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Review

Preparation of superamphiphobic polymer-based coatings via spray- and dip-coating strategies

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ABSTRACT

The widespread usage of superamphiphobic surfaces could dramatically improve our lives. For example, we may lead a life with little need for laundry, no need to clean electronic products, cars or buildings. In addition, virtually any liquid could be spilled onto a surface without causing undesirable wetness or stains. Considering the performance and technological requirements of various industrial sectors, the use of polymer-based coatings is an outstanding approach to fabricate durable and multifunctional superamphiphobic surfaces at a low cost. In this review, the processes used to prepare superamphiphobic polymer-based coatings by spray- and dip-coating methods will be highlighted, and the compositions and properties of these materials will also be discussed. It is hoped that this review will provide inspiration and help with the design of applicable superamphiphobic materials, and will demonstrate the diverse range of applications of superamphiphobic materials.

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1. Introduction

Nature is an infinite source of inspiration due to the complexity, beauty, and functionality of many biological materials. Many artificial materials have thus been designed in attempts to mimic certain aspects of natural organisms [1,2]. Superamphiphobic materials are a recently developed class of bio-inspired materials with extreme

repellency against water, surfactant-based solutions, alcohols or other organic liquids [3]. On superhydrophobic and superoleophobic surfaces, water and oil droplets respectively will have a contact angle greater than 150° with a rolling angle typically smaller than 10° [4]. Meanwhile, superamphiphobic surfaces exhibit this degree of repellency against both water and oil droplets (Fig. 1) [5]. The large contact angle and very small rolling angle exhibited by superamphiphobic surfaces make it very difficult for liquid droplets to spread on or wet these surfaces. Materials bearing superamphiphobic surfaces could thus come into contact with virtually any liquid and still remain dry and clean. The widespread application

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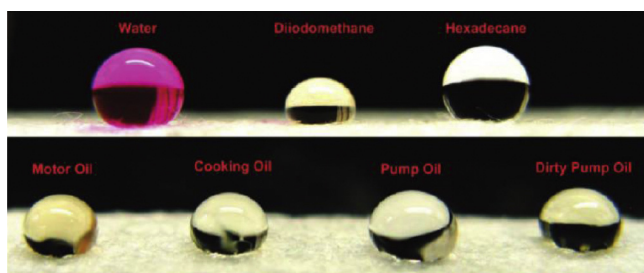


Fig. 1. Images of droplets of various liquids on superamphiphobic cotton fabrics. The water droplet appears pink because it was impregnated with rhodamine B. Reprinted with permission from the American Chemical Society, Xiong and coworkers [5]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of such amazing superamphiphobicity could dramatically improve our lives in various ways. These materials may allow us to live our lives with little need for laundry, no need to clean electronic devices, cars, buildings, or other surfaces. These materials can also be used to protect metal surfaces against corrosion [6], pipelines against clogging [7], surfaces against ice-accumulation [8], and the hulls of ships against fouling [9].

In recent years, the underlying causes of superamphiphobicity have been attributed to the surface free energy (arising from the chemical composition) and the surface's geometrical structure (particularly the roughness and the presence of re-entrant structures) [10–12]. The surface tension of oil is typically lower than that of water [13], and thus the surface energy required for a material to exhibit superamphiphobicity is even lower than that needed for a material to exhibit superhydrophobic behavior [14–16]. Consequently, low-surface-energy fluorinated compounds or polymers are frequently used to prepare superamphiphobic surfaces [17,18]. Even with the use of fluorinated polymers, the maximum achievable contact angles on flat surfaces for water, diiodomethane, and hexadecane droplets with respective surface tensions of 72.1, 50.8, and 27.5 mN/m are only $\sim 120^\circ$, $\sim 100^\circ$, and $\sim 80^\circ$, respectively [19–22]. Therefore, it becomes apparent that the intrinsic characteristics of materials alone are insufficient for attaining superamphiphobicity. In order to ensure that the contact angles of these liquids exceed 150° , surface roughness on both the nanometer and micrometer scales is required via the creation of textured surfaces. In addition, the surface should possess re-entrant structures [10], which are those that are hidden under overhangs. Examples of such re-entrant structures include the gills of a standing mushroom or the bottom half of a sphere (Fig. 2).

In terms of the composition of previously reported superamphiphobic materials, fluorinated small organic molecules [23] and polymers [24] have been used as low surface energy binders, while inorganic components such as TiO_2 [25], ZnO [26,27], SiO_2 [28], and multi-walled carbon nanotubes (MWCNTs) [29] have typically been used to fabricate rough structures. In comparison with

small molecules, fluorinated polymers exhibit an unique combination of properties that include facile processability [30,31], good durability [32], and great structural diversity. In particular, the weather resistance [33] and adhesive properties [34] of the materials could be improved and their cost could be reduced [35] by introducing acrylate-based monomers into the polymer systems. The scratch resistance [36] and flexibility [37] could be enhanced by incorporating monomers of polyurethane. Furthermore, polydimethylsiloxane (PDMS) [38] and poly(perfluoropropylene oxide) (PFPO) [39] exhibit excellent transparency, which would provide them with excellent potential for use on windows, the screens of electronic devices or lenses. Some active groups such as epoxy [40] and silanol [41] moieties have been reacted with various substrates in order to chemically bond the coatings onto the underlying substrates, thus securing them to the surface. The temperature employed during the heating treatment of coatings can also be arbitrarily adjusted by tuning the ratios of the monomers such as methyl methacrylate and butyl acrylate, which have different glass transition temperatures (T_g) [42]. In addition, the combination of the superamphiphobic properties with other characteristics, such as conductivity [43], anti-bacterial activity [44], anti-static behavior [45], flame-retardancy [46], self-healing properties [47] and other useful properties could be achieved by adjusting the structure of the polymer building blocks.

Among the methods utilized to fabricate superamphiphobic polymer-based surfaces (Fig. 3), plasma etching provides an effective method to fabricate nanotextured surfaces. However, the plasma process requires the use of expensive equipment, which can potentially limit the applicability of this technique [48]. Electrospinning can be applied to various substrates but this technique requires high voltage in order to melt the coating material [49]. The composition of a material can be adjusted easily by changing the monomers, while the curing process employed as part of the polymerization strategy typically time and energy consuming [50]. In the case of spin-coating [51], uniform coatings with different thickness can be prepared by changing the spinning speed and time, while the size of the substrate is restricted by the spinning device. In comparison, spray- and dip-coating strategies using polymers as components provide the advantages of great simplicity, scalability, speed, low cost (thus facilitating large-scale fabrication), and compatibility with almost any type of substrate [25,52]. Some attempts have been made to improve the water- and oil-repellency of polyacrylates [53,54], polyurethane [55–57], and acrylate-modified polyurethane [58,59] by introducing fluorinated units into these traditional polymers, which have traditionally been applied as coating materials onto textiles, furniture, stone and various other substrates via spray- and dip-coating techniques. However, few of these attempts have yielded applicable coating materials that exhibited superamphiphobic properties [53–59]. Although there have been some reviews highlighting various methods employed for the preparation of superamphiphobic surfaces [60–62] as well as the principles of superamphiphobicity in general [61–63], we believe that a review providing particular emphasis on the spray- and dip-coating strategies for the preparation of polymer-based superamphiphobic materials would provide a helpful resource for researchers and practitioners of this field. In this review, we thus attempt to summarize the current state of spray- and dip-coating strategies for the preparation of superamphiphobic polymer-based coatings, and describe the relative effectiveness of these coating protocols. In addition, the challenges and future directions of this technology will be discussed. It is hoped that this review will provide inspiration and assist researchers with the design of superamphiphobic polymer-based coatings with desirable properties, and will thus help to advance the development and applications of superamphiphobic polymer-based materials.

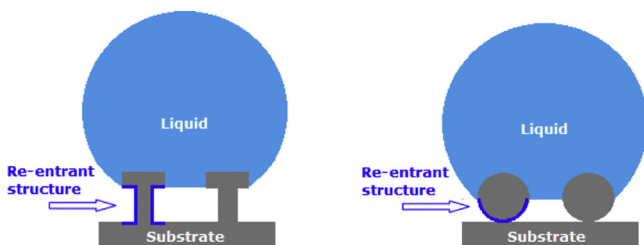


Fig. 2. Schematic illustrations of re-entrant surface structures.

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