Understanding the mechanism for building woven fabrics with wettability ranging from superhydrophobic to superamphiphobic via an aqueous process

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A B S T R A C T

We have recently developed a novel and simple approach based on aqueous solutions of block copolymer micelles for the construction of WFs with wettability ranging from the superhydrophobic to the superamphiphobic regime. That is, the copolymers were initially dispersed into water to yield a micelle solution with the insoluble fluorinated block serving as the micellar core and the water soluble block as the micellar corona. The polyethylene terephthalate (PET) or cotton WFs were then dipped into a copolymer micelle solution and then naturally dried at room temperature before they were cured at high temperature to yield WFs with various degrees of liquid repellency. Further investigation on the mechanism for the formation of either superhydrophobic or superamphiphobic WFs using this aqueous process would facilitate the commercial applications of these water-based coatings. In this contribution, polyethylene terephthalate (PET) films with different liquid repellencies based on copolymer aqueous micelle solutions were prepared via previously reported process, and AFM and XPS techniques were respectively employed to evaluate the morphology and chemical composition of the copolymer-coated PET films. The dependence of water and oil contact angles of PET films on the concentrations of the copolymer micelle solution were evaluated and further employed for the prediction different liquid repellencies of PET WFs. The mechanism for the formation of the superhydrophobic WFs or superamphiphobic WFs was also proposed.

1. Introduction

A superhydrophobic woven fabric (WF) displaying an apparent water contact angle (WCA) of more than 150° and a water sliding angle (WSA) of less than 10° is very useful as a versatile textile for clothing that could be worn in kitchens, labs, outdoors, at sports events, and as military uniforms [1]. Similarly, a superamphiphobic WF with an oil contact angle (OCA) of more than 150° and an oil sliding angle (OSA) lower than 10° that strongly repel water- and oil-borne contaminants and etchants, holds even more academic interests and has a wider range of potential applications over superhydrophobic WFs [2,3]. For example, it can be used to provide protection against exposure to hazardous chemicals and biological contaminants [2]. Therefore, these prospects and many potential applications have driven the development of various methods to prepare superamphiphobic WFs [3].

There are two key factors that govern the strategies for constructing superhydrophobic or superamphiphobic surface. One of these considerations is that the surface should be constructed from materials with low surface free energies, while the other one is that the surface should have sufficient surface roughness [4]. Since WFs consist of micro-sized fibers, superhydrophobic WFs can be produced by covalently attaching small molecules or polymers with low surface free energies without altering their roughness. This can be achieved by coating highly-fluorinated polymers onto the fibers of woven fabrics by polymerizing the fluorinated monomers via an γ-ray irradiated reaction [5] or by chemically attaching diblock copolymers containing sol-gel forming blocks and high-fluorinated blocks [6]. Additionally, it is believed that it is also necessary to introduce sub-structures with nanoscale roughness to the fibers at the surfaces of WFs in order to create superamphiphobic WFs. Through the incorporation of these nanoscale subs-

structures, the WFs are imparted with nanoscale roughness that in combination with the inherent microscale roughness of the the WF fibers yields hierarchical roughness, which is one of the key requirements of a superamphiphobic surface besides a low surface energy.

Since it's more difficult to prepare superamphiphobic WFs, there are many reports on the preparation of superhydrophobic WFs in comparison with only a few reports on the strategies for preparation of superamphiphobic WFs. This is due to the fact that oils have lower surface tensions in comparison with water [7]. These difficulties can be solved by employing materials bearing −CF$_3$ groups on the surface [8], such as perfluorooctyl components or fluorinated polymers containing perfluorooctyl components consisting of seven CF$_2$ units and one CF$_3$ unit, which have the lowest surface energy [9].

To date, there are a few reports focusing on the development of methods to prepare superamphiphobic WFs. One technique is to deposit fluorinated nano- or micro-particles onto textile fibers [10]. However, these coatings adversely affected the intrinsic properties of the textiles and exhibited poor adhesion to textile fibers [11]. The other attempts have included the grafting of perfluorooctyl compounds onto fiber surfaces of textiles, which are intrinsically rough and possess re-entrant sites on the bottom halves of the fibers and threads [12]. Unfortunately, the coatings prepared via this process did not produce WFs with the anticipated stable superamphiphobicity due to the heterogeneous coatings that were obtained as a result of surface reconstruction [13]. Recently, highly stable superamphiphobic WFs became available by grafting textile fibers with monolayers of diblock copolymers consisting of a fluorinated block and a grafting/crosslinking block [13], or by treating textile fibers with a coating solution consisting of poly(vinylidene fluoride-*co*-hexafluoropropylene), fluoroalkyl silane, and a volatile organic solvent [10]. The common drawback of these two strategies, reported so far, was their reliance on organic solvents, which should be eliminated or reduced for practical applications and environmental considerations [14]. Therefore, the development of a new strategy for the preparation of superamphiphobic WFs without using organic solvents is both attractive and challenging.

To the best of our knowledge, there are only three reports describing the pursuit of this challenge. Anish Tuteja [8] and Tong Lin [15] have prepared superamphiphobic WFs by coating substrates with a fluorinated-decyl polyhedral oligomeric silsesquioxane (FD-POSS) dispersion in ethanol, which was a relatively environment-friendly approach in comparison with other strategies that have employed toxic organic solvents. More recently, we have developed, for the first time, an aqueous process for the preparation of robust superhydrophobic or superamphiphobic WFs from a multifunctional diblock copolymer, using an A-*b*-(C-*r*-D) micelle solution in water [16]. Here, the A block provides a low surface free energy that is required to build a superamphiphobic surface. Meanwhile, the other block consists of C and D segments that respectively bear functionalities enabling the covalent attachment or crosslinking of the coating onto the substrate surface, and facilitating the dispersal of the copolymers into water. Scheme 1 provides an illustration of PFOEA-*b*-P(GMA-*r*-mOEGMA) (denoted as A-*b*-(C-*r*-D)) and its use as a precursor toward superamphiphobic WFs.

Specifically, the A block consists of poly(2-perfluorooctethyl acrylate) (PFOEA), which bears a crystal structure and an exceptionally low surface energy (9.3 mN m^{-1}) [17]. The C-*r*-D block bears units of glycidyl methacrylate or GMA (denoted as C), which provides the prepared superamphiphobic surface with high durability since the epoxy groups of GMA can react with different functional groups including carboxyl, hydroxyl, amino and anhydride groups on the surface of various substrates, such as wood, paper, silica, glass plate, sheet metal and textiles [18]. Meanwhile, the mOEGMA (denoted as D) units provide the copolymer with water dispersibility [19].

The copolymers were directly dispersed into water to yield a micelle solution with the insoluble PFOEA block serving as the micellar core and the soluble P(GMA-*r*-mOEGMA) block as the micellar corona (1 → 2 in Scheme 1). The polyethylene terephthalate (PET) or cotton WFs were then dipped into a copolymer micelle solution and then naturally dried at room temperature before they were cured at 110 °C (2 → 3 in Scheme 1). We found that fabrics that were coated by a copolymer micelle solution at different concentrations exhibited various degrees of liquid repellency. For example, fabrics coated at a copolymer concentration at 2.28 mg/mL were superhydrophobic. On these coatings, the water contact angles were ~160° and the sliding angles were ~3°, whereas peanut cooking oil exhibited a contact angle of ~104°. In contrast, fabrics coated at a copolymer concentration of 22.8 mg/mL were rendered superamphiphobic. Both hexadecane and peanut oils readily rolled off these coatings. Moreover, both the superhydrophobic and superamphiphobic coatings were mechanically and chemically robust and retained their repellent properties because they had been stabilized via the thermal crosslinking of the GMA segments.

In our previous study, we found that the coating structure would change depending on the micelle concentration [16]. At low copolymer micelle concentrations, an incomplete unimolecular layer would form. Meanwhile, high micelle concentrations would lead to the formation of a rough coating. A smooth unimolecular layer would form only around an optimal copolymer micelle concentration. Interestingly, the fibers of the superhydrophobic WF were coated by a smooth unimolecular layer, while those of the superamphiphobic WF possessed a rough coating layer. Further investigation of the formation of either superhydrophobic or superamphiphobic WFs via this aqueous process would facilitate the commercial development of this class of water-based coatings.

To further understand this novel and simple process for the preparation of superhydrophobic or superamphiphobic WFs, in this contribution we applied copolymer micelle solutions onto PET films instead of applying these dispersions onto PET WF substrates. The water and oil repellency, as well as the morphology of surfaces of the PET films were subsequently evaluated. Based on the these results observed on the PET films, the water and oil contact angles of copolymer coatings on PET WFs were predicted and found to be consistent with the measured values. A mechanism for the formation of superhydrophobic and superamphiphobic WFs was proposed. The current study on the formation of either superhydrophobic or superamphiphobic WFs using an aqueous
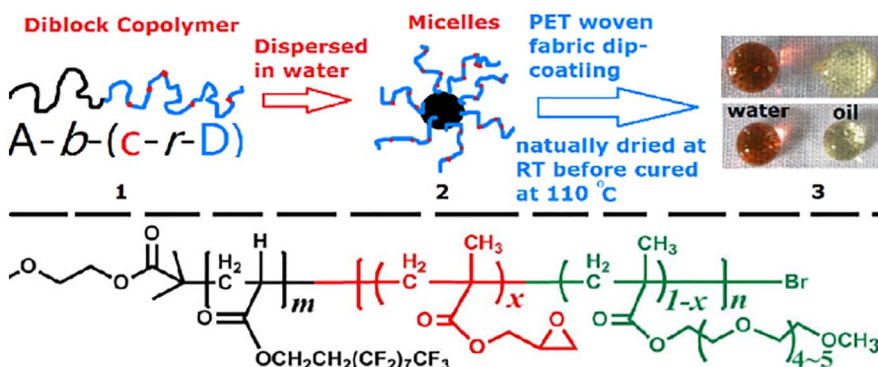
Scheme 1. Illustration of the aqueous process for the preparation of a superamphiphobic woven fabric (WF) from our diblock copolymer A-*b*-(C-*r*-D). The bottom shows the designed copolymer structure.