Preparation of Water-Based Alkyl Ketene Dimer (AKD) Nanoparticles and Their Use in Superhydrophobic Treatments of Value-Added Teakwood Products

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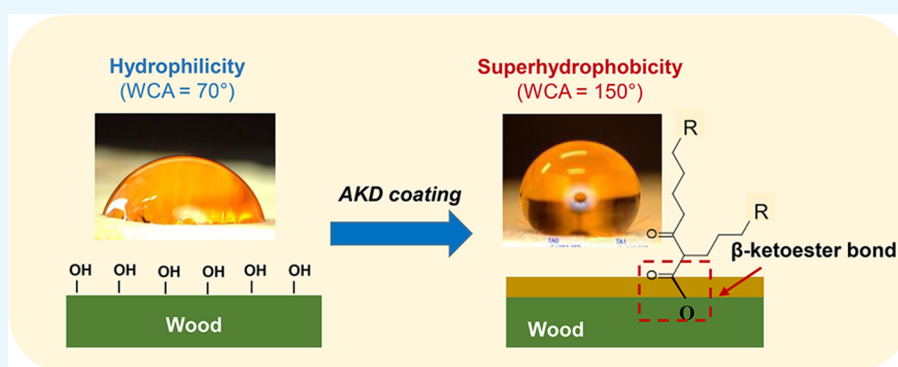
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ABSTRACT: A process for preparing emulsions of alkyl ketene dimer (AKD) nanoparticles *via* a nanoemulsion template (emulsion/evaporation) method has been developed. The effects of types and contents of stabilizing agents, *i.e.*, anionic (sodium dodecyl sulfate, SDS), cationic (cetyltrimethylammonium bromide, CTAB), amphoteric (phosphatidylcholine, PC), and polymeric (poly(vinyl alcohol), PVA), on the colloidal stability and hydrodynamic size of the AKD nanoparticles are investigated. The use of 0.1 wt % anionic SDS as a stabilizer generates nanoparticles with high stability and the smallest average size of 148 ± 5 nm. The environmentally friendly water-based emulsion prepared without halogenated compounds and harsh organic solvents is then applied to enhance the hydrophobicity of teakwood products by a simple dipping process. The properties and structures of the resulting treated woods are examined by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM), and water contact angle (WCA) measurements. The treated woods show superhydrophobicity with a WCA value of $150 \pm 2°$, as the emulsion generates a hydrophobic layer covering the wood surfaces due to the β-ketoester bond formation and the arrangement of AKD hydrophobic tails. The nanosized nanoparticles can penetrate the dense structure of the teakwood and form similar bonding for up to a 0.8 mm depth, generating a protective water-repellent layer in the wood structure. The emulsion has high potential for use in the commercial production of value-added teakwood products, with excellent water-resistant properties and high dimensional instability, without altering their physical appearances.

1. INTRODUCTION

Wood materials have been widely used in various applications, such as construction, furniture, and indoor decorations, due to their high strength, ease of fabrication, low price, and renewability. Teakwood (*Tectona grandis*) is one of the most economically important timbers in the Southeast Asian region. It is a high-value hardwood with excellent physical properties, durability, and a good aesthetic. Due to the increasing demand, most teakwood products have been fabricated from shorter cutting cycles (7−15 years).[1,2] The high proportion of juvenile teakwood, however, adversely affects the production process, wood properties, and end-product value. An important physical property of teakwood that strongly influences its product quality is surface wettability. This complex phenomenon is related to

various factors, *e.g.*, cell morphology, roughness, specific surface area, permeability, functional groups, and molecular and elemental compositions.[3] Its porous structures on the surface and high contents of hydroxyl groups adversely lead to increased water absorption, which can cause swelling, dimensional instability, cracking, and degradation of the wood. To solve this problem, many studies have focused on chemical

modifications of the wood structures by converting their hydrophilic surfaces using hydrophobic compounds, endowing the wood materials with water resistance and prolonged service life.[4−6]

Superhydrophobic surfaces have aroused enormous interest in various applications due to their high water-repellent, self-cleaning, antipollution, and anticorrosion properties. Wood materials could be used in broader applications, and their service life would be further prolonged with the properties of superhydrophobicity. For example, Cai et al. developed wood products with superhydrophobic surfaces using lauryl aldehyde and lauric acid organic reagents.[7] A silane hierarchical structure was first created on the wood surface by immersion in a solution of γ-aminopropyltriethoxysilane and lauryl aldehyde and/or lauric acid, leading to chemical bond formation. The products possessed superhydrophobicity (water contact angle > 150°) and improved stability when exposed to aggressive media, *e.g.*, acidic or basic corrosive solutions, organic solvents, and simulated seawater. Other hydrophobic organic compounds, such as fluoro-containing silica,[8] perfluoroalkyltriethoxysilane,[9] and potassium methyl siliconate,[10] were also applied in the superhydrophobic treatments of wood surfaces. However, the treatments often involve extensive chemical processing or the use of organic solvents for dispersing hydrophobic agents in solvents or an aqueous medium. Their commercial use is therefore restricted due to both environmental and consumer safety concerns. Although water-based systems are more environmentally friendly, hydrophobic agents generally do not readily disperse in water. It is challenging in terms of material selection to find suitable candidates that possess both sufficient water-repellent characteristics and processing feasibility.

Alkyl ketene dimer (AKD) is a water-insoluble solid with a melting temperature ranging between 40 and 60 °C. It is a widely used neutral sizing chemical in the papermaking industry, as the compound decreases the rate of aqueous liquid penetration into papers.[11−13] The compound possesses one unsaturated β-lactone ring and 16−18 carbons of the alkyl groups. Its β-lactone ring can readily react with hydroxyl groups of cellulose to form a β-ketoester bond, enabling its hydrophobic tails to arrange into hydrophobic domains. In the presence of water, however, the reactivity of AKD with water is faster than with hydroxyl groups, generating dialkylketone with no or low internal sizing ability, *i.e.*, the ability of additives to facilitate the water-resistant protection of a paper's surface.[14,15] Most attention in the industrial sector is given to preparing AKD in the form of emulsions.[16] Owing to a solid dictating nature of AKD, emulsion can be formed above its melting temperature in the presence of surfactants. After cooling to room temperature, liquid AKD droplets become solid particles that engage in a solid−water interfacial interaction for sizing. Cationic starch and its derivative, natural polymer surfactants, are the most widely used for emulsifying AKD.[17] However, the aqueous solutions with high density will inevitably increase the viscosity of AKD emulsions. Recently, there exists an opportunity to prepare Pickering (particle)-stabilized AKD dispersions, which may avoid the adverse effect of surfactant on emulsion properties.[18−20] Yang et al. employed nanocrystalline cellulose (NCC) as a stabilizer to prepare AKD emulsions *via* a physical blending method to produce surface-sized papers with multiple-barrier properties.[19] The particle size and ζ potential of AKD/NCC emulsions were ∼5 μm and −50 mV, respectively. After the surface-sized papers were heated, NCC formed a coating layer with water and air resistance properties. Similarly, Li et al.

prepared AKD emulsions having uniform droplets with an average size in a range of >2 μm using layered double hydroxide (LDH) particles modified with the glutamic acid (Glu) stabilizer.[21] Using Glu-modified LDH nanoparticles, the storage stability of the AKD emulsion and its sizing performance on papers were significantly improved. Although small solid particles can act as an effective stabilizer for AKD emulsions, surface modification of the particles before use is still needed. Moreover, the particle size of these AKD emulsions (particles) is large in the range of micrometric size, resulting in the limited use of AKD particles in some applications.

A nanoemulsion with droplet size in the nanoscale (typically 20−200 nm) is a versatile system for preparing nanoparticles. An oil-in-water nanoemulsion system is effective and convenient for encapsulating poorly water-soluble (hydrophobic) compounds and improving their delivery through the water-based system.[22,23] These are mainly applied in various drug delivery systems.[24,25] The advantages of this system are penetration ability because of their nanometric size, protection of compounds from environmental degradations, and preparation using single facile scalable and cost-effective methodologies. A nanoemulsion is prepared by mixing two immiscible liquids with the application of a high shear force and a stabilizing agent. Ultrasonic emulsification is a highly effective process in reducing the size of the liquid droplets. Stabilizing agents can be of different chemical natures. However, the compounds share a common feature, *i.e.*, the presence of hydrophobic and hydrophilic parts in their structures. These allow the molecules to be placed at the droplet interface, stabilizing the system, and avoiding phase separation. When an active compound is introduced into a water-based nanoemulsion system, it is commonly added in the dispersed oil phase. A few studies have been reported on preparing AKD nanoemulsions, such as Missoum et al.[26] The prepared AKD nanoemulsion was then used to modify nanofibrillated cellulose. However, the formation mechanism of the nanoemulsion was not discussed.

In this work, a process for preparing environmentally friendly water-based AKD nanoparticles is developed by a nanoemulsion template method for use in the fabrication of value-added wood products with superhydrophobic surfaces. The effect of types of stabilizing agents, *i.e.*, anionic (sodium dodecyl sulfate, SDS), cationic (cetyltrimethylammonium bromide, CTAB), amphoteric (phosphatidylcholine, PC), and polymeric (poly(vinyl alcohol), PVA), on the stability of the emulsion and hydrodynamic size of the AKD nanoparticles are systematically examined. The emulsion is then used in the treatments of juvenile teakwood samples *via* a simple dipping process, whose degree of hydrophobicity enhancement is reviewed. The cleavage ability of different stabilizing agents on the AKD nanoparticles, the adsorption mechanisms between the AKD nanoparticles and the teakwood surface, the durability and penetration ability of the AKD nanoparticles into the teakwood structure are evaluated.

2. EXPERIMENTAL SECTION

2.1. Materials. Alkyl ketene dimer (AKD) and chloroform (LabScan, AR), poly(vinyl alcohol) (PVA, M_w = 30,000−70,000 g/mol, Sigma-Aldrich), sodium dodecyl sulfate (SDS, Carlo Erba Reagent), hexadecyltrimethylammonium bromide (CTAB, Acros, Organics), phosphatidylcholine (PC, Acros, Organics), and *n*-hexane (Carlo Erba Reagent) were used as received. Juvenile teakwood samples were obtained from a local

Scheme 1. Summary of the Preparation of AKD Nanoparticles *via* a Nanoemulsion Template (Emulsion/Evaporation) Method and the Wood Treatment Process
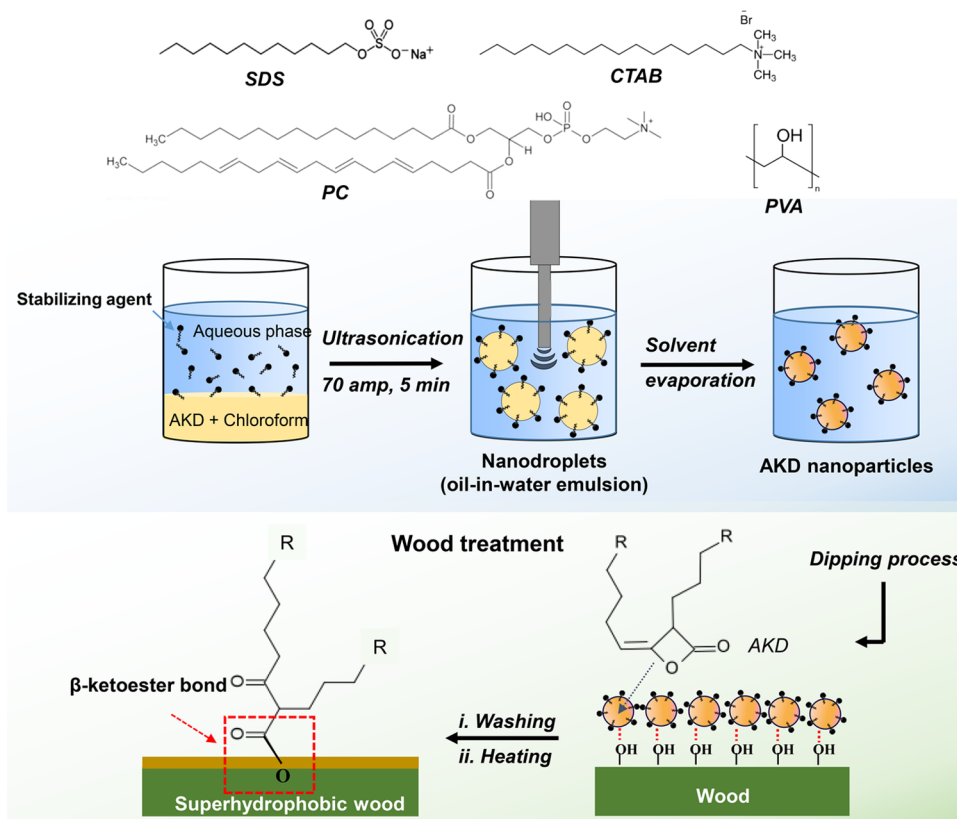
plantation in Thailand. Deionized (DI) water was used throughout the work.

2.2. Preparation and Characterization of AKD Nanoparticles. AKD pellets (7.0 g) were dissolved in chloroform (10.0 mL). In parallel, four surfactants, *i.e.*, SDS, CTAB, PC, and PVA (1.0 g), were separately dissolved in DI water (10.0 mL). The AKD solution (1.0 mL) was then poured into the aqueous phase containing the surfactant (10.0 mL). The mixture was emulsified by ultrasonication (Ultrasonic homogenizer, Branson Sonifier, 550 W, 20 kHz, tip diameter 5.6 mm) at 70% amplitude for 5 min. The as-prepared emulsion was stirred overnight in a fume hood to evaporate the solvent, leaving AKD nanoparticles suspended in the aqueous medium. The hydrodynamic diameter (D_h) and ζ potential of the AKD nanoparticles were measured using a Zetasizer (Malvern, Nano ZS). The measurement was repeated three times. The morphology of the nanoparticles was examined by scanning electron microscopy (SEM, JSM 7800F).

2.3. Treatments of Wood Samples. Teakwood samples were cut into a specimen size of $25 \times 25 \times 2$ mm^3. The specimens were polished with sandpaper, rinsed with DI water, and ultrasonically degreased in acetone for 15 min. After drying, the samples were immersed into the AKD nanoparticles dispersion for 5 h at 60 °C. The samples were finally rinsed with DI water three times before heating at 110 °C for 5 h. The reaction between AKD and the hydroxyls of cellulose occurred at these two treatment steps.

2.4. Characterization and Stability Testing. The water-repellent property of the treated wood samples was examined by measuring their water contact angle (WCA). A water droplet was dropped onto the wood's surface, whose picture was recorded on a Dino-Lite microscope at ambient temperature.

The ImageJ program was then employed to calculate its WCA value. An average value calculated from the measurements at five different spots was reported. Fourier transform infrared (FTIR) spectroscopy was utilized to analyze the chemical bonding between AKD and the cellulose structure of the wood samples. The measurements were recorded in an attenuated total reflection (ATR) mode (Nicolet iS5, Thermo Scientific). The morphology of the treated wood surfaces was observed by scanning electron microscopy (SEM). As free AKD is dissolved in *n*-hexane, the stability of the superhydrophobicity of the treated woods was evaluated by extraction with the solvent to verify chemical bonding formation. The wood samples were immersed in *n*-hexane at different times, *e.g.*, 30, 60, 90, and 120 min. The samples were then dried at 100 °C for 3 h, and their properties were re-examined.

3. RESULTS AND DISCUSSION

A facile nanoemulsion template (emulsion/evaporation) method has been developed to prepare AKD nanoparticles in water-based emulsions, with precise control of the particle size and homogeneous size distribution.[27] The resulting emulsions were employed in the teakwood treatments by a simple dipping process, leading to superhydrophobic surfaces and prolonged service life of the woodwork products. The preparation of AKD nanoparticles and the teakwood treatment processes are summarized in Scheme 1. AKD was first dissolved in chloroform and then emulsified in an aqueous solution containing a specific stabilizing agent, *i.e.*, anionic (SDS), cationic (CTAB), amphoteric (PC), or polymeric (PVA). Chloroform (solubility parameter, $\delta = 19.0$ MPa$^{1/2}$) was used as a solvent to dissolve the AKD wax ($\delta = 16.6$ MPa$^{1/2}$).[28,29] Ultrasonication was applied to

Table 1. Summary of the Average Size, Polydispersity Index (PDI), and ζ Potential Values of AKD Nanoparticles Prepared by Different Stabilizing Agents

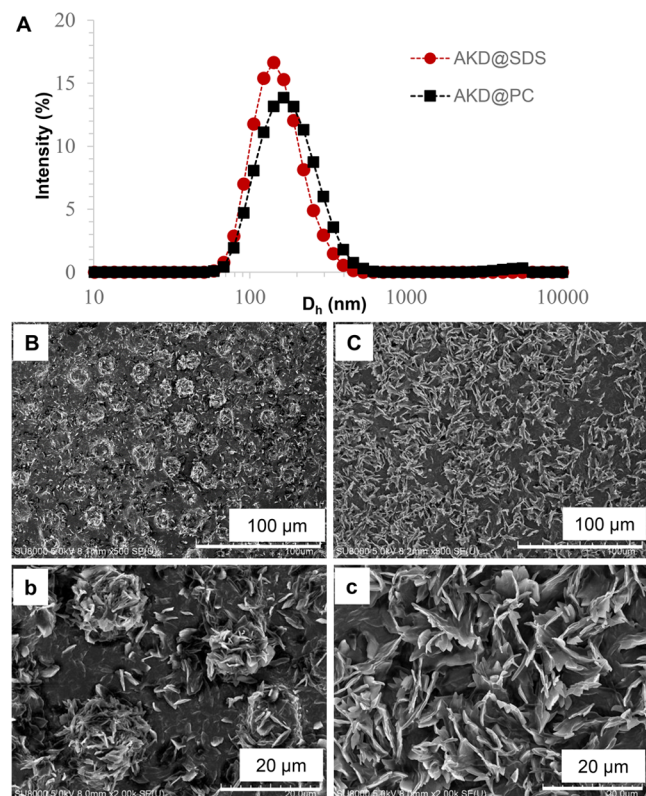| samples	surfactants		D_h (nm)	PDI	ζ potential (mV)
	type	content (wt %)			
AKD@SDS	SDS	0.1	148 ± 5	0.14	−40.0 ± 1.2
AKD@SDS-1	SDS	1.0	201, 880	0.37	N/A
AKD@CTAB	CTAB	1.0	331 ± 37	0.36	22.6 ± 0.5
AKD@PC	PC	1.0	168 ± 7	0.16	−31.3 ± 1.7
AKD@PVA	PVA	1.0	378 ± 11	0.22	−20.9 ± 2.1

Figure 1. Particle size distribution (A) and SEM images of AKD@SDS (B, b) and AKD@PC (C, c).
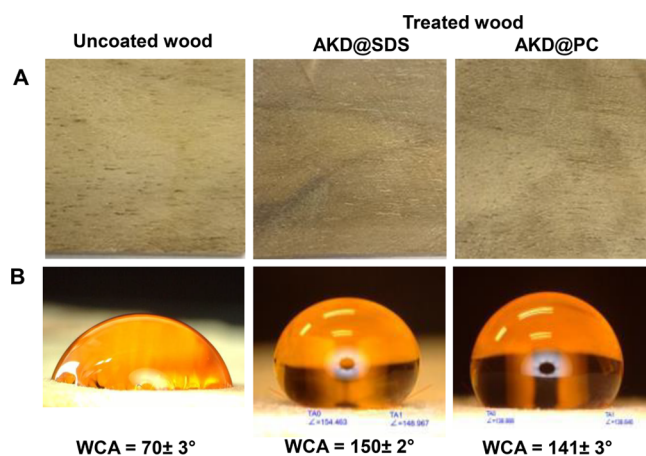

Figure 2. Appearance (A) and WCA (B) of teakwood samples before and after treating with AKD@SDS and AKD@PC emulsions.

generate stable AKD oil droplets or oil-in-water emulsions. Chloroform was subsequently evaporated in a fume hood overnight. Stable solid AKD nanoparticles or water-based emulsions were obtained. In the superhydrophobic treatment of the wood products, the teakwood samples were immersed in the water-based AKD nanoparticles for the desired time. After washing and heating, the AKD molecules reacted with the cellulose structure of the wood samples. This led to the formation of β-ketoester bonds due to the reaction between the lactone ring of AKD and the −OH groups of cellulose.[13,30,31] The wood products with superhydrophobic or water-repellent properties were finally obtained.

3.1. Preparation of AKD Nanoparticles. For the preparation of stable AKD nanoparticles, a water-based emulsion method is employed using different stabilizing agents, *i.e.*, anionic (SDS), cationic (CTAB), amphoteric (PC), and polymeric (PVA). The hydrodynamic diameter (D_h), size distribution, and ζ potential of the resulting nanoparticles were determined, as summarized in Table 1.

According to the nanoemulsion principle, the stability and diameter of nanodroplets or nanoparticles are strongly influenced by the content of the stabilizing agent, the oil/water phase ratio, and the ultrasonic parameters, *e.g.*, amplitude and time.[27] To study the effect of types of stabilizing agents on the stability and D_h of the AKD nanoparticles, other preparation parameters were fixed at 1.0 wt % stabilizing agent of DI water, 1:10 ratio of oil/water, 70% amplitude, and 5 min sonication time. In the SDS system (AKD@SDS-1), the nanoparticles possess a broad bimodal size distribution at approximately 201 and 880 nm. This is likely because the concentration of SDS is higher than that of its critical micellization concentration (CMC), resulting in the formation of micelles and connected structures with complex and rich topologies.[32] When the concentration of SDS (0.1 wt %) was decreased to lower than its CMC, the nanoparticles with monodispersity (PDI = 0.14) and an average size of 148 ± 5 nm were obtained, as denoted by AKD@SDS. The AKD nanoparticles stabilized by anionic SDS showed high stability, without agglomeration for several weeks. This is confirmed by their high negative ζ potential value of at least −40 mV due to the presence of sulfate groups of the SDS molecules.

In contrast, using cationic CTAB as a stabilizer at a concentration of 1.0 wt % produced AKD nanoparticles (AKD@CTAB) with an average size of 331 ± 37 nm and broad size distribution (PDI = 0.36). However, when a high concentration of CTAB above its CMC (0.95 mmol L$^{−1}$)[33] was employed, the bimodal size distribution could not be seen in the AKD@CTAB system. It was reported that the droplet sizes of nanoemulsions with CTAB were smaller than that of nanoemulsions with SDS due to the different amounts and structures of CTAB and SDS micelles. The CTAB structure consists of longer hydrocarbon chains ($C_{16}H_{33}$) than SDS ($C_{12}H_{25}$) and favors micelle formation due to stronger hydrophobic−hydrophobic interaction between the nonpolar hydrophobic groups. This can accommodate more oil molecules in one micelle, resulting in a better solubilization capacity for oil molecules.[33,34] In this work, a nanoemulsion with different droplet sizes is produced after the ultrasonic emulsification due to the utilization of a high concentration of CTAB (>its CMC). This is likely due to the high miscibility of the long hydrocarbon chains of CTAB and the hydrophobic tails of AKD in each droplet. As a result, varied amounts of AKD may be present in different droplets. After solvent evaporation, each particle could
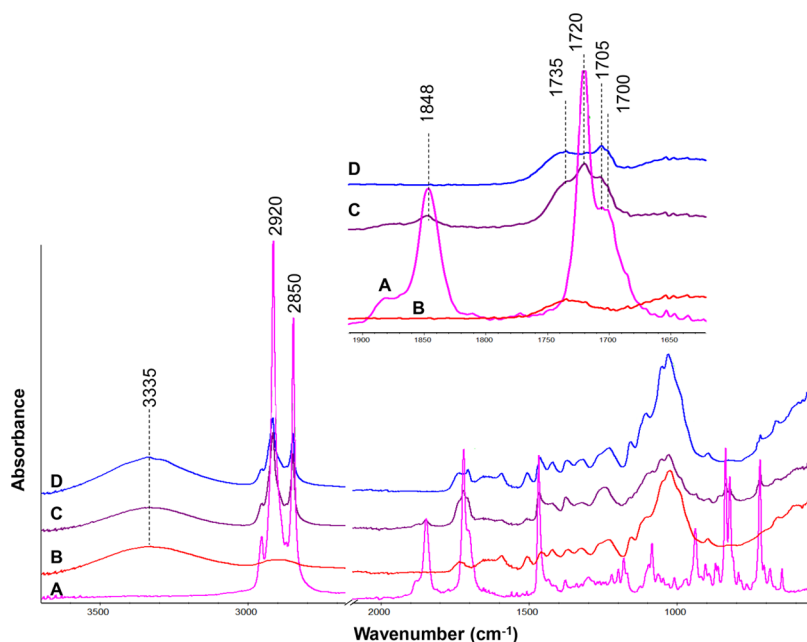
Figure 3. FTIR spectra of neat AKD (A), untreated teakwood (B), and teakwood samples treated with AKD@SDS (C) and AKD@PC (D).
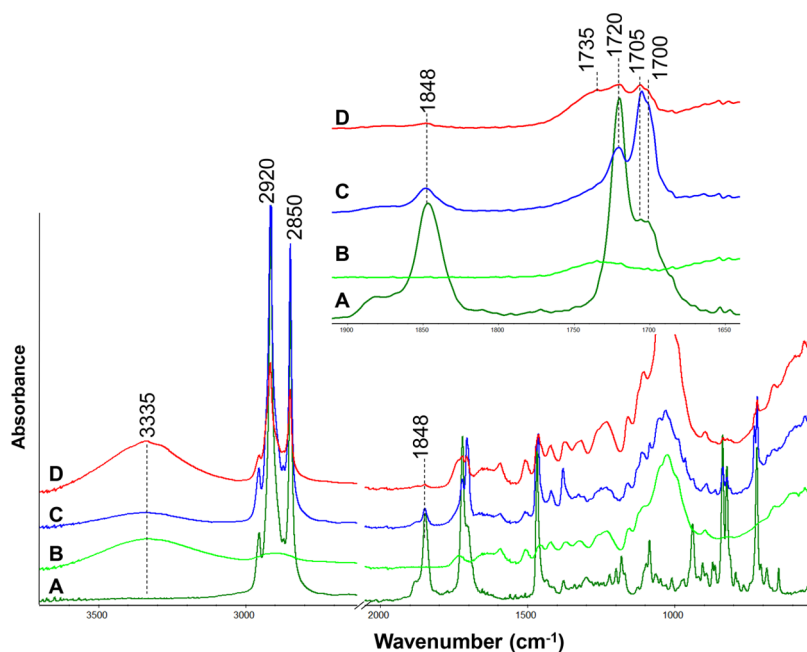

Figure 4. FTIR spectra of neat AKD (A), untreated teakwood sample (B), and treated woods after submerging into AKD@SDS dispersion (C) and after drying at 110 °C (D).

maintain its shape and size, leading to the broad size distribution of AKD nanoparticles. However, the dispersing stability of the particles was also low. When kept at room temperature for 3 days, the aggregation of the particles was observed. This agrees well with their low ζ potential value of 22.6 mV.[35,36] Using PC as a stabilizer, monodispersed AKD nanoparticles (AKD@PC) having an average diameter of 168 ± 7 nm were produced. The ζ potential of the nanoparticles exhibited a negative character at the as-prepared pH of 7.5, due to the domination of phosphate moieties of PC with imparted particle stability, on the nanoparticle surfaces. The phosphocholine polar head is a zwitterion at pHs between 3 and 11. In this pH range, the phosphate group of the polar head has a net negative charge, while the choline group $[-N^+(CH_3)_3]$ has an equal positive charge with spatial separation.[37] The application of PVA as a polymeric stabilizer significantly increased the average size of the obtained AKD nanoparticles (AKD@PVA) to 378 ± 11 nm. This behavior can be explained based on the tendency of PVA molecules to adsorb onto the particle surface as a multilayer and, hence, promote an efficient emulsification process.[38,39] The high PDI value (0.22) indicates a broad size distribution of the final particles. This result is similar to a previous study when PVA was used as a stabilizing agent in a miniemulsion/solvent evaporation process to prepare magnetic polymeric nano-particles.[40]
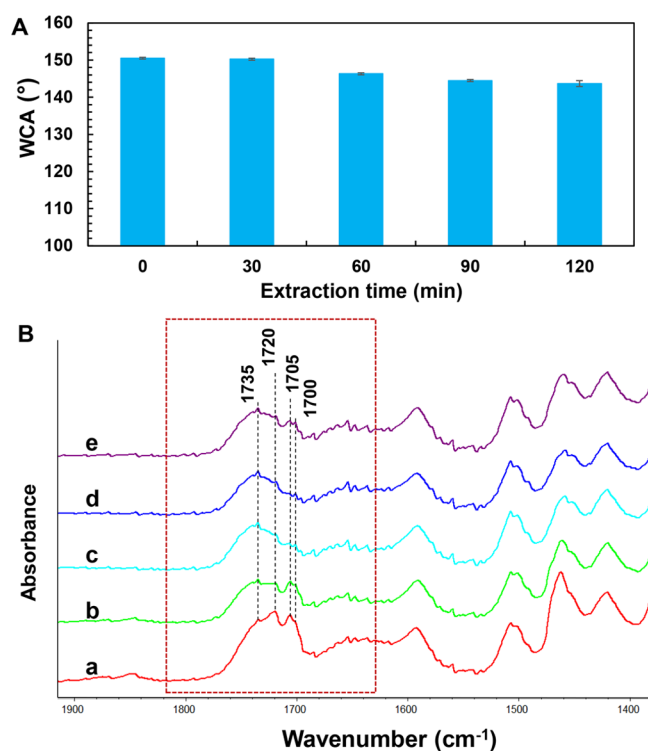
Figure 5. WCAs (A) and FTIR spectra (B) of treated teakwoods after extraction with *n*-hexane at various times: (a) 0, (b) 30, (c) 60, (d) 90, and (e) 120 min.

Figure 7. Optical micrographs of the cross-sectional area of a teakwood sample for observation of dye penetrating patterns (A), and WCA values (B) of treated teakwood samples as a function of penetration depth: 0, 0.2, 0.5, 0.8, and 1.0 mm.

AKD@SDS and AKD@PC were chosen for further experiments, as these showed high stability and small and uniform size. Their size distribution and SEM images, as shown in Figure 1, indicate that AKD@SDS and AKD@PC had small average sizes of 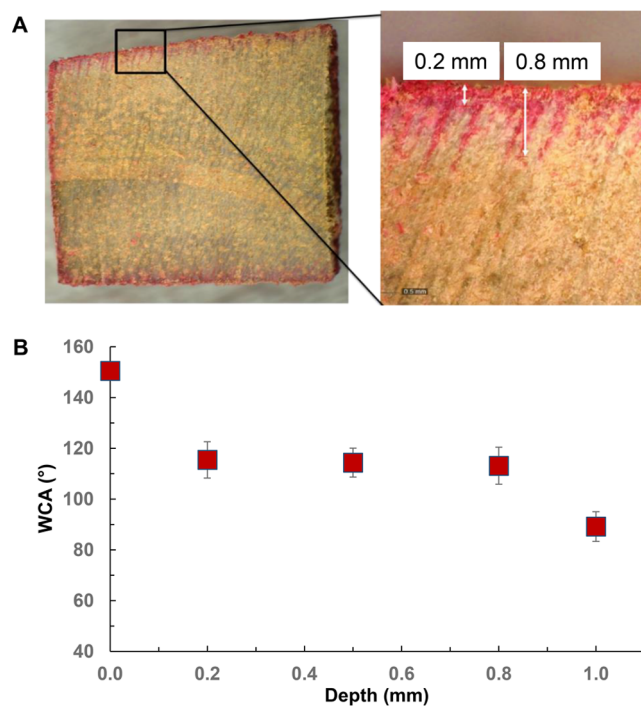148 ± 5 and 168 ± 7 nm, respectively, with monodispersity (PDI < 0.16). AKD@SDS in a dry state showed agglomeration of AKD flakes, as observed in the SEM images (Figure 1B,b). In contrast, similar features could not be seen in AKD@PC (Figure 1C,c). This is likely a result of different types and amounts of surfactants. In AKD@SDS, the amount of SDS used to stabilize AKD nanoparticles was too low (0.1 wt %). When the
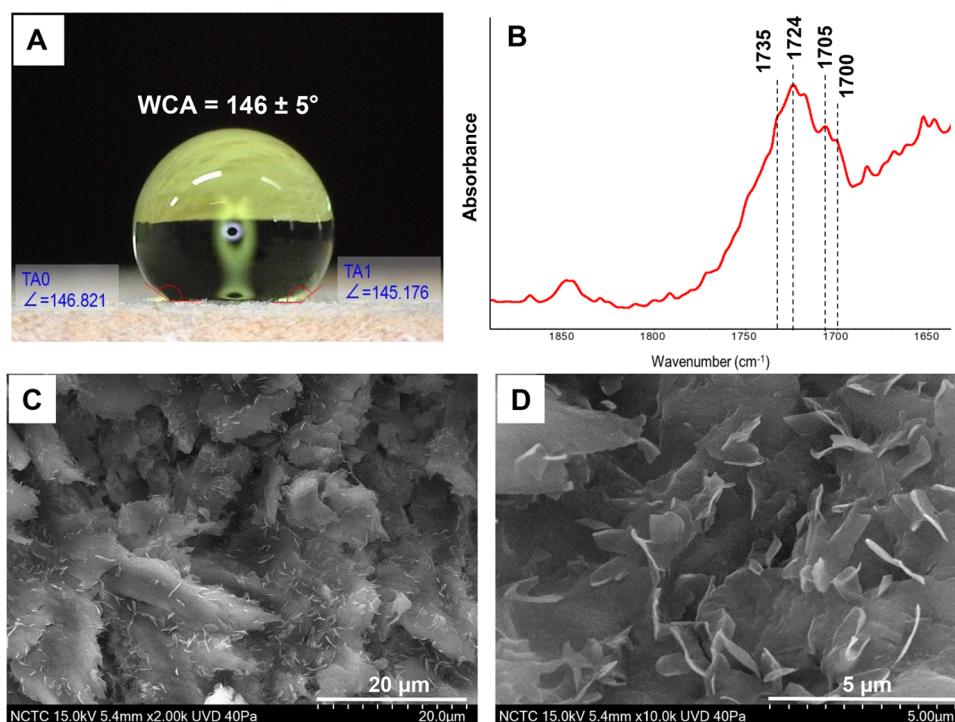

Figure 6. WCA (A), FTIR spectrum (B), and SEM images (C, D) of the treated teakwood after a service time of 2 years.
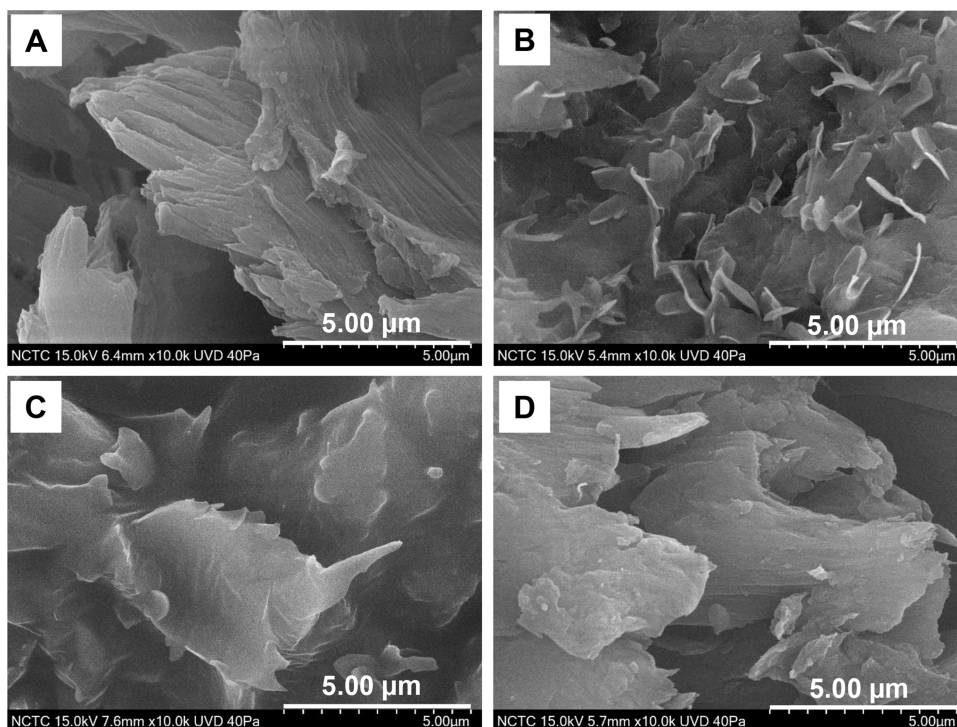
Figure 8. SEM images of the pristine teakwood surface (A) and the treated wood sample at the surface (B) at a penetration depth of 0.8 mm (C) and 1.0 mm (D).

nanoparticles are in the dry state, the coverage of the SDS surfactant is insufficient; hence, the hydrophobic character of AKD molecules was displayed, resulting in accumulation. In contrast, AKD@PC consumed 1.0 wt % PC, which is 10 times higher than SDS. Moreover, the molecular structure of PC contains both positive and negative charges, which enhances the stability of the AKD nanoparticles. Therefore, the crystal flakes of AKD in a dry state are well dispersed, as shown in Figure 1C,c.

3.2. Hydrophobic Treatments of Teakwood Products. The treatment process conditions, *i.e.*, time and temperature, play a key role in improving the surface hydrophobicity of teakwood. In this study, the teakwood samples were immersed in the AKD emulsions at 5 h to ensure optimum adsorption/ penetration of the AKD nanoparticles into the wood structure. The treatment time selection was set from the results of water penetration testing of the teakwood samples (as described in Section 3.4). As AKD is reactive toward hydroxyl groups of cellulose, the reactivity and accessibility can be enhanced when AKD is in the liquid phase, generating β-ketoester bonds with high stability and arrangement of its nonpolar tails on the cellulose surfaces for superhydrophobicity. The processing temperature was therefore raised to 60 °C (melting point of AKD: 40−60 °C)[41] compared to room temperature. The teakwood immersed in water-based AKD@SDS nanoparticles at 60 °C showed a significantly higher WCA value ($150 \pm 2°$) than that at room temperature ($137 \pm 3°$).

Although the wood treatment aims to improve its surface hydrophobicity, the appearance of the resulting wood products is also essential. If the appearance changed after the treatments, the wood products might not suit furniture or decoration applications. Therefore, the appearance of the modified woods was compared to the untreated counterpart, as shown in Figure 2A. Although the AKD emulsions appeared milky solutions (Figure S1), the appearances of the wood samples treated with

different AKD emulsions were not significantly different from that of the untreated sample. The color of the wood products remained brown, without milky or white stains from the AKD emulsions.

The wetting behaviors of the resulting teakwood products were analyzed by water contact angle (WCA) measurements. The WCA values of the woods treated with AKD@SDS and AKD@PC were 150 ± 2 and $141 \pm 3°$, respectively, implying (super)hydrophobic surfaces. The untreated wood showed a hydrophilic WCA value of $70 \pm 3°$, due to its high content of hydroxyl groups. Moreover, using AKD@SDS in the treatment led to a higher WCA value of $150 \pm 2°$ (superhydrophobic surface) compared to that of AKD@PC. This is likely due to the dissociation of SDS molecules, which have a high water solubility of 200 mg mL^{-1} and prefer to dissolve in water during the washing step. Also, partial dissociation of PC, which consists of longer hydrocarbon chains, may be possible in the washing step. As a result, its phosphocholine polar head groups interfere with AKD's alkyl chain arrangement, decreasing the product's hydrophobicity.[42]

The chemical structures of the treated teakwood samples were characterized by FTIR spectroscopy, as shown in Figure 3. The untreated sample showed a broad band at 3335 cm^{-1}, associated with the −OH groups of cellulose. The spectrum of neat AKD showed two strong bands at 2920 and 2850 cm^{-1}, corresponding to the stretching vibration of C−H in the methylene and methyl of AKD tails. The characteristic bands at 1848 (C=O in lactone ring) and 1720 cm^{-1} (C=C connected to lactone ring) were observed in the original AKD.[31,43] In contrast, these bands were not observed in the treated wood samples. The absence of the C=O stretching bands of the lactone ring reflects that no unreacted AKD molecules remain on the wood surfaces. However, a new intense band at 1735 cm^{-1} appeared, indicating the reaction between the lactone ring of AKD and −OH groups

on wood, generating β-ketoester linkages.[44] Two additional bands at 1705 and 1700 cm^{-1} were also observed. These are assigned to the C=O stretching modes of dialkylketone (stable) and β-ketoacid (unstable) structures, reflecting the cleavage of the lactone ring as a result of the hydrolysis of AKD in the presence of water molecules.[14,17,45]

To explain the formation mechanisms of the β-ketoester bonds during the treatment process, FTIR spectra of teakwood samples treated with AKD@SDS at each treatment step are compared in Figure 4. After submerging the wood sample into the AKD@SDS dispersion and washing with DI water (spectrum C), the characteristic bands of AKD at 1848 and 1720 cm^{-1} were still observed. More intense bands at 1705 and 1700 cm^{-1} were also observed, reflecting the presence of dialkylketone and β-ketone acid groups of hydrolyzed AKD. After heating the sample at 110 °C for 5 h (spectrum D), the characteristic bands of neat AKD disappeared, while the band of β-ketoester at 1735 cm^{-1} was observed.[44] However, the characteristic modes of hydrolyzed AKD were also detected. The results imply that the reaction between the lactone ring of AKD and −OH groups effectively occurs during the drying step. Yuan et al. reported that by increasing the reaction temperature from 70 to 110 °C, the grafting yield of AKD onto the nanofibrillated cellulose increased from approximately 4 to 22%.[41] The authors suggested that the increase in reaction temperature caused changes in the bond configuration of the noncrystalline regions of cellulose molecules, resulting in the swelling of fibrils, thereby improving the chemical reaction between the lactone ring of AKD and free OH− groups on cellulosic fibers. Additionally, the increase in the reaction temperature also increases the reaction rate between the −OH groups of cellulose and the lactone rings of AKD.

3.3. Stability of the Superhydrophobic Surfaces. To investigate the stability of superhydrophobicity of the treated woods, solvent extraction of free, unreacted AKD molecules physically adsorbed on the wood surface was performed. The treated samples were submerged in *n*-hexane at various times, *i.e.*, 30, 60, 90, and 120 min. The samples were then characterized by WCA measurements and FTIR analysis, as summarized in Figure 5. The WCA values of the treated teakwoods after *n*-hexane extraction for 30 min remained unchanged (around 150°) and slightly decreased at 60 and 90 min. When the extracting time was increased by 120 min, the value dropped to 143°. The results indicate that the wood treatment by the AKD emulsions effectively generates chemical bonds between the cellulose and AKD, enhancing the surface superhydrophobicity. Even extreme extraction conditions could only impose a slight effect on the stability of the surface property.

FTIR spectra (Figure 5B) show the unique band of β-ketoester bonds at 1735 cm^{-1} in all samples after the solvent extraction, even at 120 min.[44] The results confirm that the newly generated covalent bonds have high resistance to solvent extraction and play a vital role in the enhanced hydrophobicity of the wood samples. At the same time, when the extraction time was increased, the bands associated with unreacted AKD at 1720 cm^{-1} and hydrolyzed AKD at 1705 and 1700 cm^{-1} tended to disappear. This is because *n*-hexane (δ = 14.9 MPa$^{1/2}$) is a good solvent for dissolving a small amount of free AKD (δ = 16.8 MPa$^{1/2}$) and its hydrolyzed products remaining on the wood structures.[28,29] The results are consistent with the SEM images of the teakwood samples after solvent extraction at various times, as shown in Figure S2. Clusters of AKD crystalline flakes were observed on the surface of the freshly treated teakwood. When

the samples were extracted at 60 min, these flakes disappeared. This implies that the teakwood's superhydrophobicity is mainly contributed by thin layers of the chemically connected AKD at the sample interface, regardless of the presence of excess free AKD flakes.

To assess the stability of the treated teakwood products in practical use, the samples were stored in indoor ambient conditions for at least 2 years. Their appearance and hydrophobic properties were examined by FTIR, SEM, and WCA measurements, as summarized in Figure 6. The physical appearance of the samples remains unchanged. The WCA value (Figure 6A) of the treated teakwoods after the long service time slightly decreased to $146 \pm 5°$. The FTIR spectrum (Figure 6B) showed a strong band of free AKD at 1724 cm^{-1}, hydrolyzed AKD at 1705 and 1700 cm^{-1}, and a unique band of β-ketoester bonds at 1735 cm^{-1}.[14,17,44] This is supported by the SEM images (Figure 6C,D), in which clusters of AKD flakes were seen on the surface of the treated teakwood samples. The results confirm the high stability of the treatment layers on the surface of the teakwood products.

3.4. Penetration Ability of AKD Nanoparticles. Owing to a high content of hydroxyl groups and a high degree of porosity on its surfaces, wood can easily absorb water. The water molecules are not only absorbed on its surface but may also penetrate the wood structure, depending on its packing density. To investigate the water penetrating ability into the teakwood structure, the samples were submerged in an aqueous red dye solution at various times. After dying, the wood samples were cut to reveal their cross-sectional area, as shown in Figure 7A. At 5 h of submerging time, the red dye patterns on the wood samples indicate an optimum penetration depth of around 0.8 mm. As AKD@SDS has a small size of 148 ± 5 nm, the emulsion of these nanoparticles may also penetrate inside the wood matrix at a similar depth. To prove this hypothesis, the presence of AKD inside the wood structure at different depths, *i.e.*, 0.2, 0.5, 0.8, and 1.0 mm, was examined by WCA measurements, as summarized in Figure 7B. The WCA values of the treated woods decreased from 150° at the surface to 115−114° at depths of 0.2−0.8 mm, reflecting the existence of bondings between AKD and cellulose. At a depth higher than 0.8 mm, however, the WCA value was drastically decreased to 70°, similar to that of untreated wood, indicating the inaccessibility of the AKD nanoparticles to this depth level.

The morphology of the treated wood samples as a function of penetration depth was examined. The SEM images of an untreated teakwood surface and a treated sample at its surface and a depth of 0.8 mm are compared in Figure 8. Clusters of AKD crystalline flakes were observed on the surface of the treated wood (Figure 8B), which is distinctive from the untreated wood (Figure 8A). At a depth of 0.8 mm (Figure 8C), the number of AKD flakes, with a smoother surface and thinner layer structure, decreased. This reflects a lower amount of penetrated AKD nanoparticles at this high depth level. This agrees with the reduced WCA value (Figure 7), as previously discussed. The results imply that the treatments by the prepared AKD emulsion generate a hydrophobic layer covering the wood surfaces due to chemical bonding. Also, the AKD nanoparticles having a small size in the nanometer range can penetrate the dense structure of the teakwood and form similar bonding for up to 0.8 mm depth. These generate a protective water-repellent layer in the wood structure, leading to enhanced hydrophobicity and prolonged service life, as the dimensional instability from water absorption can be effectively prevented. However, at a

depth of 1.0 mm, the crystalline flakes of AKD could not be observed (Figure 8D). This is also consistent with the WCA results, indicating the inaccessibility of the AKD nanoparticles to this depth level.

4. CONCLUSIONS

A process for preparing emulsions of AKD nanoparticles *via* a nanoemulsion template (emulsion/evaporation) method has been successfully developed. Owing to the solid dictating nature of AKD, the emulsion was formed by emulsifying its oil-phase solution in the aqueous surfactant phase. After solvent evaporation, liquid AKD droplets become solid particles or AKD nanoparticles dispersed in the aqueous phase. AKD nanoparticles having a monodispersed small size of 148 nm with high colloidal stability were obtained using anionic (SDS, with a small amount of 0.1 wt %) as a stabilizing agent. The environmentally friendly water-based emulsion was employed to prepare teakwood products with enhanced water-repellent property by employing a facile dipping process. After submerging the wood sample into the emulsion for 5 h, its WCA values drastically increased to 150°, reflecting super-hydrophobicity. This is achieved because the prepared AKD emulsion generates a hydrophobic layer covering the wood surfaces due to the β-ketoester bond formation and the arrangement of AKD's hydrophobic tails. In addition, the nanosized AKD nanoparticles can penetrate the dense structure of the teakwood and form similar bonding for up to a 0.8 mm depth, generating a protective water-repellent layer in the wood structure, leading to enhanced hydrophobicity and prolonged service life. Compared to other commercial wood treatment processes, which commonly use solvent-based chemicals that form a thick protective layer on the wood surface, this water-based emulsion system utilizes chemical bonding between AKD and cellulose as thin layers at the wood surface and inside the wood structure. The emulsion has a high potential for use in facile commercial treatments and cost-effective production of teakwood products, due to their excellent water-resistant property and high dimensional instability from the effective prevention of water absorption/swelling, without altering their physical appearances.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02420.

Appearance and colloidal stability of the AKD emulsion (AKD@SDS nanoparticles) and SEM images of the surfaces of the teakwood samples after solvent extraction at various times: 0, 30, 60, 90, and 120 min (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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