Fabrication of Food-Safe Water-Resistant Paper Coatings Using a Melamine Primer and Polysiloxane Outer Layer

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ABSTRACT: Paper-based materials are highly desirable as packaging materials due to their numerous advantages that include low cost, renewability, and biodegradability. However, their hydrophilicity has limited their range of applications. Reported herein is a facile and economical approach for the preparation of biodegradable water-resistant paper for food-contact applications. Commercial printing paper and cup papers are coated with melamine, which is FDA approved for food-contact applications. Subsequently, a water-repellent outer layer is applied using poly(dimethylsiloxane) (PDMS)−isocyanate. A relationship between the PDMS concentration and water contact angles (WCAs) of the obtained coating was studied. Typically, the coated cup paper and printing paper had coating loadings of 1.61 ± 1.10 and 0.93 ± 0.74 wt %, respectively. After the coatings had been applied, the WCAs were very high (>125°), and water absorption had decreased by 70% for printing paper and by 35% for cup paper. Considering the facile fabrication method and the low-cost food-safe raw materials, herein, this approach will have great potential for the large-scale production of materials for use in food- and nonfood contact applications.

1. INTRODUCTION

The annual production of plastic has reached 407 million tons globally.1 Approximately 38% of all plastics produced is used in the packaging sector because of their excellent properties. Meanwhile, ∼244 million tons of plastic annually are disposed of either in landfills or ends in the ocean. To address this problem, greener alternatives, such as biodegradable plastic and paper-based packaging materials, are highly desirable.

Paper, paperboard, and corrugated board are widely used materials in the packaging and distribution sectors due to their numerous advantages, including their low cost, reliance on renewable feedstocks, and their biodegradable nature. Approximately 40 million tons of paper and paperboard were generated in 2014, of which 75.4% was recycled and composted in the United States according to U.S. Environmental Protection Agency.2 Despite the low cost and environmental benefits of paper and paper-based materials, they have limited applicability due to their poor water resistance.

A common approach to improve the water resistance of paper-based materials is to laminate them with a plastic film. For example, disposable paper cups bear a water-resistant low-density polyethylene (LDPE) inner liner that prevents the direct contact between a liquid and the water-absorbing paper.3 However, after use, the separation of paper from plastic is difficult, and thus paper cups end up in landfills or the ocean. Biobased plastic, such as poly(lactic acid), (PLA) inner layers are also used as alternatives to LDPE.4,5 However, PLA and paper cellulose biodegrade in different environments because PLA is compostable (biodegradable under industrial compost conditions only at temperature 60 °C in a week).6 Wax is also commonly used to enhance the water resistance, but wax has poor crack resistance as well as low thermal resistance.7,8 Thus, challenges still remain with the development of environmentally friendly water-resistant paper-based materials.

Recently, research interest has grown in the development of recyclable and biodegradable (being decomposed into basic molecules by microorganisms, and thus they can reduce the strain on our landfills) paper-based materials with good water-resistance properties for use in packaging, the medical industry, food storage, bioassay devices or microfluidics.9–11 Considerable research has been undertaken through various approaches, such as paper sizing12–16 chemical modification (layer-by-layer,17,18 grafting approach,19–21 etc.), and physiochemical modification (plasma etching, laser, etc.).22 However, most of these techniques are not applicable for practical large-scale production due to their time-consuming processes, reliance on costly raw materials, nonsuitability for food-contact applications, and the use of environmentally harmful chemicals. Thus, the development of a facile, low-cost, safe for food contact, and scalable approach remains a critical practical challenge.

The coating of paper with water-repellent materials is considered as a simple and commercially viable approach to develop biodegradable water-resistant paper. Typically, compounds with low surface energies, such as fluorinated polymers, polysiloxanes,23,24 or higher alkanes, are applied to fabricate a hydrophobic coating for paper. Although fluorocompounds render excellent water resistance due to their low surface energies, demands have arisen for the phasing out of these materials from

Received: June 22, 2018
Accepted: September 11, 2018
Published: September 25, 2018
use in paper coatings due to their toxicity and environmental concerns.\textsuperscript{35,36} Alternatively, polysiloxanes and higher alkanes have attracted great attention due to their nontoxic nature, affordability, and environmental friendliness.\textsuperscript{37} Due to their lower surface tension, polysiloxanes render greater hydrophobicity than is offered by higher alkanes.\textsuperscript{38} For example, a mechanically durable superhydrophobic coating has been applied onto fibrous cellulose surfaces.\textsuperscript{39} Considering the global importance of plastic-free water-repellent paper, Kotkamills\textsuperscript{`} has introduced a new plastic-free and easily recyclable paper AEGLE Barrier Light.\textsuperscript{40} To the best of our knowledge, however, have been no prior reports on the fabrication of water-resistant paper using fully biodegradable, low-cost materials, with suitability for food-contact applications.

In this study, water-resistant coatings for paper are reported. These coatings rely on polysiloxanes, which are affordable and biocompatible materials\textsuperscript{41} that biodegrade into nontoxic silicate minerals\textsuperscript{32–34} and thus are safe for food processing.\textsuperscript{35–37} To promote firm binding of the poly(dimethylsiloxane) (PDMS) onto paper substrates, melamine was used as a primer. Melamine is a FDA-approved material for food-contact applications (tolerable level is 0.63 mg/kg of body weight, per day)\textsuperscript{38} that exhibits superior binding to paper because it is a strong hydrogen donor as well as an acceptor, thus providing it with excellent performance as a primer. Meanwhile, the use of PDMS–isocyanate (NCO) enables the chemical grafting of PDMS to melamine via a biodegradable urea linkage formed as a result of a reaction between the NCO and amine groups of PDMS and melamine, respectively.\textsuperscript{39} In the absence of melamine, the bonding between PDMS and paper would be weak, and the PDMS could be readily washed away from the paper. As a result, water-resistant-coated paper bears PDMS as its outer layer that is firmly held onto the paper substrate by an intermediate melamine layer. This method is facile, economical, and suitable for large-scale production. The obtained melamine–PDMS coating exhibits excellent water resistance.

2. RESULTS AND DISCUSSION

In this study, a novel fabrication approach has been developed to prepare a biodegradable water-resistant paper from low-cost raw materials. To obtain biodegradable water-resistant paper via this strategy, paper (cellulose) is coated with biodegradable melamine and PDMS using a dual-layer fabrication approach. Melamine is selected because it binds strongly to the paper via hydrogen bonding. In addition, one or more of the three \textit{–NH\textsubscript{2}} moieties on the triazine core of melamine react immediately with the NCO group of the PDMS–NCO, and thus the PDMS chains bind firmly to the paper through the melamine primer. The PDMS–NCO was chosen because NCO reacts with the NH\textsubscript{2} groups of melamine cleanly and efficiently even in the presence of water. As it is critical that each PDMS–NCO chain should have at least one NCO group to react with melamine, PDMS–NCO was thus prepared by mixing PDMS–NH\textsubscript{2} with a 10-fold excess of NCO groups. It is important to note that due to the low cost and commercial availability of the raw materials (melamine, paper, PDMS), this approach is commercially viable for numerous real-world applications.

Fourier transform infrared (FTIR) analysis was performed to confirm the successful application of PDMS onto the paper. Figure 1 shows the FTIR spectra of the printed paper (a) and cup paper (b) at various stages during the fabrication process. The melamine C–N stretching in IR for the melamine-primed paper overlapped with that from the uncoated paper at 1553 cm\textsuperscript{-1}.\textsuperscript{39} The melamine–PDMS-primed paper exhibits several characteristic peaks corresponding to the PDMS. For example, the peak at 1260 cm\textsuperscript{-1} corresponds to the stretching vibration of the \textit{–CH\textsubscript{3}} groups in the Si–CH\textsubscript{3} moieties of PDMS, whereas the peak at 798 cm\textsuperscript{-1} represents the \textit{–CH\textsubscript{3}} rocking and Si–C stretching of PDMS. Thus, the FTIR spectrum indicated that PDMS had been successfully applied onto the paper substrate.

Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of the coating. As shown in Figure 2, the initial weight loss observed below 120 °C was attributed to the moisture loss. Meanwhile, the weight loss encountered between 200 and 270 °C was attributed to the decomposition of melamine,\textsuperscript{40} whereas the decomposition of PDMS occurred over the temperature range of 400–500 °C.\textsuperscript{41} The absence of peaks between 200 and 270 °C suggests the absence of free melamine presumably underwent reaction with the terminal –NCO group of PDMS–NCO. Overall, the TGA indicated that the coated paper had greater thermal stability than that of the uncoated paper, and thus the thermal stability of paper was improved after the coating. This also suggests that the coated paper is suitable for applications, in which the material may be exposed to temperatures reaching up to ~220 °C as it is thermally stable up to this temperature.

The theoretical and experimental loadings of the coating are shown in Table 1. The theoretical load value is not as accurate as the experimental load value because paper substrates were sequentially immersed into two solutions, in which there was an uncontrollable loss of substances (moisture, fillers, and sizing agent) from paper into the coating solutions. To account for the uncontrolled loss, the weight loss caused by the dipping into the acetone and water solutions was quantified using uncoated paper.

![Figure 1. FTIR spectra of (a) printing paper and (b) cup paper.](image-url)
In future, the authors intend to develop the spray method as that will overcome the above problem. The experimental loads were determined by comparing the weight gain by the coated paper and including the weight losses during the immersion into solutions. On the basis of these experimental results, the net coatings applied onto the cup paper and printing paper, were 1.61 and 0.93 wt %, respectively. Melamine loads are 0.39 and 0.16 wt % for cup paper and printing paper, respectively. And we believe that the melamine load should be lower than the obtained result because of weight loss during dipping into the PDMS−NCO solution. Unfortunately, we tried to study the weight increase before and after applying the melamine primer, but there is no statistically significant change.

![Figure 2. TGA traces of unmodified paper and melamine–PDMS primed paper for (a) printing paper, (b) cup paper.](image)

![Figure 3. Water uptake profiles of (a) printing paper and (b) cup paper.](image)

| sample      | theoretical coating load (%) | experimental coating load (%) | melamine load (%) |
|-------------|------------------------------|------------------------------|-------------------|
| cup paper   | 12.20 ± 0.47**               | 1.61 ± 1.10**                | 0.39 ± 0.045**    |
| printing paper | 3.64 ± 1.49**             | 0.93 ± 0.74**                | 0.16 ± 0.062**    |

**Values are shown as mean ± standard deviation.

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Figure 3a,b shows the water-absorbance profile for printing paper and cup paper, respectively. It is apparent that printing paper absorbed more water compared to the cup paper, possibly because printing paper had a more porous structure. As anticipated, the unmodified printing paper water gain was 123.96% for the first 0.5 h and subsequently plateaued for 24 h (the duration of water-gain test). Meanwhile, the unmodified cup paper slowly absorbed water and reached 74.22% after 24 h. For the printing paper, the melamine-primed paper (without PDMS) also showed a high water gain of ~110 wt % after 24 h, which was due to the hydrophilic nature of melamine.

The water gain exhibited by melamine–hexamethylene diisocyanate trimer (HDIT)-primed paper was reduced down to 47.51 and 48.23% for printing paper and cup paper, respectively. This was due to the relatively hydrophobic nature of the HDIT. As expected, the best water resistance among the tested samples was observed for the melamine–PDMS-primed paper. For example, the water gain was reduced down to 37.77% for the printing paper and 48.23% for cup paper. Also, the water uptake profile indicates slow water absorption by the melamine–PDMS primed paper, thus suggesting that this sample exhibited improved and robust water resistance.

The water contact angles (WCAs) were also determined for paper samples at various stages of fabrication (see Figure 4). The results indicate that unmodified printing paper was hydrophilic and showed poor resistance to water because the water droplet slowly permeated into the paper. Meanwhile, even though unmodified cup paper had a certain degree of water resistance (with a WCA of ~100°), some water marks remained on the sample after 3 min of contact with water, indicating that water had diffused into the paper substrate. We observed that the printing paper was even more hydrophobic as treatment of this printing paper with melamine reduced the WCA even further from 89° for unmodified printing paper to below 65° for the melamine-primed paper. To our surprise, the WCA for the cup paper was improved after melamine treatment. Considering that after melamine coating the water gain was reduced both for the printing and cup papers, but the decrease in the WCAs for the printing paper after melamine coating is likely originated from the highly porous structure of printing paper. Both melamine−HDIT and melamine−PDMS primed papers showed high WCAs. For example, in the cases involving melamine−PDMS primed paper, the WCAs were >125° for both types of paper,
thus indicating that they exhibited excellent water resistance. These findings were also consistent with the results obtained from the water-gain tests. The enhanced performance that was exhibited by the PDMS-coated paper is due to the strong water repellency of PDMS. It is noteworthy that both melamine−HDIT and melamine−PDMS primed papers showed no noticeable change in the WCA over time, indicating that these coated paper samples exhibited long-term water resistance.

To investigate the effect of PDMS−NCO concentrations on the WCA of the resultant coatings, both printing and cup papers were coated from PDMS−NCO solutions at different concentrations. Figure 5 demonstrates the effect of increasing the concentrations of the coating solutions and their influence on the WCA. Initially, the WCAs were improved with an increase in the PDMS concentration. For example, the highest hydrophobicity for the cup paper was achieved at a 0.5 wt % PDMS−NCO concentration, whereas for the printing paper the highest WCA was achieved at 0.1 wt % of PDMS−NCO. However, with further increases in the concentration of PDMS, the WCAs gradually began to decrease. This unexpected decrease in the WCAs with an increasing PDMS concentration can be attributed to the fact that WCAs are influenced by surface roughness as well as surface energy. Initially, increasing the PDMS concentration yielded higher WCAs because it provided a lower surface energy while the roughness of the paper surface was retained. However, further increases in the PDMS concentration beyond a certain value also likely reduced the surface roughness due to the greater number of liquid-like PDMS chains on the surface. Therefore, it is apparent that an optimum PDMS concentration exists (below 1 wt %) at which the surface energy can be reduced, whereas the roughness of the surface can be retained to provide the maximum repellency. Interestingly, the observation of the highest WCAs at a low PDMS concentration strengthens our claim regarding the low cost of this coating strategy.

Scanning electron microscopy (SEM) images of cup paper at different stages of fabrication are shown in Figure 6. Inset images are taken to get a close-up view of the samples. The unmodified cup paper is comprised of a network of fibers (Figure 6a). After the melamine coating, there is no noticeable change in the paper texture (Figure 6b), however, fiber surface became smoother upon melamine−HDIT coating (Figure 6c). It is possibly due to the flexible aliphatic HDID chains on the surface. Melamine−PDMS (Figure 6d) has fibers with much smoother texture caused by the liquid-like PDMS chains on the surface.

SEM images of printing paper at different stages of fabrications are shown in Figure 7. The unmodified cup paper is comprised of cellulosic fibers of various diameters. Except for melamine−PDMS-coated paper (Figure 7d), where the surface texture is smooth due to PDMS chains, the uncoated (Figure 7a), melamine-coated (Figure 7b), melamine−HDIT coated (Figure 7c) print papers had rough textures.

One key aspect of this coating is the biodegradability of the coated paper. On the basis of the nature of the materials (PDMS, melamine) used for the coating, we expect that the coated papers are biodegradable. Also, linkage formed by the reaction of PDMS−NCO and melamine is urea bond, and urea bonds are biodegradable. Coated paper fabricated in this study has some degrees of cross-linking due to the multifunctional nature of melamine and trifunctional HDIT, however, even cross-linked polyurea is known to biodegrade though at a slower rate. In the future, the biodegradability studies of the coated papers will be conducted.

3. CONCLUSIONS

In this study, we successfully applied a facile and economical approach for the preparation of biodegradable water-resistant paper coatings. A simple two-step dip-coating approach was used to fabricate the coated paper. The obtained surface exhibited hydrophobic properties with WCAs exceeding 125° at a 1 wt % loading of the coating. The water absorbed by the coated papers was significantly reduced in comparison with their uncoated counterparts, and also the water-gain time was enhanced, thus confirming the high water resistance of the coated paper.
This novel approach can be extended to other types of papers and cellulose-based materials. Considering the biocompatibility and full biodegradability of these coatings as well as the low cost of the raw materials, this strategy provides a viable green route for the fabrication of disposable cups and corrugated packages.

4. EXPERIMENTAL SECTION

4.1. Materials. Melamine (purity 99%), acetone (purity 98%), and monoaminopropyl-terminated poly(dimethylsiloxane) (PDMS–NH2) with a molecular weight of 2000 g/mol were purchased from Sigma Aldrich and used without further purification. Polyisocyanate (HDIT) was supplied by a
proprietary manufacturer. Printing paper was purchased at a local supermarket. Cup papers were purchased from a local coffee shop (Spartan at Michigan State University, MI). Prior to the application of the coating, the polymer layer on the commercial paper cups was carefully peeled off.

4.2. Methods and Characterization. 4.2.1. Fabrication of Water-Resistant Paper. Figure 8 shows the fabrication of the two-step approach used to achieve the desired water-resistant paper. First, melamine was applied as a primer. In the next step, PDMS–NCO solution was applied as a water-resistant coating.

4.2.1.1. Preparation of PDMS–NCO Solution. First, HDIT (100 mg) was dissolved in acetone (5 mL). Subsequently, PDMS–NH$_2$ (200 mg of PDMS–NH$_2$ in 5 mL of acetone) was added into the HDIT solution and homogenized using a vortex mixer for 30 s. The concentration of the obtained PDMS–NCO solution was recorded as the concentration of PDMS, i.e., 2 wt % in this case. All of the characterization and testing were based on the formulation of 2 wt % PDMS–NCO coating. Moreover, to study the effect of PDMS–NCO concentration on coating properties, PDMS–NCO solution with various concentrations (0.1, 0.5, 1, 2, 4, and 8 wt %) were prepared by varying the amount HDIT and PDMS–NH$_2$ proportionally, but keeping the amount of acetone constant.

4.2.1.2. Coating Application. Printing paper and cup paper were cut into 1 × 1 in.$^2$ sections prior to coating. Aqueous melamine solutions were prepared by dissolving melamine in hot water at a concentration of 0.20 wt %. Paper substrates were immersed in the melamine solution for 10 s, and they were then left under ambient conditions for 5 min to enable solvent evaporation. These paper samples were then dipped in a PDMS–NCO solution for 10 s. The paper samples were subsequently allowed to dry in open air for 5 min prior to heating at 120 °C for 1 h. The resultant coated paper samples are referred to as melamine–PDMS-primed paper.

4.2.1.3. Preparation of Reference-Coated Papers (without PDMS). Samples that were only coated with the melamine solution are from here onward referred to as melamine-primed paper. Meanwhile, samples that were dipped into the melamine solution and subsequently in the HDIT solution are from here onward referred to as melamine–HDIT-primed paper.

4.2.2. Characterization. Fourier-transform infrared (FTIR) spectra of unmodified paper, melamine-primed paper, melamine–HDIT-primed paper, and melamine–PDMS-primed paper were recorded using a Shimadzu IR Prestige21 FTIR spectrometer (Shimadzu Co., Columbia, MD) equipped with an attenuated total reflection attachment (PIKE Technologies, Madison, WI). A total number of 64 scans with a spectral range of 4000–400 cm$^{-1}$ and a resolution of 4 cm$^{-1}$ were recorded for each sample.

Thermogravimetric analysis (TGA) was recorded to determine the thermal stability and weight gain of the coated paper (from 2 wt % PDMS–NCO solution) in reference to the uncoated paper. The TGA was performed using a Q-S50 thermogravimetric analyzer (TA Instruments, New Castle, DE). The weight loss exhibited by the samples was recorded as a function of the temperature range from 23 to 600 °C at a ramp rate of 10 °C/min under a nitrogen flow with a flow rate of 40 mL/min.

The weight gain by the paper as a result of the application of the coatings was quantified via gravimetric methods. The weight of solution absorbed by paper substrates was recorded, and the theoretical loading of the coating was calculated based on the solution absorbed by the paper and their corresponding concentration. The experimental load of the coating was quantified by calculating the difference between the weight gain of the coated paper and that of the corresponding control. The weight before and after coating was recorded using a microbalance. To minimize the experimental error, the control paper substrates were dipped into pure water and subsequently into acetone. Both the control group and the coated samples were dried under identical conditions.

To study the safety of melamine in paper coating, the theoretical melamine loading on the coated paper was studied using gravimetric approaches similarly to the above-mentioned weight gain analysis. Paper substrates were dipped into deionized water as a control. Experimental melamine loading was not studied because melamine loading was too little, that there was no significant difference before and after melamine primer was applied according to preliminary test.

4.2.3. Water-Resistance Tests. Prior to testing, all of the samples were preconditioned by drying at 70 °C under vacuum for 1 h to remove moisture. Water-gain tests were conducted by dipping preconditioned samples into deionized water for periods of 0.5, 1, 2, 3, 5, and 24 h. The weight of each sample was recorded after wiping excess water from the surface with a clean tissue. Water-gain was calculated using the eq 1

\[
\text{water gain} = \frac{\text{final weight} - \text{initial weight}}{\text{initial weight}} \times 100
\]

4.2.4. Water Contact Angles (WCAs). Water contact angles (WCAs) were measured using a 590-U1 Advanced Automated Goniometer with DROPimage Advanced software (Ramé-hart Instrument Co., NJ). Deionized water droplet (10 μL) was placed onto the sample and allowed the droplet to sit for 3 min before contact angle was measured. The reported WCA values are the average of three measurements on different areas on the surface of each sample.

4.2.5. Scanning Electron Microscopy (SEM). JEOL 6610 SEM (JEOL Ltd., Japan) system was used for the SEM analysis. Samples were mounted on aluminum disks and coated with a gold layer (10 nm thickness) using a sputtering approach. All samples were examined with an accelerating voltage of 15 kV.

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**Notes**

The authors declare no competing financial interest.
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