A waterproof cellulose nanofibril sheet prepared by the deposition of an alkyl ketene dimer on a controlled porous structure

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Abstract This study prepared a waterproof cellulose nanofibril (CNF) sheet via the deposition of an alkyl ketene dimer (AKD) on the sheet’s controlled porous structure. The porosity of the CNF sheet was controlled by drying under different conditions, which included hot-press drying (HD) and solvent-exchange drying (SD), and the effect on the hydrophobization and water-related barrier performance of the sheet were investigated. When the SD sheet was immersed in an AKD wax solution, the sheet exhibited superhydrophobicity and a lower water vapor transmission rate, compared with the HD sheet. This indicated that the porous structure of the SD sheet enabled AKD to be adsorbed on both the surface and the inner surface and it filled in the pores of the sheet, thereby giving rise to excellent waterproofing properties. The performance of a hydrophobized SD sheet as a water barrier material was comparable to a linear low-density polyethylene film. This study confirms the possibility for AKD wax to be immersed in a porous CNF sheet and used as a potential barrier material in hydrogel packaging.
Graphical abstract

Keywords  Cellulose nanofibril · Alkyl ketene dimer · Hydrophobization · Porosity · Waterproof sheet

Introduction

Plastic pollution, which has many negative environmental impacts, is one of the most critical current global issues, and has been aggravated by the excessive use of plastics due to the 2019 coronavirus pandemic outbreak (Silva et al. 2021). Packaging is the largest sector to use petroleum-based plastics in many different forms, including film and foams (Geyer et al. 2017). Although plastic-based packaging materials have many advantages, e.g. convertibility, low cost, and waterproof properties, the non-biodegradable nature of petroleum-based plastics causes significant environmental problems through the production of microplastics (Stark 2016). Compounding this issue is the recycling rate of plastics is too low, particularly when compared with that of cellulose-based paper and board. As such, it is necessary to develop packaging materials that use biodegradable and renewable resources and to replace plastics and ensure a sustainable environment.

Cellulose is an abundant bio-based material that has long been used for packaging because it presents many advantages in terms of biodegradability and sustainability. Recently, it was shown that cellulose nanomaterial could be prepared and used in many forms, including films, hydrogels, and powders (Nechyporchuk et al. 2016). Cellulose nanofibril (CNF) film has been identified as having significant potential as a packaging material due to its excellent mechanical strength, and high oxygen barrier properties (Fukuzumi et al. 2009; Kumar et al. 2014; Rodionova et al. 2012). However, the water vapor transmission rate (WVTR) of CNF film is much higher compared with conventional plastic-based packaging films due to its highly hydrophilic nature (Nair et al. 2014; Wang et al. 2018). Additionally, CNF film has the disadvantage of not preventing water penetration. To improve water resistance, many researchers have investigated the surface chemical modification of cellulose, e.g., esterification (Felix and Gatenholm 1991; Pasquini et al. 2006), silylation (Gousse et al. 2004), and polymer grafting (Missoum et al. 2012) using various chemical compounds. Alkyl ketene dimer (AKD) is one of the most widely used hydrophobizing chemical and has C_{12}-C_{16} alkyl groups.
The reaction of cellulose with an AKD forms β-keto ester bonds between the lactone ring of the AKD and the hydroxyl groups of cellulose (Roberts 1997). Many researchers have proposed that AKD molecules spread when heated as a monolayer (Seppänen et al. 2000) or thin multilayer (Ström et al. 1992). The spreading of AKD molecules on a cellulose surface can be achieved by adsorption and vapor diffusion (Yu and Garnier 1997). Seppänen et al. (2000) reported that a monomolecular layer of AKD on a cellulose surface inhibited the further spreading of AKD molecules by surface diffusion in the form of an autophobic precursor and the monolayer diffusion occurred relatively slowly. To overcome the slow reactivity of an AKD with cellulose, factors promoting the reactivity of the AKD with hydroxyl groups, such as high temperatures (Yu and Garnier 1997), and relative humidity (RH) (Lee and Luner 2005) were investigated. Lee and Luner (2005) investigated the effect of RH on the hydrophobicity of paper, and showed that the sizing efficiency increased with RH up to 80%. They attributed this to an increase in the exposure of hydrophilic AKD lactone rings under a high RH (Lee and Luner 2005).

Yan et al. (2016) prepared microfibrillated cellulose (MFC) powder with the water contact angle of approximately 140° by a simple method of blending solvent-exchange of MFC with AKD dissolved in an organic solvent. Yuan and Wen (2018) also proposed to graft AKD onto the surface of CNF powder by mixing with melt AKD in an organic solvent, which further increased hydrophobicity and thermal stability than those of the untreated CNF powder. Russler et al. (2012) proposed a convenient way to modify bacterial cellulose aerogels with AKD dissolved in the CO₂ supercritical fluid. In addition, several researchers have reported the effective hydrophobization of CNF films with an AKD. For example, Fukuzumi et al. (2009) prepared a transparent and hydrophobic 2,2,6,6-tetramethylpiperidine-1-oxyl-oxidized CNF (TOCN) film using a simple immersion treatment in a cationic AKD dispersion. Their study showed that the abundant carboxyl groups in the TOCN film had a positive effect on hydrophobization with an AKD. An effective hydrophobization method for a CNF sheet was achieved by the immersion of a wet CNF sheet in an AKD emulsion and subsequent drying; the water contact angle was 118°, which was a higher value compared with the internal addition of an AKD to a CNF suspension and the immersion of a dry CNF sheet in an AKD emulsion (Goo et al. 2018).

However, CNF films hydrophobized with an AKD that exhibited high water contact angle did not reflect high water repellency and waterproof properties throughout the entire thickness direction if the hydrophobization was conducted at the surface layer. Water repellency and waterproof properties throughout the entire thickness of a CNF film are required for packaging that necessitates complete protection against water, e.g., for packaging of hydrogels such as cosmetics. Therefore, the objective of this study is to find a means of preparing waterproof CNF sheets via the reaction of an AKD on the controlled porous structure to hydrophobize not only on its surface but also in its thickness direction using an AKD as a hydrophobizing agent. To investigate the effect of structural properties on the hydrophobization of the samples, CNF sheets with different structural characteristics (a dense structure and a bulky structure, respectively) were prepared using hot-press drying (HD) and solvent-exchange drying (SD) techniques, respectively, and hydrophobized by immersion in an AKD emulsion and an AKD wax solution, respectively. The water contact angle, WVTR, and the resistance of water evaporation were evaluated.

Materials and methods

Materials

Never-dried hardwood bleached kraft pulp was used as a raw material for CNF production. A 2 wt% pulp suspension was passed through a grinder (Masscolloider, Masuko Sangyo Co., Ltd, Japan) to produce the CNF suspension. The speed of the grinder and the gap distance between grinding stones were 1500 rpm and −80 μm, respectively. The number of passes made through the grinder was 12.

The AKD wax supplied by Solenis (USA) and an AKD emulsion (EXPEL-200D) with a solids content of 20.6% (Taegwang Chemicals, Korea) were used as a hydrophobizing agent. The AKD wax was dissolved in toluene at 105 °C to prepare the AKD solutions at 5%, 10%, 20%, and 30% concentrations, and it was stirred for 10 min before use. The AKD emulsion was diluted to 1% using deionized water.
Cellulose nanofibril sheet preparation

Two drying methods, i.e. HD and SD, were used to prepare the CNF sheets with different structural properties (i.e., dense and bulky structures, respectively), and the effect of the structural properties of the CNF sheets on hydrophobization was investigated. First, CNF suspension was dewatered by vacuum filtration through a 0.2 μm membrane filter (Advantec, USA). To prepare the HD sheet, the sheet was pressed under a pressure of 30 bar at room temperature for 5 min and then hot-pressed at 105 °C and 25 bar for 10 min to dry. The grammage of the sheet was 60 g/m². To prepare the SD sheet with a bulkier structure, the CNF suspension was first dewatered by vacuum filtration and then wet-pressed at 30 bar for 30 s. The sheet was immersed in an ethanol solution for 24 h (step 1). Then, the ethanol-exchanged wet sheet was immersed in acetone for 24 h (step 2); then, it was immersed in hexane for 24 h (step 3). After each step of solvent exchange, vacuum drying was applied for 1 min. The grammage of the solvent-exchanged sheet was 60 g/m².

Evaluation of the physical and mechanical properties of the cellulose nanofibril sheet

The morphology of the CNF sheets was observed using a field-emission scanning electron microscope (FE-SEM) (SUPRA 55VP, Carl Zeiss, Germany). The specimen was sputtered with platinum at a thickness of 3 nm. Secondary electron images of the sheet were obtained with accelerating voltage of 2 kV.

The density (ρ) of the CNF sheet was calculated by dividing the oven dried weight (W) by the volume (V) of the CNF sheet. The porosity was determined using Eq. (1). The density of the cellulose (ρcellulose) was 1.5 g/cm³.

\[
\text{Porosity(\%)} = \left(1 - \frac{\rho}{\rho_{\text{cellulose}}} \right) \times 100
\]  

(1)

The dry tensile strength of the CNF sheet was measured using a universal testing machine (Instron Co., USA) after conditioning under conditions of 23 °C and 50% RH. The width of the specimen and the measurement span were 15 and 30 mm, respectively. The strain rate was 5 mm/min.

The air permeability of the CNF sheet was evaluated using a Gurley densometer (Gurley Precision Instruments, Inc., USA). The time required for 50 ml of air to flow through the sheet was measured in seconds. The specific surface area and pore size distribution of the CNF sheet were determined using Brunauer-Emmett-Teller (BET) analysis (TriStar II 3020 Version 3.02, Micromeritics Instrument Co., USA) by nitrogen gas adsorption and desorption. The sample was dried completely under a vacuum heat treatment at 105 °C for 4 h prior to the analysis.

Hydrophobization of the cellulose nanofibril sheet

The hydrophobization of the AKD was conducted by immersing the CNF sheet in either the AKD emulsion or the AKD wax solution. The immersion of the CNF sheets in the AKD emulsion was performed by soaking the HD sheet in a 1% AKD emulsion for 10 min. In the case of the SD sheet, the AKD emulsion was not used for hydrophobization because the porous structure of the solvent-exchanged CNF sheets would be destroyed during the drying process. Following the immersion in the AKD emulsion, the sheet was wet-pressed at 30 bar for 5 min to remove any excess AKD emulsion; again, it was drum-dried at 95 °C. This sheet was labeled the “HD-AKD emulsion” sheet.

Immersion in the AKD wax solution was performed for the SD and the HD sheets because doing so could maintain the porous structure of the SD sheets by inhibiting the formation of hydrogen bonds during drying. The SD sheet was immersed in an AKD wax solution for 6 h at 105 °C before being vacuum dried for 1 min at room temperature; this sheet was labeled the “SD-AKD wax” sheet. The hydrophobization of the HD sheet was also carried out by immersing the sheet in the AKD wax solution followed by vacuum drying for 1 min at room temperature; this was labeled the “HD-AKD wax” sheet.

Evaluation of the hydrophobicity of the cellulose nanofibril sheet

FT-IR analysis

A Fourier-transform-infrared (FT-IR) (Nicolet 6700, Thermo Scientific, USA) spectroscopy analysis of the CNF sheet was conducted using attenuated total
reflectance mode to confirm the reactions of the hydrophobizing agent and the CNF, and to evaluate the degree of hydrophobization. The wavenumber range was 650 to 4000 cm\(^{-1}\), and the scan number and resolution were 32 and 8 cm\(^{-1}\), respectively.

**Water contact angle**

The hydrophobicity of the CNF sheets was evaluated by measuring the water contact angle using a drop shape analyzer (DSA 100, KRÜSS GmbH, Germany) under the conditions of 23 °C and 50% RH. A 5 µl deionized water droplet was placed on the sheet’s surface and the contact angle was measured for each second for a total of 60 s.

**WVTR**

The WVTR was evaluated in accordance with T448 om-97. The method set out by the Technical Association of the Pulp and Paper Industry. An assembled cup containing dried silica gel was sealed with CNF sheets using high vacuum grease. Then, the cup was exposed to constant temperature conditions of 23 °C and 50% RH for 24 h. The WVTR was calculated using Eq. (2), where \( A \) is the exposed surface area of the CNF sheet, and \( \Delta m \) is the difference in weight before and after exposure for 24 h (t).

\[
WVTR( g \cdot cm^{-2} \cdot day^{-1} ) = \frac{\Delta m}{A \times t}
\]  

(2)

**Quantification of the alkyl ketene dimer on the cellulose nanofibril sheet**

The loading amount of the AKD on the CNF sheet was determined by measuring the oven dry weight before and after the hydrophobization of the CNF sheet. Oven drying was carried out at 105 °C for 2h. To evaluate the amount of AKD that reacted with the cellulose, a CNF sheet specimen (4×5 cm\(^2\)) was Soxhlet-extracted with dichloromethane for 24 h at 70 °C to remove any unreacted AKD. Then, the extracted CNF sheets were dried and weighed. The reacted AKD content was calculated according to the difference in the oven dried weights of the CNF sheet before and after Soxhlet extraction. The AKD loading content and the reacted AKD content were expressed in individual amounts by dividing the oven dried weight of the CNF before hydrophobization.

**Evaluation of the resistance against water transport**

The resistance of water evaporation was evaluated using a hydrogel-CNF packaging system, and a 1.33 wt% carboxymethylated CNF (CM-CNF) was used as a model hydrogel as the viscosity and water-holding capacity were high enough to test the resistance of water evaporation. Acridine orange dye was added to the CM-CNF hydrogel to visualize the water transport behavior through the CNF sheet. The hydrogel stained with acridine orange was placed in a specially designed module (8 mm diameter, 8 mm height) and covered with the CNF sheet. The contact area between the hydrogel and the CNF sheet was 50.24 mm\(^2\). Then, the modules were stored in a standard conditioning room (23 °C and 50% RH), and the hydrogel weight was measured at regular time intervals for up to 30 days. The water evaporation rate was calculated from the initial weight of the hydrogel (\( W_1 \)) and the weight of the hydrogel at time t (\( W_t \)) according to Eq. (3). A linear low-density-polyethylene (LLD-PE) film was also tested for comparison.

Water evaporation(%) = \( 1 - \frac{W_t}{W_1} \) \times 100  

(3)

**Observation of water transport behavior**

To evaluate the transport of water through the CNF sheet, the cross section of the CNF sheet in contact with the CM-CNF hydrogel was observed at regular time intervals using a confocal laser scanning microscope (CLSM) (LSM 710, Carl Zeiss, Germany). The excitation and emission wavelengths of acridine orange were 458 and 550–600 nm, respectively, and these two wavelengths were used in the CLSM observation.

**Results and discussion**

Structural properties of CNF sheet under different drying conditions

The CNF sheets were prepared under different drying conditions, i.e., HD and SD, and the appearance
and FE-SEM micrographs of four CNF sheets, which were dried under four drying conditions, are shown in Fig. 1. An HD sheet (Fig. 1a and e), and three SD sheets that were dried after the solvent-exchange steps involving ethanol (Fig. 1b and f), acetone (Fig. 1c and g), and hexane (Fig. 1d and h) revealed different network structures. The microstructure of the HD sheet was significantly denser than the SD sheets; this was because the HD sheet was dried under high temperature and pressure conditions, which increased the interfibrillar bonding. The high transparency of the sheet shown in Fig. 1a demonstrates the densified structure of the HD sheet. In contrast, the SD sheets were more porous compared with the HD sheet, and the pore structure of the SD sheets gradually increased as the solvent-exchange steps proceeded from ethanol to acetone and hexane. In particular, following the hexane-exchange as the final step, the SD sheet had a more opaque appearance and the highest porosity due to the low surface tension of the hexane.

To investigate the effect of drying conditions on the quantifying the properties of the CNF sheet, the structural properties, including thickness, density, porosity, Gurley air permeability, and specific surface and tensile strength were measured. The results are presented in Table 1. The HD sheet had the highest density of 1.25 g/cm³ and the lowest porosity among the CNF sheets which gave rise to an excellent tensile strength of 158.4 MPa. This was because extensive interfibrillar bonding was obtained in the HD process, which made the measurement of Gurley air permeability and the specific surface area of the HD sheet impossible. It was probably because most of the pores in the HD sheet were smaller than the measurement limit of the equipment (1.7 nm).

Compared with the HD sheet, the SD sheets were more porous. The porosity of the solvent exchanged SD sheet with hexane showed the highest porosity of 54.7% as well as the thickest bulk among the three SD sheets. The ethanol-exchanged and ethanol-acetone-exchanged SD sheets had 39.4% and 48.0% porosity, respectively.

Table 1 The properties of the cellulose nanofibril sheets as a result of using different drying methods

| CNF sheet         | Thickness (µm) | Density (g/cm³) | Porosity (%) | Gurley50cc (sec) | BET specific surface area (m²/g) | Tensile stress (MPa) |
|-------------------|----------------|-----------------|--------------|------------------|----------------------------------|----------------------|
| Hot-press         | 56             | 1.25            | 16.7         | N.D*             | N.D*                             | 158.4                |
| Ethanol (step 1)  | 74             | 0.87            | 39.4         | 2703             | 64.4                             | 58.6                 |
| Acetone (step 2)  | 80             | 0.78            | 48.0         | 2321             | 88.4                             | 54.4                 |
| Hexane (step 3)   | 89             | 0.68            | 54.7         | 150              | 115.0                            | 46.7                 |

*Not determined
porosity, respectively (Table 1). This showed that the polarity and surface tension of the solvent used in the final step of the solvent-exchange process played a critical role in the swelling and interfibrillar bonding of the SD sheets. Therefore, the air permeability and specific surface area of the SD sheets increased, and the tensile strength decreased with an increase in the solvent-exchange steps for the SD sheets. The hexane-exchange dried sheet (step 3) showed the highest air permeability with a more porous structure. In addition, the results of the specific surface area of ethanol, acetone, and hexane exchange drying were 64.4, 88.4, and 115 m²/g, respectively. This also demonstrated that the SD process reflected very limited aggregation of fibrils during the drying conditions compared with HD process, which induced hydrogen bonds that caused fibrils to aggregate during water evaporation. Thus, the hexane-exchange dried sheet among the three SD steps was selected as the best candidate for hydrophobization as opposed to the HD sheet.

The hydrophobicity of the cellulose nanofibril sheet

Fourier-transform infrared spectroscopy was used to determine the effectiveness of the AKD types (emulsion and was solution) and the hydrophobization method. Figure 2 shows the FT-IR spectra of the unreacted CNF, an AKD emulsion-treated sheet, and two AKD wax solution-treated sheets, including HD-AKD wax and SD-AKD wax sheets. Two absorption peaks at 2921 and 2848 cm⁻¹ were assigned to the C–H stretching vibration of –CH₂ in the alkyl groups, which was attributed to the alkyl chain of the bound AKD (Song et al. 2012). The peaks at 1024 and 3440 cm⁻¹ in all the sheets were attributed to C–O and O–H stretching, respectively (Hospodarova et al. 2018; Rosa et al. 2010). The difference between the untreated and hydrophobized CNF sheets was observable at absorption bands of 1720 and 1848 cm⁻¹, which were assigned to C=O stretching and C=O stretching, respectively (Zhang et al. 2007). These peaks demonstrated the existence of the lactone ring of the AKD and the formation of a β-keto ester group, indicating the reaction of the lactone ring with the hydroxyl groups of the cellulose. In particular, the hydrophobized CNF sheets with the AKD wax solution had higher intensity peaks compared with the AKD emulsion-treated sheet; this indicated that larger amounts of the AKD remained on AKD wax solution-treated sheets. However, the intensities of the peaks between the two AKD wax-treated sheets (the HD-AKD and SD-AKD wax sheets) were similar. Therefore, compared with the AKD emulsion sheet, the AKD wax-treated sheet, which exhibited higher intensities at the characteristic peaks of the β-keto ester, indicated that the AKD wax solution was a more effective hydrophobizing agent than the AKD emulsion.

To investigate the effect of the structural properties of CNF sheets on hydrophobicity, HD and SD sheets were immersed in AKD wax solutions with different wax concentrations. The water contact angle of the sheets was measured at 23 °C and 50% RH conditions (Fig. 3a). The water contact angle of the HD sheet treated with an AKD wax solution of 5% was 118°, while the angle of the SD sheet was 87°. The water contact angle of the SD sheet increased to 104° when a 10% AKD wax solution was used, although this was still lower than that of the HD sheet. All of the HD sheets treated with 20% and 30% AKD solutions showed similar water contact angles of approximately 120°. It was noted that the SD sheets treated with 20% and 30% AKD wax solutions showed water contact angles of 134° and 149°, respectively, which were much higher compared with the HD sheets.
Consequently, while the water contact angles of the HD sheets were similar, irrespective of AKD wax contents, the water contact angles of the SD sheets continued to increase, leading to a super-hydrophobic surface at a 30% AKD wax concentration. The water contact angle and the WVTR of the HD-AKD and SD-AKD wax sheets treated with a 30% AKD wax solution were compared with the untreated CNF sheet and the AKD emulsion sheet at 23 °C and 50% RH conditions. As shown in Fig. 3b, the water contact angle of the untreated CNF sheet is approximately 40° due to its hydrophilic properties. The AKD wax yielded a greater hydrophobicity in both the HD and the SD sheets. The WVTR of the AKD emulsion-treated sheet was lower than that of the untreated CNF sheet, which showed an approximately 30% reduction compared with the untreated CNF sheet (Fig. 3c). The AKD wax treatment substantially reduced the WVTR, which may have been due to the high accessibility and packing density of the AKD molecules in the AKD wax solution compared with the emulsion. The AKD emulsion treatment has the advantages of being an environmentally friendly process owing to its aqueous system and good adhesion onto cellulose fibers because of stabilization effected by cationic polyelectrolytes, such as cationic starch.
Conversely, the AKD emulsion comprised emulsion particles with a diameter of approximately 1 μm; accordingly, the packing density of the AKD molecules and the hydrophobicity may also have been low because of the hydrophilicity of the cationic emulsifier. The WVTR of the HD-AKD wax and SD-AKD wax sheets were approximately 37 g/m²·day and 20 g/m²·day, respectively. Specifically, the SD-AKD wax sheet showed the lowest WVTR, which, compared with untreated CNF, showed an approximately 91% reduction. That is, the 30% AKD wax-treated SD sheet demonstrated outstanding performance in terms of both water contact angle and WVTR among all of the tested samples.

The quantification of the AKD on the CNF sheet was conducted to investigate the relationship between the hydrophobicity of the SD sheet and the amount of AKD wax in the sheet. As shown in Fig. 4a, the amount of AKD loading is determined from the oven dried weights before and after hydrophobization, AKD wax sheets, and the reaction of the AKD with the two sheets. The AKD reacts with the HD-AKD sheet only on its surface, while internal penetration also occurs in the SD-AKD sheet, which increases with the AKD concentration.
which is the total amount of AKD in the sheets, including both the unbound (unreacted) and bound AKD. In the case of the bound AKD, the AKD reacted with cellulose via β-keto ester bonding. In the case of the HD-AKD wax sheet, the amount of AKD loading increased slightly as the concentration of AKD wax increased. Conversely, in the case of the SD-AKD wax sheet, the AKD wax content in the sheet linearly increased as the concentration of the AKD wax increased. Specifically, at 30%, the AKD wax content in the SD-AKD wax sheet was four times greater than in the HD-AKD wax sheet. To determine the amount of bound or reacted AKD in the sheet, Soxhlet extraction using dichloromethane was carried out for the CNF sheets, and the oven dried weights of the CNF sheets were measured before and after Soxhlet extraction. The weight difference of the CNF sheet before and after Soxhlet extraction indicated the amount of AKD that had been removed in the solvent extraction, from which the amount of bound or reacted AKD was obtained (Fig. 4b). The amount of bound AKD in the HD-AKD wax sheets was slightly reduced compared with the loading AKD amount (Fig. 4a) and was almost constant, irrespective of an AKD concentration above 5%, suggesting that no additional reaction sites were available in the HD-AKD wax sheets. Conversely, the amount of bound AKD in the SD-AKD wax sheets was greatly decreased compared with the loading amount of AKD, which was likely due to the removal of unbound AKD. However, compared with the HD-AKD wax sheet, the amount of bound AKD increased as the AKD wax concentration increased continuously (up to 30%). This demonstrated that many more reaction sites were available in the SD-AKD sheets, likely because both the outer and inner surfaces were available for AKD reactions. A schematic presentation of the AKD reaction with HD-AKD and SD-AKD sheets is shown in Fig. 4c. In the case of the HD-AKD sheets, the AKD spread and reacted only on the outer surface of the HD sheet due to its dense structure. In the case of the SD-AKD wax sheets, hydrophobization of the outer surface occurred first and proceeded into the internal structure of the sheet as the AKD concentration increased. That is, the larger the amount of AKD applied, the greater the reaction of the AKD in the internal structure of the SD-AKD sheets. This will lead to an improved WVTR for the SD-AKD wax sheet because it delays or prevents the swelling of the sheet upon exposure to water vapor.

Water transport behavior from hydrogel by cellulose nanofibril sheet

To investigate the performance of hydrophobized CNF sheets as packaging materials for hydrogels, the water evaporation of a CM-CNF hydrogel was

![Fig. 5](image)

**Fig. 5** A scheme showing the hydrogel-cellulose nanofibril (CNF) sheet packaging system, and b water evaporation from a hydrogel covered with various alkyl ketene dimer-treated CNF sheets and an LLD-PE film.
determined by measuring changes in the hydrogel weights for 30 days. The CM-CNFP hydrogel was placed in a module where it covered the CNF sheets, as shown in Fig. 5a. An LLD-PE film was used for comparison. As shown in Fig. 5b, the control sample without any barrier material on the hydrogel dried completely within 2 days. The hydrogel covered with an untreated CNF sheet also dried completely within 2 days, indicating that the untreated CNF sheet had low barrier property significance in terms of preventing water evaporation. Some improvement in preventing water evaporation was achieved when an AKD emulsion-treated sheet was used, and it took approximately 4 days to completely dry the hydrogel. In agreement with the results for the water contact angle and WVTR, the AKD-wax outperformed the AKD emulsion in preventing water evaporation from the hydrogel. The hydrogel covered by an HD-AKD wax sheet dried in 30 days, indicating that it had excellent water evaporation protection. In particular, the SD-AKD wax sheet showed better water evaporation protection than the LLD-PE film until day 10, and only 59% of water had evaporated from the hydrogel after 30 days. The performance of the SD-AKD wax sheet in terms of preventing water evaporation was comparable to the LLD-PE film. This indicated that the internal hydrophobization of the CNF sheets in the thickness direction contributed to preventing water evaporation, which provided a continuous barrier property via the thickness of the entire sheet.

To visualize the water transport behavior of the hydrogel through the CNF sheet, the hydrophobized CNF sheet was used to cover the hydrogel; a cross section of the sheet was observed using a CLSM. The HD-AKD and the SD-AKD wax sheets treated with a 30% AKD solution were compared (Fig. 6). For the HD-AKD wax sheet, water began to penetrate it after a few hours, and clear water penetration was noticed after 6 h. A deeper penetration of water was noticed over time. However, the SD-AKD wax sheet did not show any water penetration in the presence of the hydrogel for up to 48 h. This shows the importance of internal hydrophobization for preventing water evaporation from a hydrogel. In the case of the HD-AKD wax sheet that was hydrophobized only on the surface layer, water transport and evaporation occurred rapidly when the surface barrier was disrupted. Conversely, the porous structure of the SD-AKD wax sheet was advantageous for the deposition of AKDs on the inner and external surfaces of the CNF sheet. The hydrophobized internal surface of the SD-AKD sheet appeared to provide a continuous barrier that prevented water penetration throughout the entire thickness direction. The pores of the SD sheet filled with the AKD also provided an additional barrier.
against water evaporation. Thus, the SD-AKD wax sheet provided the best performance against water transport and evaporation because it had a larger amount of unbound and bound AKDs throughout its entire thickness direction.

Conclusions

To prepare waterproof CNF sheets for hydrogel packaging, an appropriate structure for the CNF sheets and an effective AKD application were investigated. HD and SD techniques were used to prepare CNF sheets with different porosities. The HD sheet exhibited high tensile strength but a porosity of 16.7%, which made it impossible to measure the BET specific surface area. However, the solvent-exchange process from ethanol to hexane resulted in a high porosity (54.7%) and specific surface area (115 m²/g) values for the sheet. The hydrophobization of the sheet was accomplished by immersion in an AKD emulsion and an AKD wax solution (toluene), respectively. Immersion in the AKD wax solution revealed a higher water contact angle and barrier property against water vapor compared with the AKD emulsion. In particular, the SD sheet immersed in a 30% AKD wax solution exhibited super-hydrophobicity (149°) and a very low WVTR value. The difference in porosity between the HD and SD sheets resulted in a difference in the loading and reacted amounts of the AKD. In the case of the SD-AKD wax sheet, the AKD was adsorbed on the outer and inner surfaces of the sheet; it also filled the pores of the sheet, which gave rise to waterproof properties and a comparable resistance against the water evaporation of a hydrogel for 30 days. The CLSM results supported the barrier performance of the SD-AKD wax sheet. Accordingly, the highly porous structure of the SD sheets with a large specific surface area allowed the AKD to penetrate the CNF sheet and hydrophobize its entire thickness. Based on these results, AKD wax immersion of the SD sheet was observed as an efficient method for preparing waterproof CNF sheet as a potential hydrogel packaging material.

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Data availability

Not applicable.

Declarations

Conflict of interest

The authors declare that there are no conflicts of interest.

Ethical approval

All authors state that they adhere to the Ethical Responsibilities of Authors. In addition, this article does not contain any studies with human participants or animals performed by any of the authors.

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