Preparation and Characterization of Epoxidized Soybean Oil-Based Paper Composite as Potential Water-Resistant Materials

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ABSTRACT: Epoxidized soybean oil-based paper composites (ESOPCs) were prepared by fabricating poly epoxidized soybean oil (PESO) with paper. With boron trifluride diethyl etherate as catalyst, epoxidized soybean oil was *in situ* polymerized on the surface of the paper and within the interspaces of the paper cellulose fibers. Fourier transform infrared analysis confirmed the polymerization of epoxidized soybean oil. Scanning electron microscopic analysis showed that ESOPCs had nanostructured wrinkle morphology on the surfaces and the PESO combined tightly with the paper cellulose fibers. The tensile strength of ESOPCs was 17.3–24.8 MPa, which was higher than that of most vegetable oil-based neat polymers. Thermogravimetric analysis indicated that ESOPCs were thermally stable up to 360°C in a nitrogen atmosphere. Water vapor permeability (WVP) tests revealed that the WVP of ESOPCs was 3.52–4.45×10^{-12} g/m/s/Pa, significantly lower than many of other biobased polymeric materials, which would promote the application of vegetable-based polymers as potential water-resistant materials. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41575.

INTRODUCTION

In consideration of depleting petroleum resources and increasing environmental concerns, polymeric materials derived from renewable resources have been paid great attention.[1–5] Celluloses are important feedstock of various polymeric products such as cellulose films[6,7] and papers.[8] However, the repeat unit of celluloses has three hydroxyl groups that make celluloses hydrophilic and sensitive to moisture, limiting their applications as water-resistant products.[9] Various polymers are applied to coat cellulose films to obtain water-resistant property. Nitrocellulose wax, polyvinylidene chloride, and polyurethane are the most common coating materials.[9–11] However, these coating materials are mostly from petroleum resources that still give rise to environmental concerns.

Plant oil is another type of important natural resources. The main composition of plant oil is triglycerides that can be converted into various monomers for producing a great variety of polymers to meet requirement of different applications.[2–4] In particular, vegetable oil-based various polymers have been used to fabricate composites with cellulosic materials as fillers.[12–14]

Although the purposes of these researches are to increase the tensile strength of the final products by incorporating cellulosic materials, combining vegetable oil polymers with cellulosic materials may suggest a good strategy for fabrication of natural water-resistant products in view of the hydrophobicity of vegetable oils. For example, castor oil-based polyurethane has been applied to coating cellulose films to develop water-resistant materials.[11] However, the content of castor oil in the polyurethane is very low (about 30%).[11]

Polyether synthesized by direct polymerization of epoxidized vegetable oils (ESO) is one class of important vegetable oil-based polymers.[15,16] The double bonds in vegetable oils are first converted into epoxy groups, and polyether networks are synthesized by cross-linking the epoxy rings.[15,16] In these polyether networks, the triglyceride frameworks are well preserved, and the long alkane fatty acid residues make the polymers highly hydrophobic. However, to our best knowledge, these vegetable oil-based polyether networks have not been applied to fabricating water-resistant materials. In the present study, a facile method was developed to fabricate poly epoxidized soybean oil
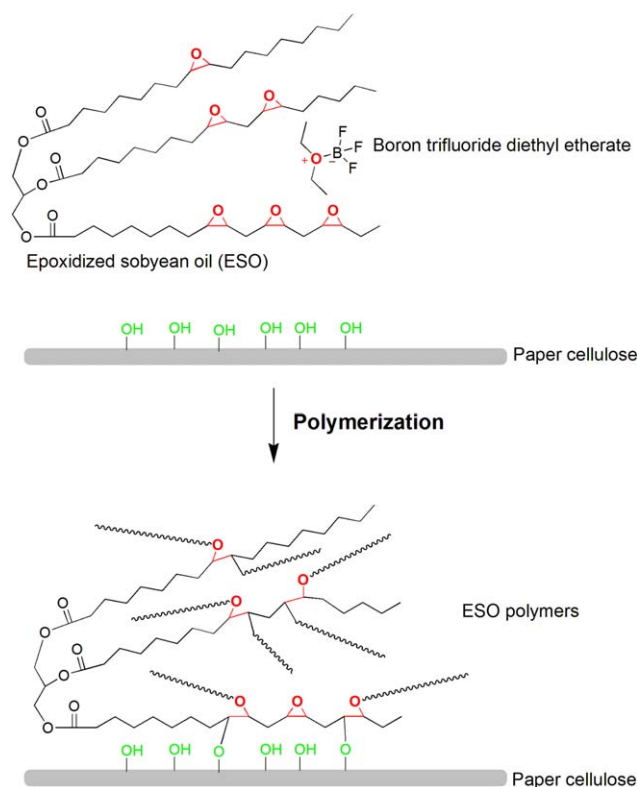
Figure 1. Schematic illustration of the preparation of the ESO-based paper composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(PESO) coated paper composites with good water-resistant property via *in situ* polymerization of ESO on the paper. The obtained ESO-based paper composites (ESOPCs) were fully characterized with Fourier transform infrared spectroscopy (FTIR), tensile test, thermogravimetric analysis (TGA), scanning electron microscope (SEM), and water vapor permeability (WVP) test.

EXPERIMENTAL

Materials and Characterization

Tetrahydrofuran and boron trifluoride diethyl etherate ($BF_3.OEt_2$) were purchased from Sigma-Aldrich. Water was Milli-Q water (Millipore, 18.2 MΩ cm at 25°C). Epoxidized soybean oil (ESO) with an average molecular weight of 930 Da and 3.2 epoxy groups per molecule were synthesized following a procedure in our previous work.[17] Paper (for printing, 210 mm × 297 mm) was purchased from Future Co., Ltd (Shanghai, China). All other reagents were of analytical grade.

A FTIR spectrometer (Nicolet Series II Magna-IR System 750, Nicolet Instrument Inc.) equipped with a horizontal germanium attenuated total reflectance accessory (ATR-FTIR) was used to monitor the reactions.

SEM photograph was obtained using a JSM 6700F machine (Japan Electron, Tokyo, Japan).

TGA was performed on a Perkin–Elmer Pyris-7 thermogravimeter in nitrogen with a gas flow rate of 20 mL/min. The samples were heated from 50°C to 650°C at a heating rate of 10°C/min.

The tensile tests were conducted according to ASTM D882-09 using an Instron universal testing machine (Model-3365) at a cross-head speed of 12.5 mm/min. The samples were cut into 30 mm wide and 100 mm long. For each sample, at least five identical specimens were tested.

The transparency of the sample was evaluated by measuring the light transmittance $T\%$ using a Unico 2800 UV–Vis Spectrophotometer by pasting a piece of sample on the side face of a quartz curvet.

WVP test was conducted according to a reported procedure (ASTM method E96 with some modifications).[18] Typically, the ESOPCs were cut into circles. The films were then sealed over with melted paraffin and stored in a desiccator at 25°C. In the cell, the relative humidity (RH) was maintained at zero with anhydrous calcium chloride. In the desiccator, a constant RH of 75% was maintained with saturated sodium chloride. Water vapor transport was determined by the weight gain of the cell. Changes in the weight of the cell were recorded as a function of time. Slopes were calculated by linear regression of weight vs time. Water vapor transmission rate (WVTR) is defined as the slope divided by the transfer area. WVP is calculated as:

$$WVP = \frac{WVTR}{P(R_1 - R_2)} \times x$$

where P is the saturation vapor pressure of water (Pa) at the test temperature (25°C), R_1 is the RH in the desiccator, R_2 is the RH in the cell, and x is the film thickness (m).

Preparation of ESOPCs

ESO was mixed with tetrahydrofuran, and the ESO weight content ranged from 10% to 60%. Boron trifluoride diethyl etherate was then added to the solution to reach a concentration of 1% (v/v). After being well mixed, appropriate amount of the monomer solution (containing 1.8 g ESO) was casted carefully over an area (100 mm × 200 mm) on the paper that was pinned on a plastic board. The tetrahydrofuran was evaporated for 24 h in a hood. Then ESOPC was taken off, and cut into pieces for characterization. According to the ESO weight content in the monomer solution, the samples were coded as PC-10%, PC-20%, PC-30%, PC-40%, PC-50%, and PC-60%, respectively.

Statistical Analysis

The results were presented as the mean ± SD of five samples. The Graphpad Prism, version 5, software was used for statistical analysis. The normality of the distribution was tested using D'Agostino and Pearson omnibus normality test. To assess multiple comparisons, a parametric one-way analysis (ANOVA) was performed with a Tukey's test.

RESULTS AND DISCUSSION

The epoxy rings, which were located in the middle of long alkane chains in ESO, were electron-donating groups. Therefore, ESO could be polymerized in the presence of cationic ions.[15,16] Lewis acids such as tin tetrachloride ($SnCl_4$) and $BF_3.OEt_2$ are the widely used catalysts, of which $BF_3.OEt_2$ is the preferred one for ring-opening polymerization of ESO in the present work since it is hydrophobic and compatible with ESO. Figure 1 schematically illustrated the reaction mechanism for preparing
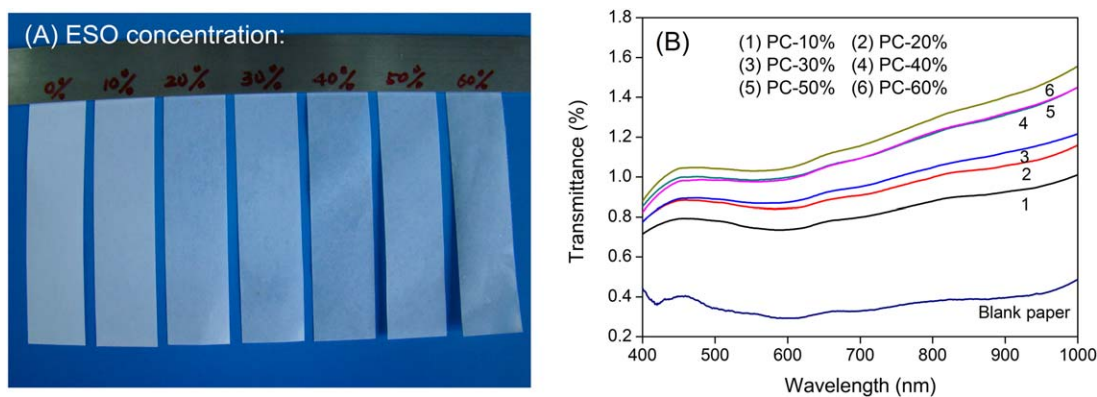
Figure 2. Photos of the paper and the ESO-based paper composites (A), and the transmittance of the samples (B). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ESOPCs. Theoretically, cationic ions were sensitive to water, alcohols, acids, and anhydrides, and the chain transfer reactions between cationic ions and hydroxyls groups could establish covalent bond connection.[19] Accordingly, when the cationic polymerization of ESO was performed on paper surface, covalent connections between PESO and paper cellulose fibers also possibly forms, though there is no direct evidence to prove this. As will be discussed later, the physical combination between PESO and paper as well as this possible covalent bond connection between them will form a strong interlock structure owing to the penetration of PESO into paper cellulose.

When $BF_3 \cdot OEt_2$ was added to the neat ESO, visible brown curd was formed immediately due to the fast cationic polymerization. Therefore, when preparing the ESOPCs, dissolution of ESO in proper organic solvent was necessary, and toluene, dichloromethane, hexane, and tetrahydrofuran were tested as solvents. When hexane was used as solvent, white precipitation was observed instantly after adding $BF_3 \cdot OEt_2$. Toluene and dichloromethane were also improper since the evaporation process of the former one was too slow while the later one was too fast. In practice, tetrahydrofuran was chosen as suitable solvent to fabricate ESOPCs. Figure 2(A) presented the photos of ESOPCs with ESO concentration ranging from 10% to 60%. The ESO concentration had a significant effect on the morphology of the composite. When the ESO concentration was lower than 40%, the ESO solution penetrated the paper, and the synthesized PESO polymer was visible both on the backside of the paper and on the supporting board. When the ESO concentration was increased to 60%, the polymerization of ESO was too fast to make the preparing process repeatable. At ESO concentration of 40% and 50%, visible bright film was formed on the frontispiece of paper surface, while no PESO was observed on the back side of the paper and on the supporting board. That is, the paper was only coated with a layer of PESO on the surface. The light transmittance results in the visible range (400–1000 nm) show that compared with the blank paper, ESOPCs is more transparent, and the transparency is positively correlated to the content of the ESO concentration within the ranges of 10%–60% [Figure 2(B)]. It was speculated that the PESO partially penetrated within interspaces between paper cellulose fibers, thus led to the enhancement in the transparency.

The ATR-FITR spectra of the blank paper, ESO, and PC-40% were shown in Figure 3. In the spectrum of the paper, the signal at 3333 cm^{-1} corresponds to hydroxyl groups, and the signal at 1034 cm^{-1} corresponds to sugar residues in cellulose. In the spectrum of ESO, the signals at 2923 and 2853 cm^{-1} correspond to CH_2 group, while the signal at 1741 cm^{-1} corresponds to ester group. In the spectrum of PC-40%, the signals of the paper at 3333 and 1034 cm^{-1} were significantly weakened, while most of the signals of ESO were clearly observable, indicating the paper was covered by a layer of ESO and PESO. BY comparing the spectrum of ESO with PC-40%, it can be seen that the signal at 823 cm^{-1} in ESO corresponding to epoxy groups disappeared in the spectrum of PC-40%, and the signal at 1074 cm^{-1} assigned to ether group came up distinctly in PC-40%, which confirms the polymerization of ESO. The ATR-FTIR spectrum of PC-50% is similar to that PC-40 (data not shown).

The penetration of PESO into the paper was confirmed by SEM. Figure 4(A) shows the SEM image of cross-section of PC-40%, indicating that the polymer was well combined with the paper and a thin film was formed on the front side of paper. The thickness of the paper and PC-40% was measured using a vernier caliper, at least seven points along edge of the samples were measured and the average values were 132.9 ± 5.1 µm and 94.4 ± 1.0 µm, respectively (Table I). Therefore, the neat thickness of PESO film was estimated to be about 38 µm. In a
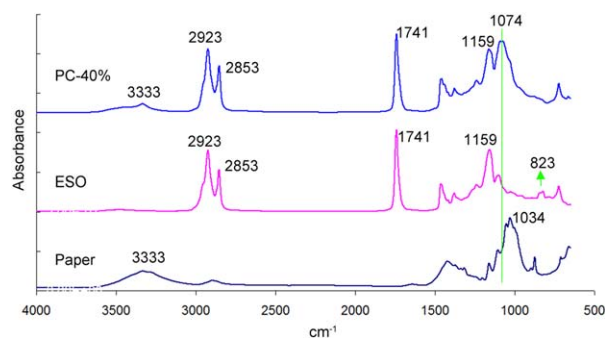

Figure 3. ATR-FITR spectra of the paper, ESO, and PC-40%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
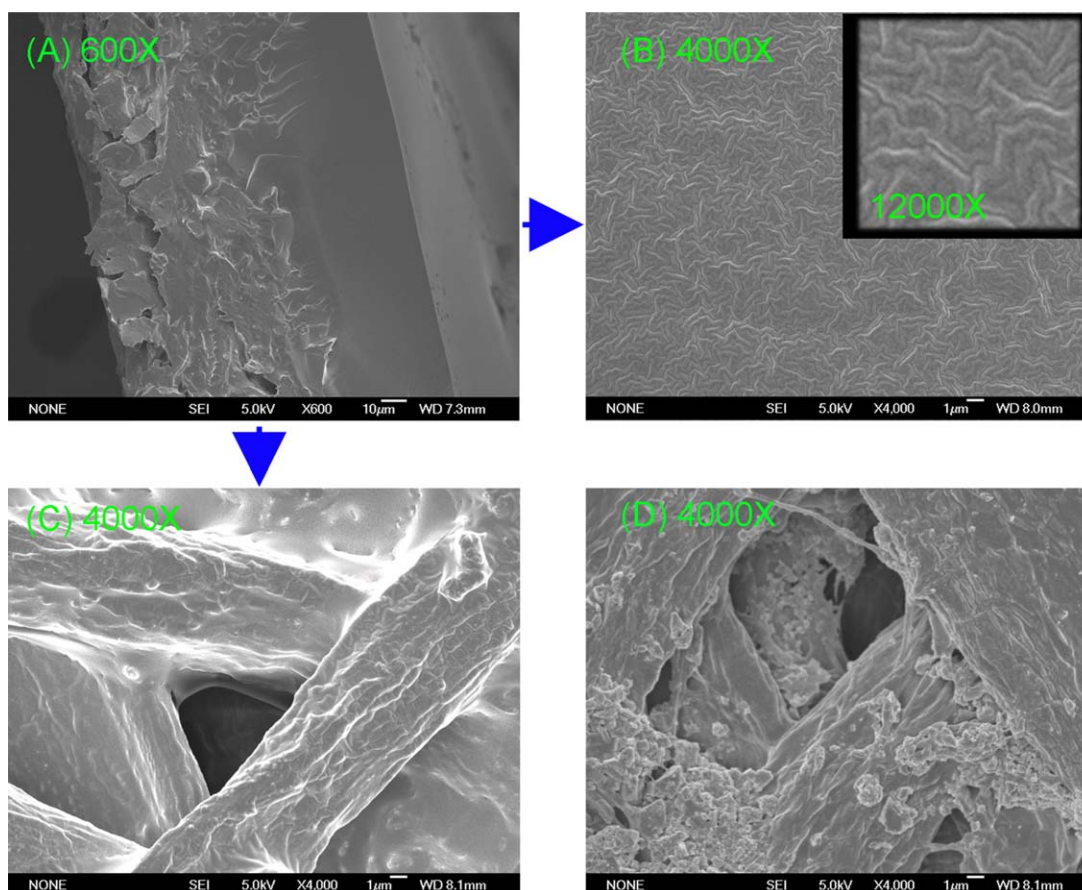
Figure 4. SEM images of the paper and PC-40%. (**A**) The cross section of PC-40%; (**B**) The PESO surface on PC-40%; (**C**) The back side of PC-40%; (**D**) The surface of the paper control. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

control experiment when the same amount of monomer solution was polymerized in a dish with size as same as the applied paper for preparing ESOPCs, a PESO film with thickness about 90 μm was formed, significantly larger than the neat thickness of PESO film formed on the paper. This suggested that a large portion of the PESO was dispersed into the interspaces between the paper cellulose fibers. In comparison to the structure of the blank paper [Figure 4(D)], the SEM image of the back side of the PC-40% indicated that although PESO was not completely penetrated, deep dispersion of PESO even to the bottom of the paper occurred and a strong combination between PESO matrix and cellulose fibers was formed.

Figure 5 schematically illustrated the dispersion and combination of PESO with paper. Both layered structure and well-dispersed structure existed in this ESO-based paper composite, which would afford the composite material excellent hydropho-

bic properties by the coating layer and a strong combination between PESO matrix and cellulose fibers by the well-dispersed structure. The SEM image of the frontispiece of the composite [Figure 4(B)] showed that the surface of the PESO film had a nanostructured wrinkle morphology (about 200 nm wide ridges). Certain nanoscale surface phenomena have been exploited to promote or prevent the attachment of living cells, and the role that these nanostructured surface properties play in the different stages of cell attachment are widely explored.[20,21] Therefore, though functionality of these nano-ridges morphology on the surface of PESO film is unknown so far, they might provide the ESOPCs with potential applications in the field of biotechnology.[20,21] Similar SEM images were also observed for sample of PC-50% (picture was not shown).

Table II listed the tensile test results of blank paper and the ESOPCs. The tensile strength of the paper was 61 MPa, while

Table I. Thickness of the Paper and the ESO-Based Paper Composites

	Thickness at different places (μm)							Average[a]
Paper	93	95	94	94	94	96	95	94.4 ± 1.0
ESO 40%	141	137	132	128	135	127	130	132.9 ± 5.1
ESO 50%	138	140	133	129	128	135	137	134.3 ± 4.5

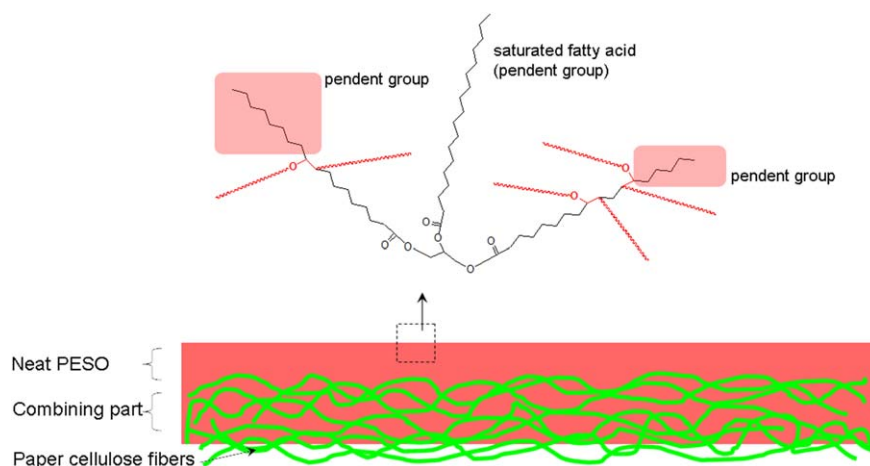[a] The difference is significant between each other ($P < 0.05$).

Figure 5. Schematic illustrations of the chemical structure of PESO, and the dispersion and combination of PESO with paper. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the tensile strength of PC-40% and PC-50% decreased to only 17 and 21 MPa, respectively. The decrease of the tensile strength and elastic modulus was attributed to the PESO layer whose tensile strength was low. At the same time, the utilization of THF as solvent during the preparation of the composites might also lead to the decrease of the tensile strength by destroying fraction of cellulose fibers in paper and even solubilizing them. It was found that the tensile strength of paper after being soaked in THF for 2 h was reduced to only around 17.6 MPa. It should be mentioned that the tensile strengths of the prepared ESOPCs were still higher than that of most of the vegetable oil-based polymers due to the contribution of high tensile strength of the paper cellulose fibers.[22] That is, as in common composites, the cellulose fibers act as tensile enhancement factor, while the PESO endows the paper composite with hydrophobic properties. The elongation at break of the composites was higher than that of the paper, but the difference was only within 1.5%.

Thermal stabilities of the paper and PC-40% were evaluated via TGA analysis, and the results were shown in Figure 6. The TGA curve of PC-50% was similar with that of PC-40% and was not shown. Evident from the appearance of a single peak on the first derivative weight loss curve, the paper had a one-step thermal degradation. While for the PC-40%, a typical two-step thermal degradation was observed. The first decomposition peak was at around 360°C due to the decomposition of the paper. The second decomposition peak took place at around 418°C due to the decomposition of the PESO. The residues were about

13%, which was probably due to other components of the paper, such as calcium carbonate.

In consideration of the hydrophobic property of the PESO coating layer, the composite might be suitable for using as water-proof materials. WVP results (Table III) showed that the WVP of blank paper was 116.76×10^{-12} g/m/s/Pa, while the values of PC-40% and PC-50% decreased to 4.45 and 3.52×10^{-12} g/m/s/Pa, respectively, which were about 25 times lower than that of blank paper. However, water contact angle measurements on the surface with PESO coating layer show that the values of PC-40% and PC-50% are 90.04° and 87.65°, respectively, which are

Table II. Tensile Test Results of the Paper and the ESO-Based Paper Composites

Sample	Stress at break (MPa)[a]	Elongation at break (%)[a]	Modulus (MPa)[a]
Paper	61.4 ± 2.0	2.0 ± 0.1	5,907.8 ± 102.3
PC-40%	17.3 ± 0.7	3.4 ± 0.5	1,784.6 ± 57.2
PC-50%	24.8 ± 9.4	2.8 ± 0.1	2,539.8 ± 851.3

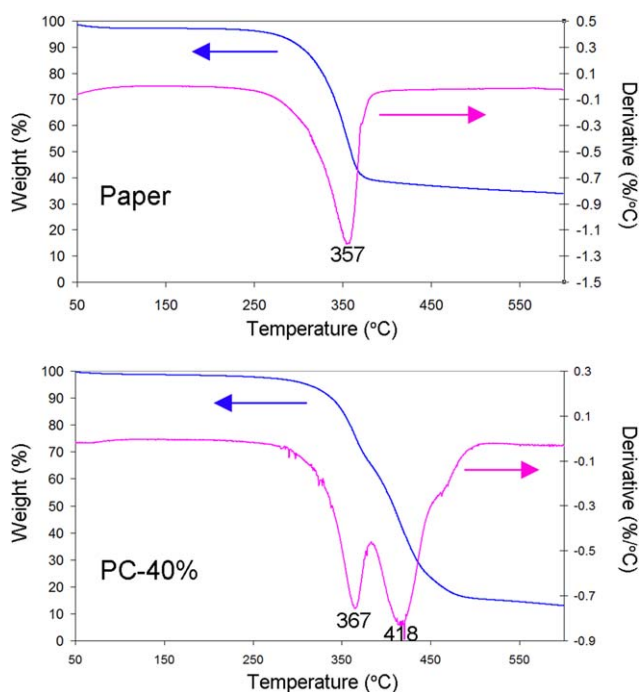[a] The difference is significant between each other ($P < 0.05$).

Figure 6. TGA plots and the first derivative curves of the blank paper and PC-40%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Water Vapor Permeability of the Paper and the ESO-Based Paper Composites

Sample	WVP ($10-10$ g/m/s/Pa)[a]	Reference
PC-40%	0.045 ± 0.005	In this study
PC-50%	0.035 ± 0.003	In this study
Blank paper	1.17 ± 0.004	In this study
Dialdehyde starch and thermoplastic dialdehyde starch	4.0–16.4	Yu et al.[18]
Kraft paper impregnated with starch acetate	1.93–9.40	Larotonda et al.[23]
Soy protein isolate/ poly(vinylalcohol)/glycerol blend films	20.3–27.8	Su et al.[25]
Poly lactic acids	0.10–0.23	Tsuji et al.[26]

[a]The difference between PC-40% and PC-50% is not significant ($P > 0.05$), but the difference between blank paper and (PC-40% or PC-50%) is significant ($P < 0.05$).

statistically lower than that of blank paper ($114.92°$). This result suggests that for the ESOPCs composite material prepared in the present work, though the hydrophobicity of the PESO coating layer is important to their good WVP, the tight combination between the PESO coating layer and the paper substrate as well as the filling of the PESO material within the interspaces of the cellulose fibril in the paper are also very important to the significant enhancement in their WVP, with which the permeation of water could be largely hindered.

The WVP values of PC-40% and PC-50% were also significantly lower than that of other bio-based materials. For comparison, Table III also lists WVP values of some reported water-resistance materials. For example, the WVP value of thermoplastic potato starch-based films was reported to be from 4.0 to 16.4×10^{-10} g/m/s/Pa, [18] which was about 89 times higher than that of the ESO-based paper composite. Kraft papers impregnated with starch acetate also had higher WVP values than PC-40% and PC-50%.[23] In comparison to starch-based films, the WVP values of soy protein isocyanate-based films were even higher (Table III). Poly lactic acids are one class of important commercial available biopolymers that are widely applied in many fields. The WVP value of poly lactic acids is in a range of 0.10 to 0.23×10^{-10} g/m/s/Pa, still significantly higher than that of the ESO-based paper composites. These large differences in WVP values are attributed to polymer properties. Both starches and proteins are naturally hydrophilic, therefore cannot provide the composite materials good water resistance property. In contrast, soybean oil is highly hydrophobic. As schematically illustrated in Figure 5, in the molecular structure of PESO coating layer, the saturated fatty acid residues in soybean oil (about 5%, mostly stearic acid)[24] form long pendent groups. At the same time the alkane chains from the chain ends to the double bonds form shorter pendent groups. The highly hydrophobic feature of soybean oil and these pendent groups provided the ESO-based paper composites with very low WVP values. Considering that the PC-40% have WVP values close to that of PC-50%, but less ESO are needed for preparing PC-40%, therefore, PC-40% would be more attractive for future applications.

CONCLUSIONS

ESOPCs were fabricated by combination of PESO with paper. ESO was diffused into the paper and polymerized *in situ*, which provided a facile protocol to prepare vegetable oil-based polymeric composites. The hydrophobic polymer networks of PESO made the WVP values of ESO-based paper composites significantly lower than that of other biobased polymeric materials. This research was considered contributing greatly to the further development of novel vegetable oil-based water-resistant composite materials for using as packaging materials.

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