Journal of Metals, Materials and Minerals, Vol.28 No.1 pp.10-15, 2018

A comparative study of nanofibrillated cellulose and microcrystalline cellulose as reinforcements in all-cellulose composites

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Received date:
18 December 2017
Accepted date:
21 January 2018

Keywords:
Cellulose
Composites
Biodegradability
Mechanical properties
Films
Rule of mixtures

Abstract

The reinforcing abilities of nanofibrillated cellulose (NFC) and microcrystalline cellulose (MCC) in composites were investigated and compared. All-cellulose composites were prepared using the dissolved MCC as the matrix, and NFC and MCC were introduced as the reinforcing phase. With the addition of MCC, tensile strength of the composites decreased; on the other hand, the higher tensile strength of the composites with NFC was found with increasing a NFC content. Strong interfacial interaction between the matrix and reinforcing phase could be obtained at a low content of the reinforcement was observed. At a higher content of the reinforcement the fiber pull-out was found from the fracture surface of the composites after tensile deformation. The reinforcing abilities of NFC and MCC were also confirmed by the comparison between values of the Young's moduli of the composites obtained from the experiments and calculations using the rule of mixtures equation. From these results it could be summarized that NFC had the higher reinforcing ability than MCC.

1. Introduction

Due to the environmental concerns and growing interest in sustainable materials, biodegradable composites have gained more attention. An all-cellulose composite, introduced by Nishino et al. [1], is a materials where the matrix and reinforcement are made from cellulose. All-cellulose composites can be prepared from various cellulose resources such as bagasse [2], pineapple leaf [3-5], regenerated cellulose [6] and microcrystalline cellulose [7]. This composite material is considered to be a potential candidate to replace polymers derived from petroleum because of high mechanical properties, transparency, environmental friendliness, degradability and recyclability [2,8,9]. All-cellulose composites have been originally prepared using the impregnation method [1]. Ramie fibers were used as reinforcement, and the matrix was prepared from craft pulp. The pre-treated pulp was immersed in a solution of lithium chloride (LiCl) and *N, N*-dimethyl acetamide (DMAc) to form a cellulose solution, while ramie fibers were unidirectionally aligned. Then, the aligned fibers were impregnated in the cellulose solution for 12 h. The tensile strength and storage modulus of the all-cellulose composites were found to be 480 MPa and 20 GPa, which were higher than those of glass fiber reinforced composites. Moreover, its co-efficient thermal expansion was about 10^{-7} K^{-1}, which was much lower than that of silica. This composite material showed superior mechanical properties and thermal performance. In 2005, Ginal and Keckes [7] announced another procedure called the surface selective dissolution method to prepare all-cellulose composites. Microcrystalline cellulose (MCC) was firstly dissolved in a mixed LiCl/DMAc solution. During the dissolution process, the outer part of MCC was dissolved, and covered the inner undissolved part of MCC acted as reinforcement. The isotropic and transparent composite films with the tensile strength of 240 MPa and modulus of 13.1 GPa were reported. It is worth mentioning that the poor interaction between the matrix and reinforcement phase can induce an inefficient stress-transfer, resulting in lower mechanical properties of composites [8,9]. Before composite preparation, the compatibility of the matrix and reinforcement should be considered. Interestingly, in the all-cellulose composites, both matrix and reinforcement are cellulose. Therefore, the composites with better interfacial compatibility between matrix and reinforcement could be obtained.

Nanofibrillated cellulose (NFC) has been of significant interest due to their renewability, biocompatibility, low density, high aspect ratio and high strength and stiffness [10-12]. NFC, web-like structure, can be prepared using only mechanical treatment. Originally, a dilute pulp solution was passed through a homogenizer under high pressure for several times to obtain nanofibers [13-16]. Then,

DOI: 10.14456/jmmm.2018.3

other techniques such as grinding, refining and microfluidizing have been purposed [15-17]. NFC has been widely used as a promising reinforcing phase to produce high performance biocomposites. For example, NFC was used to reinforce poly (lactic acid) in order to prepare green composites [18]. With the NFC content of 10 wt%, the tensile strength and Young's modulus of the composites were improved by 25 and 40%, respectively. No reduction of yield strain was observed for these composites. Next, Lu et al. [19] studied effects of NFC on properties of poly(vinyl alcohol) composites. Mechanical properties and thermal stability of the composites were enhanced with the addition of NFC. The tensile strength of the composites with 10 wt% NFC was increased by 76%, compared to that of neat resin.

The objective of this work was to prepare all-cellulose composites with the addition of NFC and MCC, and compare reinforcing abilities of NFC and MCC in all-cellulose composites. The influence of NFC and MCC on mechanical properties of the composites was investigated. This work revealed which material between NFC and MCC should be used as the reinforcement to improve mechanical properties of the cellulose matrix.

2. Experimental methods

2.1 Materials

Microcrystalline cellulose (MCC) and nanofibrillated cellulose (NFC) (CELISH) (solid content of 10 wt%) were supplied by Sigma-Aldrich Co., Ltd. and Daicel Finechem Co., Ltd., respectively, as shown in Figure 1. Acetone, methanol, lithium chloride (LiCl) and *N*,*N*-dimethylacetamide (DMAc) were purchased from Siam Beta Group Co., Ltd., Thailand. All chemical reagents were used as received.

2.2 Preparation of all-cellulose composites

MCC was immersed in a series of solvents for 24 h. each at room temperature (distilled water, methanol, acetone and DMAc). Meanwhile, 8 g of LiCl was slowly dissolved in 100 ml of DMAc, and then stirred at 120°C for 1 h. to obtain the clear solution. The activated MCC was dissolved in the prepared solution of LiCl and DMAc, and left at room temperature for 24 h. to acquire the cellulose solution. After that, a reinforcing agent (NFC or MCC) (0 – 20 wt%) was introduced in the prepared cellulose solution, and was vigorously stirred for 4 h. The suspension was subsequently poured into a petridish, and was left at room temperature for 24 h. The composite films were washed with methanol for a few times to remove the excessive solvent. The films were dried at room temperature for 24 h. and were further dried in an oven at 60°C for another 24 h. The composite films with an average thickness of ~ 120 µm were finally formed. The all-cellulose composites containing MCC of 10 and 20 wt% were coded as MCC 10 and MCC 20 while the composites with 10 and 20 wt% NFC were called NFC 10 and NFC 20, respectively.

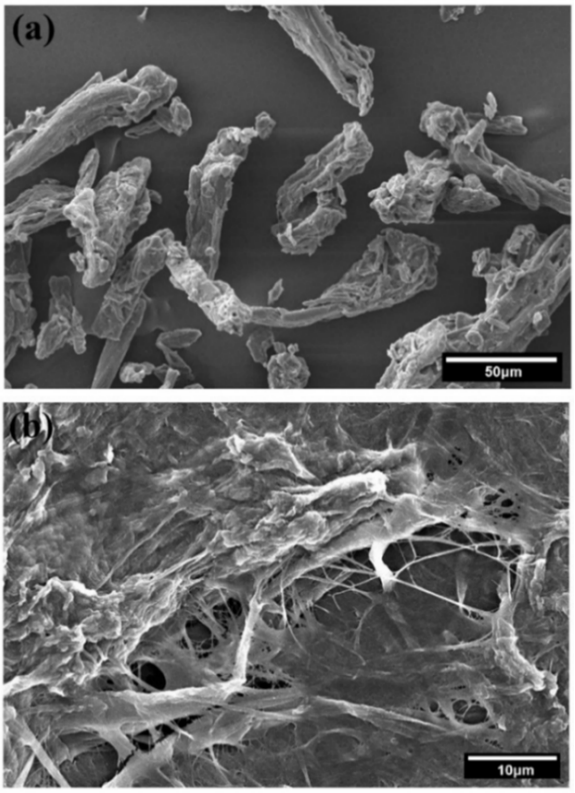

Figure 1. SEM images of (a) microcrystalline cellulose and (b) nanofibrillated cellulose.

2.3 Scanning electron microscopy (SEM)

The morphological structure of NFC and MCC was studied using a scanning electron microscope (SEM JSM-6610LV) equipped with a secondary electron detector under an accelerating voltage of 10 kV. Before examination, the samples were coated with a thin layer of gold in order to avoid charging. Also, the fracture surfaces of the all-cellulose composites with NFC and MCC after tensile deformation were investigated.

2.4 Mechanical testing

A universal testing machine (LLOYD LR 50 K) with the 1 kN load cell was used to investigate mechanical properties of the all-cellulose composites with NFC and MCC. The gauge length and crosshead speed were 20 mm and 1 mm min^{-1}, respectively, and the samples were prepared with a width of ~ 5 mm. Prior to the test, the width and thickness of each sample were measured, and for each material at least five samples were investigated to acquire the average and standard deviation values.

3. Results and discussion

Fracture surfaces of the all-cellulose composites with MCC and NFC after tensile deformation are shown in Figure 2. When NFC or MCC was higher, the rough surface could be seen. The fiber pull-out failure mechanism after tensile deformation was easily observed when MCC or NFC was over 10 wt%. This indicated that the interfacial adhesion between the matrix and reinforcing phase was not strong. This might be because with a higher content of MCC or NFC in the matrix, the fibers were aggregated. This led to the low reinforcing efficiency at a higher content of NFC and MCC.

Tensile strength and Young's modulus of the all-cellulose composites as a function of a content of MCC and NFC are compared in Figure 3, and mechanical properties of the all-cellulose composites with MCC and NFC are reported in Table 1. Results showed that with the addition of MCC, tensile strength of the composites decreased gradually, compared to the composites without the addition of the reinforcement. The tensile strength of the composites was reduced from 37.4 MPa to 34.4 with the presence of 10 wt% MCC, and the MCC 20 samples showed a value of 32.8 MPa for tensile strength. The reduced tensile strength of the composites with MCC was due to the low aspect ratio of MCC. Similar decrease of tensile strength was also reported for thermoplastic starch/poly(butylene adipate-co-terephthalate) films with addition of MCC [20]. On the other hand, the considerable improvement of tensile strength was found when NFC was added in the composites. With the introduction of 10 wt% NFC tensile strength of the composites was increased by 11.6 MPa to 49 MPa. The composites with 20 wt% of NFC showed the tensile strength of 53.4 MPa.

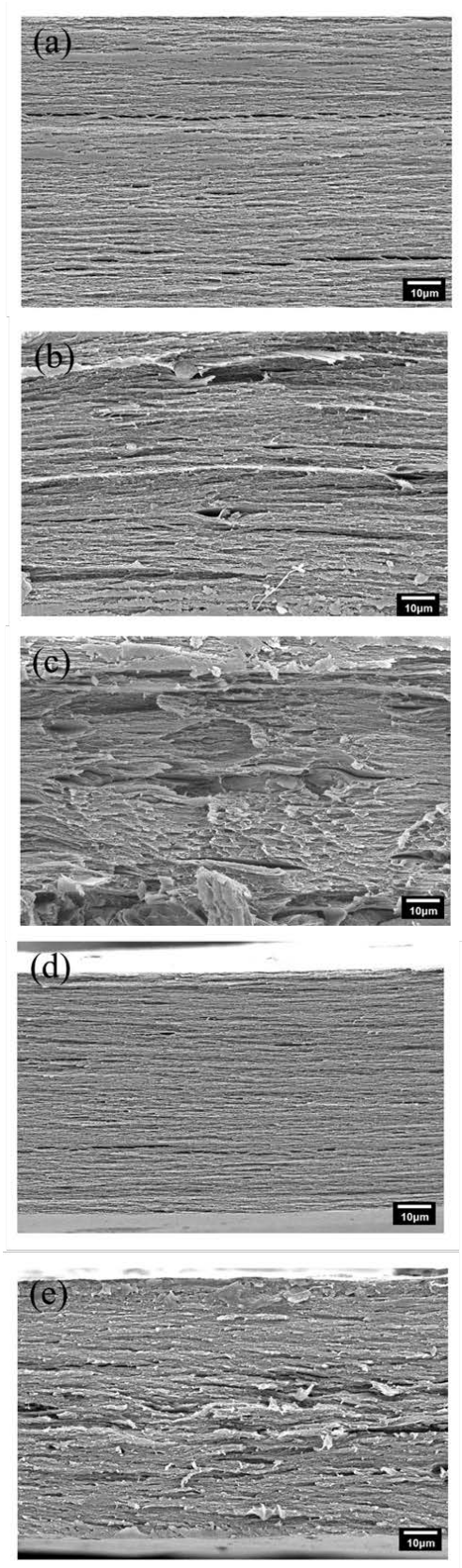

Figure 2. Fracture surface of the all-cellulose composites with MCC contents of (a) 0, (b) 10 and (c) 20 wt% and with NFC contents of (d) 10 and (e) 20 wt%, respectively.

The tensile strength improvement of 43% was detected from the NFC 20 samples in comparison to the composites without NFC. These results were an indication of the higher reinforcing efficiency of NFC over MCC. Notably, similar enhancement of Young's modulus was found from the composites with both MCC and NFC at the same fraction. With 20 wt% of NFC the Young's modulus of the composites was improved by 57% compared to the composites without NFC. The Young's modulus of MCC and NFC has been estimated using Raman spectroscopy to be 25 [21] and 29 - 36 GPa [22], respectively. This might explain why similar values of the Young's modulus could be obtained from the all-cellulose composites with NFC and MCC at the same content. The modulus of composites (E_c) can be estimated using a following equation.

$$E_c = \eta V_f E_f + (1 - V_f) E_m \quad (1)$$

where E_f and E_m are the reinforcing and matrix moduli, and V_f is the volume fraction of the reinforcing phase. Values of 25 and 29 - 36 GPa were used for the modulus of the MCC and NFC, respectively, while the modulus of the matrix was 1.4 GPa, as reported in Table 1. In the prepared composite films, MCC or NFC was randomly aligned in the matrix. Therefore, the efficiency orientation factor matrix (η) in this case is 3/8 [23]. The estimated moduli of the MCC 10 and MCC 20 were 2.1 and 2.9 GPa, respectively. On the other hand, the NFC 10 and NFC 20 had the calculated moduli in the range of 2.2 – 2.5 and 3.2 – 3.7 GPa, respectively. The estimated modulus of the all-cellulose composites with MCC was higher than the value observed experimentally. However, the estimated and experimental values of the NFC 10 samples were similar. With more than 10 wt% of NFC, the significant difference between moduli of the composites from experiment and calculation was observed. This might be due to the fiber aggregates. Mathew et al. [24] prepared biodegradable composites of MCC and poly (lactic acid) (PLA). Mechanical testing results showed the slight improvement of Young's modulus of the composites with increasing a content of MCC while the decrease of tensile strength was observed for the PLA composites with MCC, compared to the neat PLA resin. The increased mechanical properties of the all-cellulose composites with NFC was due to the higher aspect ratio of NFC than MCC. Moreover, NFC had a positive effect on tensile strain of the composites than MCC did. Fibers with a lower aspect ratio can cause shorter elongation at break and more brittleness on composites [24].

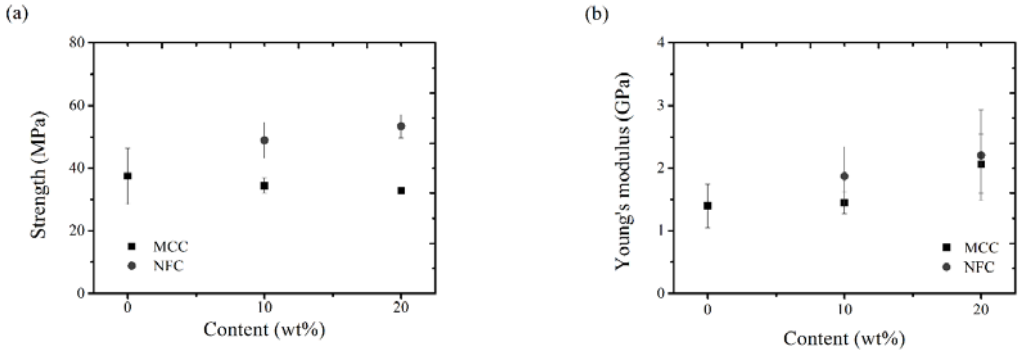

Figure 3. (a) Tensile strength and (b) Young's modulus of the all-cellulose composites with the addition of NFC and MCC.

Table 1. Mechanical properties of the all-cellulose composites reinforced with NFC and MCC.

Reinforcing phase (wt%)		Strength (MPa)	Modulus (GPa)	Strain (%)
NFC	MCC			
-	-	37.4 (8.9)	1.4 (0.3)	22.1 (8.0)
-	10	34.4 (2.4)	1.5 (0.2)	25.4 (4.9)
-	20	32.8 (0.4)	2.1 (0.5)	23.6 (4.3)
10	-	49.0 (5.7)	1.9 (0.5)	20.9 (6.2)
20	-	53.4 (3.8)	2.2 (0.7)	28.2 (8.7)

4. Conclusions

All-cellulose composites reinforced with MCC or NFC were successfully prepared. With incorporation of NFC, mechanical properties of the composites increased. At 20 wt% tensile strength and Young's modulus of the all-cellulose composites with NFC increased to 53.4 MPa (42% improvement) and 2.2 GPa (57% improvement) while values of 32.8 MPa (12% reduction) and 2.1 GPa (50% improvement) for tensile strength and Young's modulus was found for the composites with MCC. Results from mechanical testing revealed that NFC had a reinforcing ability to enhance mechanical properties of the all-cellulose composites over MCC due to the higher aspect ratio. These composites could be possibly used as an alternative material to polymers derived from fossil fuels in the near future due to advantages of biodegradability and high mechanical properties.

5. Acknowledgements

This research was supported by a new researcher scholarship of CSTS, MOST provided by Coordinating Center for Thai Government Science and Technology Scholarship Students (CSTS) and National Science and Technology Development Agency (NSTDA) (scholarship no. SCH-NR 2012-204).

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