Hydrophobicity of Alkyl Ketene Dimer-Modified Microfibrillated Cellulose Film

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Microfibrillated cellulose (MFC) is a promising bio-based material owing to its excellent mechanical, optical, and barrier properties. However, its inherent hydrophilicity limits its applicability in moisture-sensitive environments. In this study, the surface hydrophobicity of MFC films was enhanced by incorporating an alkyl ketene dimer (AKD) and thermal curing. MFC was prepared from hardwood bleached kraft pulp *via* high-pressure homogenization to fabricate AKD-modified MFC films using vacuum filtration. The water contact angles of the AKD-modified MFC films were measured after thermal curing to determine the optimum manufacturing conditions for MFC film hydrophobicity. The presence of the AKD in the MFC matrix was confirmed by the appearance of alkyl chain C–H stretching bands in the Fourier transform infrared spectroscopy spectra. The water contact angle measurements showed that the addition of AKD alone improved the hydrophobicity but did not yield contact angles greater than 90°. However, with subsequent thermal curing at 105 °C, the contact angles increased significantly, reaching 104° under optimal conditions. The highest hydrophilicities were achieved with 2% AKD and 30 min curing and with 3% AKD and 10 min curing. These findings demonstrated that thermal curing was essential for activating the hydrophobic potential of AKD and achieving uniform, water-repellent MFC films.

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Keywords: Microfibrillated cellulose (MFC); Alkyl ketene dimer (AKD); Film; Hydrophobicity; Thermal curing; Contact angle

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INTRODUCTION

The increasing global demand for sustainable and eco-friendly materials has intensified the interest in bio-based alternatives to synthetic polymers (Deng *et al*. 2016; Lambert and Wagner 2017; Marturano *et al*. 2023). Among these, microfibrillated cellulose (MFC), a micro-scale fibrous material derived from plant-based cellulose, has garnered significant attention owing to its exceptional mechanical, optical, and barrier properties (Nishiyama 2009; Lavoine *et al*. 2012). MFC exhibits a unique combination of high tensile strength, low oxygen permeability, excellent transparency, and biodegradability when fabricated into films, making it a promising candidate for diverse high-performance applications (Syverud and Stenius 2009; Aulin *et al*. 2010). However, one critical limitation of MFC films is their intrinsic hydrophilicity, which restricts their performance under humid or wet conditions and limits their applicability in moisture-sensitive environments (Deng *et al*. 2016; Yan *et al*. 2016).

To address this challenge, enhancing the hydrophobicity of MFC films has become a key research area. Recent studies have explored various strategies for enhancing the hydrophobicity of MFC films to overcome the inherent moisture sensitivity (Andresen *et al*. 2006; Deng *et al*. 2016; Bian *et al*. 2022; Li *et al*. 2022; Shi *et al*. 2022). Surface modification techniques, such as chemical grafting (Guo *et al*. 2019), plasma treatment (Iqbal *et al*. 2019), and the incorporation of hydrophobic agents (Jo *et al*. 2021; Yang *et al*. 2014), have been investigated to reduce water absorption and improve dimensional stability. For example, fatty acid derivatives (Balasubramaniam *et al*. 2020), silanes (Andresen *et al*. 2006; Bang *et al*. 2024), and fluorinated compounds have been applied to cellulose surfaces to lower the surface energy. However, some of these treatments raise concerns regarding environmental safety and long-term stability (Poothanari and Leterrier 2024). Among the more sustainable approaches, alkyl ketene dimer (AKD) has been widely studied due to its ability to covalently bond with cellulose hydroxyl groups and impart a hydrophobic character without significantly altering the mechanical or optical properties of MFC films (Yang *et al*. 2014; Yuan and Wen 2018; Oh *et al*. 2022). Previous studies have laid the groundwork for understanding the interaction between AKD and cellulose and other hydrophobic modification techniques. For example, Hubbe (2007) discussed how AKD could effectively reduce the wettability of cellulose surfaces when applied under optimal conditions. Lindström and Larsson (2008) highlighted the importance of curing temperature and time to achieve durable hydrophobicity in paper products treated with AKD. However, optimizing treatment conditions, such as dosage and curing, to achieve uniform and durable hydrophobicity across the surface of MFC films remains challenging.

This study aimed to develop AKD-modified hydrophobization tailored to MFC films, with a focus on enhancing water repellency. The MFC fibers were prepared from hardwood bleached kraft pulp (HwBKP) through high-pressure homogenization, and their characteristics were measured. After AKD was added to the MFC emulsion, the AKD-modified MFC films were fabricated using a vacuum filtration system. Following preparation and thermal curing, the measured water contact angles of the MFC films were analyzed as a function of the thermal curing time to identify the optimum manufacturing conditions for the water-repellent MFC films.

EXPERIMENTAL

Materials

The MFC was made by HwBKP (Moorim Paper Co., Ltd., Jinju, Republic of Korea). The AKD emulsion was supplied by LATON Co., LTD (Gongju, Republic of Korea), exhibiting a solid content of 15 ± 0.5%, an average particle size of 0.68 μm, and an average zeta-potential of +28 mV (at pH 7.0). The positive zeta potential provides evidence that the AKD had been stabilized by a cationic agent, possibly cationic starch. Ethyl alcohol (C_2H_5OH, 95.00%; Daejung, Republic of Korea), acetone (CH_3COCH_3, 99.9%; Fisher, USA), and n-hexane (C_6H_4, 86.18%; Daejung, Republic of Korea) were used for the solvent exchange method.

Manufacture of MFC

HwBKP at 1.57% solids was soaked in tap water and then beaten to 300 ± 5 mL CSF using a laboratory Hollander beater. To prepare the MFC suspensions, the beaten pulp slurry was diluted to 0.7% solids and fibrillated up to four times (pass numbers 1, 2, 3, and 4) using a high-pressure homogenizer (MN400BD; Micronox, Gwanju, Republic of Korea) at 20,000 psi. The microfibrillated cellulose samples were corrected at each pass (1, 2, 3, and 4).

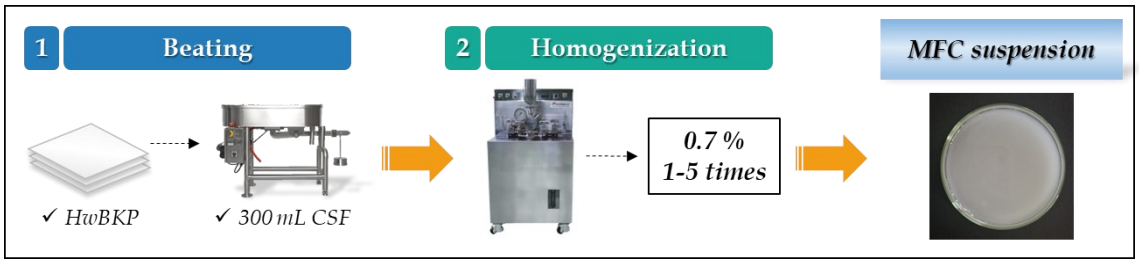


Fig. 1. Flow diagram of the manufacture of MFC suspension

Characterization of MFC

Wet MFC test specimen pads were prepared using a vacuum filtration system to measure the fiber widths. To prevent deformation during drying, the test specimens were dried using the solvent exchange method with ethyl alcohol, acetone, and n-hexane (Stelte and Sanadi 2009; Kim *et al*. 2019). After capturing field emission scanning electron microscopy (FE-SEM) (JSM-7610F; JEOL, Tokyo, Japan) images of the pads, the fiber widths of 100 individual microfibers from each MFC specimen were measured using 3D image software (MP-45030TDI; JEOL, Osaka, Japan).

The low-shear viscosity of the 1.0% MFC suspension was determined using a low-shear viscometer (DV-IP; Brookfield Engineering Laboratories, Middleborough, MA, USA) at 25 °C. The zeta-potential of the 0.01% MFC suspension was measured using a zeta-potential analyzer (Nano ZS; Malvern Panalytical, Malvern, UK).

The particle size of the MFC was measured using a particle analyzer (1090 LD; CILAS, Orleans, France). Because the MFC has a high aspect ratio, laser scattering is not an ideal method for detecting the fiber dimensions (Gantenbein *et al*. 2011). However, it was thought that the particle size data could be used to indirectly indicate the size differences among the MFC samples (Park *et al*. 2018).

MFC Film Preparation and Physical Property Measurement

To fabricate the MFC films, the MFC suspension, diluted to 0.5%, and the AKD were mixed for 30 min at 600 rpm. The dosage of AKD was 1%, 2%, 3%, 4%, and 5% of the oven-dried microfibers. MFC films with a grammage of 45 ± 2 g/m² were then formed on filter paper using a vacuum dewatering device and pressed using a laboratory press at 410 ± 10 kPa for 30 min to remove any moisture, and then carefully removed from the filter paper. The films were dried for approximately 6 min by passing them through a cylinder dryer twice at 100 °C. The fabricated films were then conditioned at 23 °C and 50% relative humidity for 24 h before their physical properties were measured.

To determine the reaction between the AKD and MFC, Fourier transform infrared spectroscopy (FT-IR; IS50, Thermo Fisher, USA) was used to determine the functional groups. To evaluate the hydrophobic effect of the AKD, the contact angles of the films

were measured after curing using aqueous ferric chloride ($FeCl_3$) solution, in accordance with TAPPI T 458, with an in-house water resistance tester (Lee *et al.* 2012, 2014) The films were cured at 105 ± 5°C for 1, 2, 3, and 4 h. Figure 2 presents the flow diagram of the MFC film fabrication, curing, and contact angle measurement (Jo *et al*. 2021).

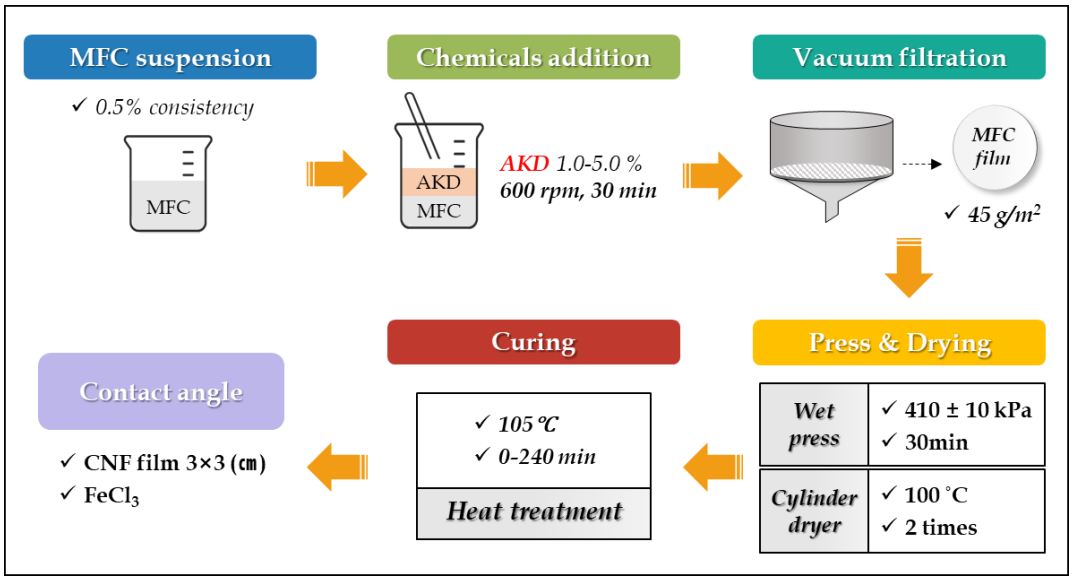


Fig. 2. Flow diagram of MFC film preparation, thermal curing, and contact angle measurement

RESULTS AND DISCUSSION

Characteristics of MFC

Table 1 summarizes the characteristics of the MFC according to the number of passes through the high-pressure homogenizer. As the number of passes increased from 1 to 4, the fiber width decreased from 47.7 to 36.2 nm, indicating the progressive fibrillation of the cellulose fibers. A corresponding increase in the viscosity from 338 to 874 cPs was observed, suggesting enhanced entanglement and network formation among the finer fibrils. The zeta-potential remained relatively stable, ranging from -15.2 to -17.2 mV, indicating consistent surface charge characteristics despite the mechanical processing. In addition, the average particle size decreased from 48.4 to 32.5 µm, further confirming the effective size reduction and dispersion of the fibrillated cellulose with increasing numbers of high-pressure homogenization passes.

Table 1. Characteristics of MFC Depending on the Number of Homogenization Passes

Pass Number	Average Fiber Width (nm)	Viscosity (cPs)	Zeta-Potential (mV)	Average Particle Size (µm)
1	47.7	338	-15.2	48.4
2	45.5	549	-17.0	42.8
3	38.4	743	-15.4	36.2
4	36.2	874	-17.2	32.5

To ensure practical relevance and consistency with commercially available materials, the MFC prepared using four high-pressure homogenization passes was selected for subsequent experiments, having a particle size of 32.5 μm, comparable to the particle size of commercial MFC products (typically around 33.6 μm).

Hydrophobicity Measurement of AKD-modified MFC Films

The effect of the AKD dosage on the contact angle of the MFC film was evaluated to assess the changes in the surface hydrophobicity. As shown in Fig. 3, the contact angle gradually increased with increasing AKD dosage from 1% to 4%, rising from approximately 54° to 66°. This trend suggests that the incorporation of AKD moieties contributed to lowering the surface energy of the MFC films, likely due to the presence of hydrophobic alkyl chains (Yang *et al*. 2012; Duan *et al*. 2023; Nadeem *et al*. 2023). Nevertheless, the contact angles of all cylinder-dried films remained below 90°, indicating that the hydrophobic effect was only partially developed under the given processing conditions. At 5% AKD, a slight decrease in the contact angle was observed, which may be attributed to the accumulation of unreacted AKD, some of which may have decomposed, and crystallized on the film surface as waxy deposits, thereby interfering with the uniform distribution of sizing agents and leading to non-uniform sizing (Goldstein 1992; Bottorff and Sullivan 1993; Lee *et al*. 2020).

The chemical structures of the AKD-dosed MFC films were analyzed using FT-IR spectroscopy. As shown in Fig. 4, a distinct absorption band appeared in the range of 2,850 to 2,920 cm^{-1}, corresponding to the C–H stretching vibrations of the alkyl chains (Yan *et al*. 2016; Khalilzadeh *et al*. 2019; Li *et al*. 2022; Nechita *et al*. 2022; Duan *et al*. 2023). This band was absent in the untreated MFC film but progressively intensified with increasing AKD content, indicating the successful introduction of the AKD hydrophobic alkyl groups into the MFC matrix.

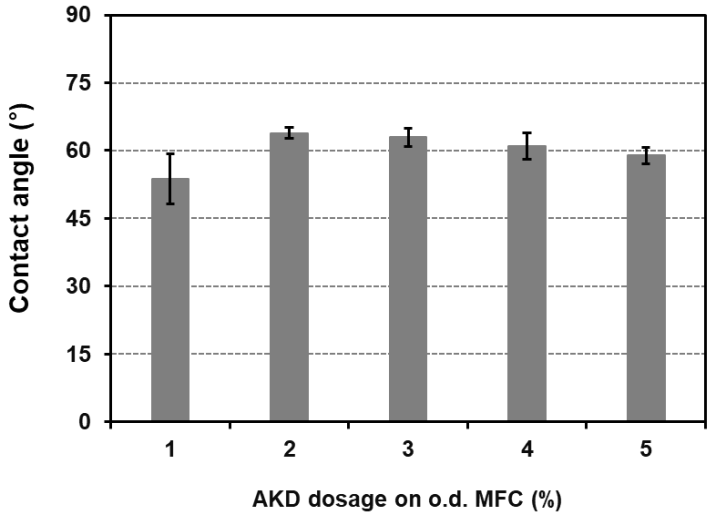


Fig. 3. Contact angle of AKD-modified MFC film depending on the AKD dosage

Despite the evidence of AKD incorporation from FTIR, the contact angles of the cylinder-dried films did not exceed 90°, as shown in Fig. 3. This suggests that the absorption of hydrophobic moieties alone did not guarantee sufficient surface hydrophobization. Additional thermal curing was therefore considered necessary to

promote both esterification with cellulose hydroxyl groups and crystalline reorientation of alkyl chains (Yan *et al.* 2016; Nechita *et al.* 2022). The limited hydrophobicity observed here can thus be reasonably attributed to the limitations of cylinder drying, which provides heat but may not enable the complete activation of AKD.

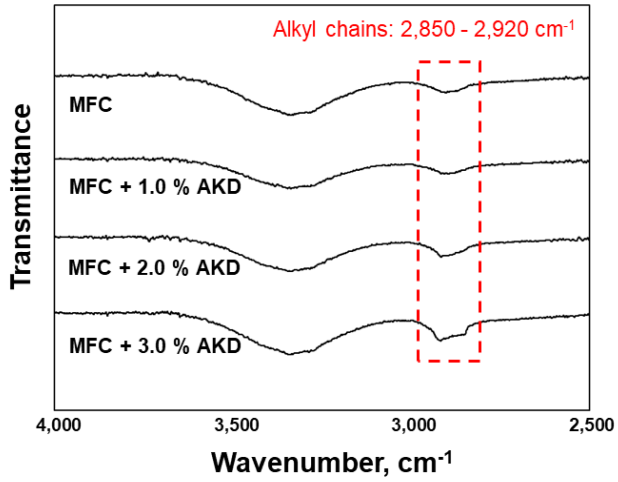
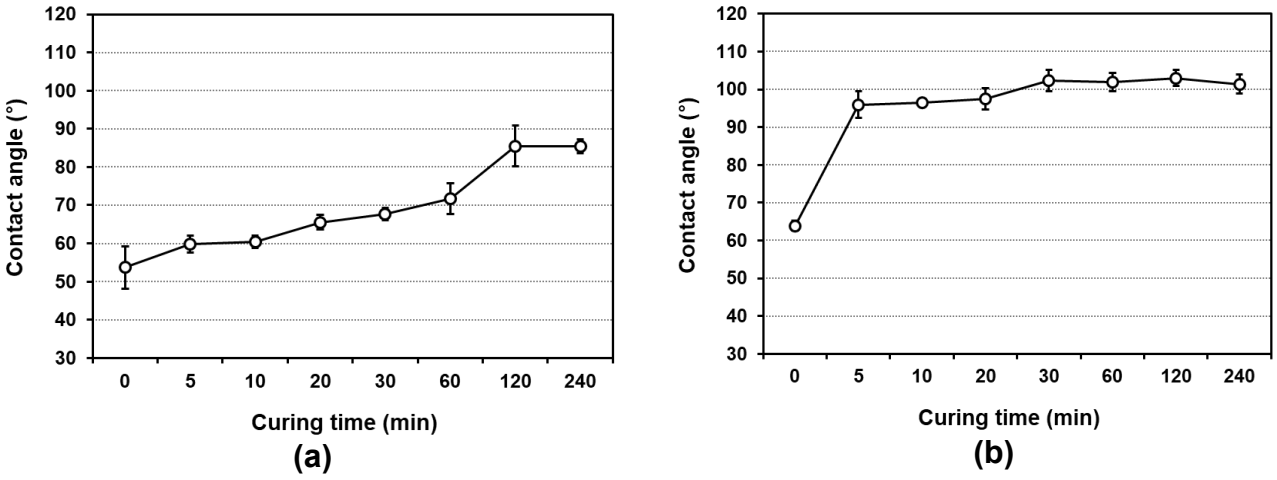


Fig. 4. FT-IR spectra of AKD-modified MFC films

Effect of the Curing Process on the Contact Angle of AKD-modified MFC Film

After the film fabrication, thermal curing was performed to fix the AKD onto the MFC film surface and induce the orientation of the alkyl chains. This was performed using a hot-air dryer at 105 °C for 0 to 240 min. Figure 5 illustrates the changes in the contact angles of the AKD-modified MFC films with varying AKD dosages and curing times. As the curing time increased, the contact angle also tended to increase, with a maximum contact angle of 104° observed at an AKD dosage of 2% (Fig. 5b). While increasing the AKD dosage accelerated the initial increase in the contact angle, an excessive dosage beyond 3% resulted in a decrease in the maximum contact angle (Figs. 5d and e). This was likely due to the increased amount of residual AKD in the film, which may have enhanced the thermal reactivity but hindered the hydrogen bonding between the MFCs due to the long alkyl chains (Aziz and Mat Salleh 2023).



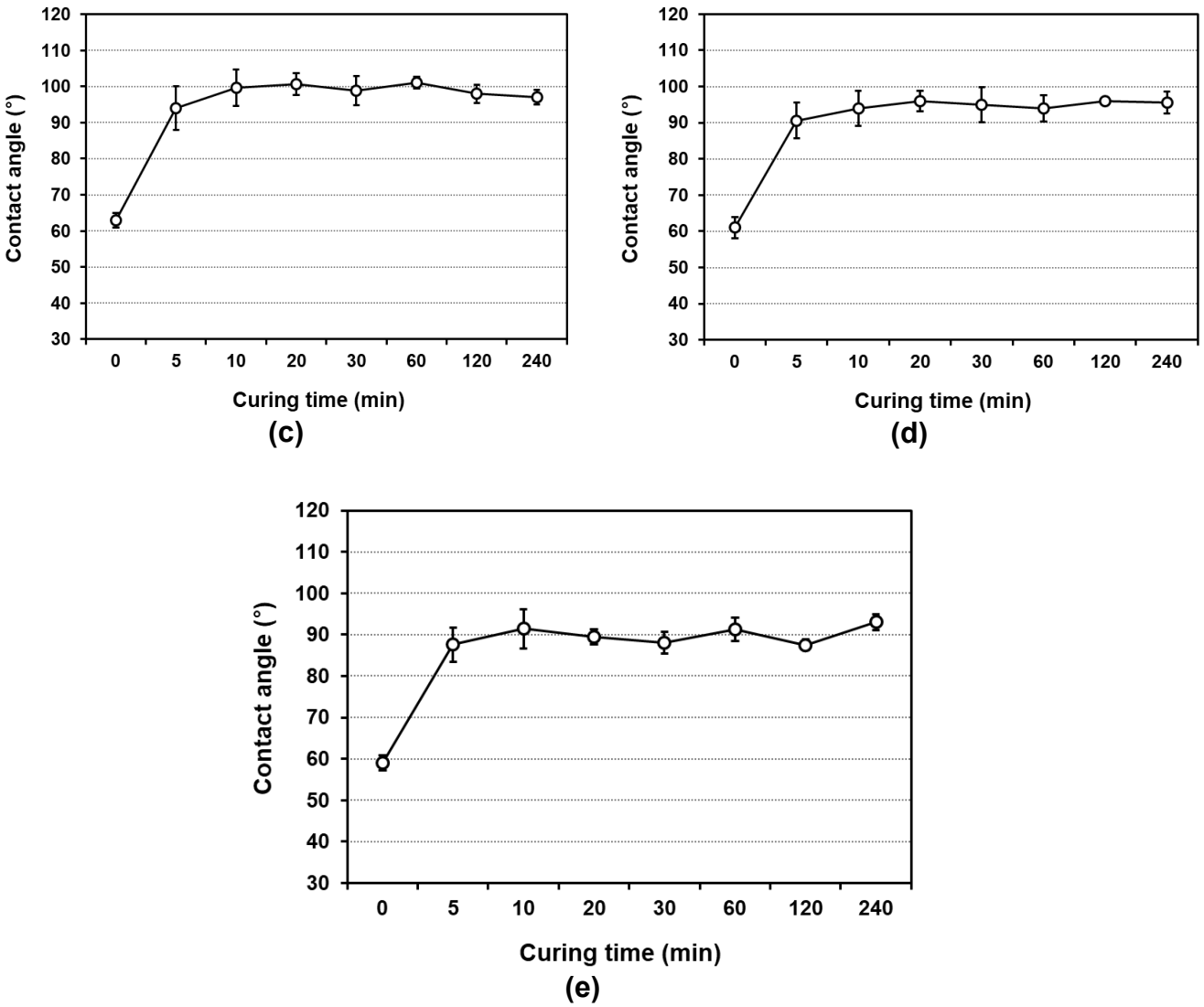


Fig. 5. Contact angle of (a) 1%, (b) 2%, (c), 3%, (d) 4%, and (e) 5% AKD-modified MFC film cured at 105 °C

Figure 6 illustrates the AKD sizing and thermal curing processes. When the AKD emulsion was added to the MFC emulsion and dried to form the MFC film, the AKD particles partially melted and reacted with the hydroxyl groups on the surface of the MFC fibers *via* esterification. Thermal curing plays a critical role in enhancing the hydrophobicity of MFC films. Upon heating, the hydrophobic alkyl chains gain sufficient mobility to reorient toward the film-air interface. This molecular rearrangement minimizes the surface energy and contributes to the formation of a continuous hydrophobic layer (Choi *et al*. 2002).

In addition, enhanced surface hydrophobicity may result primarily from alkyl chain reorientation during curing, while self-association of long alkyl chains could also contribute to the formation of hydrophobic domains. Both mechanisms likely play a role in the effective sizing performance of AKD-modified MFC films (Shen *et al.* 2001; Hubbe *et al.* 2020).

It was determined that hydrophobicity was not achieved solely by adding the AKD during the film fabrication; it required a thermal curing step to activate the effective sizing performance of the AKD. A 2% AKD dosage with 30 min of curing or a 3% AKD dosage with 10 min of curing were considered optimal to achieve a contact angle greater than 100°.

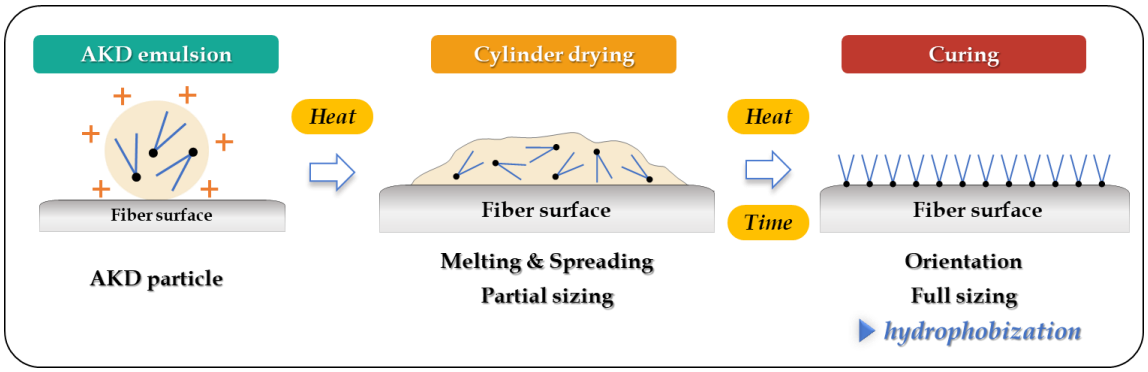


Fig. 6. Proposed mechanism of AKD sizing during the thermal curing process

CONCLUSIONS

1. The absorption of the AKD into the MFC films, followed by heated drying, contributed to enhancing their surface hydrophobicity, as confirmed by the contact angle measurements and the FT-IR analysis. The contact angles increased with AKD dosage up to 4%, accompanied by the appearance of hydrophobic C–H stretching peaks, indicating the successful absorption of the hydrophobic alkyl groups from the AKD into the MFC film matrix. However, without thermal curing, the contact angle did not exceed 90°, suggesting that the addition of AKD alone is insufficient for the effective sizing performance of the MFC films.
2. The 105 °C thermal curing process was essential for improving the hydrophobic performance of the AKD-modified MFC films. The curing promoted further redistribution of the AKD molecules within the MFC film matrix. The highest hydrophobicity, with contact angles exceeding 100°, was achieved at 2% AKD dosage with 30 min of curing or 3% AKD dosage with 10 min of curing. These results underscore the importance of curing conditions in achieving uniform and stable hydrophobic surfaces for MFC films.
3. This preliminary study represents an initial investigation and provides insights that could be useful in future research to further explore and optimize the performance of AKD-modified MFC films.

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