Nanoclay-reinforced Nanocellulose Composite Films with Improved Heat resistance, Gas Barrier Performance, and Mechanical properties

Ji Hyung Ryu, Nam Koo Han and Young Gyu Jeong*

Department of Advanced Organic Materials and Textile System Engineering, Chungnam National University, Daejeon 34134, Republic of Korea, *ygjeong@cnu.ac.kr

ABSTRACT

Since nanocellulose (NC) is known to have excellent strength, modulus, lightness, and thermal stability, it has been widely utilized for composites, electronics, sensors, papers, coatings, films, aerogels, additives, etc. In this study, to attain NC films with enhanced physical properties, a series of NC-based composite films reinforced with nanoclay are fabricated and their structural features, thermal stability, mechanical performance, and barrier property are characterized by using SEM, XRD, TGA, DMA, and gas permeability tests.

Keywords: Nanocellulose, Nanoclay, Thermal stability, Mechanical property, Gas barrier performance.

1 INTRODUCTION

Recently, environmental problems have become more important in many application fields of polymeric materials. Cellulose is a plant-based polymeric material that has an annual biomass production of about 1.5 trillion tons, making it less likely to be depleted. In recent years, various technologies have been developed to obtain nano-structured cellulose, i.e., nanocellulose (NC), such as cellulose nanofibrils (CNF), cellulose nanocrystals (CNC), and bacterial cellulose (BC). Especially, CNFs and CNCs are isolated from wood pulps or native fibers via mechanical methods with aids of high-pressure homogenizers, ultrasonic homogenizers, grinders, and microfluidizers through chemical treatments. Owing to high cristallinity and high aspect ratio, NC such as CNF and CNC is considered as eco-friendly reinforcing agents.

Nanoclays with a nano-sized layered structure having a large surface area provide sufficient interfacial regions in polymer nanocomposites, which offer tremendous improvement in physical and engineering properties of polymeric matrix.

In this study, with a objective to attain eco-friendly composite films with high performance in heat resistance, gas barrier property, and mechanical property, nanoclay-reinforced NC films were fabricated by an facile aqueous suspension casting. For the purpose, structural features, thermal stability, mechanical properties, and gas barrier property of the nanoclay-reinforced NC composites films were characterized in terms of the nanoclay content.

2 EXPERIMENTAL

An aqueous suspension with 1 wt% carboxylated nanocellulose (CNC) was supplied from Asia Nanocellulose Com. The CNC was prepared from Eucalyptus bleached kraft pulp and then carboxymethylated with chloroacetic acid ($ClCH_2COOH$, 99.0%, Sigma-Aldrich Com), acetic acid (CH_3COOH, 99.5%, Samchun Chemicals), ethanol (CH_3CH_2OH, 99.9%, Duksan Reagents), and sodium hydroxide (NaOH, 99.0%, Junsei Chemical) to enhance the dispersion stability in aqueous solutions. The degree of carboxymethylation of CNC was evaluated to be 0.3-0.5. Sodium montmorillonite (MMT) as a reinforcing nanoclay was supplied by Sigma Aldrich, Com. and it was used without further chemical modification. The cation-exchange capacity of the MMT was 250 g/m^2.

A seires of composites films composed of CNC with different MMT contents of 1-20 wt% were fabricated by an aqueous suspension casting process. Each aqeuous suspension with a predetermined CNC and MMT content was casted in a petri dish, dried on a hot plate at 50 °C for 6 hr, and finally dried in a vacuum oven at 60 °C for 24 hr. The finally fabricated CNC/MMT composite films wer named CM-x, where x denotes the weight % of MMT in the composite films.

3 RESULTS AND DISCUSSION

The surface morphological features of the composite films are examined by using SEM images, as shown in Figure 1. The surfaces of CNC film were very smooth and flat. On the other hand, the surface of the CNC/MMT composite films became rough with increasing the MMT content, which might be caused by the agglomerate formation of MMT particles in the CNC matrix.

The optical transparency of the composite films were identified from the UV/visible spectra shwon in Figure 2. The optical transparency was found to decrease with increasing the MMT content, as expected.

The thermal stability of the composite films were examind by using TGA curves, as represented in Figure 3. For all the composite films, the thermal decomposition was characterized to take place dominatly at 250-300 °C owing to the dominant decomposition of the CNC matrix and the residues at 800 °C increased with the increment of the

MMT in the composite films due to the presence of inorganic MMT with high thermal stability.

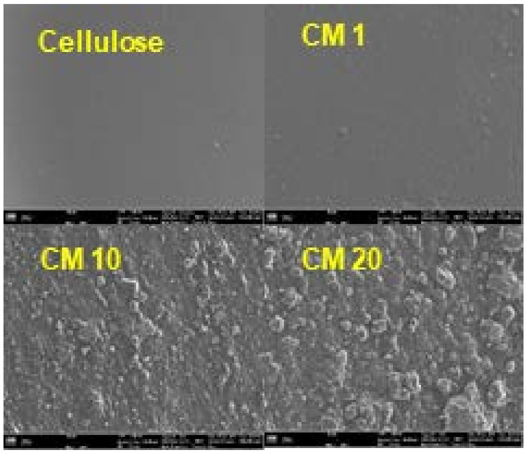

Figure 1: SEM images of CNC/MMT composite films with different MMT contents of 1-20 wt%.

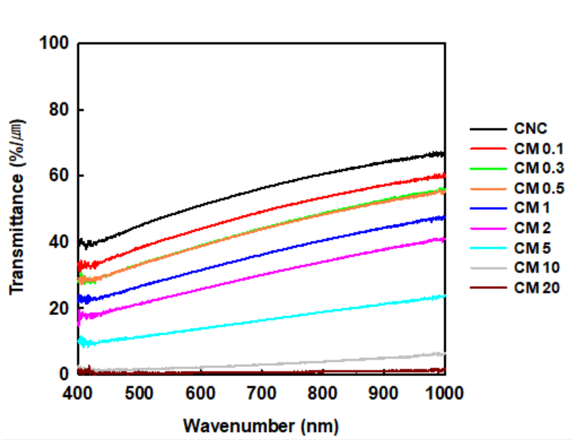

Figure 2: UV/vis spectra of CNC/MMT composite films with different MMT contents of 1-20 wt%.

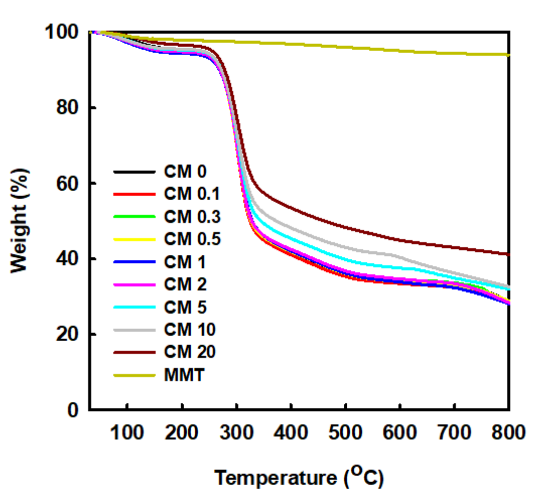

Figure 3: TGA curves of CNC/MMT composite films with different MMT contents of 1-20 wt%.

DMA analysis was performed to characterize the mechanical properties of the CNC/MMT composite films. When the content of MMT was added up to 0.5 wt%, the storage moduli of the composite films were higher than that of the neat CNC film. Th highest mechanical modulus was attached for the composite films with 0.1 wt% MMT. When the content of nanoclay exceeds 5 wt%, the storage modulus decreased, which is cused by the possibility of agglomeration of MMT in the CNC matrix.

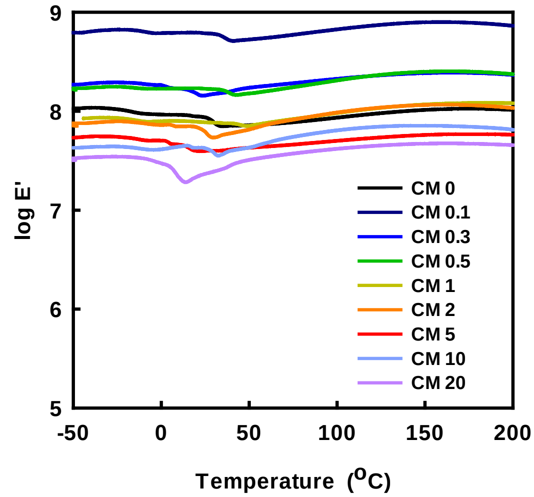

Figure 4: DMA curves of CNC/MMT composite films with different MMT contents of 1-20 wt%.

4 CONCLUSION

CNC-based composite films having different MMT contents of 0-20 wt% were prepared by a facile and eco-friendly aqueous suspension casting. The SEM images revealed that the MMT up to 1.0 wt% was dispersed uniformly in the CNC matrix. The optical transparency of the composite films decreased as the MMT content increased. The composite films were thermally stable up to ~250 °C, and their residues at 800 °C increased with the increment of the MMT content. The mechanical moduli of the composite film were foun to increase noticeable by adding a small amount of MMT of 0.1 wt%.

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