

# Facile Approach for Ecofriendly, Low-Cost, and Water-Resistant Paper Coatings via Palm Kernel Oil

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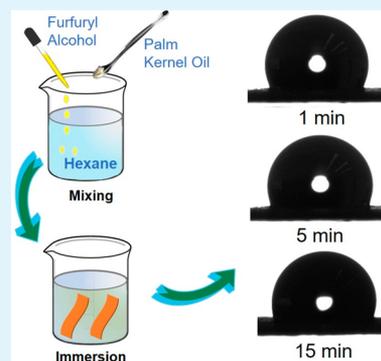
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**ABSTRACT:** Paper-based packaging is widely employed in industries ranging from food to beverages to pharmaceuticals because of its attractive advantages of biodegradability, recyclability, good strength, low cost, and lightweight. However, paper products usually have poor water barrier resistance properties because of paper and fibers porous microstructure. In this study, an ecofriendly water-resistant (hydrophobic) oil from biological origin, namely, palm kernel oil (PKO) was used to coat paper by using a facile and cost-effective dip-casting approach. PKO formulation was prepared by mixing with a solvent and furfuryl alcohol (FA). The water resistance, structural properties, and thermal and mechanical properties of the coated papers obtained under different processing conditions were reported and compared to understand the performance of coated paper. Contact angle (CA), Fourier transform infrared (FTIR), and thermal gravimetry (TGA) were used for analysis and characterization of coated papers. Data from contact angle measurements showed that the PKO formulation could considerably improve the liquid water barrier property of the paper, with a measured water contact angle (CA) of  $\sim 120^\circ$  and reduce the water vapor transmission rate (WVTR) by 22%. This novel, green, low-cost, and water-resistant paper coating made with biological and biodegradable oil is a potential candidate for replacing petroleum-based coatings used in a broad range of applications and will also be able to make an additional full use of the palm kernel oil.

**KEYWORDS:** *biobased materials, water-resistant, hydrophobic, paper coating, palm kernel oil, contact angle, furfuryl alcohol, sustainable packaging*



## INTRODUCTION

Packaging is of paramount importance to protect food, beverages, and pharmaceuticals from damage or contamination and to extend shelf life of products during handling, transporting and storage process in the supply chain.<sup>1</sup> Petrochemical-based materials, such as polypropylene (PP), polyethylene (PE), or polyethylene terephthalate (PET), have been widely used in packaging industry because of their outstanding properties, such as good water vapor resistance, high elasticity, and toughness.<sup>2</sup> However, all these materials are nonrenewable and nonbiodegradable and have induced much concern about environment pollution and human health from the public in their use. In the United States, about 254 million tons of waste of these materials are generated each year, and approximately 50% of them are put into 2000 active landfills across the country and only 10% of the waste may be recycled.<sup>3</sup> To address this grand challenge, research on developing safe and green food packaging materials with good water- and gas resistance and barrier properties has attracted increasing attention in the past decades.<sup>4–6</sup>

Paper or paper-based materials such as folding cartons, container boards, and corrugated boards have been extensively utilized in the packaging industry for food, water and drugs due to their attractive merits of low cost, biodegradability,

recyclability, good strength, and lightness of weight.<sup>7–9</sup> However, paper has poor water resistance and low barrier properties because of its porous microstructures and cannot maintain its functionality when encountering water or stored in high-relative humidity environments. Paper is hygroscopic and absorbs or desorbs water to be in equilibrium with its surrounding environment. The optimum moisture condition for paper utilization ranges from 3 to 7%. Above 7% paper becomes mushy with reduction of strength while below 3% it gets brittle. To address this problem, an additional hydrophobic coating is usually applied on the surface of paper to improve its water-resistant property.<sup>10</sup> For example, the disposable paper cups widely used in restaurants have a laminated water-resistant low-density polyethylene (LDPE) inner liner to avoid direct contact between water and the water-absorbing paper.<sup>11</sup> However, the LDPE film is difficult and costly to remove from paper during the recycling steps of

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paper into new paper, and thus paper cups are frequently landfilled after use. Wax is also used to enhance the water and oil resistance of paper. However, wax is a petroleum-based product and not completely biodegradable. Meanwhile, wax coating also has poor fracture toughness and low thermal resistance.<sup>12</sup>

Recently, research focus for paper coatings has shifted to the development of recyclable and biodegradable biopolymer materials with good water resistance for packaging and related industries.<sup>13–15</sup> Polysaccharides, lipids, and proteins derived from agricultural and forest residues provide new opportunities to develop novel coatings formulations for paper products.<sup>16–18</sup> For example, biodegradable nanocellulose fiber (NCF)/polylactic acid (PLA) composites were coated on paper surface through a cast-coating process to reduce water vapor transmission rate (WVTR).<sup>19</sup> The incorporation of palmitic acid into the chitosan film solution was shown to improve the wetting properties of Kraft paper, resulting in significant reduction of the values of WVTR and water absorption.<sup>20,21</sup> By coating Kraft paper with silylated soybean oil and curing via silanol condensation, the WVTR of Kraft paper (No. 78) reduced significantly by 53.1%.<sup>22</sup> Other various approaches have also been explored, such as the use of some internal or external sizing,<sup>23</sup> refining pulp and calendaring to control pores sizes and distribution,<sup>24,25</sup> chemical modification,<sup>26,27</sup> and physiochemical modification (e.g., plasma etching).<sup>28</sup> However, most of these approaches are not applicable for large-scale production because of their time-consuming processes (e.g., long curing period), complex conditions (e.g., higher reaction temperature), reliance on high-cost raw materials, energy consumption, and the use of toxic chemicals.<sup>2</sup> Thus, there is a strong demand to develop a facile, low-cost, ecofriendly and scalable approach for making water-resistant coated paper by using available low cost biopolymers.

Palm kernel oil (PKO) is usually considered as oil palm byproducts and needs to be processed as abundant waste and pollution from production. For instance, around 2.4 million tons of palm kernel oil was considered as production waste in Malaysia in 2015.<sup>29</sup> PKO is a typical lauric oil that mainly contains a high level of C12:0 and short and medium chain unsaturated and saturated fatty acids such as C8:0 and C10:0,<sup>30</sup> and it is a semisolid fat at room temperature with a low melting point of 26–28 °C.<sup>31</sup> Palm-based materials have promising potential for film and coating technology.<sup>32</sup> Paper coated with palm-based materials showed a similar surface compared to paraffin wax coated paper.<sup>33</sup> For example, liner board coated with palm oil from palm fruit bunch's lignin derivatives exhibited superior water-resistant properties.<sup>34</sup> Thus, we assume that PKO from the seed of palm fruit will be similar to palm oil and be consider as a potential promising candidate for edible, renewable, and biodegradable paper coating with suitable fabrication and curing process.<sup>35,36</sup> Additionally, in some regions where PKO is present, it is used as cooking and as microbial ingredients in lotions to prevent skin damages.<sup>37,38</sup>

In this work, a facile method has been proposed to fabricate an ecofriendly, low-cost, and water-resistant paper coating using palm kernel oil. Food grade hexane is used as an organic solvent for dissolving the PKO. Furfuryl alcohol (FA), which exists in many foods and is mainly generated in thermal processing and aging of alcoholic beverages,<sup>39</sup> is added into the solution as a cross-link agent for better impermeability and

interaction between PKO and paper surface. Copolymerization was detected and reported when epoxidized linseed oil reacts with FA.<sup>40</sup> Changes of wetting properties, mechanical strength, and thermal stability of coated paper were studied to further evaluate the performance of simply immersing the paper samples into PKO-FA-hexane solutions as a dip coating method for developing water resistant coatings. Migration of PKO from coated paper into food simulant was also analyzed to prove the safety of coatings used for food products. This facile fabrication method offers a new approach for low-cost, high-throughput, and large-scale fabrication of coated paper for different applications in packaging and beyond.

## ■ MATERIALS AND METHODS

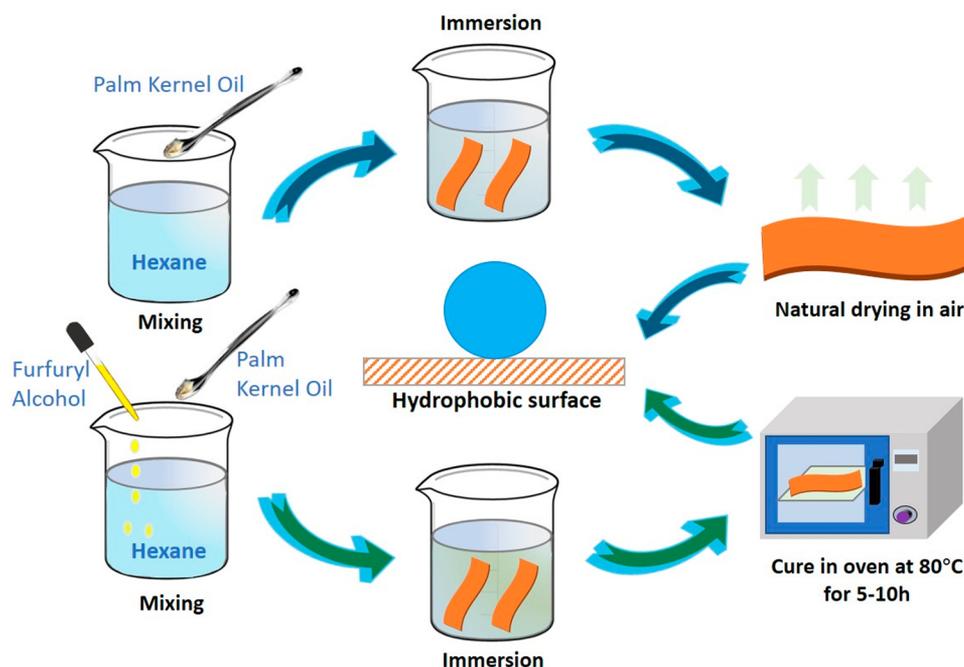
**Materials.** Palm kernel oil was purchased from a local supplier in Cameroon, Africa. N-Hexane was obtained from VWR Chemicals BDH, while furfuryl alcohol (purity 98%) and ethyl alcohol, 200 proof were purchased from Sigma-Aldrich, USA, and were reagent grade and used without further purification. The 35-liner paper (basis weight =  $188.6 \pm 2.3$  g/m<sup>2</sup>, thickness =  $0.218 \pm 0.002$  mm) unbleached Kraft paper was obtained from MI Pack Co. and used as received without further treatment. Mason jars and epoxy glue were purchased at local grocery stores. Drierite desiccant and disposable UV cuvettes were purchased from Biochemistry Research Store at Michigan State University.

**Gas Chromatography–Mass Spectrometry (GC-MS).** GC-MS was performed to quantify the average mole percentage of the fatty acid methyl esters (FAMES) in the palm kernel oil sample using an Agilent 7890A GC/single quadrupole mass spectrometer with 5975C inert XL MSD (Agilent, Santa Clara, CA) at Mass Spectrometry and Metabolomics Core, Michigan State University. One microliter of the derivatized sample was injected in a split mode (1:10) with an injector temperature of 250 °C and a flow rate of 1.0 mL/min helium. Separation was achieved on an Agilent J&W DB-23 column (30 m × 0.25 mm × 0.25 μm) (Agilent, Santa Clara, CA) using the following temperature profile: 40 °C for 2 min; 20 °C min<sup>-1</sup> to 160 °C; 3 °C min<sup>-1</sup> to 210 °C; 40 °C min<sup>-1</sup> to 250 °C; 250 °C for 3 min. Ionization employed 70 eV electron ionization and the mass spectrometer was operated in scanning mode with a scan range of *m/z* 45 to 500. FAMES were identified by comparing their mass spectra and retention time to the Supelco 37 component FAME mix (Sigma-Aldrich, St. Louis, MO). The percentage of specific FAME compared to total FAME was then reported.

**Preparation of PKO Solution.** PKO–hexane solution was prepared by dissolving PKO into hexane (weight used, ratio % between PKO and mixed solution) by stirring at room temperature for 10 min. Five different concentrations ranging from 1, 2, 4, 6, and 8 wt % were used in this work to evaluate the effect on the amounts of PKO on coating performance.

**Preparation of PKO–FA–Hexane Solution.** The PKO and FA were dissolved and mixed together in the hexane solvent. To simplify the testing, the optimal PKO concentration (2 wt %) was used for making a PKO–FA–hexane solution. The six different FA concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, 1 wt % were selected to examine a suitable or optimal FA concentration for the specific PKO–hexane solution under room temperature. In addition, 8 wt % PKO and 1 wt % FA were prepared to evaluate the performance of coated paper with higher concentration of coating materials.

**Sample Preparation for Coating Layer.** Paper samples were trimmed to be of  $50 \pm 10$  mm × 13 mm and then immersed into the prepared solution for 1 min and then completely dried in the air at room temperature. Three sample replicates were used for each treatment. To enhance the cross-link of the PKO and FA, paper samples were also cured in a convection oven at 80 °C for 5 or 10 h. For each solution of different concentration, three samples were prepared for further characterization to determine the optimal concentration of PKO, as well as FA by measuring the water contact angle.



**Figure 1.** Schematic illustration of the fabrication procedures for coating a paper sample with PKO or PKO-FA. PKO or PKO-FA is dissolved into hexane with thorough mixing. Then, the trimmed line paper is immersed into the solution for 1 min to coat the PKO layer. After that, the sample is naturally dried in air (for FA immersed samples) or cured in an oven at 80 °C for 5–10 h. The as-prepared samples are used for further experimental testing.

**Coating Loading Quantification.** The coating loading of coated paper samples was measured using a gravimetric method. Both unmodified and coated paper samples with 5 replicas, respectively, were cut into 1 cm × 1 cm squares. The load of the coating was quantified by calculating the average weight difference between the coated paper and uncoated paper using a microbalance.

**Fourier Transform Infrared (FTIR) Spectra.** FTIR spectra of the samples were studied via a Shimadzu IR Prestige21 FTIR spectrometer (Shimadzu Co., Columbia, MD) equipped with an attenuated total reflection attachment (PIKE Technologies, Madison, WI). The spectra were obtained by 64 scans at the resolution of 4 cm<sup>-1</sup> in the spectral range of 4000–400 cm<sup>-1</sup>.

**Thermogravimetric Analysis (TGA).** Thermal stability of the coated and uncoated paper samples was determined using a Q-50 thermogravimetric analyzer (TA Instruments, New Castle, DE). Sample (weighing about 5–10 mg) was placed in a standard aluminum pan, and the weight loss of the sample was reported as a function of the temperature varying from 23 to 600 °C with a ramp rate of 10 °C/min under a nitrogen flow rate of 40 mL/min.

**Measurement of Water Contact Angle.** Water contact angles (CAs) were measured using an advanced automated goniometer (S90-U1, Rame-hart Instrument Co., USA). For each group, three samples were measured for averaging the data. A deionized water droplet (5 μL) was gently deposited onto the surface of each sample, and the CAs were measured after 5 s and recorded every minute. For easy comparison, CAs measured for each sample are reported for same time period, such as 1, 3, 5, 15 min. The reported CAs were averaged by repeating measurements at five different sites on each sample. The sessile drop method (ASTM D7334) was applied and modified to analyze the contact angle.

**Measurement of Water Vapor Transmission.** Water vapor transmissions of uncoated and coated papers were evaluated via a dry cup method following the ASTM E96 standard. The paper samples were divided into 4 different groups: uncoated paper, 2 wt % PKO-coated paper, 2 wt % PKO + 0.3 wt % FA-coated paper and 8 wt % PKO + 1 wt % FA-coated paper, with three replicates in each group. Twelve half-pint (8 oz) size mason jars with a wide mouth of 75 mm diameter were used in the experiments. The effective permeation area was the open area of the mason jars mouth and calculated as 0.0044

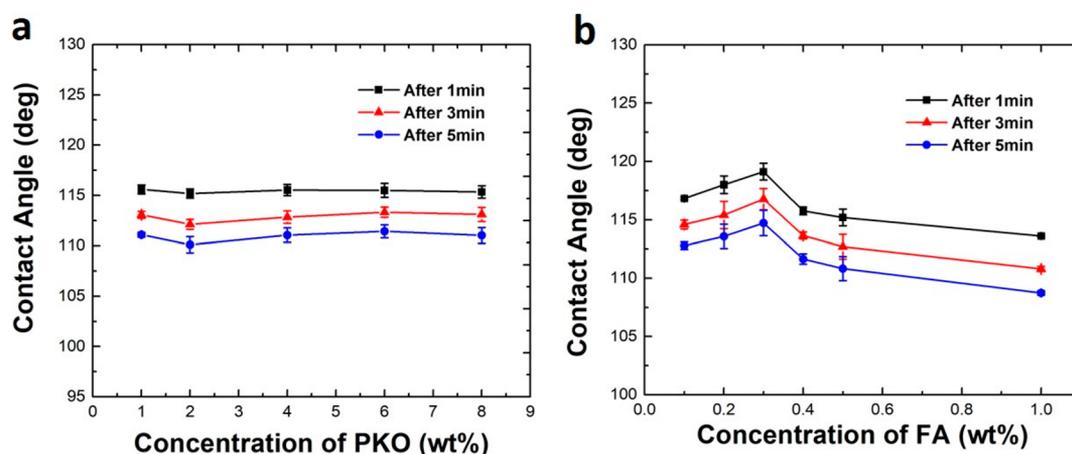
m<sup>2</sup>. The jars were filled with desiccant with the total weight of the whole system reaching 270 g, which was also defined as original weight. Instead of the lids, the jars were sealed with the paper samples on the top and epoxy glue on the mouth rims. Thus, the paper samples on the top will provide the only portal for water vapor to permeate into the jars. Total weight of each jar was recorded via gravimetric methods every 10 h. Water gain as  $Q_t$  in every 10-h frame was calculated by subtracting the original weight (270 g). By plotting every net weight gain  $Q_t$  versus time, the relationship from linear trendline with a slope  $k$  was obtained. Then, the WVTR can be calculated by

$$\text{WVTR} = \frac{k}{\text{permeation area}}$$

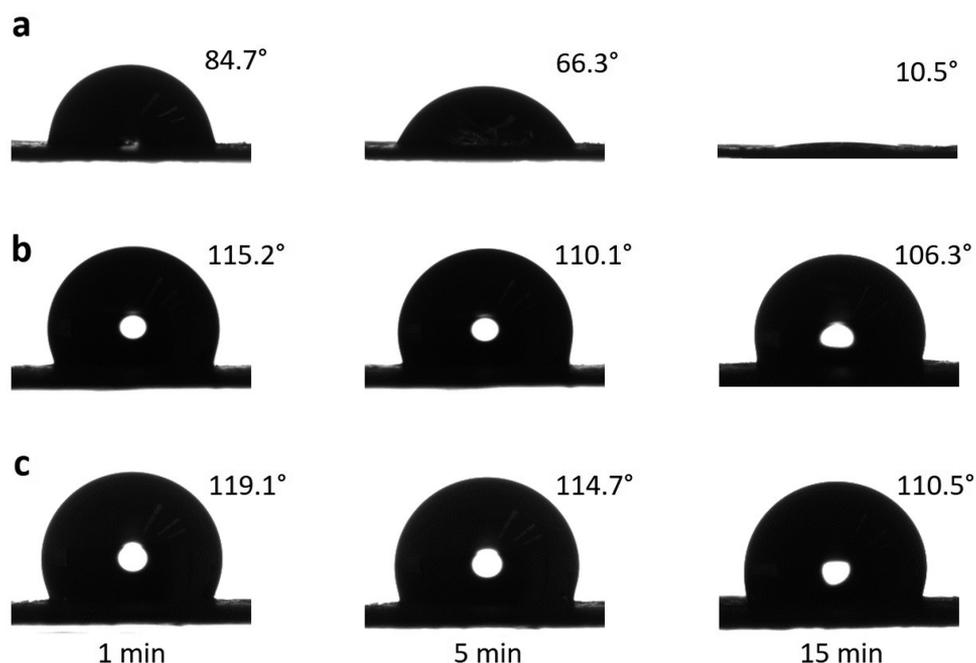
**Scanning Electron Microscopy (SEM).** The Zeiss EVO LS 25 VP-SEM (CARL ZEISS Ltd., Germany) system was used for the SEM analysis. The samples were fixed on aluminum stubs and coated with a thin layer of platinum (5–10 nm thick) via a Denton Desk II sputter coater. All samples were examined with an accelerating voltage of 2 kV.

**Mechanical Testing of Tensile Strength.** The mechanical tensile tests were performed by using an Instron Universal Testing Machine (model 5565), following the ASTM 828 standard. The stress–strain curves were measured at a speed of 25.4 mm/min. The uncoated and coated papers were cut into small strips of 25.4 × 254 mm for testing. Five replicas were made for two groups. The tensile stresses at the maximum load and the tensile strains at break were recorded and calculated.

**Migration Testing of Coated Paper.** UV–vis spectrophotometry was used to determine the migration of PKO from coated samples in food simulant. In line with the application of the coated paper, food simulant (10% ethanol–90% DI water) for low fat, aqueous, and acidic foods was prepared following the guidance from FDA.<sup>41</sup> Unmodified liner paper was first cut into small square pieces of 1 cm × 1 cm and then washed with food simulant three times, each time for 5 min. The paper samples were then coated with 2 wt % PKO + 0.3 wt % FA following the same procedure mentioned above. Coated samples were immersed into the food simulant for 10, 20, 30,



**Figure 2.** Contact angle measurements of paper samples processed in PKO solutions with different concentrations. (a) Variation of contact angles of a coated paper as a function of PKO concentration. (b) Variation of contact angles of a coated paper as a function of FA percentage in a PKO–FA–hexane solution. The PKO concentration is kept at 2 wt %.



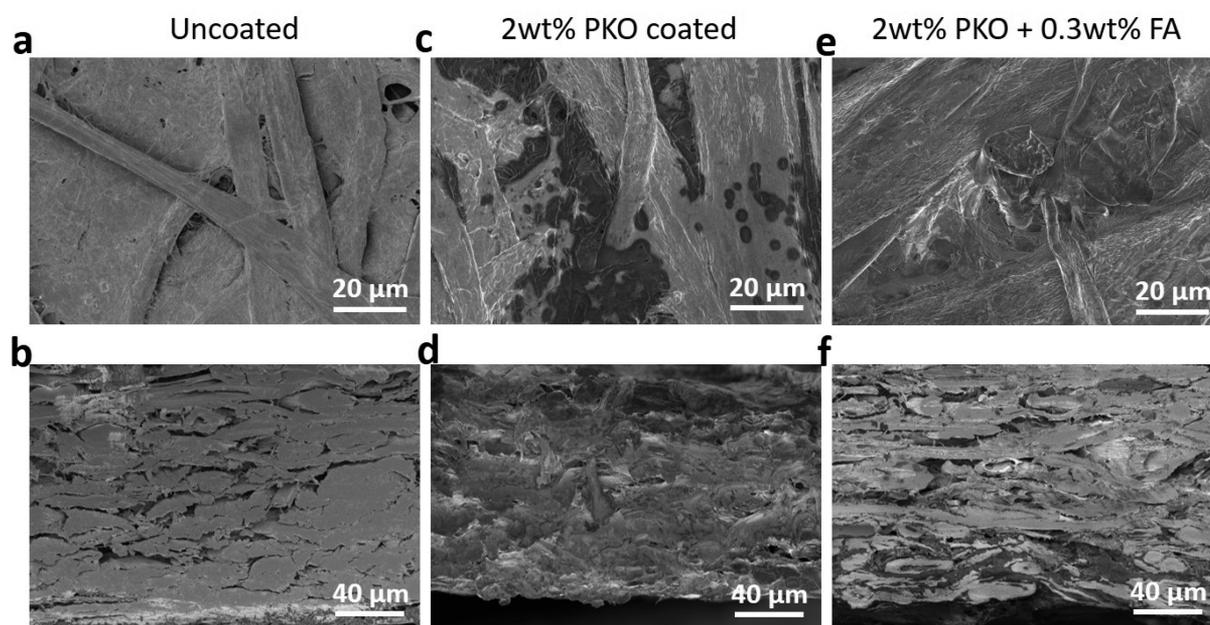
**Figure 3.** Water droplet profiles and their contact angle variations with time on paper coatings: (a) uncoated liner paper, (b) 2 wt % PKO solution-coated liner paper, and (c) 2 wt % PKO + 0.3 wt % FA solution-coated liner paper.

40, and 50 min, respectively. After collecting the immersed paper samples, the food simulant was analyzed to evaluate the migration level by using UV–vis spectroscopy. To find the typical wavelength range of the coating material, different concentration (from 4.76% to 33.33%) of 8 wt % PKO + 1 wt % FA + 91 wt % hexane was added into food simulant to locate the range of wavelength. The presence of unsaturated double bond with UV peak around 285 nm was assumed and confirmed by using GC MS analysis. The UV1800 UV–vis spectrophotometer (Shimadzu Co., Columbia, MD) was employed for the migration test of coated paper.

## RESULTS AND DISCUSSION

As shown in Figure 1, the paper coating is fabricated with a facile immersion-drying method. The palm kernel oil (PKO) is first diluted with hexane, which is a food grade additive widely used in food industry.<sup>42</sup> The liner paper strip is then immersed into the uniform PKO solution for 1 min. After that, the so-

treated paper sample is removed from the solution and dried on a Petri dish at room temperature in air. PKO is easily soluble in hexane at room temperature at concentration lower than 10 wt %. Thus, the five different concentrations used in this study from 1–8 wt % are selected as independent parameters. The wetting properties of the dried samples were further tested using a sessile droplet method by a goniometer. The identification of fatty acids presents in PKO was carried out by GC-MS. The 8 major FAMES present in the PKO sample are shown in Figure S1. Fatty acids between C8:0 and C18:2, such as octanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, octadecanoic acid, octadecenoic acid, and octadecadienoic acid, are revealed through the analysis, which is in line with Kılıç's study.<sup>30</sup> Meanwhile, except for the high level of saturated fatty acid, around ten mole percent of C18:1 and C18:2 demonstrates the



**Figure 4.** SEM images of the top surfaces and cross sections of (a, b) uncoated liner paper, (c, d) 2 wt % PKO-coated liner paper, and (e, f) 2 wt % PKO + 3 wt % FA-coated liner paper.

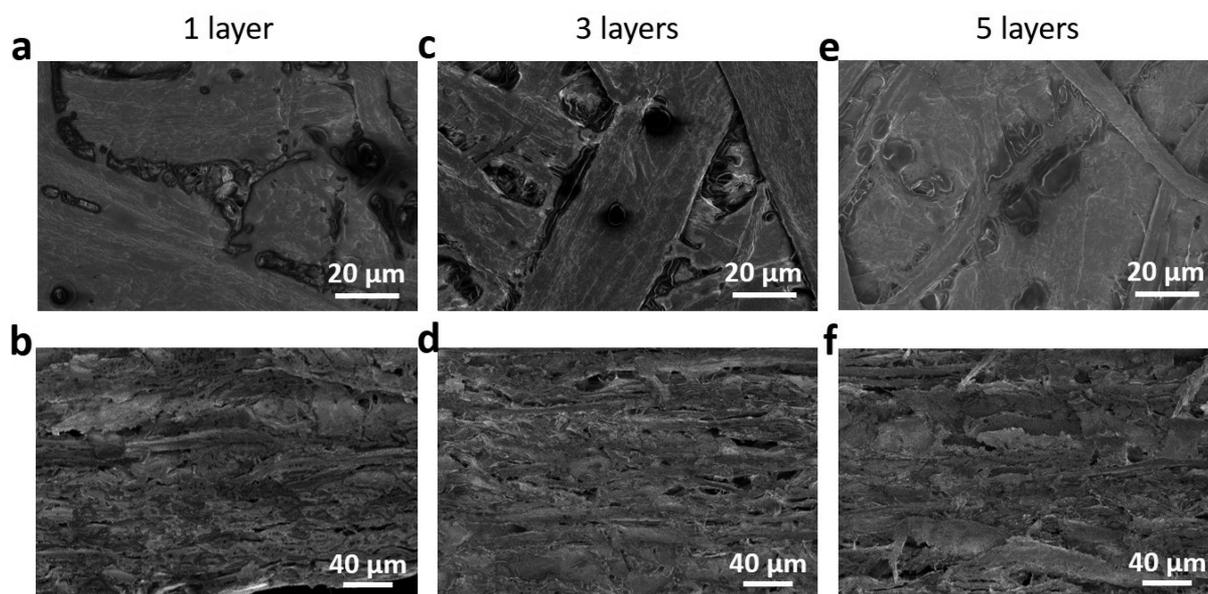
existence of unsaturated fatty acid. It is noted that the biobased PKO as a byproduct of plants can be easily biodegraded and will generate no or much less pollution from production.

Figure 2a shows the measured contact angles (CAs) of the coated paper samples after processing in PKO solution of different concentrations. It can be seen from Figure 3 that the untreated liner paper is hydrophilic and has poor water-resistance and the water droplet slowly diffused into the paper ( $\sim 65^\circ$  after 5 min), while on the contrary, the PKO-coated samples exhibit good water resistance with a CA larger than  $115^\circ$  at 1 min and  $110^\circ$  at 5 min. However, the concentration of PKO has no obvious influence on the CA of the paper surface, with a CA of about  $115.5^\circ$  for various PKO concentrations. Therefore, in the following experiments, we take the 2 wt % PKO solution as an example to examine the coupling effect of PKO and FA on the water resistance of paper.

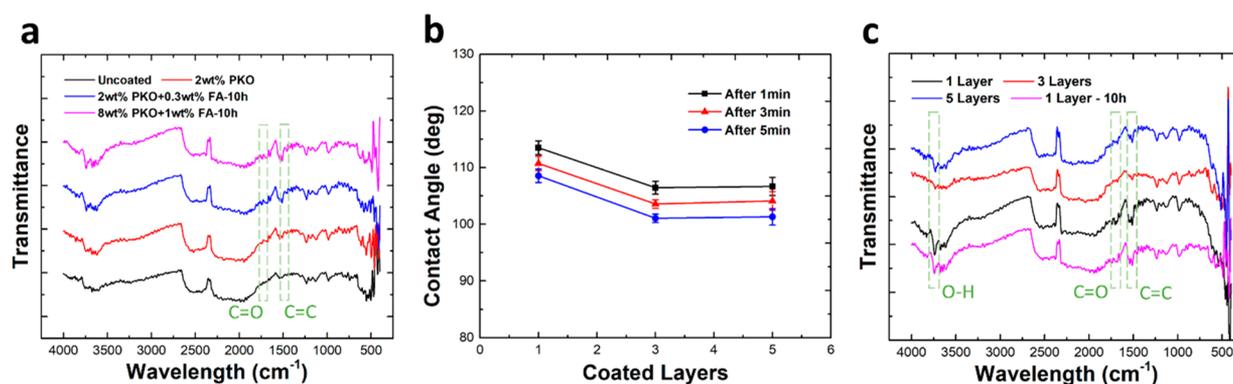
FA is used as a cross-linking agent because it reacts with the cellulose of paper via hydrogen bonding. It is assumed that FA will cross-link with PKO in hexane solvent to form strong bonds for a stable coating layer firmly bound onto the paper. This will further improve the hydrophobic or water resistance of the paper coating and increase its durability in applications. To find the optimal percentage of FA, we have utilized six different concentrations of FA: 0.1, 0.2, 0.3, 0.4, 0.5, and 1 wt % for a 2 wt % PKO solution. It is found that when 0.5 wt % of FA is mixed into the 2 wt % PKO solution, a small amount of brown residual FA can be visually observed after thorough stirring. This indicates that the 2 wt % PKO can only react with less than 0.5 wt % of FA. As shown in Figure 1, for the PKO-FA coating, similar to the only PKO coating, the immersion-drying method is used for coating the paper samples. After the raw paper samples were immersed into the PKO-FA solution for 1 min, they are lifted out and then dried in a conventional oven at  $80^\circ\text{C}$  for a few hours. It is found that the curing time varying between 5 and 10 h has not much effect on the CA of the paper coating and the variation induced by curing time can be ignored. Figure 2b illustrates the variation of the CA of the

coated paper by PKO-FA with a different concentration of FA. It is interesting that there is an optimal concentration (0.3 wt %) for better CA performance for a fixed PKO concentration (2 wt %). The CA of the paper coating reaches  $119^\circ$  at the 0.3 wt % FA concentration and gradually reduces to  $114^\circ$ , when FA concentration increases to 1.0 wt %. This may be due to the residual FA on the surface increasing the water absorption capability of the paper due to FA's hydrophilia.<sup>43</sup> Similarly, the contact angles of the paper coated with PKO-FA coating also decrease with increase time evolution (Figure 3). Thus, 2 wt % PKO + 0.3 wt % FA was chosen as optimal coating concentration for paper samples. The load of 2 wt % PKO + 0.3 wt % FA-coated samples was calculated as  $20.2\text{ g/m}^2$  via gravimetric methods. It is also verified that if the paper sample was only processed with FA solution, no obvious change occurred for the water resistance of the paper. Thus, we assume that the FA has cross-linked with PKO to form stable bonds in the solution. It is noted that the CA of the coated samples will further decrease with the wetting time (Figure S2), so that they are not suitable for long time use (e.g., >1 h).

Figure 4 shows the SEM images of the top surfaces and the cross sections of uncoated liner paper, 2 wt % PKO-coated liner paper, and 2 wt % PKO + 3 wt % FA-coated liner paper. The cross sections are cut with a knife blade. In the uncoated liner paper, cellulose fibers of a variety of diameters can be observed on the porous surface. The size of open pores varies from a few microns to  $\sim 50\ \mu\text{m}$  in the uncoated paper (Figure 4a and b). After being coated with PKO, almost all the pores are covered by dark mottling with a few open gaps remaining. From the cross-section view in the SEM images, it is seen that aggregation of greasy substances appears (Figure 4c and d). On the other hand, from Figure 4e and f, it is observed that the PKO- and FA-coated paper shows an enhanced coverage of its surface by the barrier coating. Different from the paper coated solely by PKO, the cellulose fibers in the paper can still be observed at the cross-section view. However, the open pores are filled with greasy substances, indicating that after curing the cross-linked PKO and FA has penetrated the paper and formed



**Figure 5.** SEM images of the top surfaces and cross sections of (a, b) 8 wt % PKO + 1 wt % FA-coated paper, single layer, (c, d) 8 wt % PKO + 1 wt % FA-coated paper, three layers, and (e, f) 8 wt % PKO + 1 wt % FA-coated paper, five layers.



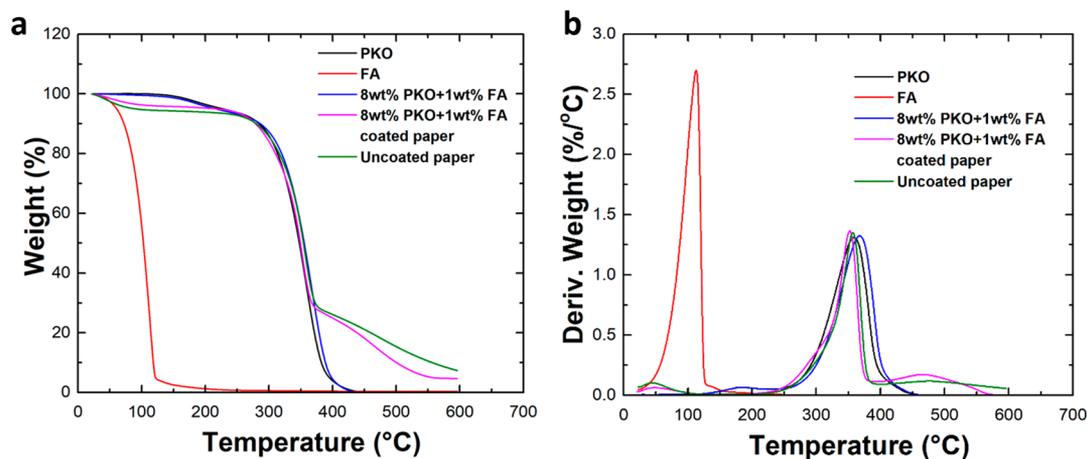
**Figure 6.** Characterization of the coated liner paper. (a) FTIR spectra of liner paper with or without coating. (b) Variation of water contact angles with the number of coating layers (2 wt % PKO + 0.3 wt % FA). (c) FTIR spectra of liner paper with multiple coating layers (8 wt % PKO + 1 wt % FA).

a barrier inside of the paper. From the atomic force microscopy (AFM) scanning (Figure S3), the thickness of the coating layer (may not continuous) is estimated to be a few micrometers after coating three times, similar to the wax coating ( $\sim 4\text{--}50\ \mu\text{m}$ ) for porous paper or metal substrates.<sup>44</sup> Ideally, at increased concentration of PKO and FA, more fibers will be covered by hydrophobic substances and more gaps between fibers will be filled in, resulting in a better impermeability of water, which is further verified later by measuring the WVTR of coated and uncoated papers.

To further confirm the successful application of PKO onto the paper, we perform the Fourier transform infrared (FTIR) analysis for the paper samples obtained under different treating conditions. Figure 6a shows the FTIR spectra of liner paper samples with or without coating applied. The PKO-FA-coated paper exhibits additional characteristic peaks because of the presence of the PKO and FA. For example, the peaks at  $1744\ \text{cm}^{-1}$  correspond to the stretching vibration of the  $\text{C}=\text{O}$  in the fatty acids ester group of PKO.<sup>45</sup> In contrast to the coated paper, no typical peak at  $1744\ \text{cm}^{-1}$  is presented from the uncoated paper. Meanwhile, the peaks at  $1503\ \text{cm}^{-1}$  represent the  $\text{C}=\text{C}$  stretching of furan ring in FA.<sup>46</sup> An increase of the

FA concentration along with the increment of the peak's intensity at  $1503\ \text{cm}^{-1}$  is also revealed. Thus, the FTIR spectrum results confirmed the presence of the PKO and FA coating, indicating that PKO and FA are successfully applied onto the paper substrate.

To check the performance of multiple layer coatings, we also repeatedly coat the samples for 1, 3, and 5 times in the 8 wt % PKO + 1 wt % FA solution by the immersion-dry procedures. In each coating cycle, the samples are cured in an oven at  $80\ ^\circ\text{C}$  for 1 h. The SEM images of the paper surface becomes smoother with more coating materials filled into the porous structure of the paper to form a thicker layer (Figure 5). Interestingly, the water contact angles of the coated paper decrease with the number of coating layers applied on the surfaces (Figure 6b). However, the contact angle became very stable after having more than 3 layers of coating. As shown in Figure 6c, the peaks ( $3750$ ,  $1744$ , and  $1503\ \text{cm}^{-1}$ ) in the FTIR spectra of the coated liner paper become smaller after coating multiple coating layers (8 wt % PKO + 1 wt % FA). Compared with the FTIR spectra of the coated sample by PKO-FA curing at  $80\ ^\circ\text{C}$  for 1 h, the samples postcured in an oven at  $80\ ^\circ\text{C}$  for 10 h show no obvious difference, indicating



**Figure 7.** (a) TGA curves of PKO, FA, 8 wt % PKO + 1 wt % FA coating solution, uncoated liner paper and liner paper coated with 8 wt % PKO and 1 wt % FA. (b) Derivative weight loss curves of PKO, FA, 8 wt % PKO + 1 wt % FA coating solution, uncoated liner paper, and liner paper coated with 8 wt % PKO and 1 wt % FA.

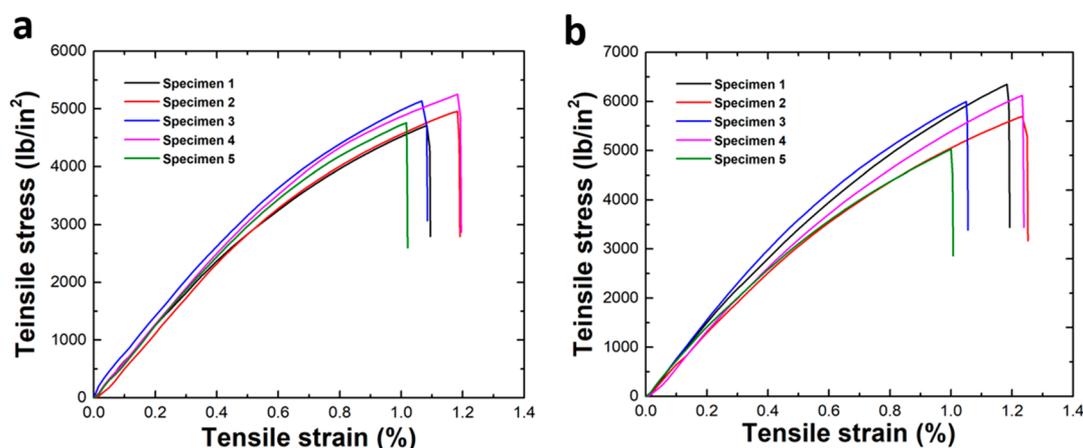
that the thermal drying time actually has little influence on the quality of the applied coatings. This indicates that less layers can be used for getting paper products with good water-resistant performance to further reduce the manufacturing cost in large-scale fabrications in industry. We have also studied the adhesion (dissolubility) of the coating layers on paper samples. As-prepared samples with PKO or PKO-FA coatings are further immersed into the water or hexane under strong stirring for a few hours. Afterward, they are taken out for contact angle measurement after natural drying. It is found that the contact angles of the samples obtained from different coating processing conditions show ignorable changes in water resistance, only about  $2^\circ$ .

The stability of the PKO-FA coating is further examined by the migration tests of the samples in food simulants (Figure S4). FA is a biobased material derived from biorefinery lignocellulosic biomass. In the experiments, all the paper samples used for the migration tests are washed three times (5 min per time) with food simulant to remove the possible interference of lignin inside the unmodified paper, which is important for maintaining the mechanical properties of paper. Peaks around 285 nm indicates the presence of benzene ring in the lignin structure, which is considered as an indicator to evaluate any migration from coated samples to food simulants.<sup>47</sup> As shown in Figure S4a, with the increased concentration of PKO-FA solution, the peak around 285 nm grows only for coating materials. It can be seen from Figure S4c that there is no peak appearing around 285 nm in the UV-vis absorption spectra, indicating a strong bonding of coating and paper substrates. This result verified that the coated paper with this facile approach can be safely utilized for food packaging.

Thermogravimetric analysis (TGA) is performed to evaluate the thermal stability of the coating layer. Higher concentration coatings (8 wt % PKO + 1 wt % FA) are chosen for testing here to emphasize the coating effect. Coated samples, as well as the coating mixture itself, are cured at  $80^\circ\text{C}$  for 10 h. Figure 7a shows the TGA traces of the main coating materials and coated liner paper with high concentration coating solutions, including PKO, FA, 8 wt % PKO + 1 wt % FA coating mixture and liner paper coated with 8 wt % PKO and 1 wt % FA. The uncoated samples are also tested for comparison. The first derivative of the weight loss curve in Figure 7b is provided

to indicate the point at which the weight loss is most apparent. The FA sample exhibits only one degradation step which occurs above  $50^\circ\text{C}$ , indicating the volatile aspect of FA. PKO sample has two major degradation phases. The first degradation phase starts from  $150^\circ\text{C}$ , which involves scission of the weaker chemical bonds. The next degradation phase appears at the range of  $250\text{--}450^\circ\text{C}$  with the mass gradually decreases to zero. The 8 wt % PKO + 1 wt % FA coating mixture shows similar degradation steps with PKO. However, the temperature range of second degradation step of mixed coating material slight shifts to the right. All the tested paper samples show three steps of thermal degradation. Initially, all paper samples exhibit a significant weight loss between 50 and  $100^\circ\text{C}$  which corresponds to the presence of moisture.<sup>48,49</sup> Less weight reduction is found in coated paper below  $100^\circ\text{C}$ , proving that paper with coatings has better water-repellent ability. Decomposition of coating materials and paper substrate almost occur simultaneously between 260 and  $390^\circ\text{C}$ . In the temperature range of  $400\text{--}600^\circ\text{C}$ , the degradation contributes to the additives inside the paper. Additionally, larger weight loss can be found in coated paper, which may indicate the appearance of new cross-linking structure. From the TGA, it is illustrated that the additional coating does not affect the thermal stability of original uncoated paper.

Water vapor transmission plays a very important role in food packaging applications. Thus, in this research, we test the water vapor transmission of the coated liner papers with a desiccant method. As shown in Figure S5a-c, test desiccant is filled in a jar stored at  $23^\circ\text{C}$  and 50% RH in a controlled chamber for 150 h. The results show that coated papers with different kinds of coating layers can reduce the WVTR of liner paper (Figure S5d). A lowest WVTR at  $15.84\text{ g/h}\cdot\text{m}^2$  is found in 8 wt % PKO-1% FA-coated papers, representing a 22% reduction compared to  $20.30\text{ g/h}\cdot\text{m}^2$  for uncoated paper. Meanwhile, 2 wt % PKO-coated paper with WVTR at  $18.45\text{ g/h}\cdot\text{m}^2$  and 2 wt % PKO-0.3% FA-coated paper with WVTR at  $18.31\text{ g/h}\cdot\text{m}^2$  present certain water barrier capability. The outcome can be explicated in terms of the microstructure change of the coated papers in comparison with porous uncoated papers. The pores are filled with PKO-FA, which prevent the passage of water vapor molecules through the void spaces between cellulose fibers. As the concentration of the coatings increases, more gaps in the microstructure tend to be filled.



**Figure 8.** Representative stress and strain curves of the (a) uncoated liner paper and (b) coated liner paper with 2 wt % PKO + 0.3 wt % FA solution, measured in tensile tests by a micromechanical analyzer.

It is important to ensure that the mechanical strength of the coated paper maintains at the acceptable level after experiencing the coating process in the PKO or PKO–FA solutions. To verify this, stress and strain curves of the uncoated and coated liner paper with a 2 wt % PKO + 0.3 wt % FA solution are measured by a micromechanical analyzer. As shown in Figure 8, the experimental results demonstrate that the coated paper has slightly higher tensile strength than uncoated papers, indicating a slight enhancement of its mechanical strength. This may be explained by the fact that the PKO and FA coating materials have penetrated the porous cellulose structures of the paper and the cross-linking between FA and cellulose can serve as a reinforcement of the paper in addition to a barrier for the water vapor.<sup>50</sup>

## CONCLUSION

In this study, we have developed a facile dip-coating approach to enhance the water vapor resistance property of liner paper by using palm kernel oil and furfuryl alcohol produced from agriculture wastes. The biobased coating layer significantly improves the water resistance of liner papers with a contact angle increasing from zero to about 120°, and simultaneously reduces the water transmission rate of 22% in comparison with uncoated paper. Although we mainly used the liner paper as an example in this work, it can be extended to other paper-based materials like corrugated boxes and disposable cups. Thanks to the simple processing procedures and conditions, as well as the low cost and commercial availability of the raw materials (PKO, FA, and paper), this approach has great potential and commercial viability for large-scale industrial applications. This new green coating and fabrication method offers an alternative solution to substitute the current petrochemical-based, non-biobased products widely used for a broad range of applications in food packaging, pharmacy, and e-commerce, and thus, it has the potential to reduce the environmental pressures that are faced by human beings.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c00067>.

GC-MS results of PKO, variation of the water contact angles for long time testing, AFM images of coated and uncoated liner paper samples, UV–vis absorption

spectra of paper samples, and water vapor transmission of liner paper samples by desiccant method (PDF)

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### Notes

The authors declare no competing financial interest.

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