COMPARATIVE EVALUATION OF SURFACTANT-ASSISTED AND SURFACTANT-FREE BEESWAX EMULSIONS FOR DIP-COATING OF CMC-MODIFIED PAPER

MOGHADASE AKBARI,[*,**] ELYAS AFRA,[**] SEYED MAJID ZABIHZADEH[*] and MOHAMMADREZA DEHGHANI FIROUZABADI[**]

[*]*Department of Wood and Paper Science, Faculty of Natural Resources, Sari Agricultural Sciences and Natural Resource University, P.O. Box 737, Sari, 4818168984, Iran*
[**]*Department of Paper Science and Engineering, Faculty of Wood and Paper Engineering, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, 49189-43464, Iran*
✉ *Corresponding author: E. Afra, m.akbari.a.30@gmail.com*

Received July 5, 2026

This study compares two beeswax-in-water emulsion systems – surfactant-assisted (Tween 80/ultrasonication, TUBW) and surfactant-free (ultrasonication-only, UBW) – for coating cellulose-based paper sheets modified with carboxymethyl cellulose (CMC). TUBW exhibited a smaller mean droplet diameter (425.5 nm vs 822 nm) and a more negative zeta potential (−8.4 vs −2.4 mV) than UBW. After 10 days of storage, TUBW showed greater stability, with less droplet aggregation and phase separation than UBW. Dip-coating with TUBW under ambient conditions yielded a maximum water contact angle (WCA) of 135°. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses revealed changes in surface morphology and roughness after coating. Although beeswax coating reduced tensile strength, the 15 wt% concentration provided a favorable balance between barrier performance and mechanical integrity.

Keywords: biopolymers, hydrophobic paper, barrier properties, paper-based packaging

INTRODUCTION

Recent efforts in paper-based packaging focus on improving moisture, vapor, and grease resistance, while maintaining recyclability and sustainability.[1] Conventional methods for improving cellulosic packaging include adding fillers, sizing agents, and wet-strength additives, as well as applying petroleum-derived coatings, such as polyethylene (PE), and polyethylene terephthalate (PET). Although effective, these approaches can increase production costs, raise environmental concerns, and compromise recyclability.[2-3] These limitations have intensified interest in simple, green, and single-layer coating systems compatible with established industrial techniques, such as dip-coating, size press, and extrusion.[4-5]

Among bio-based hydrophobic agents, natural waxes have attracted considerable attention due to their inherent hydrophobicity, chemical stability, and compatibility with lignocellulosic fibers.[5-6]

Beeswax contains more than 300 chemical constituents, including hydrocarbons, long-chain fatty acid esters, and alcohols.[7] Its hydrophobic composition makes it a promising candidate for improving the moisture-barrier properties of cellulosic materials.[8-9] Additionally, the ability to readily separate wax from cellulose fibers during the repulping process has contributed to the commercial attractiveness of wax-coated paper.[10] However, prior beeswax-paper coating strategies, including ethanol-dissolved wax[11] and hot-pressed wax films,[12] have frequently led to rapid solidification, uneven deposition, or greasy surfaces. Studies have investigated wax-based coatings to enhance the barrier performance of paper substrates.[13]

The performance of beeswax coatings depends strongly on their interactions with other coating components, which may also affect biodegradability and repulpability. For example, a

beeswax–silica dispersion produced a textured surface that enabled liquids such as yogurt to roll off after annealing, despite reduced hydrophobicity.[14] Microcrystalline-wax coatings on starch-pretreated paper improved oil resistance, reducing $Cobb_{60}$ by 84% and WVP by 81.9%.[15] Similarly, a beeswax-in-water emulsion stabilized with 0.6–0.9 wt% CNF produced a moderately hydrophilic surface (WCA ≈ 96°) with WVP below 100 g/m²·day, although still inferior to PE-coated paper.[16] Despite these advances, some strategies used to enhance barrier properties – particularly cellulose nanomaterials – may raise safety concerns in food-contact applications because of limited toxicological evidence.[17] Therefore, developing well-controlled dispersion approaches remains essential to achieve uniform and reliable beeswax-based coatings for sustainable paper packaging.

Achieving a stable and homogeneous dispersion of wax in water remains a significant formulation challenge. One promising solution is using oil-in-water emulsions for wax application in paper manufacturing. This approach offers two key advantages: it facilitates wax coating application and allows wax to be effectively removed from pulp fibers during repulping.[18] Oil-in-water emulsions can be produced through various approaches, with surfactant-assisted emulsification being one of the most widely adopted methods.[19] Surfactants adsorb at the oil–water interface, where their hydrophobic and hydrophilic segments interact with the oil and aqueous phases, respectively. This arrangement reduces interfacial tension and can limit droplet coalescence. For instance, a nonionic fluorosurfactant has been used to stabilize beeswax emulsions for producing hydrophobic coatings on metal and glass.[20] However, the coating exhibited poor thermal and structural stability, and the fluorinated surfactant raised environmental and health concerns due to its potential for bioaccumulation and toxicity. In addition, beeswax/carnauba wax coatings stabilized with cetyltrimethylammonium bromide (CTAB) can provide strong hydrophobicity.[21] However, the incorporation of CTAB, a petroleum-derived, non-biodegradable surfactant associated with significant human and environmental toxicity, markedly restricts their suitability for sustainable packaging applications.[22]

Polysorbate 80, also known as Tween 80, is a nonionic surfactant and a complex mixture primarily composed of a hydrophilic sorbitan polyoxyethylene (POE) moiety linked to an oleate (C18) ester.[23] Ultrasonication is an effective method for producing nanoscale emulsion droplets, primarily through acoustic cavitation, which involves the formation, expansion, and collapse of vapor bubbles under high-intensity ultrasound. Ultrasound power, liquid properties, and processing conditions influence cavitation characteristics, with power typically controlled by adjusting the amplitude as a percentage of its maximum level.[24]

This study compares a surfactant-assisted (Tween 80/ultrasonication) and a surfactant-free (ultrasonication-only) strategy for preparing beeswax-in-water emulsions. These aqueous emulsions offer practical advantages for paper treatment, including straightforward dip-coating without specialized equipment and application at ambient temperature. This eliminates the need to handle molten wax during coating. We evaluated the effects of the emulsification strategy on the surface wettability, barrier performance, and mechanical properties of beeswax-coated paper.

EXPERIMENTAL

Raw materials

Dried bleached softwood kraft pulp (BSKP) was used as raw material and was supplied by the Mazandaran Wood and Paper Industry (MWPI) mill, Iran. The pulp was refined using a PFI mill to reach a freeness of 350 mL CSF. Double-purified beeswax was purchased from Momila (Iran). Carboxymethyl cellulose (CMC) was obtained from Merck (Germany) and dissolved in distilled water at room temperature under continuous stirring until a homogeneous solution formed. All other chemicals used in this study were of analytical grade and were used as received without further purification.

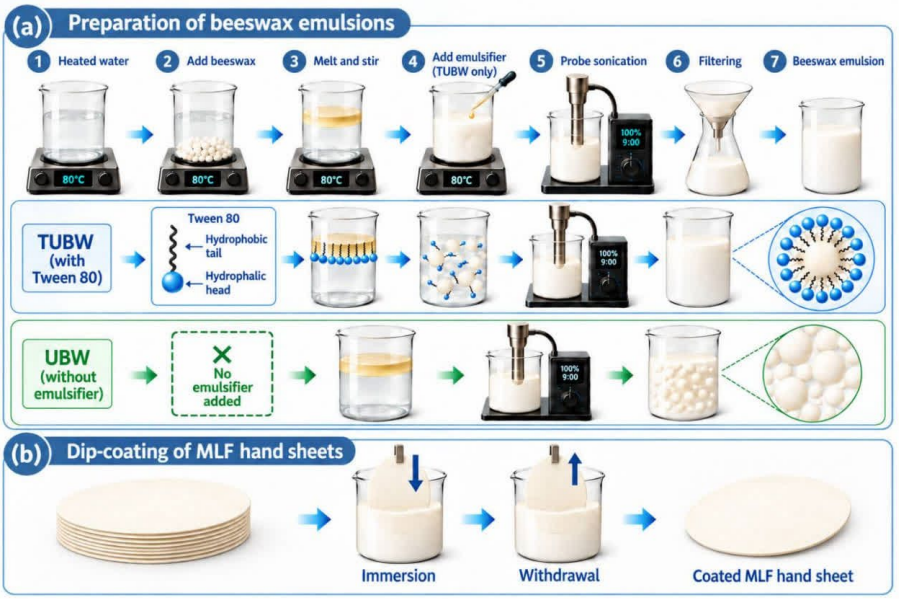
Preparation of CMC-treated cellulose fibers and handsheets

CMC-treated cellulose fibers were prepared following the method reported by Wu and Farnood.[25] Handsheets with a grammage of 60 g/m² were prepared according to TAPPI standard T 205 (2002). Refined BSKP was blended with 30 wt% CMC-treated fibers to produce modified long-fiber sheets (MLF). Handsheets prepared entirely from untreated fibers were also produced under identical conditions and used as reference samples (LF). The MLF sheets were subsequently treated with wax emulsions by dip-coating.

Preparation of beeswax emulsions

Beeswax emulsions were prepared by heating distilled water to approximately 80 °C and adding

beeswax to obtain concentrations of 1, 5, 10, 15, and 20 wt%. After the beeswax completely melted, the mixture was ultrasonicated using a Qsonica Q700 sonicator (700 W, 20 kHz) at 100% amplitude for 9 min, with a pulse cycle of 3 s on and 1 s off. To prepare TUBW emulsions, Tween 80 was added at 10 wt% relative to the beeswax content, and the mixture was magnetically stirred for 5 min before sonication. In contrast, no emulsifier was added during the preparation of UBW emulsions. After sonication, the emulsions were filtered to remove coarse particles and obtain a more uniform dispersion. The resulting emulsions were then used to treat the paper handsheets by dip-coating. The preparation of TUBW and UBW emulsions and the dip-coating of MLF handsheets are illustrated in Scheme 1.



Scheme 1: (a) Preparation of TUBW and UBW emulsions, and (b) dip-coating of MLF handsheets

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of CMC, LF paper, and MLF paper were obtained using an Agilent Cary 630 FTIR spectrometer (USA) over the wavenumber range of 4000–600 cm^{-1}. All spectra were recorded without any special sample preparation.

Zeta potential and particle size analysis

The particle size and zeta potential of the prepared emulsions were measured using a Nanotrac Wave II/Zeta analyzer (Microtrac Inc., USA) based on dynamic light scattering (DLS).

Microstructure of beeswax emulsions

We examined the macroscopic and microscopic characteristics of the TUBW and UBW emulsions immediately after preparation and after 3 and 10 days of storage. Macroscopic appearance was visually inspected and photographed. For microscopic analysis, a drop of each emulsion was placed on a clean glass slide, gently spread to form a thin film, and covered with a coverslip to avoid bubble formation. Micrographs were then captured using an optical microscope (Sairan N-180M, Iran).

Thickness and grammage

The thickness of the handsheets was measured at five randomly selected points on each sheet using a digital micrometer (Mitutoyo, Japan; 0–25 mm range, 0.001 mm resolution), and the mean thickness was recorded. Grammage (g/m^2) was determined according to TAPPI T 410 om-02.

Opacity and brightness measurements

ISO brightness and opacity of the paper samples were measured using a Chromameter (Model ZB-A, Hangzhou Zhibang Automation Technology Co., Ltd., China). ISO brightness was determined according to TAPPI 452 om. Paper opacity was measured according to TAPPI T425 om-16.

WCA and Cobb test

Surface wettability was evaluated by depositing a 5 µL droplet of distilled water onto rectangular handsheets (50 mm × 15 mm) at ambient temperature. Droplet images were captured immediately after deposition using a digital microscope (Dino-Lite) and analyzed via Image-J software. Measurements were performed with five replicates for each sample, and the average values were reported. Water absorption was measured using the Cobb test according to TAPPI T 441 om-09.

Water absorbency time

Water absorbency was evaluated by depositing a 10 µL droplet of distilled water onto handsheet specimens (25 mm × 25 mm) at ambient temperature using a

micropipette. The absorption time was recorded immediately after droplet deposition using a stopwatch and was defined as the time required for the water droplet to completely disappear from the paper surface. Measurements were performed with five replicates for each sample, and the average values were reported.[26]

Air resistance

Air resistance was determined using a Gurley-type densitometer (Model 4110, Gurley Precision Instruments, Troy, NY, USA) in accordance with TAPPI T460 om-02. The air resistance value was obtained by measuring the time required for a fixed volume of air to pass through the specimen under a gravity-loaded cylinder and liquid seal system.

Tensile index

Tensile index (Nm/g) was measured according to TAPPI T494 om-96 using a universal testing machine (SANTAM STM-20, Iran) equipped with a 100 N load cell. Paper strips (14 × 1.5 cm) with a gauge length of 10 cm were tested at a crosshead speed of 20 mm/min.

SEM and AFM analysis

Surface morphology of untreated MLF handsheets and beeswax emulsion-treated handsheets (TUBW and UBW) was examined using SEM (Pemtron PS-230 MH, Korea) after gold sputter-coating. Surface topography and roughness were further analyzed using AFM (Nanosurf Easyscan2 Flex, Switzerland) with a scan size of 5 µm × 5 µm. The average roughness (Ra) and root-mean-square roughness (RMS/Rq) values were recorded.

RESULTS AND DISCUSSION

FTIR analysis of LF, CMC and MLF handsheets

FTIR spectroscopy was used to investigate the chemical structure and functional groups of LF, CMC, and MLF samples. As shown in Figure 1, the spectra exhibit the typical absorption bands of cellulose. The broad band observed at 3200–3600 cm^{-1} corresponds to O–H stretching vibrations associated with intermolecular and intramolecular hydrogen bonding in cellulose. The peak near 2890 cm^{-1} is attributed to C–H stretching vibrations of aliphatic groups.[27-28] Characteristic cellulose bands are also observed at approximately 1423 cm^{-1} (CH_2 scissoring), 1313 cm^{-1} (O–H bending), and within the 1160–1020 cm^{-1} region, which corresponds to C–O–C and C–O stretching vibrations in the pyranose ring of cellulose. The presence of a band around 896 cm^{-1}, assigned to the β-glycosidic linkage between glucose units, confirms the typical cellulose backbone structure.[27-28]

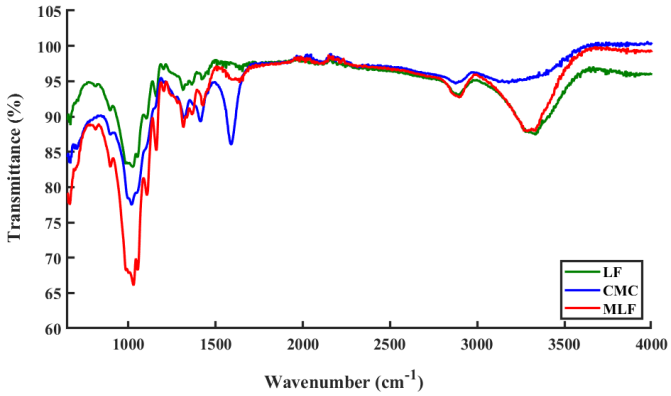


Figure 1: FTIR spectra of LF, CMC and MLF

For the CMC spectrum, a band around 1588 cm^{-1} is attributed to the asymmetric stretching vibration of carboxylate groups ($–COO^-$), indicating the presence of carboxymethyl functional groups.[27] Additional bands near 1413 and 1320 cm^{-1} correspond to CH_2 scissoring and O–H bending vibrations, which are consistent with the structure of CMC.

In the MLF sample, the FTIR spectrum shows absorption bands at approximately 3330, 2896, 1426, 1363, 1314, 1159, 1105, 1052, 1028, and 896 cm^{-1}, indicating the coexistence of functional groups related to both cellulose and CMC. A slight broadening of the O–H stretching band around 3330 cm^{-1} suggests enhanced hydrogen bonding interactions between hydroxyl groups of cellulose and carboxylate groups of CMC. Minor changes in the intensity of bands around 1426–1314 cm^{-1} may be associated with the presence of additional functional groups introduced by CMC and modifications in the hydrogen-bonding network within the fiber structure. Furthermore, the bands in the 1159–1028 cm^{-1} region become slightly more pronounced, reflecting contributions from C–

O–C and C–O stretching vibrations of both cellulose and CMC chains. The persistence of the characteristic β-glycosidic band at 896 cm^{-1} indicates that the fundamental cellulose backbone remains preserved after modification, confirming the successful incorporation of CMC into the fiber matrix

Emulsion characterization

Surface charge and particle size

The surface charge and particle size of the prepared emulsions (TUBW and UBW) were determined using dynamic light scattering (DLS), and the results are presented in Table 1. The TUBW emulsion exhibited a smaller particle size (425.5 nm) compared with UBW (822 nm). This reduction in particle size can be attributed to the combined effects of adding an emulsifier and applying ultrasonic treatment during emulsification. In the TUBW method, the emulsifier was added to the hot water–beeswax mixture prior to ultrasonic treatment, allowing it to adsorb at the wax–water interface and reduce interfacial tension. Subsequent ultrasonic treatment facilitated the disruption of larger wax droplets into smaller particles, leading to improved dispersion of the wax phase. In contrast, ultrasonic treatment in the absence of an emulsifier (UBW) resulted in larger particle sizes due to the limited stabilization of the dispersed wax droplets. Zeta potential analysis was conducted to evaluate the surface charge of the emulsion particles. The zeta potential values of TUBW and UBW were −8.4 mV and −2.4 mV, respectively, indicating that both emulsions carried a net negative surface charge. The more negative zeta potential observed for TUBW indicates relatively greater electrostatic repulsion between particles compared with UBW, which may contribute to improved dispersion and reduced particle aggregation in the emulsion system.

Table 1
Surface charge and particle size of TUBW and UBW emulsions measured by DLS

Treatment	Particle size (nm)	ZP (mV)
TUBW	425.5	-8.4
UBW	822	-2.4

Macroscopic and microscopic characterization of emulsions

Macroscopic and microscopic characterizations of the TUBW and UBW emulsions were performed immediately after preparation and after 3 and 10 days of storage, as shown in Figure 2 (a–c). Initially, both emulsions exhibited droplets dispersed within the continuous aqueous phase; however, the TUBW emulsion presented smaller and more uniformly distributed droplets (Fig. 2 a). After 3 days of storage, the TUBW emulsion maintained a relatively homogeneous droplet distribution, indicating a stable microstructure. In contrast, the UBW emulsion began to show signs of destabilization, including droplet aggregation (Fig. 2 b). After 10 days, the TUBW emulsion exhibited only slight localized aggregation, whereas the UBW emulsion showed clear flocculation and noticeable phase separation, as evidenced by both macroscopic and microscopic observations (Fig. 2 c). These results suggest that the TUBW emulsion exhibits improved storage stability compared with UBW, likely due to more effective interfacial stabilization by the emulsifier during the emulsification process.

Physical properties of handsheets: thickness and grammage

As shown in Figure 3, beeswax treatment increased both paper thickness and grammage, with more pronounced effects observed at higher emulsion concentrations. UBW-treated papers generally exhibited greater thickness, whereas TUBW-treated papers showed higher grammage. This difference may be attributed to the presence of Tween 80 in the TUBW emulsion. By reducing interfacial tension, Tween 80 produces finer droplets that interact more effectively with the fiber network. Consequently, a more uniform distribution of wax within the paper structure may contribute to the increased mass per unit area, since grammage represents the mass per unit area of paper.

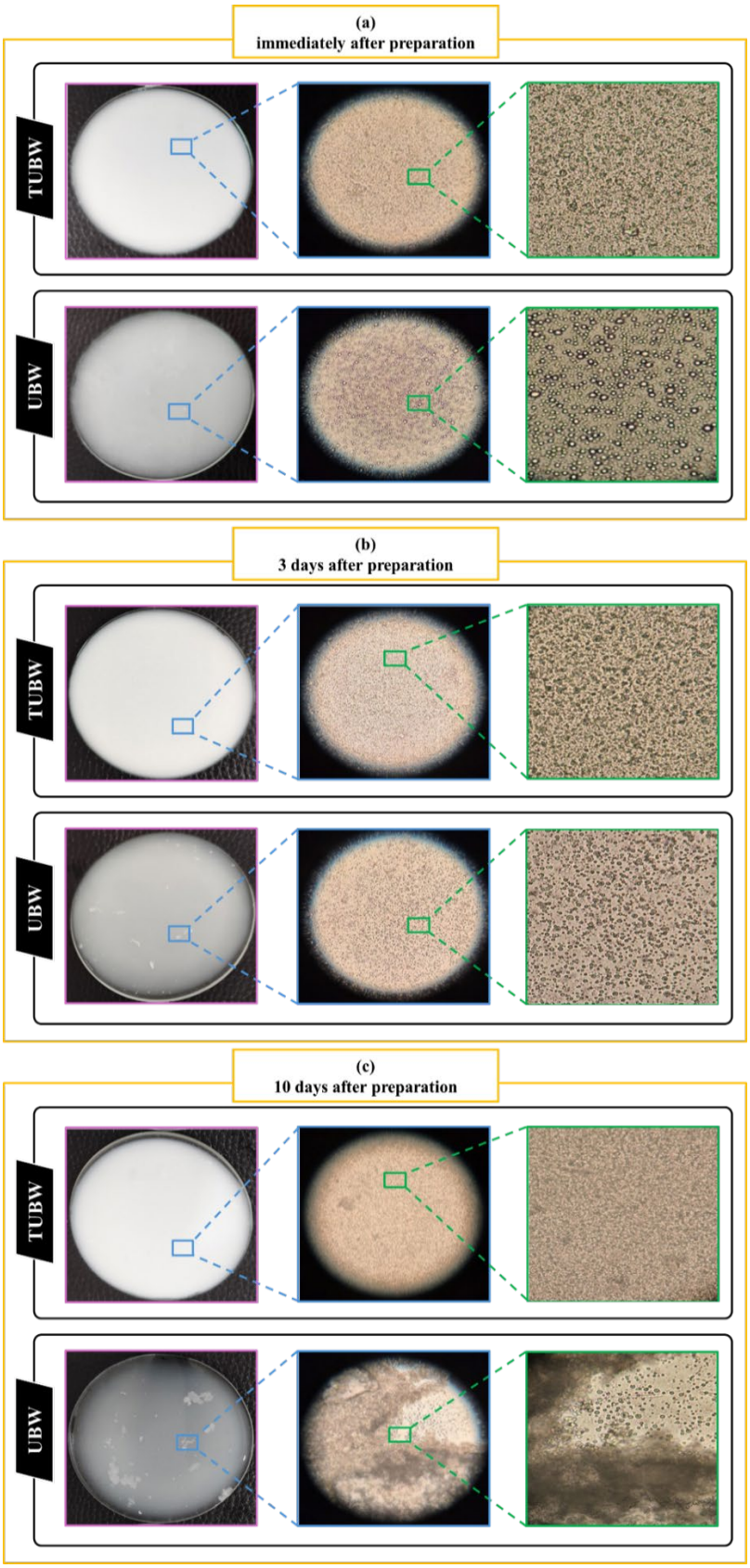


Figure 2: Macroscopic and microscopic images of TUBW and UBW emulsions at different storage times: (a) immediately after preparation, (b) after 3 days, and (c) after 10 days

Coating weight was determined by subtracting the grammage of the uncoated paper from that of the corresponding coated sample. As shown in Table 2, coating weight increased with increasing beeswax concentration in both systems. TUBW consistently achieved higher coating weights than UBW at concentrations of 5–20 wt%, reaching 25.00 g/m² at 20 wt%, compared with 7.29 g/m² for UBW. This difference may be attributed to the presence of Tween 80, which may enhance beeswax dispersion and facilitate its retention within the paper structure.

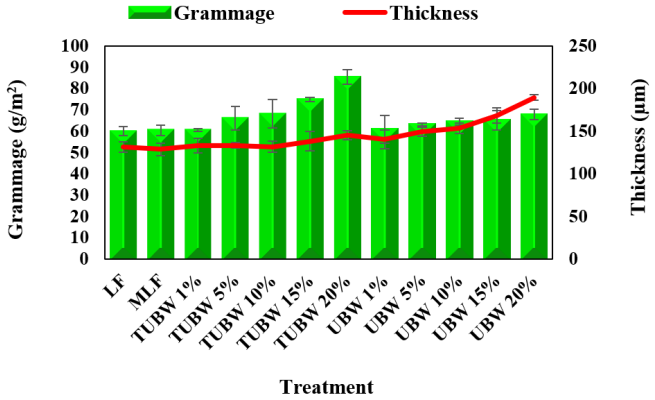


Figure 3: Thickness and grammage of LF, MLF, and papers treated with different concentrations of TUBW and UBW emulsions

Table 2
Coating weight of papers treated with different concentrations of TUBW and UBW emulsions

Beeswax concentration (wt%)	Coating weight (g/m²)	
	TUBW	UBW
1%	0.01	0.41
5%	5.62	2.7
10%	7.7	3.95
15%	14.37	4.58
20%	25	7.29

Optical properties: brightness and opacity

ISO brightness represents the ability of paper to reflect light at a wavelength of 457 nm.[29] As shown in Figure 4, the brightness of MLF paper was slightly higher than that of LF, which can be attributed to the incorporation of CMC, consistent with previous reports indicating that CMC can improve the optical properties of paper.[30] The addition of beeswax emulsions affected brightness differently depending on the formulation. Papers treated with TUBW showed a gradual decrease in brightness with increasing emulsion concentration. This reduction may be associated with the yellowish appearance of Tween 80 and with light absorption and scattering caused by the deposited wax layer. In contrast, UBW-treated papers exhibited only slight variations in brightness compared with the control samples. As illustrated in Figure 4, opacity decreased with increasing TUBW concentration. This behavior may be related to the penetration of wax into the pores and partial filling of surface irregularities, which can reduce internal light scattering within the paper structure and consequently increase transparency. In contrast, treatment with UBW emulsion did not produce a significant change in opacity.

Barrier properties of beeswax-treated papers

WCA and Cobb

Figure 5 presents the WCA and Cobb measurements (Fig. 5a) and the water droplet behavior before (Fig. 5b) and after (Fig. 5c) treatment with the TUBW and UBW hydrophobic emulsions. As illustrated in Figure 5 a-c, LF and MLF papers exhibited pronounced hydrophilicity, with WCA of 31.1° and 18.3°, respectively. The relatively low WCA values are attributed to the abundance of hydroxyl groups present in the cellulose fibers, which promote strong interactions with water. The further decrease observed for MLF can be associated with the presence of carboxymethyl cellulose (CMC), which introduces

additional hydrophilic functional groups on the fiber surface.[31] The application of beeswax emulsions (TUBW and UBW) markedly increased the WCA of the treated papers compared with the untreated MLF sample, indicating a substantial improvement in surface hydrophobicity. For the TUBW series, the WCA increased from approximately 110° to a maximum of about 135° at intermediate concentrations, followed by a slight decrease at the highest concentration. A similar but less pronounced trend was observed for the UBW-treated papers, where WCA values increased to approximately 120 – 125°. Overall, the TUBW-treated samples exhibited higher WCAs than the UBW-treated ones at comparable concentrations.

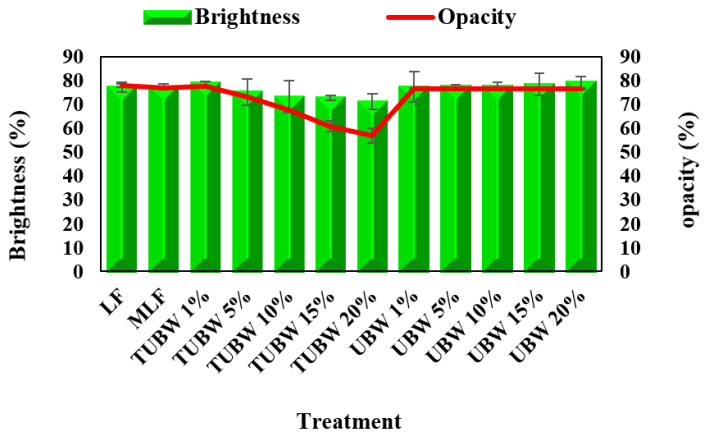


Figure 4: Brightness and opacity of LF, MLF, and papers treated with different concentrations of TUBW and UBW emulsions

Cobb test results (Fig. 5a) showed that the LF and MLF papers exhibited the highest water absorption, with Cobb values of 96.65 ± 0.18 and 96.70 ± 0.10 g/m², respectively. Both wax emulsions substantially reduced water absorption relative to the untreated MLF paper, indicating enhanced water resistance. The reduction in Cobb values was more pronounced for TUBW-treated papers than for UBW-treated papers. The enhancement in hydrophobicity can be attributed to the deposition of beeswax particles on the paper surface, which reduces the surface energy and partially covers the hydrophilic cellulose fibers. Such wax-based coatings are known to impart water-repellent characteristics to paper materials by creating a more hydrophobic surface layer.

Air resistance and water absorption times

Air resistance generally increased with increasing concentrations of TUBW and UBW emulsions (Fig. 6). The immersion treatment promoted the deposition of beeswax on fiber surfaces and partial penetration into inter-fiber voids, which likely reduced pore volume and produced a denser paper structure with fewer air pathways. This interpretation is consistent with the SEM observations and previous reports indicating that hydrophobic coatings can decrease both water and air permeability.[32] The increase in air resistance was more pronounced in TUBW-treated papers than in UBW-treated ones, suggesting that the TUBW formulation produced a more compact surface layer.

As also shown in Figure 6, the application of beeswax emulsions markedly increased the water absorption time compared with the untreated papers. The longest absorption times were observed for the TUBW-treated samples, whereas UBW-treated papers showed a moderate but noticeable improvement. In general, increasing beeswax concentration led to longer water absorption times, which can be attributed to the hydrophobic nature of beeswax that limits water penetration into the paper structure.

Tensile index

Tensile strength is a key parameter for evaluating the maximum stress that paper packaging materials can withstand before failure.[33] As shown in Figure 7, the incorporation of CMC-modified fibers increased the tensile index compared with LF paper. The reinforcing effect of CMC in papermaking has been widely reported.[34] This improvement is generally attributed to enhanced

fiber–fiber bonding and the formation of bridges between adjacent fibers, which increase the effective bonded area within the paper network.[33] In contrast, the treatment of paper with both types of beeswax emulsions led to a gradual decrease in the tensile index as the emulsion concentration increased.

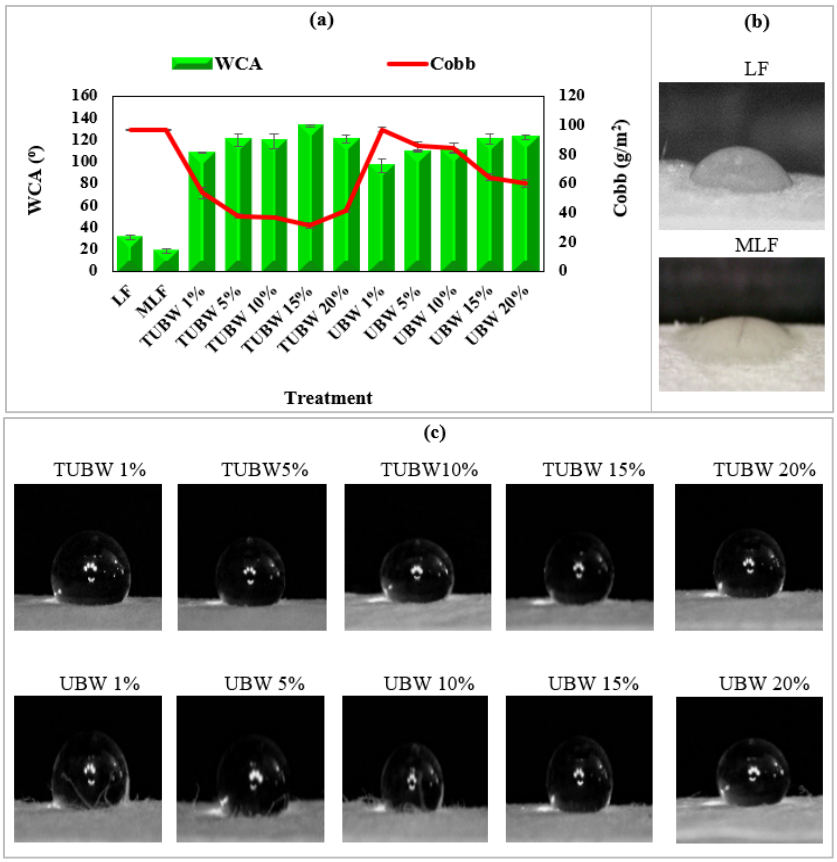


Figure 5: (a) WCA and Cobb measurements; (b) Water droplet behavior before UBW and TUBW treatment, (c) Water droplet behavior after UBW and TUBW treatment

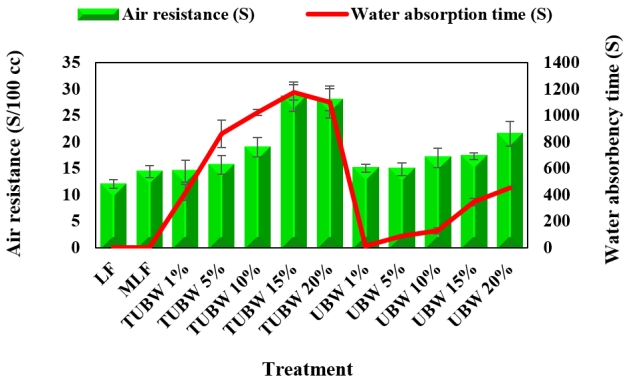


Figure 6: Air resistance and water absorption time of LF, MLF, and MLF papers treated with different concentrations of TUBW and UBW beeswax emulsions

The presence of beeswax particles within the fiber network can weaken inter-fiber bonding by occupying the voids between fibers and forming a thin hydrophobic layer on the fiber surfaces. This low-surface-energy layer limits direct fiber–fiber contact and interferes with the formation or re-establishment of hydrogen bonds during drying, thereby reducing the mechanical strength of the paper.[35] In addition, the immersion process facilitates the penetration of the aqueous emulsion

into the paper structure, which may further disturb the hydrogen-bonding network within the cellulose matrix. These findings are consistent with previous studies reporting that the incorporation of wax generally improves barrier properties while reducing the mechanical strength of cellulose-based materials.[36] For instance, Hendrawati[37] indicated that wax-based coatings typically have limited or slightly negative effects on the bursting, tensile, and tear properties of paper. Moreover, the decrease in tensile index was more pronounced in papers treated with TUBW than in those treated with UBW. This behavior may be related to the greater penetration of the TUBW emulsion into the paper structure, which can more effectively interfere with inter-fiber bonding within the fiber network.

The emulsion concentration of 15% was selected based on the combined evaluation of WCA and tensile strength. For the TUBW emulsion, the 15% concentration exhibited the highest WCA, indicating enhanced surface hydrophobicity. In the UBW emulsion, the difference in WCA between 15% and 20% was relatively small; however, increasing the concentration to 20% resulted in a more pronounced reduction in tensile strength. Therefore, considering the balance between hydrophobicity and mechanical performance, 15% was selected as the most suitable concentration for both emulsions and was used for subsequent comparisons.

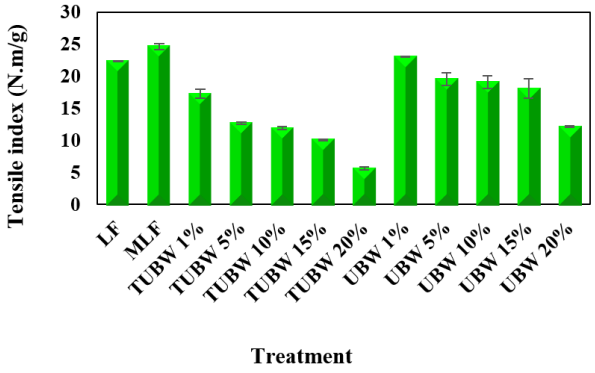


Figure 7: Tensile strength index of LF, MLF, and MLF papers treated with UBW and TUBW beeswax emulsions

SEM and AFM

SEM was used to examine the surface morphology of the prepared handsheets.[32] The SEM micrographs of untreated MLF paper (Fig. 8 a) and papers treated with TUBW (Fig. 8 b) and UBW (Fig. 8 c) emulsions are presented in Figure 8. The untreated MLF paper exhibited a typical fibrous network with a rough surface and visible voids between interlaced fibers. After treatment with beeswax emulsions, the surface morphology changed noticeably, as wax partially filled the pores within the fiber network and covered portions of the fiber surfaces, resulting in a more compact and relatively smoother structure compared with the untreated paper. The differences between the two treatments are related to the dispersion characteristics of the emulsions. Emulsifiers containing both hydrophilic and hydrophobic groups reduce the interfacial tension between wax and water and stabilize the dispersed phase.[38] Consistent with the DLS results, the TUBW emulsion showed a smaller particle size (425.5 nm) than the UBW emulsion (822 nm), indicating a finer dispersion. The smaller wax droplets in the TUBW system likely facilitated better penetration and more uniform distribution within the porous paper structure, whereas the larger and less stable droplets in the UBW emulsion tended to aggregate and remain on the surface, forming localized wax clusters.

AFM analysis further supported these observations in Table 3. The untreated MLF paper exhibited the highest surface roughness (Ra = 43.33 nm; RMS = 57.17 nm), while the roughness decreased after wax treatment to 19.05 nm (Ra) and 21.88 nm (RMS) for TUBW and to 37.33 nm (Ra) and 44.52 nm (RMS) for UBW. This reduction in roughness is attributed to wax deposition within surface depressions and partial coating of the fiber surfaces, with TUBW producing a more homogeneous and smoother surface than UBW.

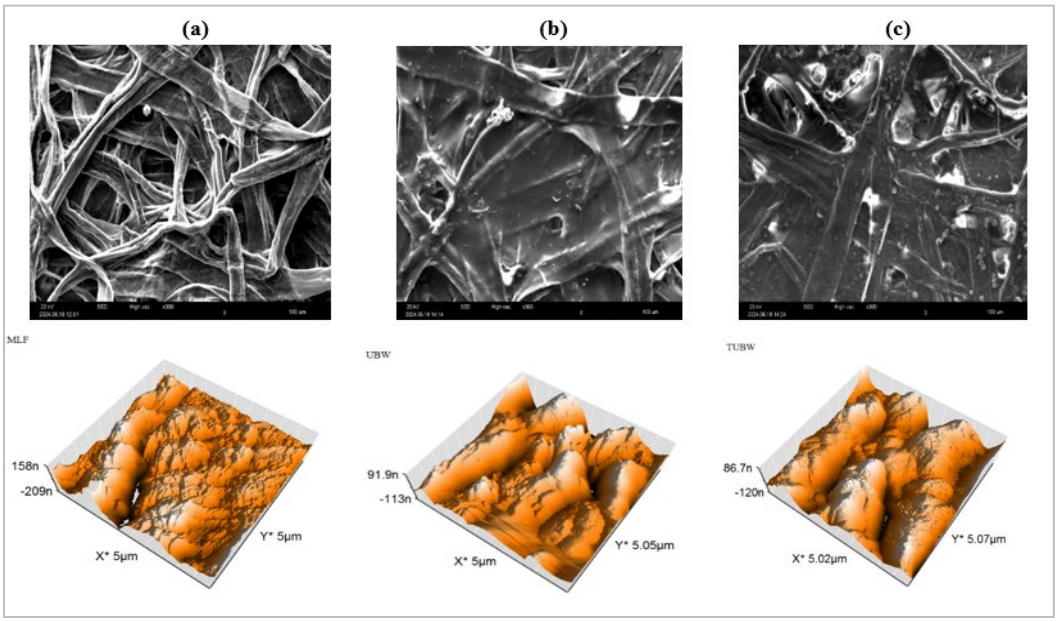


Figure 8: SEM and 3-dimensional AFM of untreated MLF handsheets (a) and handsheets treated with 15% TUBW (b) and treated with UBW emulsions (c)

Table 3
Ra and RMS of untreated and treated handsheets with 15% TUBW and UBW emulsions

Sample	Ra (nm)	RMS (nm)
MLF	43.33	57.174
TUBW	19.05	21.88
UBW	37.33	44.52

CONCLUSION

This study demonstrated that beeswax-in-water emulsions can be effectively utilized as sustainable hydrophobic coatings for cellulose-based paper packaging through a simple dip-coating process under ambient conditions. Comparative evaluation showed that the surfactant-assisted system (TUBW) produced finer and more stable emulsions than the surfactant-free system (UBW), resulting in more homogeneous wax distribution across the paper surface. The improved dispersion characteristics of TUBW contributed to superior hydrophobicity, enhanced air resistance, prolonged water absorption time, and a smoother surface morphology, as confirmed by WCA, SEM, and AFM analyses. Although both coating systems caused a reduction in tensile strength due to partial disruption of inter-fiber hydrogen bonding, optimization of coating concentration indicated that 15 wt% provided the most appropriate balance between barrier performance and mechanical properties. The findings highlight the potential of beeswax emulsions as bio-based alternatives to conventional petroleum-based coatings for paper applications.

REFERENCES

[1] L. Abenghal, J. Bley, B. Tolnai, G. Njamen and B. Chabot, *Future Foods*, **11**, 100540 (2025), https://doi.org/10.1016/j.fufo.2025.100540
[2] S. Basak, M. S. Dangate and S. Samy, *Prog. Org. Coat.*, **186**, 107938 (2024), https://doi.org/10.1016/j.porgcoat.2023.107938
[3] R. V. Gadhave, C. R. Gadhave and P. V. Dhawale, *Green Sustain. Chem.*, **12**, 9 (2022), https://doi.org/10.4236/gsc.2022.122002
[4] V. K. Rastogi and P. Samyn, *Coatings*, **5**, 887 (2015), https://doi.org/10.3390/coatings5040887
[5] D. Wang, J. Huang, Z. Guo and W. Liu, *J. Mater. Chem. A*, **9**, 1495 (2021), https://doi.org/10.1039/D0TA10638K
[6] K. Arunprasath, P. Senthamaraikannan, I. Suyambulingam, T. Y. Gowda, S. Avudaiappan *et al.*, *Int. J. Biol. Macromol.*, **338**, 149642 (2025), https://doi.org/10.1016/j.ijbiomac.2025.149642
[7] G. Chen, J. Qian, Y. Bei, Z. Qi, D. Cianciosi *et al.*, *Bee Products–Chem. Biol. Prop.*, 495 (2025), https://doi.org/10.1007/978-3-031-89049-9

[8] Y. Zhang and W. Zhang, *Biomater. Sustain. Food Packag.*, 327 (2026), https://doi.org/10.1007/978-3-032-08027-1_11
[9] M. Kumari, S. Kodan and I. Khangwal, *Trends Edible Packag.*, 107 (2026), https://doi.org/10.1007/978-3-032-13199-7_4
[10] K. Ren, T. Fei, K. Metzger and T. Wang, *Ind. Crop. Prod.*, **140**, 111654 (2019), https://doi.org/10.1016/j.indcrop.2019.111654
[11] P. Bian, Y. Dai, X. Qian, W. Chen, H. Yu *et al.*, *RSC Adv.*, 4, 52680 (2014), https://doi.org/10.1039/C4RA08437C
[12] J. Chungsiriporn, P. Khunthongkaew, Y. Wongnoipla, A. Sopajarn, S. Karrila *et al.*, *Ind. Crop. Prod.*, **177**, 114541 (2022), https://doi.org/10.1016/j.indcrop.2022.114541
[13] D. Zhang and H. Xiao, *ACS Appl. Mater. Interfaces*, **5**, 3464 (2013), https://doi.org/10.1021/am400585m
[14] J. Wan, P. Wang, X. Qian, M. Zhang, S. Song *et al.*, *ACS Sustain. Chem. Eng.*, **8**, 9906 (2020), https://doi.org/10.1021/acssuschemeng.0c03187
[15] D. Liu, Y. Duan, S. Wang, M. Gong and H. Dai, *Polymers*, **14**, 1786 (2022), https://doi.org/10.3390/polym14091786
[16] G. Bayés, R. J. Aguado, Q. Tarrés, J. Planella and M. Delgado-Aguilar, *Nanomaterials*, **13**, 2353 (2023), https://doi.org/10.3390/nano13162353
[17] R. Mu, X. Hong, Y. Ni, Y. Li, J. Pang *et al.*, *Trends Food Sci. Technol.*, **93**, 136 (2019), https://doi.org/10.1016/j.tifs.2019.09.013
[18] T. Fei, J. A. Walker, K. L. Vickerman, L. M. Stanley, D. Jarboe *et al.*, *J. Ind. Eng. Chem.*, **58**, 113 (2018), https://doi.org/10.1016/j.jiec.2017.09.015
[19] M. Daizy, Y. Zhang, D. W. Bousfield, L. Li, J. Wang *et al.*, *Sustainability*, **18**, 852 (2026), https://doi.org/10.3390/su18020852
[20] S. Naderizadeh, J. A. Heredia-Guerrero, G. Caputo, S. Grasselli, A. Malchiodi *et al.*, *Adv. Mater. Interfaces*, **6**, 1801782 (2019), https://doi.org/10.1002/admi.201801782
[21] W. Zhang, P. Lu, L. Qian and H. Xiao, *Chem. Eng. J.*, **250**, 431 (2014), https://doi.org/10.1016/j.cej.2014.04.050
[22] O. Kaczerewska, R. Martins, J. Figueiredo, S. Loureiro and J. Tedim, *J. Hazard. Mater.*, **392**, 122299 (2020), https://doi.org/10.1016/j.jhazmat.2020.122299
[23] L. Bai, Y. Zhang, C. Zhang, Y. Lu, Z. Li *et al.*, *J. Pharm. Biomed. Anal.*, **233**, 115496 (2023), https://doi.org/10.1016/j.jpba.2023.115496
[24] L. Liu, J. Niu and J. Y. Wu, *J. Mol. Liq.*, **380**, 121776 (2023), https://doi.org/10.1016/j.molliq.2023.121776
[25] T. Wu and R. Farnood, *Carbohyd. Polym.*, **114**, 500 (2014), https://doi.org/10.1016/j.carbpol.2014.08.053
[26] P. Vaithanomsat, K. Kongsin, C. Trakunjae, J. Boonyarit, A. Jarerat *et al.*, *Polymers*, **13**, 1733 (2021), https://doi.org/10.3390/polym13111733
[27] P. Laddawan, S. Auecharoenrat and C. Tongsook, *ACS Omega*, **10**, 17296 (2025), https://doi.org/10.1021/acsomega.4c09928
[28] O. Chand, L. Chopra, N. N. Raju, N. Asthana, A. Malik *et al.*, *J. Mol. Struct.*, **1319**, 139325 (2025), https://doi.org/10.1016/j.molstruc.2024.139325
[29] A. K. Bharimalla, S. Patil, J. Dhakane-Lad, M. K. Mahawar, V. Nadanathangam *et al.*, *Sci. Rep.*, **15**, 11788 (2025), https://doi.org/10.1038/s41598-025-96213-1
[30] H. Mousavipazhouh, M. Azadfallah and I. R. Jouybari, *Maderas Cienc. Tecnol.*, **20**, 703 (2018), https://doi.org/10.4067/S0718-221X2018005041601
[31] M. Akbari, E. Afra, S. M. Zabihzadeh and M. D. Firouzabadi, *J. Polym. Res.*, **32**, 403 (2025), https://doi.org/10.1007/s10965-025-04626-3
[32] J. Iewkittayakorn, P. Khunthongkaew, Y. Wongnoipla, K. Kaewtatip, P. Suybangdum *et al.*, *J. Mater. Res. Technol.*, **9**, 5056 (2020), https://doi.org/10.1016/j.jmrt.2020.03.023
[33] Y. He, H. Li, X. Fei and L. Peng, *Carbohyd. Polym.*, **252**, 117156 (2021), https://doi.org/10.1016/j.carbpol.2020.117156
[34] A. Strand, A. Khakalo, J. Kouko, A. Oksanen, A. Ketola *et al.*, *Nord. Pulp Pap. Res. J.*, **32**, 324 (2017), https://doi.org/10.3183/NPPRJ-2017-32-03-p324-335
[35] H. Li, Y. He, J. Yang, X. Wang, T. Lan *et al.*, *Carbohyd. Polym.*, **211**, 22 (2019), https://doi.org/10.1016/j.carbpol.2019.01.107
[36] H. Li, J. Yang, P. Li, T. Lan and L. Peng, *Carbohyd. Polym.*, **160**, 9 (2017), https://doi.org/10.1016/j.carbpol.2016.12.018
[37] N. Hendrawati, A. A. Wibowo, R. D. Chrisnandari and R. Adawiyah, *IOP Conf. Ser. Mater. Sci. Eng.*, **1073**, 012006 (2021), https://doi.org/10.1088/1755-1315/1446/1/012006
[38] C. K. Saurabh, S. Gupta, P. S. Variyar and A. Sharma, *Ind. Crop. Prod.*, **89**, 109 (2016), https://doi.org/10.1016/j.indcrop.2016.05.003