BIOMIMICKING HYDROPHOBICITY USING MICROSCALE STRUCTURES FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

Hydrophobic surfaces provide special characteristics for biomedical applications ranging from tunable protein adsorption, cellular interactions, and hemocompatibility to antibacterial coatings. In this research, we biomimic the hair-like micro-whisker structures of magnolia leaf using a synthetic polymeric formulation. Optical and scanning electron microscopy images revealed the presence of micro-whiskers resulting in higher water contact angles. The top layer of the magnolia leaf had a contact angle of 50º as compared to the hydrophobic bottom layer at 98º. A synthetic polymeric formulation was coated on different materials to study its effect on hydrophobicity. The coating was replicated (n=3) on each of the materials used such as glass, polymer, fabric, wood, and stainless steel. A surface tensiometer was used to measure the transition from hydrophilic to hydrophobic interactions between water and the substrate materials. Contact angle measurements revealed an increase in hydrophobicity for all the materials from their original uncoated surface. Glass displayed the highest increase in contact angle from 37º to 90º. Phase analysis of the coated region was performed to characterize the surface exposure of glass substrate to the synthetic polymeric formulation. An increase in the coated region showed a significant increase in contact angle from 50º to 95º. This research lays the foundation to develop and understand hydrophobic coatings for several biomedical applications including non-fouling implant surfaces, lab-on-chip devices, and other diagnostic tools.

Keywords: Biomimicry, Hydrophobicity, Biomedical Applications, Nanotechnology, synthetic polymer, FTIR spectroscopy, micro-whiskers, Scanning Electron Microscopy (SEM)

INTRODUCTION

Hydrophobic surfaces serve a crucial role in the biomedical field, creating pathways for drug delivery and substrates for bacterial growth [1]. Nature possesses water-repelling surfaces on plants such as magnolia tree leaves, lotus leaves, and insect (cicada) wings [2], [3], [4]. Microscopic hair-like structures and a waxy coating on several plant leaves and structures seem to be responsible for the hydrophobic property. Magnolia leaves often use hydrophobicity as a self-cleaning mechanism [5]. Likewise, hydrophobic surfaces can be re-purposed for the development of self-cleaning photovoltaic cells [6], and more importantly, diagnostic, and surgical tools [7]. In particular, hydrophobic tools have been used to protect surgical instruments from fluid contamination [8]. Improvements in the level of hydrophobicity and the creation of superhydrophobic surfaces can aid in minimizing contamination in surgical settings [9]. Further, prior research has implemented hydrophobic surfaces to limit bacterial growth on implants such as knee or hip implants [10]. Other applications of hydrophobic surfaces include creating scaffolding surfaces for patterned cell growth and controlling drug delivery [11], [12], [13]. Hydrophobic surface properties have also been used to serve as antibacterial coatings on silicone rubbers [14]. In the past, a polytetrafluoroethylene (PFTE) powder cured with UV radiation has been used to create (super)hydrophobic surfaces. These surfaces have been used for enabling the evaporation of samples to detect bacteria and other markers in the blood [11]. However, the varying degrees of hydrophobic surfaces have not been widely studied. Further, the investigation of the optimal number of polymer coatings to maximize hydrophobic properties is vital in improving cost-efficiency and effectiveness of the surface. Since the degree to which a surface repels liquids may have a maximum threshold, after a certain number of coatings the polymer may no longer improve the hydrophobic properties. Therefore, applying multiple coats even after the maximum threshold will be expensive and inefficient.

This research aims to replicate the hydrophobic property of magnolia leaves by coating multiple surfaces with a synthetic polymeric formulation. Further, this study investigates the effect of multiple polymer coatings on the intensity of hydrophobicity – which is assessed using contact angle measurements. Former research establishes surface geometry and categorizes degrees of hydrophobicity (without investigating the optimal degree of hydrophobicity) [15], [16]. This research lays the foundation for creating hydrophobic surfaces at varying repelling degrees using a synthetic polymer.

METHODS

This research was conducted in three parts: (a) scanning electron microscopy (SEM) imaging of magnolia leaf properties, (b) chemical analysis of synthetic polymer, and (c) hydrophobic polymer testing. The magnolia leaves were initially imaged using a BX51 Olympus optical microscope. However, in order to acquire more accurate imaging results, SEM was conducted using the Zeiss Auriga SEM. In stage two, chemical analysis of synthetic polymer was conducted using Fourier-transform infrared (FTIR) spectroscopy on Shimadzu ATR FTIR. Lastly, the effectiveness of synthetic polymer was analyzed using contact angle measurements on the Drop Shape analyzer (KRUSS-DSA25E). The synthetic polymer was applied on surfaces including acrylonitrile butadiene styrene, steel, wood, glass, and cloth fibers to assess the extent to which each surface repelled water after single or multiple coatings of the polymer. To ensure accurate and statically significant results, each contact angle measurement trial was conducted three times (n = 3).

Magnolia Leaf Imaging

Magnolia leaf was freshly plucked from the tree and stored at room temperature (20°C) for 2 hours before performing optical and electron microscopy. The storage at room temperature was intended to eliminate any excess moisture and prevent dehydration of the leaf surfaces. The top and bottom surfaces of the magnolia leaf were imaged using optical and electron microscopy. A BX51 Olympus optical microscope was used to acquire preliminary imaging data including the phase analysis. The Zeiss Auriga SEM was used to conduct detailed imaging and measurements to characterize micro-structure size. The leaf surfaces were cut into small sections (10 mm x 10 mm) and sputtered with a gold-palladium alloy for SEM imaging.

Synthetic Polymer Chemical Analysis

Aqueous and solid states of synthetic polymer were tested in FTIR spectroscopy performed on Shimadzu ATR FTIR. Since the synthetic polymer is in the aqueous state at STP condition (t = 20ºC), the polymer solution was dried at 45ºC to form a thin solid film for FTIR analysis. The aqueous solution is the original state of the synthetic polymer whereas, the gel state was obtained using the above-mentioned drying procedure to enable FTIR measurement. The aqueous synthetic polymer contained 80% water content and balance polymeric and volatile components. The gel state represented primarily the polymeric and coagulated volatile compounds with minimal water content. The gel state was preferred for the FTIR analysis as it presented dominant peaks of the formulation content over the aqueous state as explained within the results section.

Hydrophobicity Coating Testing

After chemical analysis, a single coat of synthetic polymer was applied to the following materials: Acrylonitrile Butadiene Styrene, steel, wood, glass, and cloth fibers. The optimal testing materials were chosen based on their routine usage and wide range of applications. An aliquot of 0.5 mL synthetic polymer was uniformly applied to each of the surfaces and allowed to dry for 20-30 minutes. The contact angle between water and the respective surface was measured using Drop Shape analyzer (KRUSS-DSA25E) with the sessile drop method at room temperature. This measurement was repeated (n=3) for each surface with no coating (control), single coating, and double coating. The effectiveness of synthetic polymer was assessed based on the degree of contact angle measurement.

RESULTS

Magnolia Leaf Imaging

Micro-structured whiskers on the bottom surface of the magnolia leaf were present based on optical and electron microscopy imaging results (Figure 1). Based on SEM observations, each hair-like micro-structure was approximately 15 µm in width. Contrastingly, the top surface of the magnolia leaf (which has a waxy texture) appeared to be relatively smooth based on imaging results (Figure 2). Therefore, it can be determined that the micro-structured whiskers on the bottom surface of the leaf are largely responsible for the leaf's hydrophobic properties. This finding can be further explained using the contact angle measurements discussed in subsequent sections.

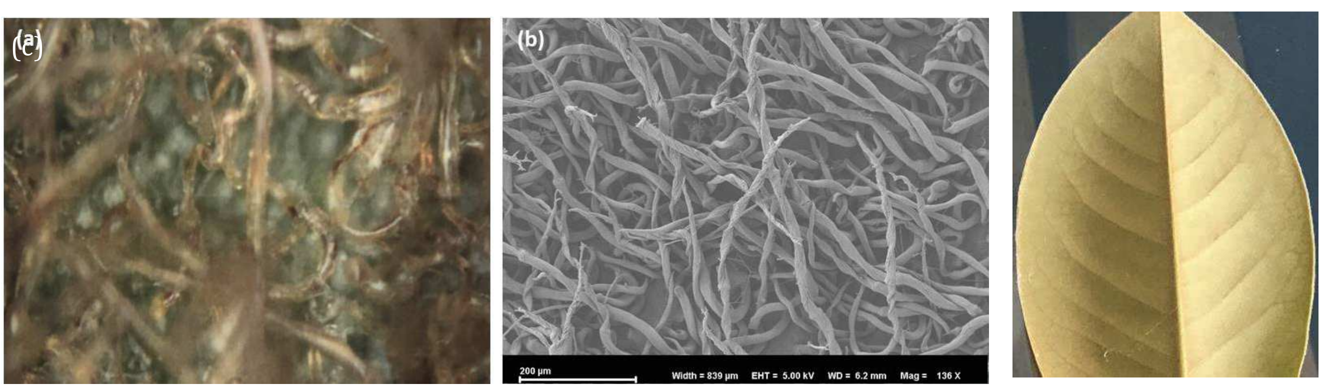

Figure 1. Bottom hair-like surface of magnolia leaf using (a) Optical microscopy (b) SEM image and (c) actual leaf surface

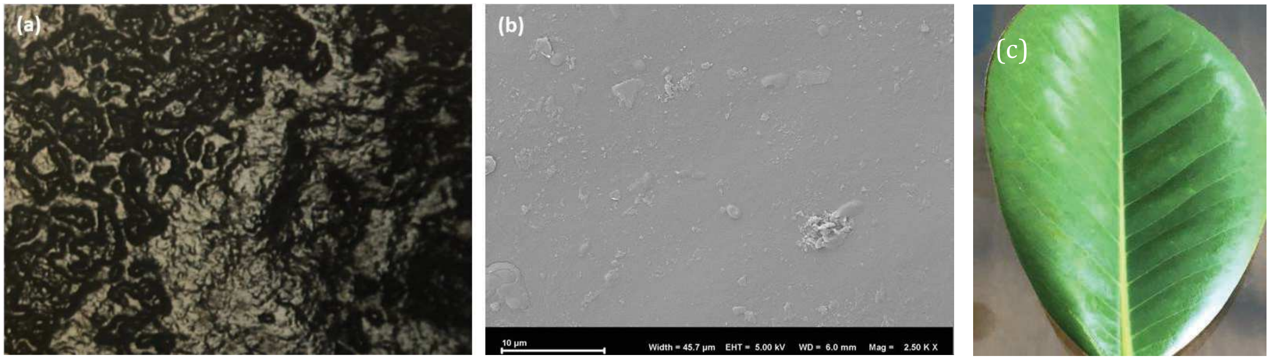

Figure 2. Top smooth surface of a magnolia leaf using (a) optical microscopy (b) SEM imaging and (c) actual leaf surface.

Chemical Analysis

Based on the FTIR analysis (Figure 3), both the solid (gel) and aqueous samples of synthetic polymer had peaks around a wavelength of 700-900 cm^{-1}, 1000-1250 cm^{-1}, and 2900-3300 cm^{-1}. These peaks indicated the presence of the following compound classes: benzene derivatives, alkene, amine, silicon oxygen bands, alkane, and (primary) alcohol. However, the alcohol peak in the aqueous sample was more prominent compared to the peak (around 3000) in the solid sample. This may be due to the degradation/evaporation of chemical compounds during the heating of the solid sample.

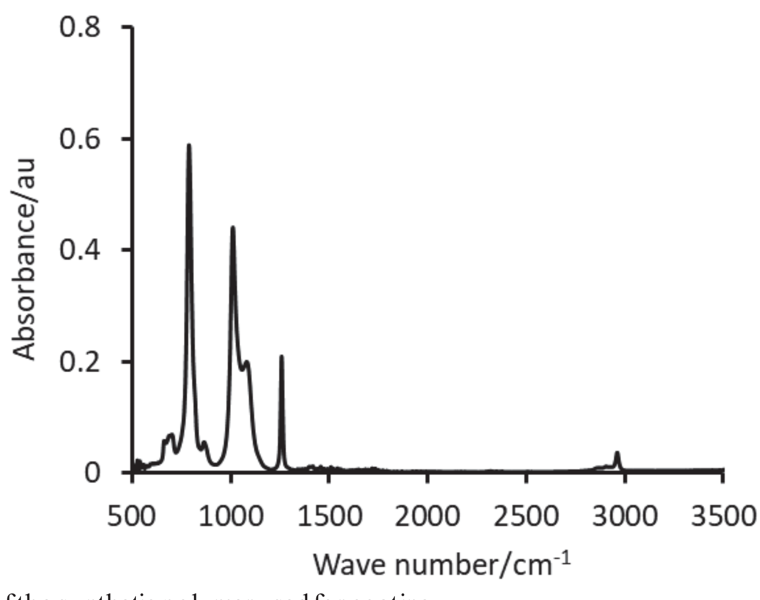

Figure 3. FTIR spectrum of the synthetic polymer used for coating.

Contact Angle Measurements

A comparative analysis of contact angle measurements based on number of coatings was conducted for different materials as shown in Figures 4 and Figure 5. A sample size of (n=3) was used for all experiments. Based on the data, glass had the lowest non-coated contact angle measurement, and the magnolia leaf bottom surface had the highest non-coated measurement. Due to the natural super-hydrophobic property of the bottom surface of the magnolia leaf, it was not coated with the synthetic polymer. The surface with the largest increase in hydrophobicity was glass (contact angle increased by 53º), followed by wood. Each of the coated materials showed a significant increase in hydrophobicity following each additional coating. The second layer of coating resulted in a superhydrophobic surface behavior based on the increased surface area coverage with micro-whiskers.

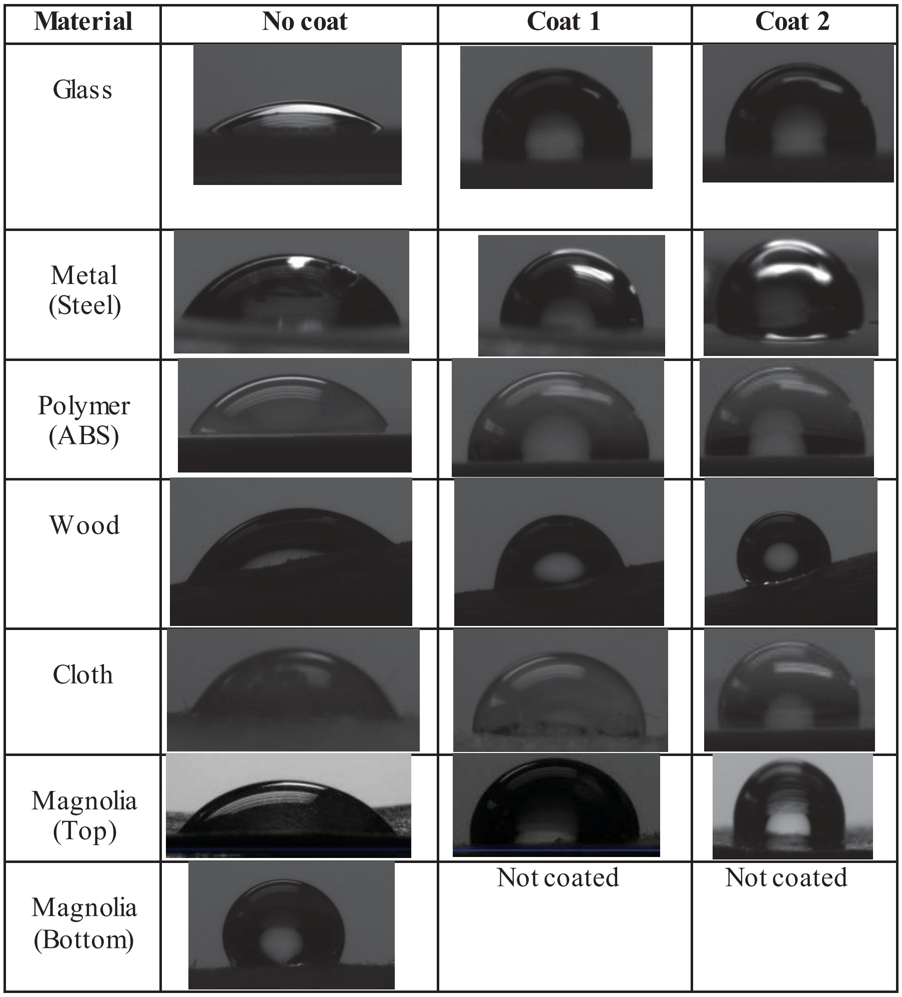

Figure 4. Contact angle measurements based on the number of coatings for different materials.

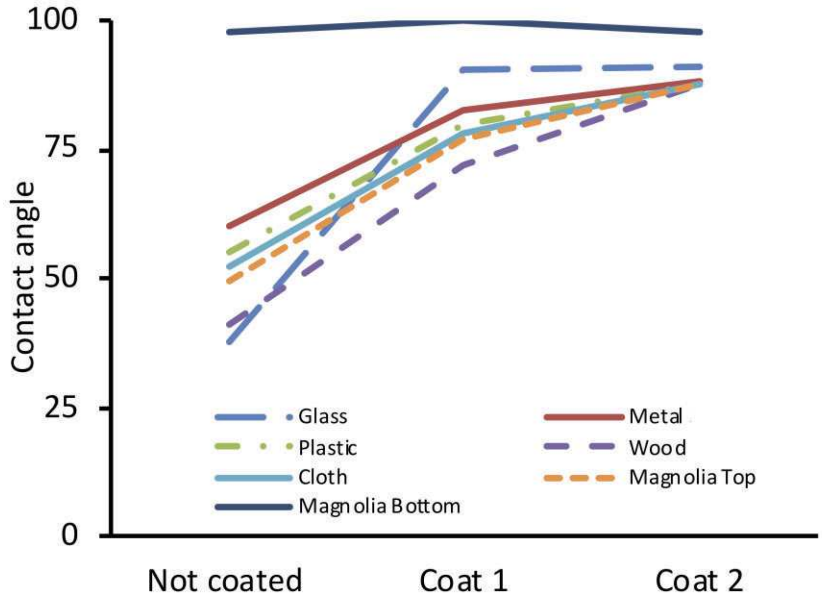

Figure 5. Comparison of the effectiveness of the hydrophobic coating based on the material and number of coatings.

Micro-whiskers in Synthetic Polymeric Coatings

Figure 6 shows the coating and magnified view of the micro-whiskers. Figure 6(a) shows a rough surface of the coating whereas; Figure 6(b) shows micro-whiskers ranging rising from the substrate ranging from 3 to 10 micrometers in dimensions. It is evident that the presence of micro-whiskers mimics the bottom surface of the magnolia leaf analogous to Figure 1(b). To understand the effect of the surface coverage of micro-whiskers on the hydrophobicity an experiment was conducted to test the different levels of (polymer) surface exposure. Glass microscope slides of 75mm x 26mm were used as the substrate, since they are a super hydrophilic surface in nature. Different layers of synthetic polymer were coated as shown in Figure 7 (Left) increasing the coverage area of micro-whiskers.

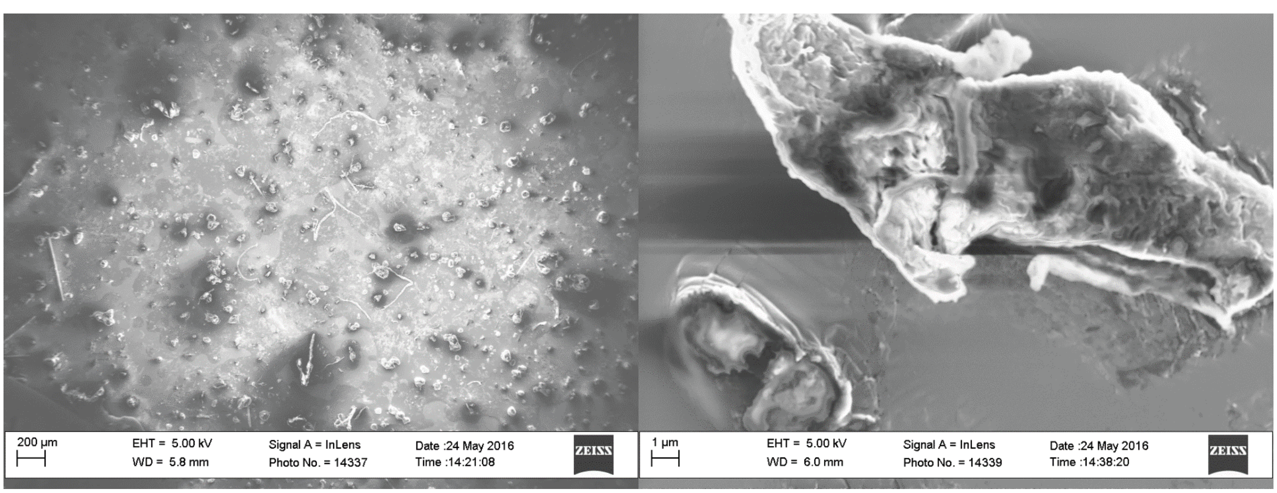

Figure 6. SEM image of microscale whiskers of the super-hydrophobic surface at low magnification and high magnification.

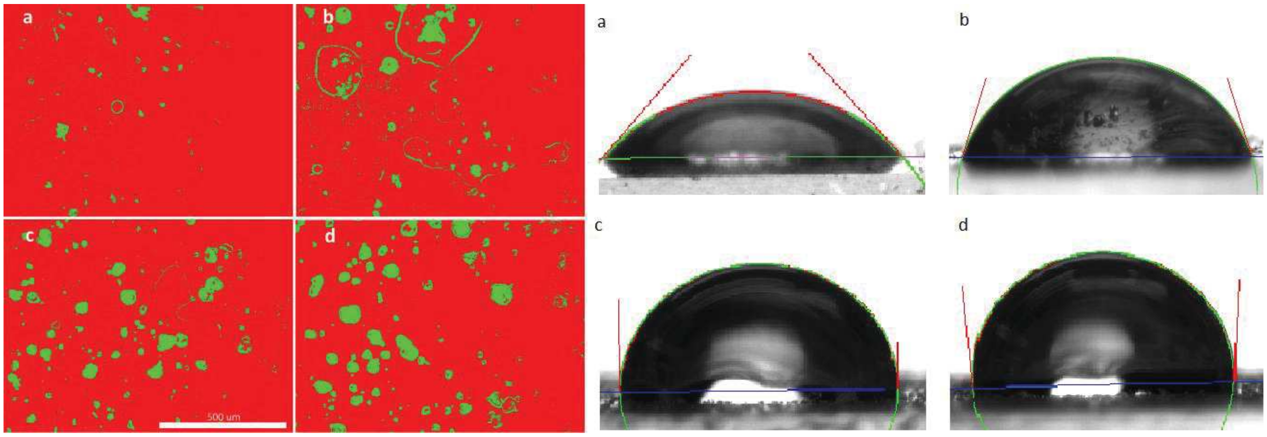

Figure 7. (Left) Phase analysis image of the surface of glass slides substrates. The glass surface exposed (red) is reduced as the concentration of hydrophobic spots (green) in the substrate. **(Right)** Contact angles of corresponding substrates with synthetic polymeric coatings.

The red portion of Figure 7 (Left) represents the exposed glass surface (hydrophilic) while the green portion of the image represents the hydrophobic portion (micro-whiskers) of the substrate. Figure 7 (Right) shows a corresponding increase in contact angle with an increase in green regions which represent micro-whiskers. The contact angle increased from 30° to 110° state with a higher number of coatings and subsequent increase in micro-whiskers.

DISCUSSION

The results indicated an increased hydrophobicity with multiple coatings of the polymeric formulation as confirmed with prior literature [17]. Multilayer coatings on porous materials such as wood and cloth showed a higher increase in hydrophobicity as the coatings assisted in closing the pores with micro whiskers. This clearly shows that synthetic polymeric coatings enable the transition of material surfaces from a Wenzel state to a Cassie-Baxter state resulting in increased hydrophobicity [18]. The top surface of the Magnolia leaf had a smoother surface texture and coating it with polymers introduced micro whiskers transitioning its surface to a Cassie-Baxter state [19]. Moreover, the phase analysis confirmed that an increase in surface exposure to the micro whiskers resulted in higher contact angles [20]. Similarly, nonfouling of the superhydrophobic Si nanowire substrate was attributed to a stable Cassie–Baxter state, limiting the contact with the culture medium [21]. Thus, biomimicking of magnolia leaves can be used to develop more effective hydrophobic coating technologies. Alternate micropatterns of hydrophilic and hydrophobic surfaces have been shown to promote multi-cell lineage growth [22]. Hydrophobic thin films have been used to prevent biofilms for indwelling medical devices [23]. This research provides alternate pathways for hydrophobic coatings in biomedical applications.

CONCLUSIONS

This research investigates the hydrophobic properties of magnolia leaves and aims to biomimic the microstructures of the leaves using a synthetic polymer formulation. Optical and scanning electron micrographs of the magnolia leaf top surface revealed a smooth surface texture. Contrastingly, the bottom surface had a maze of micro-whiskers. FTIR analysis of the synthetic polymer indicated the presence of organic compounds blended to provide a hydrophobic coating. Contact angle measurements of different materials with multiple coatings revealed an increase in the hydrophobicity. The synthetic polymer was effective in coating the voids in porous materials such as cloth and wood with micro-whiskers. SEM imaging of the coatings displayed hair-like micro-whiskers ranging from 3 to 10 micrometers (μm) in length. A phase analysis was conducted by coating multiple layers of the synthetic polymer on a glass slide and observing an increase in the hair-like micro-whiskers. Contact angle measurements of corresponding samples demonstrated a consistent increase in the hydrophobicity with the increase in surface area coverage of the micro-whiskers. This research provides a biomimicking strategy to coat different substrate materials for biomedical applications.

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DISCLOSURES

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Conflicts of Interest: None of the authors have conflicts of interest to report

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