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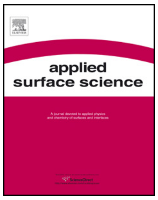

Imparting super hydro/oleophobic properties to cotton fabric by means of molecular and nanoparticles vapor deposition methods

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Super hydro/oleophobic cotton fabrics were prepared using nanoparticle vapor deposition and molecular vapor deposition techniques. The surface was roughened by trimethylaluminum/water nanoparticles followed by functionalization with (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane. This process imparted unique hydro/oleophobic properties (contact angle >160°). In contrast to wet chemistry processes, the chemicals used and the thickness of the coatings produced by this method could be controlled precisely, which allowed for the minimization of waste generation while preserving the original properties of the fabric. Dynamic contact angles were measured and the fabrics that were coated using this technique showed low-contact-angle hysteresis properties. Scanning electron microscopy and universal attenuated total reflectance Fourier transform infrared spectroscopy confirmed the formation of a nanostructure-roughened surface. Drop dynamics such as the force of droplet movement, work of adhesion, and surface free energy were also calculated.

1. Introduction

In recent years, superhydrophobic surfaces have become attractive for many applications in which water-repellency, anti-sticking, self-cleaning, and anti-fouling are needed [1–4]. Superhydrophobic surfaces are found in nature, but many artificial surfaces, which are made based on natural surface structures [5] such as rose petals, can be considered superhydrophobic [5,6]. Superhydrophobic surfaces generally have a static water contact angle of more than 150° and a sliding angle of less than 10°. The structures of these surfaces have been investigated by scientists to gain a better understanding of highly hydrophobic surfaces. Some natural, superhydrophobic surfaces consist of 20–40-μm particles that are each covered by smaller-scaled, rough surfaces [7]. This structure with two length scales (the nanoparticle structure and the roughness structure on each nanoparticle) has been shown to lead to a superhydrophobic structure. However, this type of structure is not necessarily the only one that leads to a superhydrophobic surface because many other examples of nanostructured surfaces with high contact angles have been shown.

Although repellency and wetting are opposing terms, mastering one of these techniques is nearly impossible without knowing the other. In the case of fabrics, repellency is the ability of the fabric to withstand the penetration of liquid when the existing forces consist of only capillary forces and the weight of the drop [8], and this definition can be used for oils and water. Wetting can occur when the solid–liquid or the liquid–air interface is replaced with a liquid–liquid interface. When no external forces are present, the liquid expands on the solid surface until it reaches thermodynamic equilibrium. In this case, *spontaneous wetting* occurs. However, if external forces such as thermodynamic or mechanical forces are applied, then the solid–liquid interface expands beyond static equilibrium, and *forced wetting* has occurred [8]. Wetting of a fibrous structure is a complex phenomenon because various simultaneous wetting mechanisms are involved, such as immersion, spreading, capillary penetration, and adhesion [8].

Highly hydrophobic surfaces can be applied in many areas of industry such as piping, boat hulls, and microfluidics, and it is believed that the number of applications will increase as the technology of non-wettable surfaces matures [7]. It is difficult to obtain a rough surface with fluorocarbons, so these compounds are blended with or linked to other materials that are easier to roughen [7]. A surface can be treated in two ways to impart superhydrophobic properties: a rough coating can be applied to the surface using low-surface-energy materials, or a rough surface can be modified with low-surface-energy materials to achieve a superhydrophobic nature [7]. In this study, to roughen a surface, we used a vapor phase reaction to form nanoparticles, which imparted roughness to a surface. Several materials, such as silicones [9,10] and fluorocarbons [11–14] or organic and inorganic materials, can be used as low-surface-energy materials, and different methods have been used to apply these materials to a surface. For example, a high

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contact angle was achieved by polydimethylsiloxane (PDMS) after being treated with laser technology [15] or a nanocasting method [16]. In the nanocasting method, an artificial lotus-leaf template was produced that had the same structure and superhydrophobicity. It is common to identify natural and artificial surfaces that can repel water, but it is rare to find surfaces that can repel low-surface-tension liquids such as hydrocarbons, and these types of surfaces are referred to as superoleophobic [17]. The only repellents that impart hydrophobicity and oleophobicity are fluorinated repellents [8]. Because fluorocarbon-based finishes impart water and oil repellency with high washing durability, they are more expensive than other chemicals [18]. Some surfaces with high repellency toward low-surface-tension liquids have been fabricated by combining low-energy materials and surface topography [19–22].

For many years, wet chemistry methods have been the main tool used to apply these types of materials to surfaces. Liquid processes have many disadvantages, such as the need to dispose of organic solvents, incomplete wetting of high-aspect-ratio structures, diffusion-limited transport of reactants, and poor control of reactant supply [23], when compared with gas-phase processes. In this study, coatings have been applied to cotton fabric surface in the gas phase.

Chemical vapor deposition (CVD) may be defined as a chemical reaction in the vapor phase that takes place where deposition of a solid on a heated surface occurs. This process is a class of vapor-transfer processes that are atomistic in nature, which means that the deposition species include atoms, molecules, or both. CVD is not a new process. The development of this technique dates back to the 1880s when incandescent lamps were produced to improve the strength of filaments by coating them with carbon or metal [24].

CVD and atomic layer deposition (ALD) are methods in which a binary reaction occurs [25]. In the past, CVD has been used to create hydrophobic surfaces [26]. ALD is a special type of gas-phase treatment. ALD is a self-limiting reaction because the number of reaction sites is limited; therefore, the amount of coating that can be deposited on the surface is constrained. One of the advantages of the ALD process is the low and precise thickness (Angstrom scale) and high uniformity of the resultant coating. Because the process is performed in the gas phase, the reaction can even take place in the pores of the substrate surface [24]. Because of the sequential nature of the reaction, the coating thickness is not limited to one layer; therefore, the thickness is controllable and depends on the number of sequences. In some cases, thick coatings (centimeters-thick) can be achieved [24]. Using the ALD process, aluminum oxide (Al_2O_3) can be deposited onto a surface. Trimethylaluminum (TMA)/water (H_2O) can be used as the binary chemicals in the CVD and ALD processes to add additional layers through a sequential reaction. The reaction is as follows [27]:

$$2\ \mathrm{Al(CH_3)_3} + 3\ \mathrm{H_2O} \rightarrow \mathrm{Al_2O_3} + 3\mathrm{CH_4} \quad (\Delta H) = -376\ \mathrm{kcal}$$

Sequentially, the final layer, which is composed of a fluorocarbon chain that is termed (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (FOTS), is placed on the surface and imparts hydrophobicity to the substrate.

The CVD method is often called nanoparticle vapor deposition (NVD), and it is similar to ALD. The only difference between these methods is that in NVD, two binary chemicals are injected simultaneously or when the other chemical is present. However, in ALD, each chemical is added to the reaction chamber separately. By using this method, Al_2O_3 nanoparticles are deposited on the substrate instead of a conformal coating, which leads to an increase in the roughness of the surface. Then, the fluorocarbon component is reacted with the hydroxyl groups of the nanoparticles to form the final surface layer. Super hydro/oleophobic surfaces can be prepared by using this method to add roughness to the substrate.

By definition, coatings using the CVD technique should have a thickness of less than 10 μ. Currently, CVD has mostly been applied in coating industries, but the use of CVD in other areas, such as in the production of powders, fibers, monoliths, and composites, is growing rapidly. Research on CVD is still an important research topic. Organizations such as the Department of Energy (DOE), Department of Defense (DOD), and NASA in the U.S., MITI and NIRIM in Japan, and CNRS in France have played leading roles in the development of CVD. CVD technology combines several scientific and engineering disciplines such as plasma physics, thermodynamics, fluid dynamics, kinetics, and chemistry.

2. Experimental section

2.1. Materials

The bleached, desized, and scoured cotton fabrics (C1, C6, and C9) that were used in this study were obtained from Testfabrics, Inc. (Testfabrics, West Pittston, PA, USA). Fabrics were identified as C1 (yarn size = 36 × 40 Ne and weight = 118.7 g/m^2); C6 (yarn size = 41 × 40 Ne, weight = 109.3 g/m^2); and C9 (yarn size = 22 × 13 Ne, weight = 229.0 g/m^2). Distilled water was deionized in a Milli-Q plus system from Millipore (Billerica, MA) to reach a final resistivity of 18.2 MΩ-cm. Water and varying volumetric concentrations of isopropyl alcohol (IPA) were used to assess the hydrophobic properties of the treated cotton fabrics.

2.2. Methods

2.2.1. Pretreatment of the substrate

Fabrics were cleaned by a microwave plasma (PLASMAtech, Erlanger, KY) using a generator of 2.45 GHz. The samples were exposed to N_2-plasma for 120 s at 500 W, and a 60 ml/min N_2 flow rate and pressure of 25 Pa were used.

2.2.2. MVD and ALD

The RPX-550 system was used for vapor phase deposition (Integrated Surface Technologies, USA; Menlo Park, CA) and consisted of five containers for chemical reactants, each with independently controlled temperature, a vacuum pump, and a sample chamber. Inside the chamber, a perforated plate was used to deliver the gases to the samples, and this configuration enhanced the deposition of nanoparticles on the substrate. Nitrogen was used to transfer the reactants, in the vapor phase, from the containers to the chamber through heated delivery lines. The chemicals that were used for all of the treatments were as follows: water, (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (FOTS, $(Cl)_3Si(CH_2)_2(CF_2)_5(CF_2)_3$), a blend of bifunctional trichlorosilanes, and trimethylaluminum (TMA, $Al(CH_3)_3$). The fabrics were treated following the protocols listed below and the chamber was maintained at 55 °C during all of the processes. The temperature of the chemical containers was maintained at 40 °C, and that of the transfer lines were maintained at 45 °C to avoid condensation. Due to the low vapor pressure of FOTS, the container for this reactant was held at 90 °C, and the transfer line was maintained at 95 °C. Each individual process is briefly described below.

- *Treatment T0* represents a substrate that was only pretreated with N_2-plasma (control).
- *Treatment T1* represents pretreatment of the substrate with N_2-plasma, followed by MVD deposition of FOTS (MVD FOTS layer).