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# Heat-Treated Polyvinyl Alcohol/Cellulose Nanocrystal Film with Improved Mechanical Properties and Water Resistance

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# 내수성 및 기계적 물성이 향상된 열처리된 폴리비닐알코올/셀룰로오스 나노결정 필름

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# ABSTRACT

In this study, the water resistance and mechanical properties of heat-treated polyvinyl alcohol (PVA)/cellulose nanocrystal (CNC) films were investigated. PVA is the most commonly used synthetic biodegradable polymers owing to its excellent properties. However, the water/moisture sensitivity and relatively poor mechanical properties of PVA limits its applications. Although heat treatment is a conventionally used method to improve the mechanical strength and water resistance of PVA, the effectiveness of this method is insufficient. Therefore, CNC was used to further improve the mechanical properties and water resistance of the heat-treated PVA film. PVA/CNC nanocomposites containing CNC contents of 0, 1, 3, 5, and 10 wt% were fabricated using solvent casting and subsequent heat treatment. The mechanical properties and water resistance of PVA/CNC films were significantly improved. The tensile strength and wet strength of the PVA/CNC film with a CNC content of 5 wt% (PVA/CNC 5%) were 184.5% and 136.0% higher than those of the untreated PVA, respectively. In addition, the water absorption and solubility of PVA/CNC 5% were 56.6% and 68.2% lower than those of the untreated PVA.

Key Words : Polyvinyl alcohol(폴리비닐알코올), Cellulose nanocrystal(셀룰로오스 나노결정), Water resistance 방수), Mechanical properties(기계적 성질)

### 1. Introduction

Petroleum-based polymers are widely used in daily life. However, these conventional polymers have

several negative effects on the environment and human health. Therefore, reducing the use of conventional polymers and developing biodegradable polymers are considered as viable solutions for this problem. Polyvinyl alcohol (PVA) is the most commonly used synthetic biodegradable polymer. PVA has various advantages<sup>[2]</sup> such as excellent

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film-forming properties. remarkable flexibility, biodegradability, high chemical biocompatibility, resistance, excellent oxygen/oil barrier properties, and good adhesive properties. Therefore, PVA is extensively used in numerous applications such as food packaging<sup>[9]</sup>, paper coatings, textiles, functional membranes, and wood/paper adhesive<sup>[4,10]</sup>. However, the inherent poor water/moisture resistance of PVA due to the presence of numerous hydroxyl groups in its structure has restricted its widespread applications<sup>[5]</sup>. In addition, PVA has a relatively low mechanical strength compared with that of conventional polymers.

Cellulose nanocrystal (CNC) is fabricated using acid hydrolysis from cellulose – the most abundant renewable organic polymer on Earth. CNC is a small crystalline part of cellulose fibers with a rod-like shape (3–10 nm in width and 5–500 nm in length). CNCs possess superior properties such as high specific surface area, excellent mechanical strength, biodegradability, biocompatibility, low density, and low thermal expansion coefficient. Therefore, CNC is used to improve the mechanical/thermal properties of polymers in composite materials. Multiple previous studies have used CNC as nanofillers to improve the mechanical/thermal properties of PVA<sup>[2]</sup>. However, PVA/CNC exhibits poor water/moisture resistance due to the hydrophilic nature of PVA and CNC<sup>[1]</sup>.

Improving the water resistance of PVA is crucial to range of applications. broaden its Chemical crosslinking and heat treatment are two common methods to enhance the water resistance of PVA. In crosslinking process, the the chemical reaction between PVA and crosslinking agents changes hydroxyl groups of PVA into ester groups, which significantly improves water resistance. Various types of crosslinking agents have been studied, including glyoxal, glutaraldehyde, and formaldehyde. Although these typical crosslinking agents significantly enhance the water resistance of PVA, they are relatively toxic<sup>[6]</sup>. Therefore, there is a concern about the

toxicity of chemically crosslinked PVA and crosslinking processes. Heat treatment improves water resistance by increasing the crystallinity of the PVA structure. This method is considered as a green method that can ensure the safety of PVA products. However, the improvement in water resistance is insufficient, particularly for PVA with a low degree of hydrolysis<sup>[6]</sup>. A few studies have demonstrated that treatment heat significantly improves the mechanical/thermal properties of PVA/nanocellulose composites containing nanofibrillated cellulose<sup>[7]</sup> and microcrystalline cellulose<sup>[8]</sup>. However, a study on the mechanical properties and water resistance of heat-treated PVA/CNC has not been conducted.

Therefore, the effect of CNC on water resistance and mechanical properties of heat-treated PVA/CNC were investigated in this study. PVA solution was mixed with various concentrations of CNC suspension to form different PVA/CNC mixtures. PVA/CNC films were obtained by solvent casting and subsequent heat treatment. The water resistance of the heat-treated PVA/CNC was evaluated by water absorption, solubility, and wet strength. In addition, the mechanical properties, morphology, and chemical interaction of composite were characterized using tensile testing, scanning electron microscopy (SEM), and Fourier-transform infrared (FTIR) spectra.

# 2. Experimental

#### 2.1 Materials

PVA beads ( $M_w$  85,000–124,000; 99+% hydrolyzed) were purchased from Sigma-Aldrich. CNC powder (width of 10–20 nm; length of 300–900 nm; crystallinity of 92 %) was supplied by Nanografi (Ankara, Turkey). The materials were used as received without modification.

#### 2.2 Preparing heat-treated PVA/CNC film

Fig. 1 shows the process of fabricating heat-treated PVA/CNC films. Initially, a 3 wt% PVA solution was



Fig. 1 Fabrication of heat-treated PVA/CNC films

prepared by adding PVA beads to deionized (DI) water at room temperature (22–25°C) while stirring. The mixture was heated to 90°C, and it was maintained at this temperature for 2 h to completely dissolve the PVA beads, and then cooled at room temperature. An aqueous CNC suspension (1wt%) was prepared by adding CNC powder to DI water at room temperature while stirring on a magnetic stirrer for 24 h. Subsequently, the CNC suspensions were sonicated in a sonication bath at 25°C for 10min.

PVA/CNC mixtures with different CNC contents (Table 1) were fabricated from PVA solutions and CNC suspensions. The mixtures were stirred for 2 h and then poured into Petri dishes. The films were obtained by natural air-drying. Heat-treated PVA/CNC films were obtained by performing heat treatment in an oven at 120°C for 1 h. An untreated PVA film was prepared for reference using the similar method of fabrication as PVA/CNC 0% without heat treatment.

#### 2.3 Characterization methods

A FTIR spectrometer (IRAffinity-1S, Shimaru) was used to investigate the chemical interaction between PVA and CNC. The samples were studied within a wavenumber range of 4000–500cm<sup>-1</sup>. The morphology of PVA/CNC films was investigated using SEM (SU-70, Hitachi). The samples were coated with platinum to avoid charging effects.

A water absorption test of PVA/CNC films was

| Case          | PVA (g) | CNC (g) | Heat treatment |
|---------------|---------|---------|----------------|
| Untreated PVA | 3.500   | 0.000   | No             |
| PVA/CNC 0%    | 3.500   | 0.000   | 120 °C, 1h     |
| PVA/CNC 1%    | 3.465   | 0.035   | 120 °C, 1h     |
| PVA/CNC 3%    | 3.395   | 0.105   | 120 °C, 1h     |
| PVA/CNC 5%    | 3.325   | 0.175   | 120 °C, 1h     |
| PVA/CNC 10%   | 3.150   | 0.350   | 120 °C, 1h     |

Table 1 The formulation of PVA/CNC films

performed according to ASTM D570-98. The samples were conditioned at 50°C for 24 h. After cooling to 23°C, the samples were weighed. The samples were immersed in DI water at 23°C for 24 h. Excess water present on the surface of the sample was removed before measuring the wetting weight of the samples. Swollen samples were re-conditioned at 50°C for 24 h before weighing. Water absorption and solubility were calculated using the following equations:

Water absorption (%) =  $\frac{m_{wet} - m_{re-dry}}{m_{dry}} \times 100(\%)$  (1)

Solubility (%) = 
$$\frac{\mathrm{m}_{\mathrm{dry}} - \mathrm{m}_{\mathrm{re-dry}}}{\mathrm{m}_{\mathrm{dry}}} \times 100(\%)$$
 (2)

where  $m_{dry}$ ,  $m_{wet}$ , and  $m_{re-dry}$  are the mass of the PVA/CNC sample after conditioning, immersing, and re-conditioning, respectively.

Tensile testing of PVA/CNC films under dry and wet conditions was performed using a tensile testing machine (JP/AGS-5kN, Shimadzu). A die-cutting tool was used to prepare the rectangular specimens. The drawing and the tensile specimen are shown in Fig. 2. A small piece of paper was glued to the ends of samples to prevent slipping. In dry conditions, the drip distance, load cell, and crosshead speed were 20mm, 100N, and 10mm/min, respectively. For testing at wet conditions, samples were immersed in DI water at 25°C for 1 h and immediately tested after removing excess water. The grip distance, load cell,



Fig. 2 (a) Drawing and (b) photograph of the sample prepared for the tensile test

and crosshead speed were set to 20mm, 50 N, and 10mm/min. The tests were performed at  $23^{\circ}$ C and 50% RH.

#### 3. Results and Discussion

#### 3.1 Mechanical properties

Fig. 3(a) represents the stress-strain curves of PVA/CNC films. The untreated PVA film exhibited excellent elongation, but it had a low tensile strength Young's modulus. Heat treatment and is conventional method used to improve the mechanical strength of PVA films. The tensile strength of heat-treated PVA (PVA/CNC 0%) was 49.4 % higher than that of untreated PVA. However, the elongation decreased from 302.3% (untreated PVA) to 126.2% (heat-treated PVA). These changes are explained by the increase in the crystallinity of PVA after heat treatment.

As shown in Fig. 3(b), the tensile strength and Young's modulus of the PVA/CNC film exhibited a similar trend, continuously increasing as the CNC content was increased to 5wt% and decreasing at higher CNC content. The highest tensile strength was observed in the case of PVA/CNC 5%, which was 90.4% and 184.5% higher than that of PVA/CNC 0% and untreated PVA. There are two reasons for these enhancements. First, CNC possesses excellent tensile strength and Young's modulus. The theoretical tensile strength and Young's modulus of CNC are 7.5–7.7 GPa and 105–143 GPa, respectively<sup>[3]</sup>. Second, as CNC and PVA are hydrophilic polymers, they have



Fig. 3 (a) Stress-strain curves, (b) tensile strength and Young's modulus, and (c) strain at break of PVA/CNC films

an excellent interaction with each other. Therefore, external stress is easily transferred from softer PVA chains to stiffer CNC filler.

Fig. 3(c) shows the effect of CNC content on the elongation of PVA/CNC films. The elongation was continuously reduced with an increase in the CNC content. The presence of CNC filler inside the PVA matrix decreases the hydrogen bonds between the PVA chains, which reduces the elongation of PVA/CNC films.

#### 3.2 Water resistance

The water resistance of PVA/CNC film is characterized by water absorption, solubility, and wet strength.

Fig. 4 presents the water absorption and solubility of PVA/CNC films. The untreated PVA film exhibited a high water absorption (298.7%) and solubility (14.8%) due to the presence of multiple hydroxyl groups in PVA. Heat treatment reduces the water absorption and solubility of PVA film by increasing its crystallinity. The addition of CNC further improved the water resistance of PVA. The water absorption and solubility of PVA/CNC films decreased with an increase in the CNC content up to 5 wt%. However, these values increased at a higher CNC content (10 wt%).

The wet strength is an important property to characterize the water resistance of materials. As shown in Fig. 5, the wet strength of untreated PVA was significantly low at 8.6MPa. Heat treatment slightly increased the wet strength of the film to 10.7MPa. CNC significantly enhanced the wet strength of PVA/CNC films with CNC content up to 5wt%, then decreased at a higher CNC content. The highest wet strength was obtained with PVA/CNC 5%, which was approximately 1.89 times that of PVA/CNC 0%.

The enhancement of water resistance of PVA/CNC films was attributed to the increase in hydrogen bonds between PVA and CNC. In addition, the water resistance of CNC, which has a significantly high crystal structure, is higher than that of PVA.

#### 3.3 FTIR analysis

FTIR spectra of PVA films are presented in Fig. 6(a). The FTIR spectrum of heated PVA was similar to that of untreated PVA due to the absence of chemical modification. Heat treatment increases the intensity at 1142cm<sup>-1</sup> (stretching of C–O), and 1086cm<sup>-1</sup> (out of the plane of C–O vibration) due to the change in the degree of crystallinity. Additionally, there is a change in the –OH frequencies of 3000 to



Fig. 4 (a) Water absorption and (b) solubility of PVA/CNC films



Fig. 5 Wet strength of PVA/CNC films

3600 cm<sup>-1</sup>. The absorption peak was shifted to relatively lower frequencies (Table 2), which implied that additional hydrogen bonds were formed in heated PVA.

The spectra of PVA/CNC films are shown in Fig. 6(b)–(d). CNC in PVA/CNC films was determined by the presence of cellulose peaks such as 1163 cm<sup>-1</sup>



(asymmetric ring breathing mode), 1058cm<sup>-1</sup> (C-O vibrations), and 1034cm<sup>-1</sup> (O-C-O vibrations). There are significant changes in -OH frequencies with an increase in the CNC content. The absorption peaks were stronger and broader. In addition, the absorption peaks were shifted to relatively lower frequencies as shown in Table 2. These characteristics demonstrate that more hydrogen bonds were formed when the CNC content was increased. However, at a higher CNC content (10wt%), the number of hydrogen bonds decreased. which can be explained bv the agglomerations of CNC in the PVA matrix.

| Items         | Peak (cm <sup>-1</sup> ) |  |
|---------------|--------------------------|--|
| Untreated PVA | 3284                     |  |
| PVA/CNC 0%    | 3276                     |  |
| PVA/CNC 1%    | 3273                     |  |
| PVA/CNC 3%    | 3271                     |  |
| PVA/CNC 5%    | 3268                     |  |
| PVA/CNC 10%   | 3270                     |  |

Table 2 The absorption peak of -OH frequencies

 $(3000-3600 \text{ cm}^{-1})$ 



Fig. 7 SEM images of (a) untreated PVA, (b) PVA/CNC 0%, (c) PVA/CNC 1%, (d) PVA/CNC 3%, (e) PVA/CNC 5%, and (f) PVA/CNC 10%

#### 3.4 Morphology

The morphology of PVA/CNC films was studied using SEM. Fig. 7 shows the surface micrographs of untreated PVA and PVA/CNC films. The films exhibit surfaces without any micropores or cracks, which demonstrates a good interaction between the PVA matrix and the CNC filler. The untreated PVA film presented a smooth, homogenous, and flat surface (Fig. 7(a)). Compared with that of the untreated PVA film, the heated PVA film (Fig. 7(b)) exhibited a rougher surface due to the effect of heat treatment. The addition of CNC increased the rough of the film surface. Agglomerates were observed on the surface of the PVA film after adding CNC. The rate and size of aggregates were observed to be proportional to that of the CNC content in PVA/CNC films (Fig. 7(b)-(f)). The uniform distribution of CNC was observed until 5wt% of CNC. At a higher CNC content, cluster formation of CNC was observed (Fig. 7(f)).

# 4. Conclusion

study, CNC was used to fabricate In this heat-treated PVA/CNC film with excellent water resistance and mechanical properties. Since CNC has remarkable mechanical strength and good interaction with PVA, the mechanical properties of PVA/CNC films significantly were improved by the reinforcement effect of CNC. The tensile strength of PVA/CNC 5% was observed to be 90.4% and 184.5% higher than those of PVA/CNC 0% and untreated PVA, respectively. The increase in hydrogen bonds and improvement in the low water sensitivity of the CNC contributed to the high water resistance of the PVA/CNC film. The water absorption and solubility of the PVA/CNC film 5% were 56.6% and 68.2% lower than that of untreated PVA film. In addition, the wet strength of PVA/CNC 5% was 1.89 times and 2.36 times higher than that of PVA/CNC 0% and untreated PVA, respectively. These findings indicate

that PVA/CNC can be used in potential applications such as adhesive materials, biodegradable packaging, and disposable tableware.

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