

Fig. 6 Swelling ratio of PAA-CNCk and PAA-CNCr hydrogels at pH 3, pH 7, and pH 11 [11]

PAA can be contemplated as polyelectrolyte polymers as it possesses a lot of ionizable pendant acidic groups. The sudden rise in the equilibrium swelling ratio observed at pH 7 with the addition of CNCk was due to the ionization of the COOH groups (pKa = 4.25) of PAA into COO- ions [19]. The resultant repulsive electrostatic force generated from COO- ions caused the hydrogel network to expand and thus increased the swelling ratio. Any further increase in pH caused the swelling ratio of hydrogel to decrease. This is due to the presence of too many negative charged groups in the solution forcing the COO^- ions reversed back into COOH groups [20].

However, the high equilibrium swelling ratio was observed at pH 11 with the addition of CNCr. Furthermore, based on the observation, it can be concluded that the PAA-CNCr hydrogel is pH-responsive. The swelling percentage has increased from pH 3 to pH 7, and reached the highest at pH 11. The swelling percentage of hydrogels is low at acidic pH due to unsuitable conditions for the COOH group to ionize into carboxylate ion (COO^-). When the pH exceeds 4.25, the swelling percentage increase as the COOH group starts to ionize and form a negatively charged COO^- ion, as shown in the Eq. (2) [19]. An electrostatic repulsion has been formed between the ionic chains and resulting in greater free volume space and finally increased the swelling ratio [21].

$$RCOOH + OH^- \rightleftharpoons RCOO^- + H_2O \quad (2)$$

Rheological properties of PAA-CNC biocomposites

Figure 7 presents the storage modulus of the semi-IPN hydrogel at 10 wt% of fibres loading as a function of shear frequency. The rheological properties of a viscoelastic material are usually characterized by its storage modulus. Storage modulus is a measurement of elasticity or the solid-like behavior of a material. The storage modulus of the hydrogels as the incorporation of CNC was expected to increase the mechanical properties of the hydrogel (hydrogel will behave more solid-like).

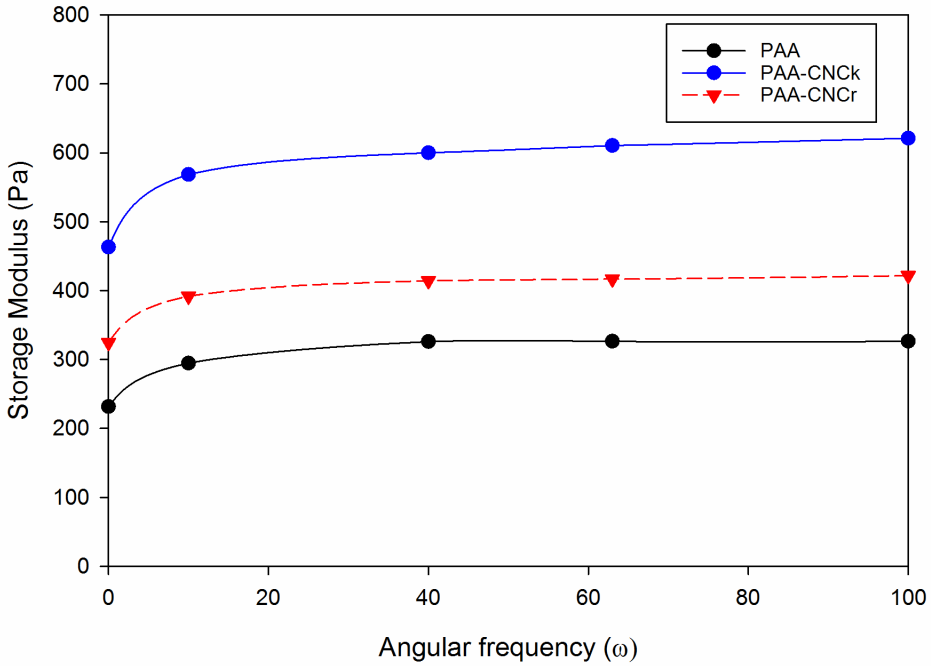

Fig. 7 The storage modulus of PAA-CNCk and PAA-CNCr hydrogels [11]

It is clearly shown in Figure 7 that the storage modulus of CNCk hydrogel is higher than that of CNCr hydrogel. This shows that hydrogels became tougher and more rigid with the addition of CNCk. The results obtained are consistent with the crystallinity index values of each CNC fibres. The high crystallinity index of kenaf CNC results in increased storage modulus of hydrogels. Besides, PAA/CNCk hydrogel showed a higher storage modulus compared to PAA/CNCr hydrogel could be due to the high aspect ratio of kenaf CNC. A crystalline structure with a higher average aspect ratio helps to improve the adhesion between the polymer chains and filler indirectly [22], thus, providing a higher strengthening in the hydrogels matrix, and thereby, increasing the rigidity in the hydrogels [23].

CONCLUSION

CNC from natural fibres had been successfully isolated using the acid hydrolysis method. The average length and the optimum aspect ratio value recorded by TEM are 5-20 nm and 10-25 nm respectively. Mechanical properties of bio-nanocomposites increased with the increase of CNC content with the optimum at 4-6% filler loadings. For biocomposite, it was found that kenaf CNC biocomposite shows better improvement in mechanical and morphological properties compared to rice husk CNC biocomposite. Hydrogels with different sources of CNC were utilized and their swelling and mechanical properties showed different results. Kenaf CNC hydrogel and rice husk CNC hydrogel achieved maximum swelling at pH 7 and pH 11, respectively. The hydrogel reinforced with kenaf CNC shows high modulus compared to rice husk CNC hydrogel. In conclusion, kenaf CNC performed much better than rice husk CNC in terms of improvement in mechanical, swelling and morphological properties when compounded with starch and PAA. The lower performances of rice husk CNC compared to kenaf CNC could be mainly attributed to the difference in the aspect ratio of the fibress which plays a crucial role in determining the

performance of the biocomposites. The higher is the aspect ratio, the higher is the mechanical property.

ACKNOWLEDGMENT

The authors acknowledge financial support from the Ministry of Higher Education, Malaysia (MOHE) and Universiti Kebangsaan Malaysia (UKM) under research grants GUP-2018-028 and MI-2019-020.

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