MORPHOLOGICAL, THERMAL, AND MECHANICAL PROPERTIES OF STARCH BIOCOMPOSITE FILMS REINFORCED BY CELLULOSE NANOCRYSTALS FROM RICE HUSKS

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A series of glycerol-plasticized starch composites reinforced by rice-husk cellulose nanocrystals was successfully fabricated through the solution casting technique. The rice husks must undergo alkali treatment, bleaching, and sulphuric acid hydrolysis before cellulose nanocrystals can be produced. The cellulose nanocrystal content used as filler was varied from 0 to 10 wt%. The thermal stability of the composite were analysed by thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG). The starch biocomposite films reinforced with rice-husk cellulose nanocrystals showed improved tensile strengths and tensile moduli. Transmission electron microscopy (TEM) was used to determine the diameter and length distribution of the cellulose nanocrystals. Field emission scanning electron microscopy (FESEM) showed that the cellulose nanocrystals (CNCs) were well distributed in the matrix. At the optimum 6% filler loading, the cellulose nanocrystals exhibited a higher reinforcing efficiency in the plasticized starch biocomposites than at any other filler loading.

Keywords: Rice husk; Cellulose nanocrystals; Starch biocomposites; Solution casting

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INTRODUCTION

Over the years, concerns about environmental problems associated with conventional plastics have generally increased, including their non-biodegradability, the release of toxic pollutants, litter, and their impact on landfills. These problems are the result of the production of petroleum-based plastics from non-renewable resources, as well as their disposal. In response to the growing need for biodegradable materials, researchers have been attempting to replace synthetic polymers with natural polymers. Most researchers have focused on materials that have properties comparable with those of the conventional polymeric materials. From this perspective, starch biocomposites (SBs) are seen as among the promising candidates to be developed as biodegradable materials.

Starch is a natural renewable polymer obtained from a variety of crops. Among its advantages, starch is cheap, abundant, and biodegrades quickly (Famá *et al.* 2006; Teixeira *et al.* 2009). In recent years, starch has been used to produce biodegradable plastics (John and Thomas 2008). Even so, in order to prepare SBs with better properties, a few drawbacks of this material need to be overcome. Poor mechanical properties and poor resistance to humidity are the main two disadvantages of SBs. However, these limitations can be overcome using several approaches.

Previous studies have demonstrated that the addition of water (Hulleman *et al.* 1998) and glycerol as plasticizers (Fishman *et al.* 2000) is one way to improve the mechanical properties of SBs. Other approaches include blending the starch composites with certain synthetic polymers (Averous and Fringant 2001), chemically modifying the starch by adding crosslinking agents or through esterification (Reddy and Yang 2010; Averous 2004; Chatakanonda *et al.* 2000; Shogren *et al.* 1998), or adding lignin (Baumberg *et al.* 1998). In addition, fibres can be used as reinforcements for SBs to overcome these problems. Various types of fibres have been discussed in the literature, including cellulosic microfibrils (Dufresne and Vignon 1998), natural fibres (Wollerdorfer and Bader 1998), and commercial regenerated cellulose fibres (Funke *et al.* 1998).

Although a number of studies have been carried out on the use of a combination of starch and natural fibres to form plastic films, no research on using cellulose nanocrystals (CNCs) from rice husks for reinforcement in SBs has been reported. In the present study, CNCs from rice husks were used as a reinforcing agent for the preparation of starch nanocomposites.

The reinforcing effect of the CNC loading on a starch nanocomposite was evaluated using morphological studies and measurements of the mechanical and thermal properties. In this study, cassava starch is used, which is generally composed of 17% amylose and 83% amylopectin; the diameter of a starch granule is approximately 4 to 35 μm and is an oval shape (Alexander 1995).

EXPERIMENTAL

Materials

The rice husks used as raw materials were obtained from Bernas Malaysia Sdn. Bhd. Native cassava starch was supplied by Thye Huat Chan Sdn. Bhd. Sodium hydroxide, acetic acid, sulphuric acid (95% to 98% purity), and glycerol (99.5% purity) were purchased from System ChemAR. Sodium chlorite (80%) was purchased from Sigma-Aldrich.

Methods

Preparation of CNCs from rice husks

CNCs were extracted from rice husks using the acid hydrolysis method. Briefly, a mixture of ground rice husks and 4 wt% alkali solution (NaOH) was refluxed under mechanical stirring at around 90 ^{o}C for 2 hours. For the bleaching treatment, acetate buffer, aqueous chlorite (1.7 wt%), and distilled water were added and refluxed at a temperature of 90 ^{o}C for 4 hours, and this process was repeated 4 times.

Acid hydrolysis was conducted on the cellulose particles at 45 °C with 65 wt% sulphuric acid (heated) for 30 minutes under mechanical stirring. The fibre content for the hydrolysis treatment was in the range of 4 to 6 wt%. The hydrolysed cellulose was then centrifuged several times at 10000 rpm and 10 ^{o}C for 10 minutes. The suspension was dialyzed against distilled water for several days until a constant pH in the range of 5 to 6 was reached.

Preparation of SB films

The fabrication of the SB films was based on the solution casting technique and the evaporation process. Cassava starch was first mixed with the plasticizers (glycerol) and the filler (CNC) in distilled water; the mixture was heated at 100 ^{o}C under continuous stirring until the mixture gelatinized. The mixture contained 5 wt% cassava starch, 2.5 wt% glycerol, and 92.5 wt% water, respectively.

Various filler loadings of the CNC were used for the production of SBs: 2%, 4%, 6%, 8%, and 10% (dry weight basis). The CNC particles must be sonicated for 10 minutes using a power of 60 W before being added into the plasticised starch mixture. The mixture was then cast in a petri dish and dried at 60 ^{o}C overnight to obtain SB films with a thickness of approximately 0.30 mm. A neat matrix of SB film was also prepared using the same process mentioned above, except that there was no filler added to the composites. The films were kept in a dry cabinet at 30% relative humidity before the tests.

Characterization

Transmission electron microscopy (TEM)

The dimensions of the CNCs from rice husks were determined using transmission electron microscopy (Philips CM 12) with an accelerating voltage of 80 kV. A drop of diluted suspension (1 wt%) was dispersed on the surface of a copper grid and coated with a thin carbon film.

To enhance the contrast in TEM, the CNCs were negatively stained in a 2 wt% solution of uranyl acetate (a heavy metal salt) in deionized water for 1 minute and dried at ambient temperature. TEM analysis was carried out to determine the length and diameter range of the cellulose crystals on a nanometre scale.

Tensile tests

The mechanical performance of the films was evaluated in terms of their tensile strengths and Young's moduli with a universal testing machine (Instron model 5560) at room temperature with a crosshead speed of 50 mm/min and load cell of 50 N. The specimens were cut into dumbbell shape according to specification of ASTM D412-68 standard to ensure the breakage of samples occurs within the gauge length. The average value obtained from five tests was taken for each sample.

Field emission scanning electron microscopy (FESEM)

The fractured cross-section of the cast SB strips was examined using a field emission scanning electron microscope (Philips XL-3) operating at an acceleration voltage of 20 kV. SB strip samples were cooled in liquid nitrogen and then broken. The fractured cross-section of films was vacuum-coated with gold for SEM.

Thermogravimetric analysis (TGA)

TGA was carried out using a Mettler Toledo thermogravimetric analyser (TGA/SDTA 85-F) apparatus. All measurements were performed under a nitrogen atmosphere with a gas flow of 10 mL min^{-1} by heating the SB film from room temperature to 600 ^{o}C at a heating rate of 10 ^{o}C min^{-1}.

RESULTS AND DISCUSSION

Morphology of the Cellulose Nanocrystals

A transmission electron micrograph of the rice-husk CNCs obtained after the hydrolysis with sulphuric acid is shown in Fig. 1. In the cellulose fibres, the sulphuric acid hydrolysis could usually cleave the amorphous region of the microfibrils transversely. This could eventually reduce the sizes of the fibres from microns to nanometres (Azizi Samir *et al.* 2005). The averages and frequencies of the diameter distribution and aspect ratio distribution for 100 samples of CNCs from rice husks are given in Table 1. The most likely diameter range for the CNCs was between 15 and 20 nm, which accounts for 35% of the sample, while the most likely aspect ratio range for the CNCs was 10 to 15, which account for 39% of the sample.

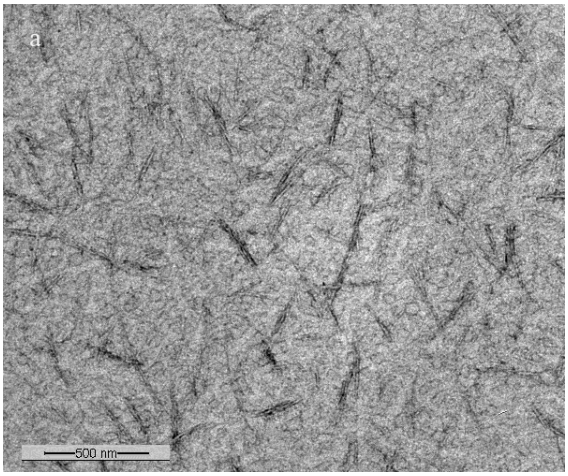

Fig. 1. TEM micrograph of CNCs from rice husks

Table 1. Averages and Frequency Range of the Diameter and Aspect Ratio Distribution of CNCs

Frequency Range	Diameter		Aspect Ratio	
	Average (nm)	Frequency (%)	Average	Frequency (%)
0-5	2.88 ±0.56	14	4.53 ± 0.23	3
5-10	9.43 ± 0.65	3	7.58 ± 1.46	36
10-15	12.64 ± 1.56	28	12.28 ± 1.58	39
15-20	17.28 ± 1.39	35	17.32 ± 1.33	16
20-25	22.13 ± 1.35	16	23.64 ± 2.04	6
25-30	26.68 ± 1.36	4	-	-

Tensile Tests

The evaluation of the tensile strength and tensile modulus as a function of CNC loading is shown in Fig. 2. As shown in the figure, it is obvious that the matrix at 0% CNC had the lowest tensile strength at 4.1 MPa. However, after CNCs were added to the composites as reinforcing fillers, the value of the tensile strength began to increase, and the optimum filler loading is about 6%. The improvement can be seen with the increment of 47% from 4.25 MPa (0% CNC) to 6.03 MPa at the optimum filler loading. Meanwhile, at higher percentages of cellulose loading, the tensile strength decreased slightly but

remained high compared to the matrix. The tensile modulus also showed a steady increase with the addition of CNCs, but the value dropped at 8% and 10% CNC loading.

It can be seen from Fig. 2 that the lowest value of the tensile modulus was for the matrix at 97.63 MPa, while the highest value was for the SB filled with 6% CNCs at 261.7 MPa. The mechanical behaviours of the starch nanocomposite films in this work were improved and enhanced with the presence of reinforcement as compared to the neat matrix at 0% CNC. This may be due to the strong interaction between the matrix and the CNC filler, which makes CNCs an effective reinforcing agent. This enhancement also indicates good dispersion of CNCs in the matrix, as can be seen from the FESEM micrographs discussed below. However at higher loading of CNC at 8% and 10%, the tensile properties slightly dropped compared to lower CNC loading. The low tensile values at high CNC loadings might be due to fibre agglomeration and high numbers of fiber ends in the composites (Fowler *et al*. 2006). The aggregation and agglomeration of CNC may happen as the fibre is in nano-phase and the tendency to form larger structures increase especially at higher CNC loading. This phenomenon resulted on fibre-fibre interaction not for the fibre-matrix interaction.

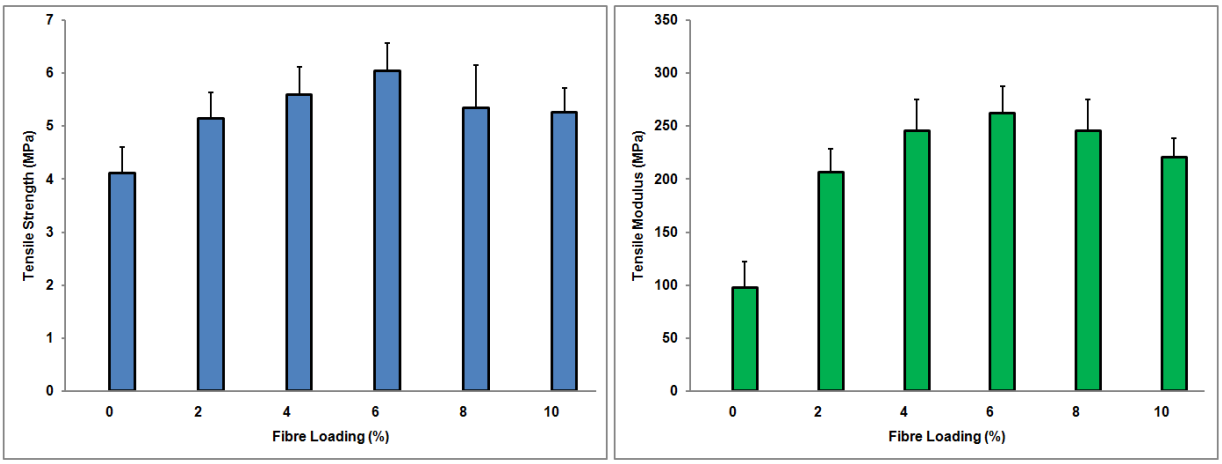

Fig. 2. Mechanical properties of SB films reinforced by CNCs

Morphology of the SB Film

Figure 3 shows macroscopic visual images of the SBs with 0% and 6% CNC content. The films in these two images appear very similar, and the hand can be clearly seen through both SB films. This highlights one benefit of using CNC as filler in the preparation of SBs: the physical appearance of the film does not change much, and it can be considered to be the same as that of the matrix.

On the other hand, as shown in Fig. 4, FESEM micrographs were taken of the fractured cross-section of (a) the neat matrix film and (b) the SB film reinforced with 6% CNC in order to investigate more details of the SB structure. The micrograph clearly shows that the neat matrix film display had a relatively smooth surface. The surface of the SB film filled with 6% CNCs, however, was rougher. This was due to the incorporation of CNCs, which caused the morphology of the composite to be more structured and produced a rougher surface. The CNCs appear as the white domains randomly distributed on the fractured cross-section of the SB film. The strong interaction between the CNCs and the polymeric phase can also be seen, as the filler was completely

covered by the matrix. This is attributed to the chemical similarity of starch and CNC fibres which provides good compatibility between these two. Good dispersion and adhesion between the CNCs and the polymer matrix are important factors contributing to the improvement of the mechanical performance. This is necessary to define a good fibre-matrix interface that can transfer externally-applied loads to the reinforcement via shear stresses over the interface (Fowler *et al.* 2006). These morphological observations suggest that these factors contributed to the improvements in the tensile test results discussed above. This result is also in good agreement with previous studies reported in the literature (Averous and Boquillon 2004; Lu *et al.* 2006).

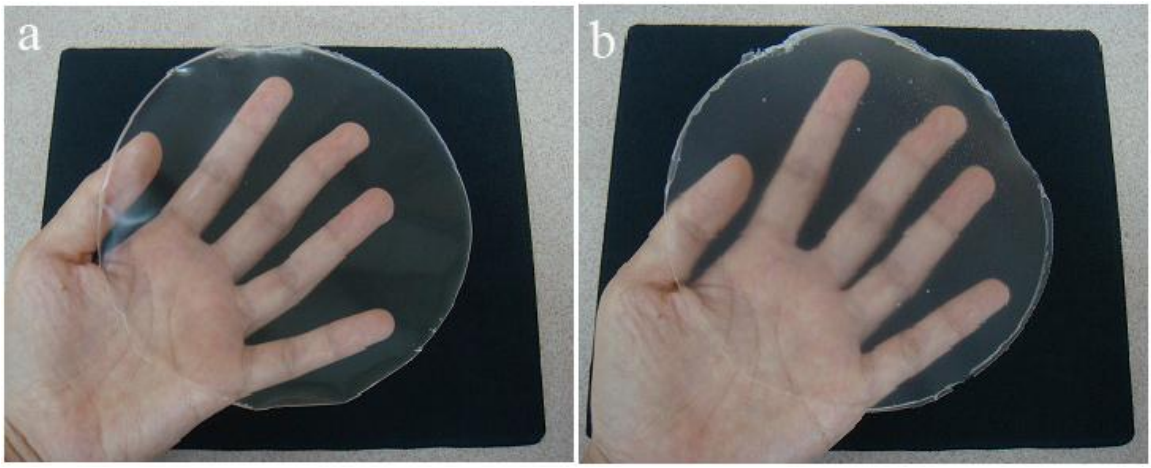

Fig. 3. Macroscopic visual images of (a) SB matrix and (b) SB with 6% CNC loading

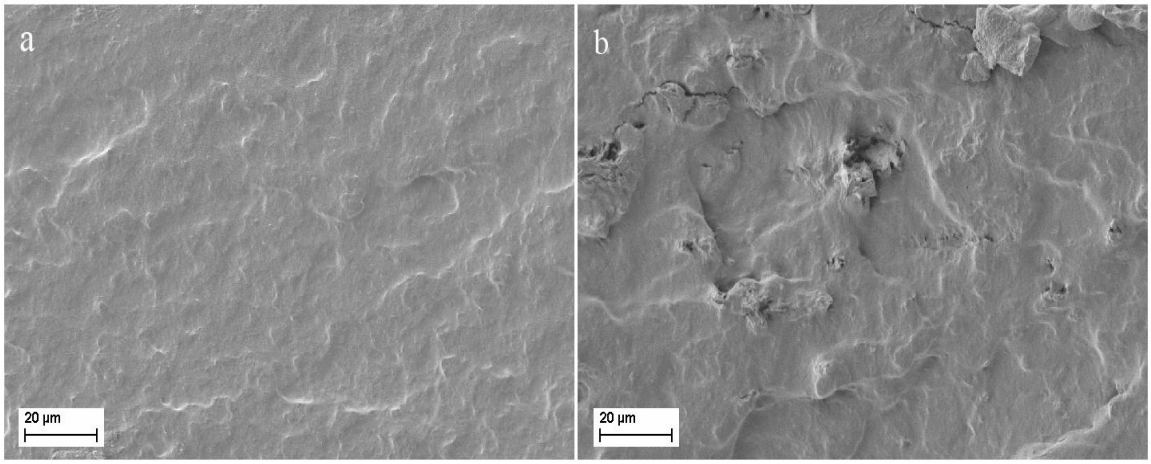

Fig. 4. FESEM micrographs of fractured surfaces of (a) SB matrix and (b) SB with 6% CNC loading

Thermal Analysis

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) were carried out to observe the thermal behaviour of the SB films, as shown in Table 2 and Fig. 5. In the early stage of the degradation of the SB films at temperatures below 100 ^{o}C, the loss of water and low-molecular-weight compounds occurred. It can be seen from Fig. 5b that there was a significant weight loss from the SB films in the temperature

range of 250 °C to 350 °C, which represents the decomposition of the CNCs and glycerol. This result is in agreement with that of Cyras *et al*. (2006), who reported that the nanocrystals and glycerol started to degrade above 180 °C. Thermograms with similar patterns have also been reported by others (Alemdar and Sain 2008; Averous and Boquillon 2004) as part of their work on the preparation of thermoplastic starch using different types of fibres. The thermal stability of the SB film reinforced with CNC was improved compared to that of the neat matrix at 0% CNC loading, and 6% filler loading of CNCs produced the best thermal stability. This result can be attributed to the introduction of the CNCs into the polymeric phase of the SB and the good interaction between the matrix and filler. Thus, better thermal stability can be achieved by the addition of CNCs into the matrix.

Table 2. Thermal Degradation Temperature (T_d) for Neat Starch Matrix and the Nanocomposites Filled with 2%, 4%, 6%, 8%, and 10% CNC Content

Sample	T_d, 5% (°C)	T_d, 10% (°C)	T_d, 15% (°C)	T_d, 20% (°C)	T_d, 50% (°C)	Residue (%)
Neat Matrix	86	154	218	248	309	10
2% CNC	86	139	208	248	309	10
4% CNC	77	129	188	228	309	8
6% CNC	90	153	212	253	314	12
8% CNC	82	139	193	228	309	16
10% CNC	82	139	193	233	314	15

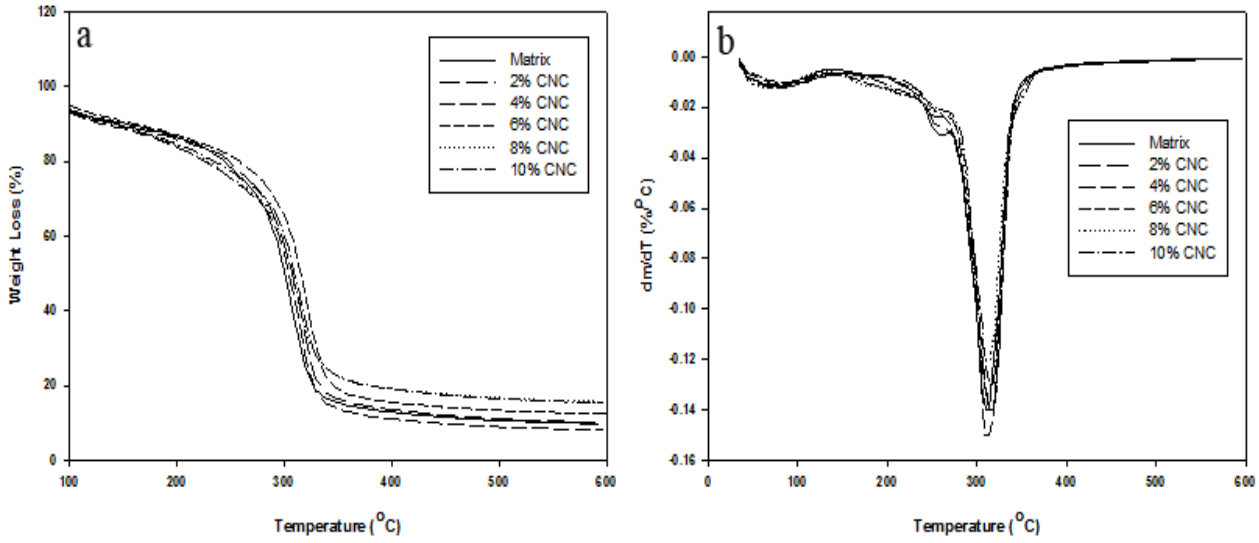

Fig. 5. TGA and DTG curves of the starch matrix and the nanocomposites filled with 2%, 4%, 6%, 8%, and 10% CNC content

CONCLUSIONS

1. CNCs from rice husks have been successfully isolated using the acid hydrolysis method. The most common average length and aspect ratio values of the 100 samples of CNCs recorded by TEM were 15 to 20 nm and 10 to 15, respectively.
2. The mechanical properties of the SB film can be improved by the addition of CNCs into the polymeric phase of the composites.
3. FESEM micrographs revealed a good distribution of the CNCs and good adhesion between the CNCs and the matrix in the SB films.
4. The SB film reinforced with CNCs exhibited better thermal stability than the original matrix as a result of the addition of the CNCs.
5. All the reported analyses suggest that the SB film reinforced with a 6% filler loading of CNCs had the best properties compared to the matrix and the films with any other filler loading level.

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