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The facile preparation of self-cleaning fabrics

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ABSTRACT

Self-cleaning surfaces can repel both water and oil, and they have various applications as materials that can protect surfaces against contamination. These surfaces typically exhibit hierarchical surface structures with roughness on both the microscale and the nanoscale, and they are composed of low surface energy components. Such surfaces are normally mechanically weak, and they are prepared using fluorinated solvent-based suspensions consisting of potentially toxic fluorinated compounds. As described in this report, we have demonstrated for the first time, the use of poly(perfluoropropylene oxide) glycol as an environmentally-friendly precursor and a novel acetone-based suspension that only utilized commercially available components for the preparation of self-cleaning cotton fabrics with superhydrophobic and highly oleophobic properties. The coating exhibited outstanding mechanical and chemical durability, and had little influence on the softness or color of the fabric. It is anticipated that these convenient and versatile formulations will facilitate the application of these materials in various fields.

1. Introduction

The development of novel materials has always been and will continue to be one of the driving forces providing society with improved living standards. Self-cleaning materials are known for their extreme repellency against both water and oil, which readily roll off of these surfaces [1–3]. The high degree of repellency allows self-cleaning or highly amphiphobic materials to come into contact with virtually any liquid and still remain clean and dry [4–6]. The widespread application of these materials may allow us to save a lot of time and money that would otherwise be devoted toward laundering, as well as cleaning electronic devices, automobiles, or the potentially dangerous task of cleaning the windows of tall buildings. In addition, these materials can be used to protect metal surfaces against corrosion [7], pipelines against clogging [8], surfaces against ice-accumulation [9], and the hulls of ships against fouling [10].

Among the methods utilized to fabricate self-cleaning surfaces such as electrospinning [11], etching [12], and molding [13], coating strategies provide the advantages of great simplicity, scalability, speed, low cost, and compatibility with virtually any type of substrate [14,15]. In recent years, researchers have found that the key requirements for achieving high degrees of amphiphobicity can include the presence of intricate surface textures (in particular, having roughness on both the micro- and nanoscale as well as re-entrant surface structures) and a low surface energy (due to the chemical composition) [16–18]. Based on these fundamental principles, various superamphiphobic coatings have been prepared using components such as TiO_2 [14], ZnO [19,20], SiO_2 [21], and carbon nanotubes [22] to construct rough structures, and using fluorinated small molecules [23] and polymers [24] as low surface energy binders. Research involving self-cleaning coatings has advanced rapidly in recent years [16–18,25], although there are still unresolved challenges that need to be addressed in order to facilitate further improvements and the commercial application of these materials. Some of these challenges include the limited durability of existing coatings (particularly in regard to their robustness and their adherence to substrates), reduce the costs of

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these materials, and find environmentally-friendly formulations (by avoiding the use of potentially toxic fluorinated components and solvents) without compromising their functional performance.

The intricate surface textures required for effective self-cleaning surfaces are typically very delicate and prone to damage when they are subjected to physical wearing [26,27]. In addition, the low surface energy components required for a self-cleaning coating typically exhibit poor adhesion to the underlying substrate, thus adding a further challenge to achieving durable amphiphobic coatings [28]. Due to these two inherent characteristics of self-cleaning coatings, it has been extremely difficult to prepare a coating that is both highly amphiphobic and durable. One strategy that has been developed to enhance the durability of amphiphobic coatings has involved the formation of covalent bonds between the coating and its substrate during the curing process. In particular, sol–gel reactions with small molecules [29–32] and polymers [15,33–36] bearing alkoxysilane groups have been used to generate covalent bonds and enhance the durability of amphiphobic coatings. Lin et al. fabricated durable superamphiphobic polyester fabrics by taking advantage of the bonding properties of perfluorodecyltriethoxysilane [29–32] with low surface energy components such as 1H,1H,2H,2H-heptadecafluorodecyl polyhedral oligomeric silsesquioxane (FD-POSS) [29,30] or poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VDF-*co*-HFP)) [31,32]. They found that the coated fabric was able to withstand over 200 cycles of standard machine laundry washing without losing its superamphiphobicity [29–32]. Inspired by the unique combination of properties available to block copolymers that provide them with the versatility required for various potential applications [37,38], Liu and coworkers prepared a series of poly[3-(triisopropyloxysilyl)propyl methacrylate]-*block*-poly[2-(perfluorooctyl)ethyl methacrylate] (PIPSMA-*b*-PFOEMA) block copolymers via sequential anionic polymerization [15,33] as well as atom transfer radical polymerization (ATRP) [34–36]. The sol–gel-forming PIPSMA blocks were employed because of their ability to enhance the coating durability, while the PFOEMA blocks were utilized for their ability to provide a low surface tension. The PIPSMA-*b*-PFOEMA block copolymers were used alone [33] and in combination with silica nanoparticles [15,34,35] as well as with raspberry-like polymer particles [36] to fabricate various superamphiphobic coatings. The coated fabrics were very robust and withstood more than 50 cycles of simulated washing treatment in detergent solutions [33]. The coatings prepared via the one-pot approach adhered strongly to the glass plates and withstood physical wearing [34]. More recently, Parkin et al. [25] used commercial adhesives to bind coatings based on an ethanolic suspension of perfluorosilane-coated TiO_2 nanoparticles onto various substrates and thus enhance their durability. Although the surfaces were not oleophobic, their superhydrophobicity was retained after they were wiped with a finger, scratched with a knife, and even subjected to 40 abrasion cycles.

Although the durability of amphiphobic coatings has been improved by incorporating components with alkoxysilane-bearing groups [15,29–36] or by the use of commercial adhesives [25], the challenges associated with the high cost and potential toxicity of these materials remains unresolved. In particular, these coatings typically require tailor-made fluorinated compounds [15,29,30,33–36], and utilize costly fluorinated solvents [15,33–36] or solvents (such as *N*,*N*-dimethylformamide, DMF) with a slow evaporation rate [31,32]. In addition, the potential of long-chain perfluorinated compounds to undergo bioaccumulation in wildlife and to enter the food chain has raised environmental concerns [39,40]. Due to these potential health and environmental hazards, the use of these materials has been restricted in many jurisdictions [41]. Unfortunately, these compounds have traditionally been the favored choice as low surface energy components for superamphiphobic [15,29–36] or superhydrophobic [25] materials, and thus a search for their replacement is needed.

We have recently discovered that poly(perfluoropropylene oxide) glycol (PFPG), which is widely believed to be an environmentally-friendly material [42–44], may have great potential as a replacement for long-chain perfluorinated compounds as precursors for amphiphobic coatings. To the best of our knowledge, however, there have been no reports describing the use of this polymer for the fabrication of highly amphiphobic coatings. Furthermore, by taking advantage of the condensation reaction that takes place between the isocyanate groups of 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI) and the hydroxyl groups of PFPG as well as the hydroxyl groups on the surfaces of SiO_2 nanoparticles and a cotton fabric, covalent bonds can be generated to enhance the durability of the resultant coatings. This condensation reaction between isocyanate groups and hydroxyl groups is a novel method for the preparation of durable self-cleaning coatings. In addition, all of the components utilized for this method are commercially available and readily dispersible in acetone, which is an inexpensive common organic solvent with a rapid evaporation rate.

2. Experimental section

2.1. Materials

A poly(perfluoropropylene oxide) glycol derivative (PFPG, with an average equivalent weight of 750, fluorine content of 57%, surface tension (at 20 °C) of 23 mN/m, kinematic viscosity (at 20 °C) of 115 cSt, glass transition temperature of -100 °C, and specific gravity (at 20 °C) of 1.73 g/cm^3) was purchased from Solvay, and distilled under reduced pressure prior to use. 3-Isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (IPDI, >99.0%), tetraethoxysilane (TEOS, >99.0%), ammonia (28%–30%), ethanol (>99.5%), acetone (>99.5%), diiodomethane (>99.0%), and hexadecane (>99.0%) were purchased from Aldrich and were used as received. Dibutyltin dilaurate (97.5%) was purchased from J&K and was used as received. Cotton fabric samples were purchased from a local factory, and they were rinsed with a 1.0 wt% aqueous detergent solution and with distilled water before use. Sandpaper (Standard glasspaper, Grit No. 400) was purchased from a local store.

2.2. Preparation

The silica particles were synthesized according to our previously described method [34]. In a typical procedure, 300 mL of ethanol and 30 mL of ammonia were mixed together in a 500 mL three-neck round-bottom flask equipped with a condenser. The mixture was heated to 70 °C and stirred at 300 rpm for 15 min, and 15 mL of tetraethoxysilane was subsequently added into the flask over a period of ~30 min. The reaction was continued for an additional 24 h at 70 °C. The resultant silica particles were settled via centrifugation at 10,000 *g* for 10 min. The supernatant was then discarded before the particles were re-dispersed into 50 mL of absolute ethanol via ultrasonication. These particles were subsequently settled and re-dispersed into absolute ethanol thrice (3 × 50 mL) before they were finally settled and dried overnight under vacuum.

In order to fabricate the coatings, the precursor solution consisting of 1 wt% IPDI in acetone and a second solution consisting of PFPG (x wt%), SiO_2 particles ($1-x$ wt%), and dibutyltin dilaurate (0.1 wt%) in acetone were initially created as separate solutions. The cotton fabric was initially immersed into the IPDI solution for 40 min at room temperature. The fabric was subsequently removed