

Improving the Barrier and Mechanical Properties of Paper Used for Packing Applications with Renewable Hydrophobic Coatings Derived from Camelina Oil

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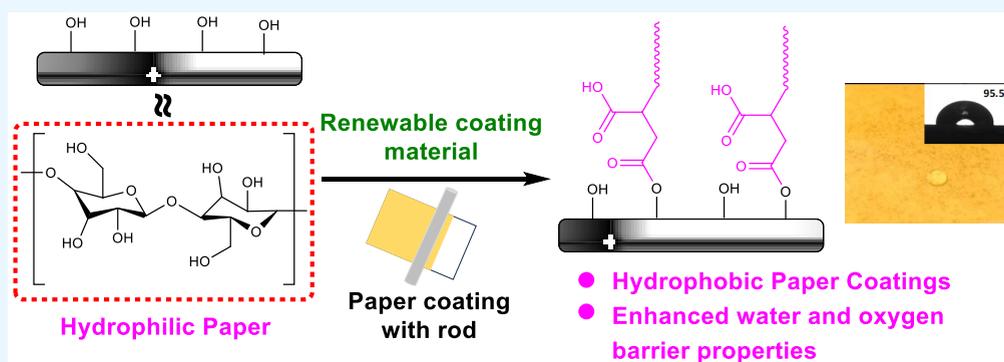
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ABSTRACT: This study looked at using modified camelina oil to develop sustainable coatings that could replace those derived from petroleum-based materials for use in packaging and other industrial sectors. Solvent-free synthesis of maleic anhydride grafted camelina oil (MCO) was carried out at two different temperatures (200 and 230 °C) to obtain sustainable hydrophobic coating materials for paper substrates. Maleic anhydride grafting of camelina oil was confirmed with attenuated total reflectance-Fourier transform infrared and NMR spectroscopic techniques, and up to 16% grafting of maleic anhydride was achieved, as determined by the titration method. MCO, obtained at different reaction temperatures, was coated onto cellulosic paper and evaluated for its hydrophobicity, mechanical, oxygen, and water vapor barrier properties. Scanning electron microscopy indicated the homogeneous dispersion of coating material onto the paper substrate. MCO-coated papers (MCO-200C paper and MCO-230C paper) provided a water contact angle of above 90° which indicates that the modified oil was working as a hydrophobic coating. Water vapor permeability (WVP) testing of coated papers revealed a reduction in WVP of up to 94% in comparison to the uncoated paper. Moreover, an improved oxygen barrier property was also observed for paper coated with both types of MCO. Analysis of the mechanical properties showed a greater than 70% retention of tensile strength and up to a five-fold increase in elongation at break of coated versus uncoated papers. Overall, the results show that camelina oil, a renewable resource, can be modified to produce environmentally friendly hydrophobic coating materials with improved mechanical and water vapor barrier properties that can serve as a potential coating material in the packaging industry. The results of this research could find applications in the huge paper packaging industries, specially in food packaging.

1. INTRODUCTION

Cellulose paper is abundant, renewable, biodegradable, non-toxic, flexible, lightweight, cheap and has adequate mechanical strength. These properties make cellulose paper one of the most useable materials in the packaging industry, which also uses other common resources like plastic, wood, and glass.^{1,2} However, the applicability of cellulose paper in various applications, specifically in the field of packaging,^{1,3–6} is limited by its structural composition. The porous network of cellulose imparts a high natural hydrophilicity, which results in poor water barrier properties and low sealability strength. Therefore, the use of cellulosic material alone is not suitable

for manufacturing the majority of packaging materials commonly used. Generally, paper-derived materials are utilized after incorporating various types of nonrenewable additives or coatings to enhance their barrier, mechanical, and sealing properties. Use of these fossil-based polymeric additives or

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coatings compromises the biodegradability of paper, eventually contributing to negative environmental impact through increased pollution.⁷ This has led to an increased global effort to develop renewable derived materials as potential replacements for conventional additives and polymeric materials within the coating industry.

Various biopolymers from renewable resources like proteins, polysaccharides, lipids, and their combinations have been studied to explore their potential for various applications including paper coatings due to their numerous advantages such as biodegradability, biocompatibility, nontoxicity, recyclability, and low-cost compared to their conventional counterparts.^{8–14} However, paper coated with protein or polysaccharide-derived biopolymers lacks water resistance due to the hydrophilic nature of these coatings, which limits their desired performance in real-world applications. A dual-layer coating approach, which uses food-safe materials like chitosan with zein, chitosan with poly(dimethylsiloxane) and zein (chitosan–PDMS–zein), and starch–zein has been reported to improve the moisture resistance and hydrophobicity properties of the coatings.^{15–17} Recently, Rabnawaz et al.¹⁸ developed renewable hydrophobic chitosan-grafted sunflower oil-based coatings for paper substrates by treating partially epoxidized sunflower oil with chitosan, which resulted in 46% reduction in the water vapor transmission rate (WVTR) with a contact angle of 98.3°. Unlike proteins and polysaccharides, which are hydrophilic and can compromise the water resistance of paper coatings, lipids are hydrophobic in nature and are thus preferred for paper coating applications. However, while lipid coatings on paper provide good moisture resistance, they come with disadvantages such as a lack of homogeneity, brittleness, and oily feeling surfaces. This suggests that further functionalization of lipids to enhance their hydrophobicity and interaction with the cellulosic paper would be beneficial.

Plant oils are renewable, biodegradable, nontoxic, inexpensive, and widely available raw materials which can be easily functionalized via single or multistep chemical processes such as maleation, silylation, acrylation, transesterification, hydrogenation, hydroxylation, ozonolysis, epoxidation, metathesis of unsaturated carbon–carbon double bonds, and thiolene addition reactions.^{19–25} Most recent reports have revealed the development of silylated plant oils via two or more steps of chemical modification for use as renewable hydrophobic moisture barrier coatings for paper substrates. Parvathy et al.²⁶ described the synthesis of silylated castor oil from epoxidized castor oil and investigated its hydrophobicity and moisture resistance as a paper coating. They reported an improved water contact angle (WCA) of up to 97° (hydrophobicity) and improved moisture barrier properties, showing a 77.5% reduction in the WVTR.²⁶ Thakur et al.²¹ developed hydrolyzable silane-modified downstream corn oil which, after its epoxidation, was cross-linked to filter paper through a condensation process. The coated paper demonstrated a WCA of 129.4° and a 67% reduction in the WVTR compared to the uncoated paper.²¹ A biobased hydrophobic coating derived from palm kernel oil and furfuryl alcohol was developed and studied by Zeng et al.²⁷ The coated paper demonstrated a 22% reduction in the WVTR with a contact angle of ~120° compared to uncoated paper.²⁷ However, no reports were found that utilize maleic anhydride-grafted vegetable oils as paper coating materials for the packaging industry. To fill this gap, the current study was carried out to explore the utility of camelina oil as a renewable hydrophobic

coating material after its single-step modification with maleic anhydride in the absence of solvent or any additional catalyst. Camelina oil has the potential to replace petroleum-derived coatings and additives because it is renewable, nontoxic, and highly unsaturated.^{28,29} Maleic anhydride, as a source of alkenyl succinic anhydride, is known to increase the hydrophobicity of the material or product.³⁰ Newly developed maleic anhydride-grafted camelina oil, as a sustainable hydrophobic coating material, was characterized and evaluated for its hydrophobicity, mechanical, and moisture barrier properties on paper substrates that could potentially be utilized in the paper packaging industry.

2. MATERIALS AND METHODS

2.1. Materials. Camelina oil was purchased from Smart Earth Company (Saskatoon, Canada). Maleic anhydride, dichloromethane, and Whatman paper No 1. (Fisher brand Qualitative grade) were purchased from Fisher Scientific (Canada). Toluene, water, phenolphthalein, potassium hydroxide, ethanol, magnesium nitrate hexahydrate, and sodium chloride were purchased from Sigma-Aldrich (Canada) except where specified.

2.2. Maleic Anhydride Grafting of Camelina Oil. Maleic anhydride grafting of camelina oil (MCO) was carried out by following a previously reported method³⁰ with slight modifications at two different temperatures (200 and 230 °C) to investigate the extent of maleic anhydride grafting and their impact as paper coating materials. In brief, 50 g (1 eq) of camelina oil and 25.3 g (4.5 eq) of maleic anhydride were placed into a 600-mL steel vessel (parr reactor 4563) equipped with a pressure gauge, an inlet gas line, an outlet line for sampling, a thermocouple thermometer, a mechanical stirrer, extra ports, and a 4848 digital temperature controller. The reactor vessel containing the reaction components was properly screwed, sealed, and then degassed by bubbling nitrogen gas into the reaction mixture for 10 min. After that, the temperature of the reactor was increased to 200 °C. The reaction was run for 4 h while the sample was collected from the reaction mixture through the sampling tube every 60 min during the reaction. The color of the reaction mixture changed from a light yellow and less viscous to a dark brown and highly viscous liquid with the passage of time as can be seen from the images provided in Figure S1. These samples were analyzed by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) to monitor the progress of the reaction (see Figure S2). After the reaction completion, the dark brown, highly viscous reaction contents were cooled and dissolved in 100 mL dichloromethane. The organic layer was washed with water (3 × 750 mL) to remove any unreacted maleic anhydride, and a brine solution was added to break up the emulsion if needed. The washed organic layer was dried with anhydrous magnesium sulfate, filtered, and evaporated on rotavapor to get dark brown colored viscous product named as MCO-200C (prepared at 200 °C). A similar procedure was used for the synthesis of maleic anhydride-grafted camelina oil at 230 °C (MCO-230C).

2.3. Characterization of Maleic Anhydride-Grafted Camelina Oil. NMR spectra were collected on a Bruker AVANCE III spectrometer with an operating frequency of 600 MHz, using a 5-mm TCI cryoprobe. All NMR experiments were recorded in CDCl₃.

Maleic anhydride-grafted camelina oil (MCO) and coated samples were characterized by Fourier transform infrared

(FTIR) spectroscopy while using attenuated total reflectance (ATR) mode. The spectra of all samples were collected by a Nicolet 6700 instrument (Thermo Scientific, Massachusetts, USA), while 64 scans were performed with a resolution of 4 cm^{-1} .

2.4. Measurement of Percent Grafting of Maleic Anhydride. The extent of maleic anhydride grafting onto the camelina oil triglycerides (developed at 200 and 230 °C) was measured by back-titration after slight modification of the method used by Muthuraj et al.³¹ In brief, 0.5 g of MCO was placed into a conical flask and dissolved in 50 mL toluene. After that 5 mL of water was added and the solution was heated at 50 °C under gentle stirring for 30 min. After cooling the mixture, 1 mL of phenolphthalein as an indicator was added and titrated against 0.1 M KOH in ethanol until a pink color appeared and persisted. The percentage of maleic anhydride grafting was calculated from eq 1.

$$\text{MA Grafting (\%)} = V_{\text{KOH}} \cdot C_{\text{KOH}} / 2G \times 98.06 \times 100 \quad (1)$$

where V represents the volume of alcoholic KOH consumed in liters for titration, C is the molar concentration of alcoholic KOH used, and G denotes the weight of the sample in grams.

2.5. Coating of Paper with MCOs. Prior to coating the paper, 50 g of each MCO (MCO-200C and MCO-230C) were individually dissolved in 15 mL dichloromethane while heating at around 50 °C. The homogeneous solution of MCO was coated onto Whatman paper No 1. To do so, the filter paper was clipped onto a glass plate, and about 25 mL of the coating solution was poured on the edge of the paper and spread over the paper using a wire bar coater (Art No. AB3050, 320 mm or 4 μm , TQC Sheen company). The coated papers were dried for 72 h at room temperature, after which a second coating was performed in the same manner as described for the first one. Uncoated paper was used as a control.

2.6. Basic Weight and Thickness. To determine the basic weight of uncoated paper and paper coated with either MCO-200C or MCO-230C, a specific size of paper was measured and weighed. For this, the papers were cut into a size of 5 cm \times 5 cm and weighed. Three samples of each paper were weighed individually, and the average value was reported in g/m^2 of the paper. To determine thickness, papers were measured using a digital hand-held digimatic micrometer with a precision of 0.001 mm. Five random locations of the uncoated and coated papers were used to evaluate the average thickness. Coating weight and thickness of the coating material on the paper were calculated by subtracting the weight and thickness of the uncoated paper from the coated papers, respectively.

2.7. Morphology of Coated Papers. Surface and cross-section morphology of uncoated and MCO-coated papers were analyzed using a Phenom ProX scanning electron microscope operated at 15 kV. The morphology of both coated surfaces and cross-sections of samples were observed. To obtain the cross-section of samples, a piece of paper from the sample was taken, frozen in liquid nitrogen, and fractured. Prior to observing the morphology of samples, the sample surfaces and the cross-sections were sputtered with conductive metal (gold) to obtain high-quality images of the samples.

2.8. Water Contact Angle. To measure the WCA of uncoated and coated papers (MCO-200C paper and MCO-230C paper), a Ramé-hart standard goniometer (260-U1) was used. For this purpose, $2.5 \times 2.5\text{ cm}$ squares of coated and uncoated papers were placed on the horizontally moveable stage of the contact angle analyzer. A drop of 5 μL deionized

water was applied on to the surface of the paper using a microsyringe, and the WCA was measured immediately. To calculate the contact angle of the water droplet from the left and right sides, the DROPimage advanced software was used with the resolution of 0.01, accuracy of ± 0.1 , and stage set at 0°.

2.9. Mechanical Properties. Tensile properties were tested in an Instron universal testing machine (Instron, Canada) following the procedures outlined in ASTM standards D828. A crosshead speed of 25.4 mm/min was used for testing.

2.10. Oxygen and Water Vapor Permeability. The oxygen permeability of the uncoated and coated papers was analyzed using an oxygen transmission rate (OTR) tester (Oxtran 2/23, Mocon), operated at a temperature and relative humidity (RH) of $23 \pm 0.1\text{ °C}$ and 0%, respectively, according to the ASTM F3985. Test samples (5 cm^2) were placed in between the two test chambers. The flow rate of high-purity nitrogen gas (carrier gas) was fixed at 10 cc/min for the cells in OTR testers, respectively. The conditioning time for test was fixed for 30 min before starting the analysis, which was critically required to purge the test cell and confirm the removal of existing air in the system line. After purging, the test started, and the permeating oxygen gas was carried to the sensor by nitrogen gas. Finally, the amount of oxygen gas was recorded in terms of oxygen permeability. Two tests were repeated for each sample, and the data are presented in terms of average value and standard deviation.

WVP of filter paper neat (uncoated) and coated with either MCO-200C or MCO-230C was determined gravimetrically using a previously reported standard method with slight modifications.³² The samples were cut into $7.5 \times 7.5\text{ cm}$ squares, which were directly mounted horizontally on the top of WVP measuring cups containing 30 g of oven-dried silica. The weight of the cups was measured, and the cups were subsequently placed in a desiccator with constant temperature and humidity controlled at 25 °C and 55% RH. The RH of 55% was obtained by using a saturated solution of magnesium nitrate. Initially, the samples were placed inside the desiccators and conditioned for 1 h, after which the initial weight was recorded. Samples were then weighed every 2 h over the following 24 h. The results obtained are shown in Table 4. WVTR was calculated from the slopes (linear) of the steady-state portion of weight gain of the cup versus time curve. Then, the WVP of the films was calculated in $\text{cc mil/m}^2\text{ day}$ as follows (eq 2):

$$\text{WVP} = \text{WVTR} \times L / \Delta p \quad (2)$$

WVTR ($\text{g/m}^2\text{ s}$) measured through the paper/samples, L represents the mean thickness of the paper in meters, and Δp denotes the partial water vapor pressure difference in pascal (Pa) across the two sides of the paper. Three tests were repeated for each sample, and the data are presented in terms of average value and standard deviation.

2.11. Statistical Analysis. All experiments were carried out in triplicate except the oxygen permeability experiment. Statistical analysis was carried out using one-way analysis of variance (ANOVA), and the results are presented as mean \pm SD (standard deviation). The significance of each mean value was determined ($p \leq 0.05$) by Duncan's tests using the SPSS software (SPSS Inc., Chicago, IL, USA).

Scheme 1. Synthesis of MCO by the Reaction of Camelina Oil Triglycerides with Maleic Anhydride

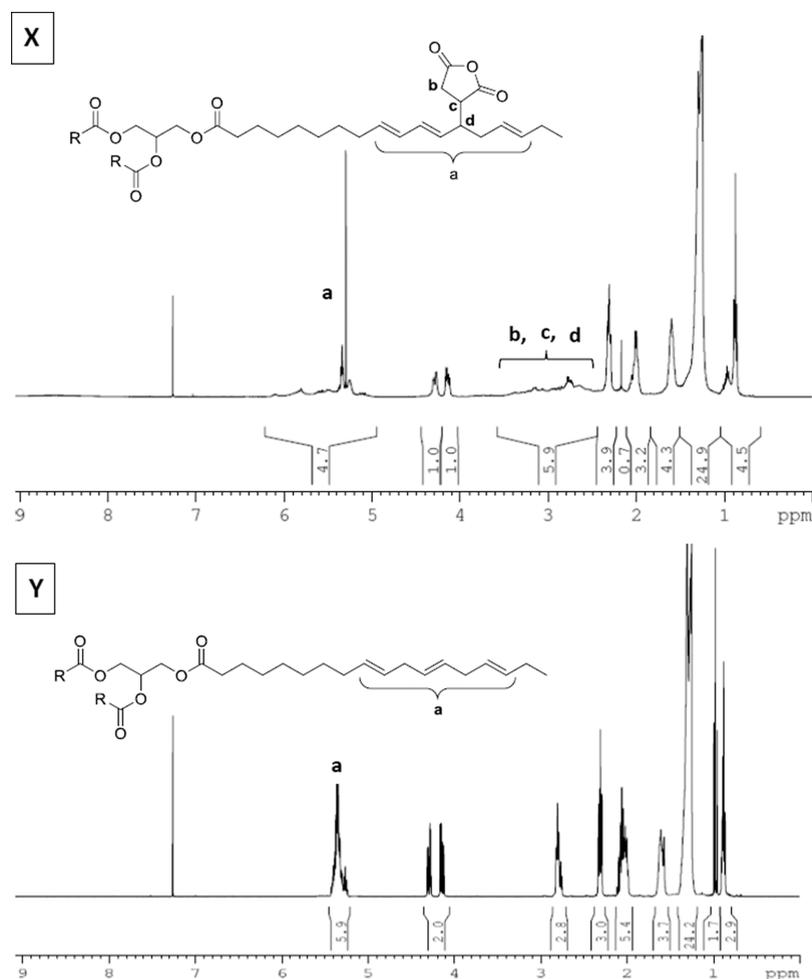
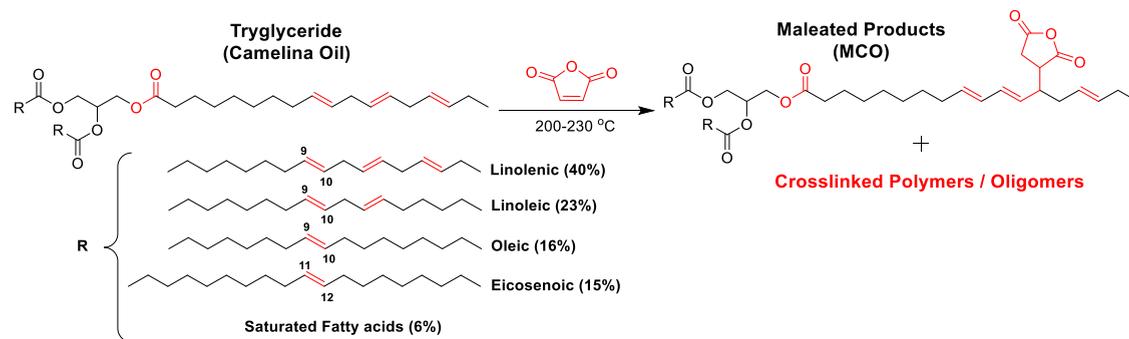


Figure 1. ^1H NMR spectra of camelina oil (Y) and MCO (X).

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of MCO. Camelina oil from an emerging oil seed crop *Camelina sativa* contains a high proportion of the unsaturated fatty acids linolenic acid (40%), linoleic acid (23%), oleic acid (16%), and eicosenoic acid (15%).²⁹ For this reason, camelina oil was chosen to be used as a hydrophobic coating material for paper substrates after its grafting with maleic anhydride. MCO was synthesized in a closed reactor vessel via a single-step chemical modification by treating camelina oil with maleic anhydride at either 200 or 230 °C for 4 h, which is a relatively green, simple, and efficient approach (Scheme 1). Grafting of maleic

anhydride involves an Alder-ene reaction between an allylic hydrogen of alkene from a nonconjugated double bond (ene) with the carbon–carbon double bond of maleic anhydride (enophile). The reaction progress was monitored by ATR-FTIR with samples collected every 60 min during the reaction. The ATR-FTIR results showed the reduction of the absorption band corresponding to the unsaturated carbon–carbon double bond at 3008 cm^{-1} and an increase in the signal intensity attributed to the anhydride functional group at 1862, 1780, and 917 cm^{-1} (see Figure S2). Moreover, the digital images of the collected samples during the reaction show the increased viscosity and the color change from light yellow to dark brown are shown (Figure S1).

The MCO was a highly viscous dark brown liquid that was characterized by ^1H NMR and ATR-FTIR. The NMR spectrum of camelina oil and MCO is provided in Figure 1. The reduction in the signal intensity of alkene ($-\text{CH}=\text{CH}-$) protons labeled as “a” at chemical shift ranging from 5.32 to 5.37 ppm in the spectrum of camelina oil (Figure 1Y), and the presence of new signal in between 2.7 and 3.4 ppm labeled as “b, c, d” associated to succinic anhydride methine and methylene protons in MCO spectrum (Figure 1X) confirms the successful reaction of the camelina oil with maleic anhydride as has been reported elsewhere.³³ Moreover, ATR-FTIR analysis of both MCOs obtained at either 200 or 230 °C (MCO-200C and MCO-230C) (Figure 2) also shows

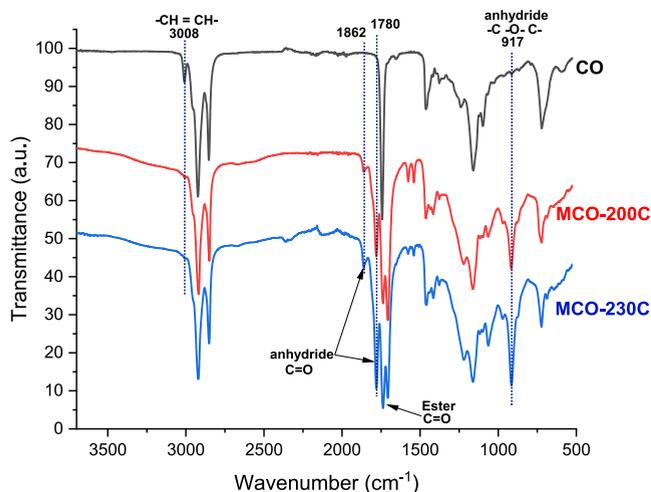


Figure 2. FTIR spectra of camelina oil (CO) and MCOs (MCO-200C and MCO-230C).

successful grafting of maleic anhydride with camelina oil triglycerides as the signal corresponding to the unsaturated carbon–carbon double bond of triglycerides (camelina oil, CO) at 3008 cm^{-1} has almost disappeared and new signals related to the substituted maleic anhydride functional group, which is converted to succinic anhydride during conjugation, can be seen at 1780 cm^{-1} ($>\text{C}=\text{O}$) and 1860 cm^{-1} ($>\text{C}=\text{O}$), and 917 cm^{-1} ($-\text{C}-\text{O}-\text{C}-$).^{33,34}

The total maleic anhydride-grafted content of MCO prepared at either 200 °C (MCO-200C) or 230 °C (MCO-230C) was determined by the previously reported back-titration method.³¹ Maleic anhydride-grafted contents of 171.31 and 183.2 mg/g were determined for MCO-200C and MCO-230C, respectively (Table 1). This shows that

Table 1. Extent of Maleic Anhydride Grafting on Camelina Oil at 200 °C (MCO-200C) and 230 °C (MCO-230C)

samples	reaction temperature (°C)	extent of grafting (mg/g)
MCO-200C	200	171.31
MCO-230C	230	183.2

MCO prepared at the higher reaction temperature (MCO-230C) has a higher level of maleic anhydride grafting compared to the MCO obtained at a lower temperature (MCO-200C).

3.2. Basic Weights and Thickness of the Coated Paper. The basic weight and thickness of the coated and uncoated papers are provided in Table 2. The basic weight and

thicknesses of the MCO-coated papers were $250.09 \pm 15.6\text{ g/m}^2$ and $0.23 \pm 0.015\text{ }\mu\text{m}$ for MCO-200C paper and $247.60 \pm 6.6\text{ g/m}^2$ and $0.23 \pm 0.015\text{ }\mu\text{m}$ for MCO-230C paper, respectively. It is notable that the basic weight and thickness of the coated papers are significantly higher as compared to the uncoated paper which has a basic weight of $90.29 \pm 1.8\text{ g/m}^2$ and a thickness of $0.13 \pm 0.01\text{ }\mu\text{m}$. Moreover, the results in Table 2 show that paper coated with MCO-200C or MCO-230C have similar basic weights, thicknesses, coating weights, and coating thicknesses. This also shows that the use of a coating bar to apply the solution is a highly effective method for achieving a homogeneous and evenly distributed coated surface. Similar reports were reported by Shankar et al.³² when wrapping paper was coated with a ternary blend of alginate, carboxymethyl cellulose, and carrageenan with grapefruit seed extract. Similar to the present study, Shankar et al.³² also observed a higher percentage increase in weight compared to thickness.

3.3. Visual Appearance and Morphology of Coated Papers. The digital images of the MCO-coated papers and uncoated paper are shown in Figure 5. It is apparent from the images that the surface of the coated papers is homogeneous and smooth which is also obvious from the scanning electron microscopy (SEM) images given in Figure 3. To evaluate the surface morphology and thickness of the coated layer on the paper, SEM images of the surface and cross-sections of the MCO-coated papers and uncoated paper were taken (Figure 3). Figure 3 shows that the uncoated paper is porous with gaps between the cellulosic fibers (Figure 3a). These features have been completely covered in the coated papers as evident from their surface images (Figure 3b,c). Moreover, the coated surface of the paper is very smooth and uniformly distributed with no cracks or voids even after drying. This represents good compatibility of the coating material with the cellulose paper. In addition, the cross-section images of the coated and uncoated papers show the extent of coating permeation into the porous structure of the cellulosic paper. SEM images of the cross-section of the coated papers reveal the layer of coated material thickness on the paper is in the range of 117–150 μm . The higher thickness of the coated layer is due to the presence of coating material which was applied twice with a coating bar to avoid any gaps or voids on the paper after coating.

3.4. ATR-FTIR Spectroscopy. ATR-FTIR spectra of uncoated paper, MCO and papers coated with MCO-200C or MCO-230C are shown in Figure 4. The results given in Figure 4 revealed that the broad and intense signal due to the stretching vibration of cellulose hydroxyl groups of uncoated paper at $3200\text{--}3600\text{ cm}^{-1}$ has been greatly reduced for papers coated with MCO (MCO-200C paper and MCO-230C paper). This shows that the surface hydroxyl groups of cellulose have been consumed after application of MCO as coating material. Moreover, the absorption bands at 1862 and 1780 cm^{-1} corresponding to anhydride carbonyls ($>\text{C}=\text{O}$) and 917 cm^{-1} associated with the $-\text{C}-\text{O}-\text{C}-$ of the anhydride group of MCO have been substantially reduced or eliminated by application of the coating material on the paper surface as shown in the spectra of MCO-200C paper and MCO-230C paper. These results indicate the possible reaction of cellulose surface hydroxyl groups with the succinic anhydride grafted on MCO.

The application of warm MCO to the paper surface may have facilitated the reaction of cellulose surface hydroxyl groups with the anhydride group of the MCO coatings as

Table 2. Basic Weight, Thickness, Coating Weight, and Coating Thickness of Uncoated and Coated Papers^a

samples	basic weight (g/m ²)	thickness (mm)	coating weight (g/m ²)	coating thickness (mm)
uncoated paper	90.29 ± 1.8 ^a	0.13 ± 0.01 ^a	ND	ND
MCO-200C paper	250.09 ± 15.6 ^b	0.23 ± 0.015 ^b	159.8 ± 17.27 ^a	0.10 ± 0.01 ^a
MCO-230C paper	247.60 ± 6.6 ^b	0.23 ± 0.015 ^b	157.31 ± 7.26 ^a	0.10 ± 0.01 ^a

^aND: not determined. The values are presented as mean ± standard deviation. Different letters in superscript within the same column indicate significant differences ($p < 0.05$).

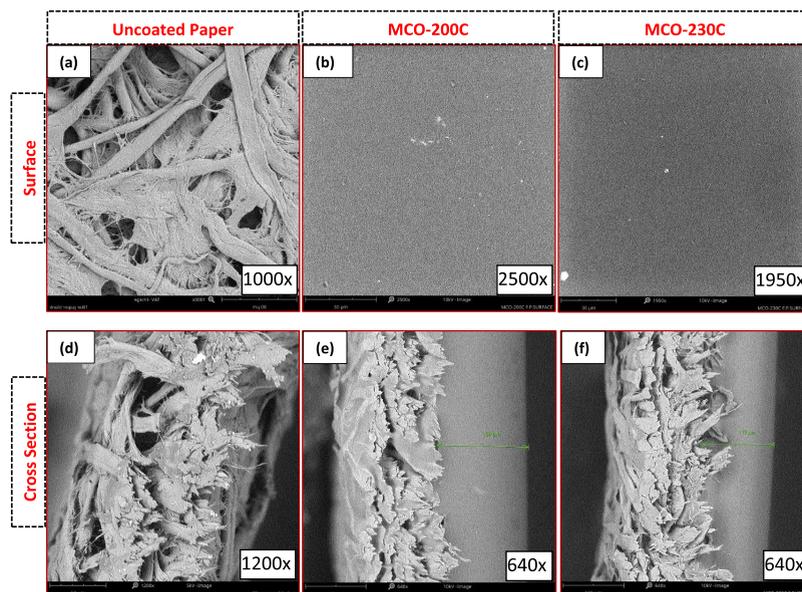


Figure 3. SEM micrographs of the surface and cross section of uncoated paper (a,d), MCO-200C-coated paper (b,e), and MCO-230C-coated paper (c,f). The number in the figure inset shows the magnification of the image.

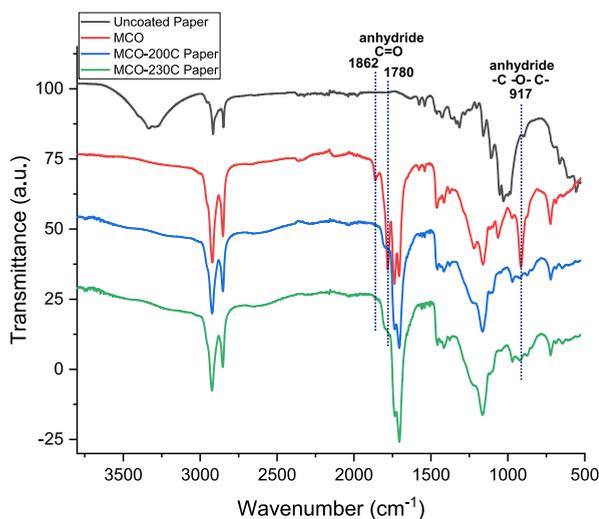


Figure 4. ATR-FTIR spectra of uncoated paper, MCO, and papers coated with either MCO-200C or MCO-230C.

shown by FTIR results and SEM images. The proposed reaction of cellulose surface hydroxyl groups with the anhydride group of MCO is shown in Scheme 2. A similar potential reaction between cellulose and anhydride groups has also been reported in the literature.³⁵ This interaction of anhydride groups with the hydroxyl groups of cellulose also suggests good compatibility of MCO with the cellulosic paper, providing a smooth and homogeneous coating onto the surface

of paper, which provides more exposed hydrophobic groups of the MCO coating.

3.5. Water Contact Angle. One of the important parameters to be evaluated for packaging material is WCA, which assesses the hydrophobic or hydrophilic nature of the surface. To determine the WCA of coated and uncoated papers, the water droplet was applied to the surface of coated and uncoated papers as shown in Figure 5. When applied to the surface of uncoated paper, the water droplet was absorbed rapidly, and the WCA was reduced very quickly to zero as no contact angle was observed during measurement. However, the MCO-coated papers have contact angles of 93.3° for MCO-200C and 95.5° for MCO-230C, which indicated a reduction in the hydrophilicity. The reason for this would be that the available surface hydroxyl groups of the cellulose paper reacted with the anhydrides of the coated MCO, which increases the hydrophobicity of the surface as has been shown in the ATR-FTIR results for the coated papers. Similar results have been reported for a silane-modified plant oil used for paper coating.³⁶

In addition, the WCA of MCO-coated papers (MCO-200C paper and MCO-230C paper) was also determined at different time intervals after the application of a water droplet onto the coated surface. A slight reduction in the WCA for both coated papers was observed after 20 min (Figure 6). This indicates the hydrophobic nature of the coated papers. Among both coated papers, the paper coated with MCO-230C has shown slightly higher WCA as compared to the paper coated with MCO-200C, which can be ascribed to higher hydrophobicity of the paper coated with MCO-230C. The higher hydrophobicity of

Scheme 2. Proposed Schematic Representation of Reaction between Cellulosic Paper and Modified Hydrophobic MCO after Coating

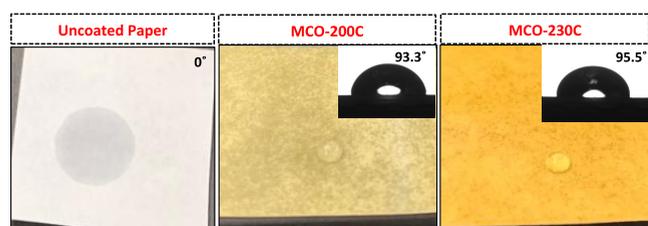
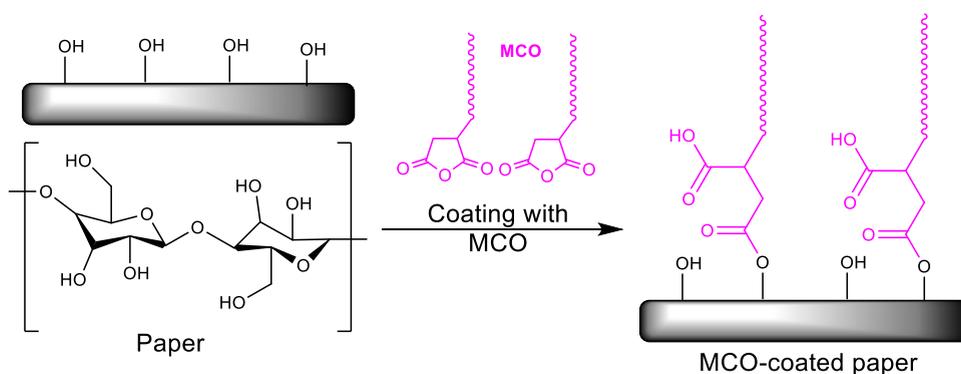


Figure 5. Digital images of neat paper, MCO-200C, and MCO-230C with the water droplet on the surface (inset showing WCA with water).

the MCO-230C coating material may be attributed to a higher level of grafting of maleic anhydride with the camelina oil as reported in Table 1.

3.6. Tensile Properties. The mechanical properties of the uncoated paper and MCO-coated papers (MCO-200C paper and MCO-230C paper) were studied to investigate their brittleness and rigidity. Tensile data of all samples is provided in Table 3. The results indicate that tensile strength, tensile modulus, and elongation at break of the paper were influenced significantly after coating with MCO. The tensile strength of uncoated paper was 15.78 ± 0.29 MPa, which was reduced to 11.24 ± 0.82 and 11.35 ± 0.65 MPa for MCO-200C paper and MCO-230C paper, respectively. This indicates the coated papers still retain more than 70% of their tensile strength. A comparable trend was observed for the tensile modulus of coated papers (Table 3), when compared with the uncoated paper. However, a significant increase in elongation at break of

8.3 ± 0.77 for MCO-200C paper and 6.4 ± 1.32 for MCO-230C paper was noticed which is up to fivefold higher than that measured for uncoated paper (elongation at break = 1.6 ± 0.12). This increase in elongation at break of coated papers can be attributed to cross-linking between the MCO and the cellulosic paper which enabled them to become elongated to a greater extent with less rigidity as compared to the uncoated paper. Similar mechanical behavior of papers coated with modified plant oils was also reported by Rabnawaz et al.³⁷ Moreover, no significant difference was observed for the mechanical properties of the two coated papers (MCO-200C paper and MCO-230C paper) as is obvious from the results provided in Table 3.

3.7. Oxygen and Water Barrier Properties. The oxygen permeability of coated papers was analyzed to determine the effect of coating on the transfer rate of oxygen across the paper, and results are shown in Table 4. In the case of uncoated paper, the oxygen permeability was over the detectable range of the machine ($4000 \text{ cc mil/m}^2 \text{ day}$). However, the oxygen barrier properties of the paper improved after coating. The oxygen permeability of MCO-200C and MCO-230C papers was ~ 814 and $\sim 1224 \text{ cc mil/m}^2 \text{ day}$, respectively. The higher oxygen barrier in MCO-200C paper might be due to the difference in the percentage of maleic anhydride grafting.

Water vapor barrier properties were determined by measuring the WVP of the papers, and the results are also presented in Table 4. The WVP of uncoated paper was $2017 \text{ g mil/m}^2 \text{ day}$, which indicates a high permeability to water vapor of the paper due to the porous structure of the cellulose fibers

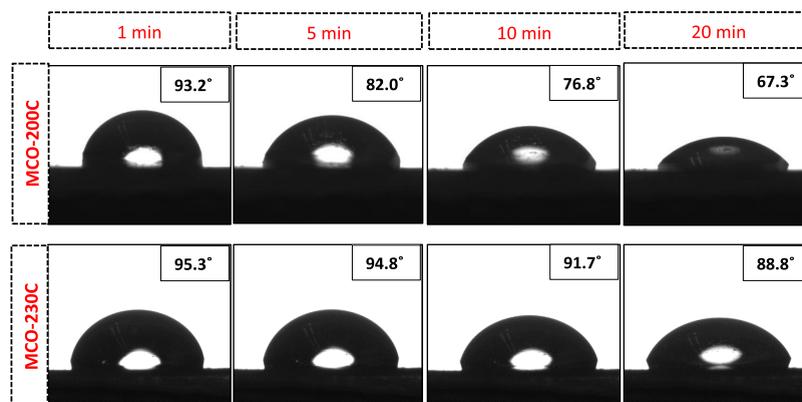


Figure 6. Contact angle of water droplet on coated papers MCO-200C and MCO-230C at different times.

Table 3. Tensile Properties of MCO-Coated Papers and Uncoated Paper^a

samples	tensile strength (MPa)	tensile modulus (MPa)	elongation at break (%)
uncoated paper	15.78 ± 0.29 ^b	1411.54 ± 17.37 ^c	1.6 ± 0.12 ^c
MCO-200C paper	11.24 ± 0.82 ^a	796.60 ± 63.25 ^b	8.3 ± 0.77 ^b
MCO-230C paper	11.35 ± 0.65 ^a	714.20 ± 64.89 ^a	6.4 ± 1.32 ^a

^aThe values are presented as mean ± standard deviation. Different letters in superscript within the same column indicate significant differences ($p < 0.05$).

Table 4. Oxygen Permeability and WVP of Uncoated and Coated Papers^a

samples	oxygen permeability (cc mil/m ² day)	WVP (g mil/m ² day)
uncoated paper	ND	2017 ± 125 ^b
MCO-200C paper	814 ± 124 ^a	175 ± 64 ^a
MCO-230C paper	1221 ± 0 ^b	121 ± 23 ^a

^aND: not determined. The values are presented as mean ± standard deviation. Different letters in superscript within the same column indicate significant differences ($p < 0.05$).

as observed in the SEM images (Figure 3). The WVP of the paper was drastically reduced to 175 and 121 g mil/m² day when coated with MCO-200C and MCO-230C, respectively. In contrast to oxygen permeability, the WVP of MCO-230C paper was found to be lower than MCO-200C paper which was due to the higher hydrophobicity of MCO-230C. The decreased WVP was due to the reduction in the number and size of pores in the paper matrix by application of the coating materials which made the papers less permeable to water vapor. Similarly, Thakur et al.³⁶ also reported a decrease in WVP of paper coated with a coating material prepared by the hydrolyzable silane groups in the downstream corn oil backbone. They explained that the decrease in WVP was due to the condensation reaction between the hydroxyl groups of paper and SECO, and as a result, the number of surface hydroxyl groups was reduced, forming a hydrophobic surface on coated paper.

4. CONCLUSIONS

In this study, we explored the potential of nonedible camelina oil as a renewable hydrophobic coating material. This was achieved through a single-step modification with maleic anhydride, eliminating the need for solvents or additional catalysts. Spectroscopic techniques (ATR-FTIR and NMR) and titration confirmed grafting levels of up to 16% maleic anhydride. Maleic anhydride-grafted Oils at 230 °C exhibited slightly higher grafting (16%) than those at 200 °C (15%). Both grafted oils increased the hydrophobicity of the paper surface with static WCAs of 93.3° (MCO-200C) and 95.5° (MCO-230C). A reduction in the tensile strength (15.78 ± 0.29 MPa) of uncoated paper to 11.24 ± 0.82 MPa for MCO-200C paper and 11.35 ± 0.65 MPa for MCO-230C paper was observed after coating with MCOs. However, an improved elongation at break was noticed for MCO-coated papers, which was up to five times higher compared to uncoated paper. Moreover, the MCO-coated papers (MCO-200C paper and MCO-230C paper) displayed increased hydrophobicity with up to a 94% decrease in WVP as compared to the uncoated papers. In addition, both MCO-200C and MCO-230C coated papers had lower oxygen permeabilities of ~814 and ~1224 cc mil/m² day, respectively. In summary, our findings highlight the potential of MCO as a sustainable, biodegradable

hydrophobic coating. Its enhanced water barrier properties position it as a promising alternative to conventional petroleum-derived packaging materials, paving the way for more sustainable packaging solutions. The developed coated paper, with its high water vapor and oxygen barrier properties, has the potential to be used in packaging of food products, which are typically moisture and oxygen sensitive.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c07213>.

Images of the reaction mixture of camelina oil grafted with maleic anhydride at different time intervals and ATR-FTIR analysis of reaction mixture of maleic anhydride-grafted camelina oil collected at different time intervals (PDF)

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Notes

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