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Fabrication of Namib Beetle Inspired Biomimetic Amphi-Phobic Surfaces Using Adsorbed Water as a Monomer

Stephanie OYOLA-REYNOSO^A, Ian TEVIS^a, Jiahao CHEN^a, Jean Francis BLOCH^b, Martin THUO^{a*}^aDepartment of Materials Science and Engineering, Iowa State University, Ames, IA^bDepartment of Paper, Print Media, and Biomaterials Grenoble Institute of Technology, Grenoble, Fr.

Abstract

Chemical grafting of small molecule reagents onto polymeric fibrous materials, like paper, has been used to modify their wetting properties. Several reagents like trichlorosilanes, which can react with water or hydroxyls, have been used with the expectation that a monolayer, single molecule or polymerized single-molecule layer, is formed on the paper fiber surface. Presence of adsorbed water, however, would complicate the formation of a monolayer, especially in case of polyvalent reagents. We hypothesized that adsorbed water is a good co-monomer for polyvalent water-reactive reagents, therefore chemical grafting with polyvalent molecules would give polymeric gels instead of a monolayer. Reaction of trivalent reagents with paper *in vacuo* leads to formation of polymeric gels. By optimizing surface energy mismatch, through felicitous choice of chemical moieties on the monomer, self-assembly leads to formation of nano- to micro particles on the surface of paper fibers. We observe that, as expected, the wetting properties correlate well with the size and distribution of particles. We conclude that the recently reported ultra-hydrophobicity of chemically modified paper is not only due to inherent roughness of the paper fibers, but also due to a secondary roughness introduced by surface polymerization. Using this technique, we prepared amphi-phobic biomimetic surfaces inspired by the namib beetle. This talk will also address potential utility of such surfaces.

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1. Introduction

Since the existence of human kind, Nature has been a great source of inspiration for technological advances. Evolution, and the need to survive, has led to development of complex surface properties in some animals. In the case of the Namib Desert beetle, *Stenocara gracilipes*, surviving in harsh environments is largely due to its ability to harvest water from fog.¹⁻² The surface structure of the beetles wings are Biphobic, that is, it has hydrophilic bumps that helps in water droplet adhesion/collection and hydrophobic valleys that act as collector channels for the water droplets. This beetle has been the inspiration for developments of various materials, such as metal surfaces for use in aerospace engineering and self-cleaning materials for biological purposes.²⁻⁵ These applications, however, often require sophisticated nano-patterning, expensive equipment, and a skilled personal to reproducibly generate these kinds of surfaces. The ability to create energy efficient materials, in a sustainable and affordable approach that can be applied in remote areas is desired.³⁻⁶

Amphiphobic surfaces have a wide range of applications and methods to fabricate these important materials are highly limited, and often employ complex and/or expensive methods or technology.⁵⁻⁶ The process of self-assembly is one that has been used over the past years due to its advantages in ease of use and cost.⁷⁻⁹ Surface modification of paper, and analogous fibrous polymeric materials, with poly-functional reagents has the potential to create textured materials, which in turn would be amphiphobic.⁹⁻¹⁰ Reaction of

* Corresponding author. Tel.: +1-515-294-8581

E-mail address: mthuo@iastate.edu

polyvalent (here valence means number of reactive units) molecules, like trichlorosilanes and water, can lead to significant cross-linking that in turn can lead to gel formation under the correct proportions. Where such a process involves step-growth polymerization, with its inherent large range in low degrees of polymerization, one can envision formation of gel particles of different sizes in a controllable manner. We hypothesized that during the surface functionalization process, the size of surface adsorbed particles can be controlled by controlling the degree of polymerization which in turn can be controlled by the reaction time. To test our hypothesis, we employed the synthesis of polysilsesquioxanes with concomitant surface energy driven self-assembly, to synthesize particles on paper.

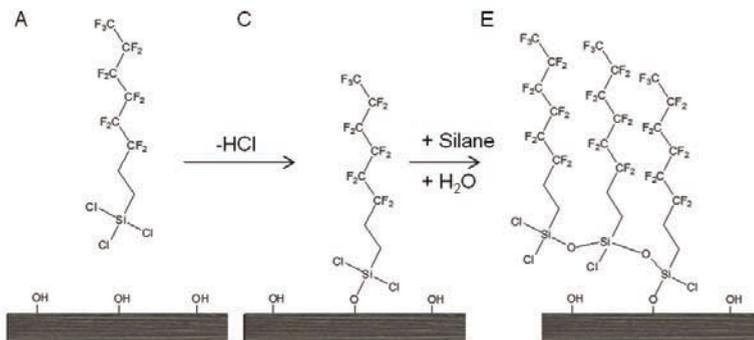


Figure 1. Reaction of surface hydroxyl groups with fluoroalkyl silane vapor to form hydrophobic surface. Condensation of the silane with any available hydroxyls releases HCl and gets cross-linked to give a polymeric layer.

2. Results and Discussion

First, we treated different types of papers with perfluoro octyltrichlorosilane (PFOTS) and observed that most of the papers became ultra-hydrophobic (static contact angle with water, θ_s , > 120).¹¹⁻¹² To understand the origin of this ultra-hydrophobicity, we compared different types of paper; i) chromatography paper – 100% cellulose, high porosity, ii) card stock paper – cellulose with fillers, and, iii) NYX beauty paper – high density with infused fillers. We also used a perfluorinated and non-fluorinated reagents to investigate the role of surface tension of the reagents, relative to that of the surface, on the gel formation which we had hypothesized to be the origin of the ultra-hydrophobicity.

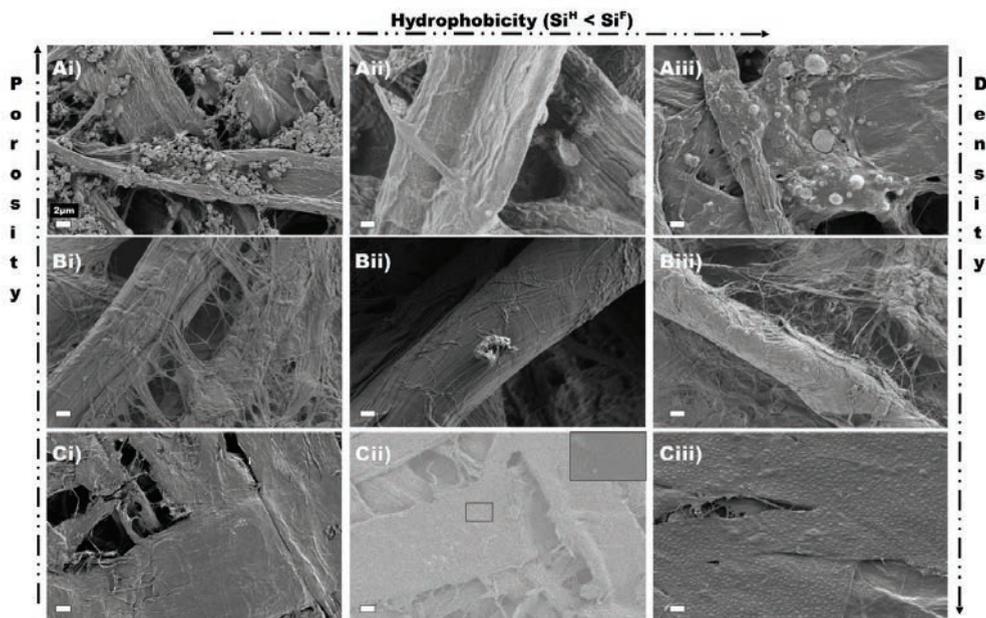


Figure 2. Chemical modification of representatives types of paper with non-fluorinated silane and fluorinated silane. Ai) highly porous, mostly cellulose paper represented here by chromatography paper No. 1. Aii) Chromatography paper upon chemical modification with non-fluorinated silane (Si^H) and Aiii) Chromatography paper upon chemical modification with fluorinated silane (Si^F). Bi) A porous paper containing filler materials represented by cardstock paper which contains PCC filler material. Bii) Cardstock paper upon salinization with Si^H , occasionally particulate were observed in the surface of the paper while in Biii) A more noticeable particle formation can be observed with the fluorinated silane (Si^F). Ci) Dense paper represented by NYX blotting paper. Cii) Upon silanization with the Si^H presence of particles are shown while in Ciii) Upon treatment with Si^F large amount of particles are formed.

Absorbed surface water: Scanning electron microscopy (SEM) images were collected from the control paper and the treated ones over different reaction times. Imaging the control paper, showed anisotropy in fiber orientation and structural composition. As

expected, different types of paper gave a variety of results upon treatment with the silanes (fluorinated and non-fluorinated silane). When a low grammage (more porous) pure cellulosic material was subjected to silanization there were no noticeable difference between the controls (Figure 2b (i)) and the treated (Figure 2b (ii) and (iii)). We chose two approaches to minimize the amount of absorbed water; additives and increase in grammage. Most papers, like cardstock, contain filler materials and we decide to use a paper that would support our polymerization by eliminate the HCl by-product upon treatment. Precipitated calcium carbonate (PCC) is a commonly used filler material, and the filler in card stock paper, reacts with the HCl byproduct, hence, pushing the silane reaction towards the desired product. Cardstock was therefore used to test the hypothesis that adding additives would reduce the amount of surface area onto which water would adsorb onto the paper fibers, while abetting the reaction by eliminating the reaction's by-products. Due to the uneven distribution of adsorbed and available, hence adsorbed surface water to react with the silanes, we hypothesized that large particles that were randomly distributed would be observed and the PCC would vanish due to reaction with the acid by-products. Figure 2a(i) show the control cardstock paper sample with a few clusters of the PCC filler visible. Figure 2a(ii) shows the silanized cardstock paper. With the perfluorinated reagent, large particles were observed upon treatment (Figure 2a(iii)) but these were absent from the non-fluorinated silane (Figure 2a(ii)). When the high grammage paper was similarly treated (Figure 2c(ii)), we observed very small particles with non-fluorinated reagent and a large correction of particles on the surface of the paper upon treatment with the PFOTS.

Further investigate of the NYX paper, high grammage, through a time course-analysis of the particle size and subsequent correlation with hydrophobicity showed that the particles became large in size (Figure 3) and created an amphiphobic surface that eventually became hydrophobic due to confluence in surface coverage with the cross-linked silane gel. There was a strong correlation between wetting and particle size (Figure 3) with a maxima around 30 minutes of the solid-gas reaction with this type of paper.

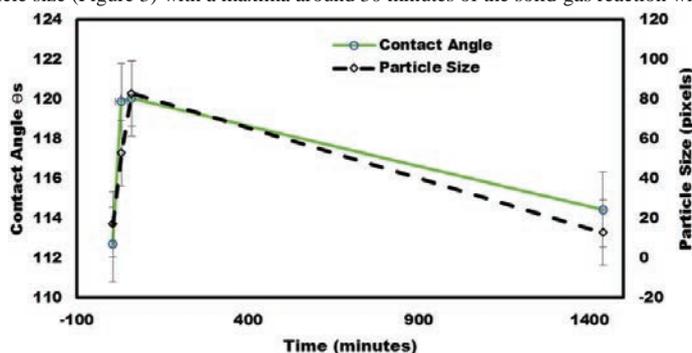


Figure 3. Contact angle correlates with particle sizes with a maximum around 30 minutes of reaction at 95°C.

Particle characterization: We characterized particles derived from different reaction times using scanning electron microscopy (SEM) and measured the average cross-section length from the images: Figure 3 gives a summary of the size of the particles as discussed above. Gandini and co-workers reported that treatment of a cellulosic material with trichloromethylsilane gave 'inorganic particles' on the surface presumably due to the formation of polysilicate on the surface of the material. Since we employed a trichlorosilane, there was a need to characterize the composition of our particles to ascertain if they were organic or inorganic. Upon imaging our surfaces with SEM, EDS was used to map elemental composition of the particles. We observed that the proportion of silicon in these particles was low enough to suggest that these particles were not inorganic. To understand the physical form of these particles, we coated the surface of perfluorinated blotting paper with 10 nm Au (to avoid charging) and used accelerated Ga ions in an SEM-FIB (scanning electron microscope- fast ion bombardment) to cut through a sample of the formed particle. We observed that the particles had a solid core, although sometimes a hole was observed near the particle fiber interface which would indicate presence of trapped gases of gaseous by-products arising from the reaction. Further comparison of elemental composition from EDS and XPS analysis indicated to us that the ratio of Si:F was in agreement with the PFOTS which confirmed that these particles were polymerized PFOTS and not inorganic as observed by Gandini and co-workers. Further analysis of changes in the amount of hydroxyl units by FTIR in the paper showed a slight decline in the OH peak, with the remaining amount being strongly hydrogen bonded. This indicates to us that the reaction is likely affecting the surface, as opposed to the core, of the paper.

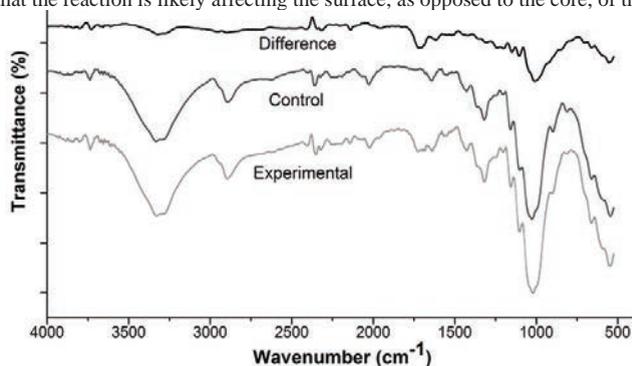


Figure 4. FTR-ATR spectra for NYX blotting paper treated with SiF at 95°C for 24 hours.

3. Conclusion

The correct understanding of the process behind the functionalization of hydrophobic paper is presented here. The gel formation upon polymerization model can help predict the formation of polymer particles, hence hydrophobicity of, cellululosic surfaces. The selection of surfaces is a key component when working with porous materials. Here we have validated that the previously used silanization reaction¹¹⁻¹³ involves adsorbed surface water, proving that the surface area, density, and porosity are important parameter to have an efficient surface polymerization. Our data indicates that the previously assumed formation of a monolayer, or cross-linked monolayer, is incorrect at least within the gel-formation step-growth conditions. This process has generated amphi-phobic surfaces analogous to the namib beetle, albeit with inverse properties, and demonstrate that bio-inspired surface engineering approach to materials synthesis is one of the most promising approaches to advanced functional materials and can be used to develop green devices compared to existing technology.¹⁴

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