ECO-FREINDLY PREPARATION AND CHARACTERIZATION OF CARBON NANOTUBES-FILLED CARBOXYMETHYL CELLULOSE NANOCOMPOSITE FILMS

Yeong-Rae Son[1], Hyo In Lee[2], Yifan Zhang[3] and Soo-Jin Park[4]*

[1] Department of Chemistry, Inha University, Inharo 100, Incheon 22212, Korea, Email: rosysky2010@naver.com
[2] Department of Chemistry, Inha University, Inharo 100, Incheon 22212, Korea, Email: hoin1992@naver.com
[3] Department of Chemistry, Inha University, Inharo 100, Incheon 22212, Korea, Email: zyf9106@gmail.com
[4] Department of Chemistry, Inha University, Inharo 100, Incheon 22212, Korea, *Email: sjpark@inha.ac.kr

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ABSTRACT

Carbon nanotubes-loaded sodium carboxymethyl cellulose (CMC/CNT) nanocomposite films were fabricated by a simple solution casting method. The CNT can be homogeneously dispersed in water with a small quantity of CMC and was used as reinforcement into CMC polymer matrix. The crystal structure and morphologies of pure CMC, pristine CNT, and CMC/CNT nanocomposite films were investigated by using X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. The mechanical behaviors of pure CMC and CMC/CNT nanocomposite films were measured by universal testing machine (UTM). As a result, the tensile strength and Young's modulus of CMC/CNT nanocomposite films were improved according to the CNT amounts.

1 INTRODUCTION

Biodegradable films are normally fabricated from biopolymers such as polysaccharides, proteins and lipids. Biodegradable films have attracted attention as promising alternatives for synthetic polymers because of their potential benefits such as food protection, preservation during storage, outstanding optical properties, and alleviation of environmental pollution. Biopolymer films, however, suffer from inferior mechanical properties. Therefore, many researches have aimed to improve the mechanical properties of biopolymer-based films by addition of hydrophobic or inorganic materials [1, 2].

Sodium carboxymethyl cellulose (CMC) belonging to polysaccharide is one of the most important industrial biopolymers. CMC is semi-synthetic derivative of cellulose produced by partial substitution of the 2, 3, and 6 hydroxyl groups of cellulose by carboxymethyl groups. CMC is an anionic linear biopolymer, soluble in water, non-toxic, and non-allergenic having a high viscosity. Because of these characteristics, various applications are being used such as detergent, textile, paper, food, pharmaceuticals *etc*. [3, 4].

The major disadvantages of polysaccharide films like CMC are their weak mechanical properties. Recently, carbon nanomaterials, such as graphene, graphene oxide (GO) and carbon nanotubes (CNTs), have extremely attracted enormous attention in the past 40 years. These carbon materials have been considered significantly as reinforcement improving the mechanical properties of polysaccharide-based films. In particular, CNTs can be a very suitable material to improving the mechanical properties of CMC film owing to their extraordinary mechanical, electronic, and thermal properties [5-7]. However, CNTs can't be dispersed in water due to its hydrophobicity. To make stable CNT

dispersion in water, dispersing agents have been used but they lead to decline of mechanical properties of biopolymer films [8].

In this work, CNTs were dispersed in water with very slight amount of CMC. Subsequently, CMC/CNT nanocomposite films were prepared by simple and environmentally harmless approaches through a solution mixing-evaporation method [9]. The mechanical properties of the CMC/CNT nanocomposites were investigated as a function of the amount of CNTs incorporated into the composites.

2 EXPERIMENTAL METHOD

2.1 Materials and methods

Sodium carboxymethyl cellulose (CMC, average Mw ~250,000) was purchased from Sigma Aldrich Korea. CNTs (purity >95 wt%, average diameter ≤10 nm, and length 10–20 μm) were supplied by Nanosolution Co., Korea.

2.2 Preparation of CMC/CNT Nanocomposite Films

Stable and homogeneous CNT dispersion in aqueous solution was prepared using a small quantity of CMC and by sonication process. Afterwards, CMC/CNT nanocomposite films were prepared by a simple solution mixing-evaporation method. CMC/CNT 1 wt% nanocomposite film was prepared according to following procedure; 1.98 g of CMC was dissolved in 49 mL of deionized water. 0.02 g of CNT was dispersed in 50 mL of aqueous solution with a small amount of CMC dissolved for 30 min using probe type ultrasonicator. CMC solution and CNT dispersion were mixed and stirred for 30 min. Finally, the mixture was poured onto a glass plate and dried under vacuum at 60^{o}C until completely dry.

2.3 Characterization

UV/Vis spectrophotometer (SCINCO S-3100) was used to analyze the dispersing ability of CMC as dispersing agent for CNTs (weight ratio of CMC to CNTs (1:1 or 1:4)).

X-ray diffraction (XRD) was conducted to analyze the crystal structure of CNTs, pure CMC film, CMC/CNT nanocomposites using D2 PHASER (Bruker) instrument with a Lynx-Eye detector using Cu Kα radiation at 30 kV and 10 mA (λ = 1.5406 Å).

High resolution scanning electron microscope (HR-SEM, SU 8010, Hitachi Co.) was used to investigate the morphologies of CNT and CMC/CNT nanocomposite films. Before observation, all samples were sputter-coated with platinum.

The mechanical properties of CMC/CNT nanocomposite films were measured by universal testing machine (UTM, LR5KPlus, LLOYD Instruments Ltd.) according to ASTM D638-05 at a loading rate 2 mm min^{-1} with a gauge length of 25 mm.

3 RESULTS AND DISCUSSION

Fig. 1 displays dispersing ability of CMC to disperse CNTs in water. UV/Vis spectra of CMC/CNT (1:1) dispersion and (1:4) dispersion show almost same absorbance trend in entire wavelength range. Therefore, it was confirmed that very slight quantity of CMC corresponding to a quarter of CNTs amount can play a role as dispersing agents and can form the stable CNT dispersion in water.

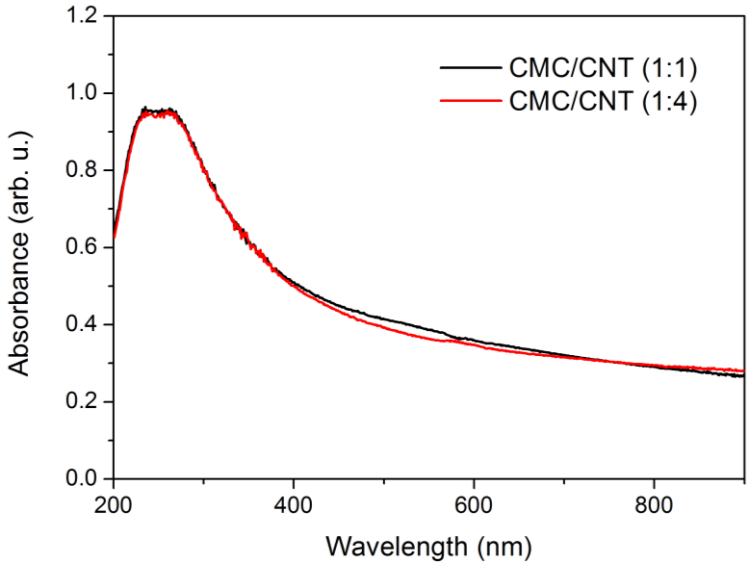

Figure 1: UV/Vis spectra of CNT dispersion with CMC .

Fig. 2 exhibits the digital photographs of pure CMC and CMC/CNT 1 wt% nanocomposite films. While pure CMC film is transparent, the CMC/CNT 1 wt% nanocomposite film is dark black and it is confirmed that the loaded CNTs are homogeneously dispersed without transparent part.

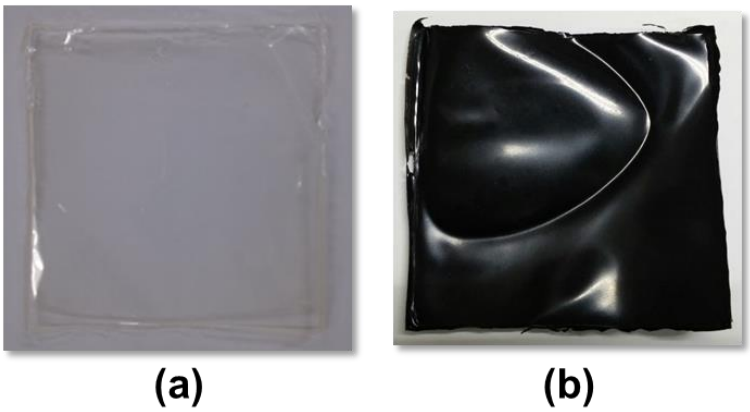

Figure 2: Digital photographs of (a) pure CMC film and (b) CMC/CNT 1 wt% nanocomposite film.

Fig. 3 shows the XRD patterns of pristine CNTs, pure CMC, and CMC/CNT nanocomposite films. The XRD patterns were collected in the 2θ range of 5° to 50°. A single peak of CNTs was shown at 2θ = 26°. XRD pattern of pure CMC film has broad pattern from 2θ = 7 to 28°, corresponding to its amorphous crystal structure. However, Peaks related to CNTs were not shown in the CMC/CNT nanocomposite films. This result indicates that the CNT is homogeneously dispersed inside the CMC matrix, not on the surface of films.

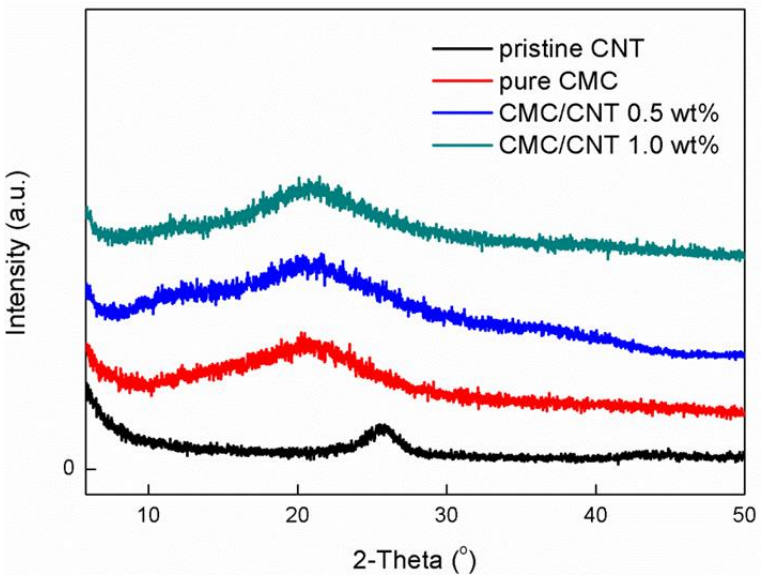

Figure 3: XRD patterns of pristine CNTs, pure CMC film, CMC/CNT 0.5 wt% and 1 wt% nanocomposite films.

The morphologies of the surfaces (Fig. 4) and fracture surfaces (Fig. 5) of pure CMC and CMC/CNT 1 wt% nanocomposite film was observed by SEM. Fig 4a showed CNTs used as reinforcement of CMC. As shown in Fig. 4b, the large CMC agglomerates were observed on the surface of pure CMC film. However, in CMC/CNT 1 wt% nanocomposites (Fig. 4c), much smaller agglomerates and smooth surface were confirmed. Fig. 5a and b showed the fracture surface of pure CMC film and CMC/CNT 1 wt% nanocomposite film, respectively, after tensile test. The fracture surface of CMC film was smooth. However, as shown in Fig. 5b, the CMC/CNT 1 wt% nanocomposite film had a rough fracture surface. Furthermore, The CNTs were homogeneously and individually dispersed into CMC matrix. Consequently, failure mode of CMC change from ductile to brittle by addition of CNT in CMC matrix as reinforcement.

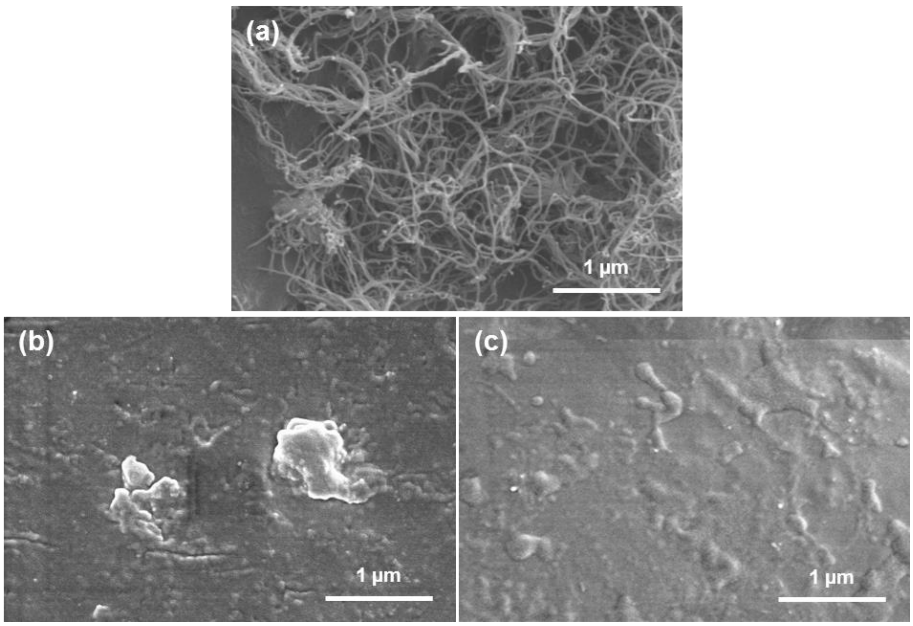

Figure 4: SEM images of (a) CNTs and surface of (b) pure CMC and (c) CMC/CNT 1 wt% nanocomposite film.

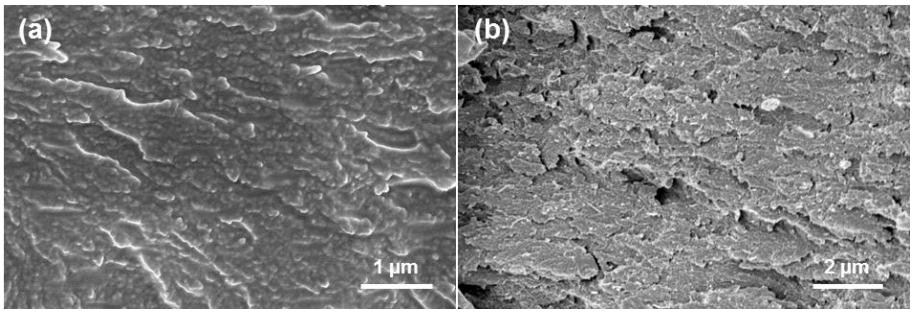

Figure 5: SEM images of fracture surface of (a) pure CMC film and (b) CMC/CNT 1 wt% nanocomposite film.

The mechanical properties (tensile strength and Young's modulus) of pure CMC and CMC/CNT nanocomposite films are measured by UTM. As shown in stress-strain curve (Fig. 6), nonlinear behavior was observed for pure CMC from yield stress to maximum stress except CMC/CNT nanocomposite films. As shown in Fig. 7, the tensile strength and Young's modulus of the CMC film were measured as 37.28 MPa and 1.89 GPa, respectively. The tensile strength of CMC/CNT 0.5 wt% and 1 wt% was increased from 37.28 MPa to 79.14 MPa and 81.79 MPa, respectively. Also, the Young's modulus of CMC/CNT 0.5 wt% and 1 wt% was increased from 1.89 GPa to 3.79 GPa and 3.76 GPa, respectively. However, the strain was reduced compared to pure CMC film, indicating that the failure mode changed from ductile to brittle, as mentioned in SEM analysis. Therefore, it was found that the CNTs can interact effectively with CMC to improve the mechanical properties of CMC by strong interaction which is van der Waals interaction.

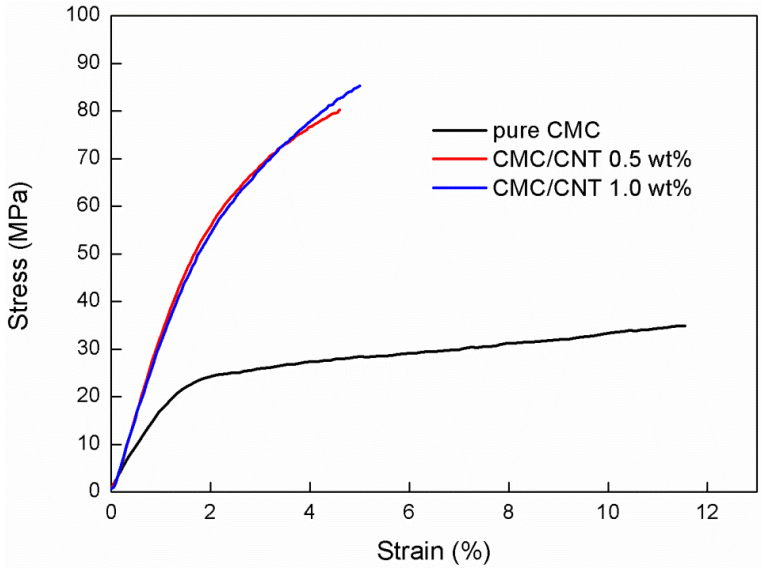

Figure 6: Stress-strain curves of pure CMC film and CMC/CNT nanocomposites.

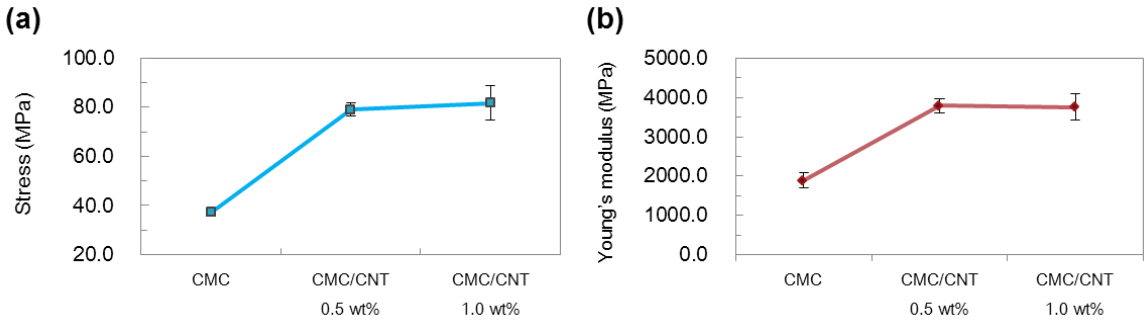

Figure 7: (a) tensile strength and (b) Young's modulus of pure CMC film, CMC/CNT 0.5 wt%, and 1wt% nanocomposite films.

4 CONCLUSIONS

In this study, Sodium carboxymethyl cellulose/carbon nanotubes (CMC/CNT) nanocomposite films were fabricated by a simple solution casting method. The CNTs can be homogeneously dispersed in water with a slight quantity of CMC and was used as reinforcement into CMC polymer matrix. The crystal structure and morphologies of pure CMC, pristine CNTs, and CMC/CNT nanocomposite films were investigated by using X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. Consequently, the CNTs were homogeneously and individually dispersed in CMC matrix. The mechanical behaviors of pure CMC and CMC/CNT nanocomposite films were measured by universal testing machine (UTM). As a result, the tensile strength and Young's modulus of CMC film were improved significantly by addition of the CNTs.

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