Fabrication of durable superamphiphobic PA-66 fabrics with wear-resistance performance

1 | INTRODUCTION

In the past decades, surfaces with special wettability have received great interest [1]. Among them, the superamphiphobic surfaces have contact angles greater than 150° and sliding angles less than 10° for both water and low-surface-tension organic liquids [2]. Therefore, superamphiphobic surfaces are very promising in many applications, including those requiring self-cleaning [3, 4], super-antiwetting [5, 6], corrosion resistance [7, 8], anti-freezing [9] and liquid separation [10]. It is well-recognized that the combination of materials with extremely low surface free energy and hierarchical micro-nano dual scale structures is crucial for the preparation of superhydrophobic surfaces [2, 11]. Up to now, many techniques have been applied to fabricate superamphiphobic surfaces, for instance, etching, sol-gel processing, templating, electrospinning, and wet-chemical coating [12–16].

Although superamphiphobic surfaces are very valuable for both basic research and commercial applications, one of the greatest challenges to their practical applications is poor mechanical durability, because the nano-scaled or micro-scaled structure is easily damaged. In addition, most of fabricating methods usually request expensive devices, complicated fabricating conditions, and costly raw materials. All these shortcomings greatly hinder their widespread applications. Some researchers have made some explorations to overcome these shortcomings. For instance, Zhou et al. reported the fabrication of superamphiphobic polyethylene terephthalate (PET) fabrics by dip coating silica nanoparticles, perfluorodecytrithoxysilane and poly (vinylidene fluoride) [17]. The modified fabrics showed good resistance to mechanical abrasion. Yearken et al. prepared superamphiphobic fabrics by a two-step coating method using polytetrafluoroethylene micro particles and fluorinated alkyl silanes on aramid fabrics. The coated fabrics could withstand at least 200 cycles of abrasion and 10 cycles of washing without significant changes in its superamphiphobicity [18]. Qu et al. developed a facile approach for the fabrication of superamphiphobic coatings by employing quartz sand particles and organic silane via a drop coating method. The coatings could maintain their superamphiphobicity after abrasion with a piece of sandpaper over a length of 280 cm [19].

It is well known that acrylate adhesives provide certain advantages, such as the ability to bond a wide variety of surfaces, good environmental and solvent resistance [20]. Hence, the fluorine-containing acrylate copolymer was selected to strengthen the resistance to mechanical abrasion of superamphiphobic surface. MMT is a sort of natural resourced nanomaterials with eco-friendliness, low cost and applied to fabricate micro-nano roughness on the fabrics [21]. Moreover, PA-66 fabrics were selected as the substrate owing to its excellent properties such as wear resistance, fatigue resistance and low cost. In this study, we report the preparation of durable superamphiphobic PA-66 fabrics by the combination of a fluorine-containing acrylate copolymer coating and MMT particles. The PA-66 fabrics were coated by the amphiphobic emulsion, and then further treated by MMT dispersion. The surface morphology and surface chemical composition of the prepared fabrics were studied by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. Mechanical durability and self-cleaning performance were also investigated.

2 | EXPERIMENTS

The amphiphobic emulsion was synthesized as follows: 1 g Span-20, 0.6 g dodecyl benzene sulphonic acid and 50 mL water were added into a flask, then stirred for 1 h. Subsequently, 50 mg ammonium persulphate, 18 g vinyl-substituted MQ silicone resin (SR) and 5 g hexafluorobutyl acrylate (HFA) were added into the flask, and then reacted for 8 h at 60 °C. Then the amphiphobic SR-HFA copolymer emulsion was prepared.

The MMT dispersion was prepared as followed: 1 g MMT, 0.3 g 1H, 1H, 2H, 2H-perfluoroalkyltriethoxysilanes and 60 g water were added into a flask, and stirred for 24 h at room temperature. Then the MMT dispersion was obtained.

The superamphiphobic PA-66 fabrics were prepared by dip-coating of the amphiphobic emulsion and the MMT dispersion: PA-66 fabrics (4 cm × 4 cm) were degreased in a sodium hydroxide solution (2 g/L) for 30 min in an ultrasonication bath, then thoroughly washed by deionized water. The pre-treated fabrics were dipped in the as-prepared amphiphobic emulsion and stirred at 100 rpm for 20 min, followed by drying in an oven for 20 min at 40 °C. This dip-coating-drying procedure was repeated three times. The resulting fabrics were immersed in the MMT dispersion, and stirred at 100 rpm for 20 min, then dried.
at room temperature for 3 h. This MMT dip-coating-drying procedure was repeated three times, and then the superamphiphobic PA-66 fabrics were obtained.

The surface morphology of the superamphiphobic PA-66 fabrics was observed by SEM (Quanta-450, FEI, USA) operating at 10 kV. An energy dispersive X-ray spectrometer (EDS, X-MAX 50, Oxford, United Kingdom) was performed for element analysis. XPS (Axis Ultra, Kratos, United Kingdom) was performed to confirm the surface chemical composition of the fabrics. Contact angle and sliding angle measurements with water and other liquids at room temperature were conducted with an optical contact angle analyser (JGW-360A, China). The contact angle and sliding angle values of five positions were recorded to calculate average values.

3 RESULTS AND DISCUSSION

The surface morphology of the superamphiphobic PA-66 fabrics was observed by SEM under different magnifications, and illustrated in Figure 1. As shown in Figure 1(a), the fibre surface was rough and covered by MMT particles. And the diameters of the individual fibre arranging from 10 to 15 µm, demonstrated the micro-scaled structures on the fabrics surface. In Figure 1(b), it was found that the single MMT particle was composed by numerous MMT lamellas. The edges of the MMT lamellas were crimped, and had a typical thickness of 20–60 nm.

Therefore, MMT played the vital role in forming the nano-scaled structures on the PA-66 fabrics surface. Consequently, the micro-nano hierarchical rough structure endowed the fabrics surface with the capability of trapping air, which was one of the essential characteristics of superamphiphobic surfaces [2].
The element compositions of the PA-66 fabrics surface were investigated by EDS, and shown in Figure 2. The C, O, F, Al and Si elements were detected in the EDS spectrum. It was clear that SR-HFA copolymer and MMT were incorporated on the fabrics surface.

The chemical compositions of the superamphiphobic PA-66 fabrics surface were analysed by XPS, as shown in Figure 3. The F 1s (689.6 eV), O 1s (532.9 eV), N 1s (403.5 eV), C 1s (284.8 eV), Si 2s (154.5 eV), Si 2p (102.1 eV), and Al 2p (75.4 eV) peaks were detected in XPS survey spectrum (see Figure 3(a)). The presence of above elements further confirmed that the SR-HFA copolymer and MMT were covered on the fabrics surface. As shown in Figure 3(b), the corresponding C 1s high-resolution spectrum could be curve-fitted into four peaks, which could be identified as: CF₃ (292.2 eV), CF₂ (290.9 eV), C O (286.8 eV) and C C/H/C H (284.88 eV) groups, respectively [22, 23]. In Figure 3(c), The Si 2p peak could also be deconvoluted into two components with binding energies at 101.6 and 100.4 eV, which could be attributed to Si-O and Si C bonding, respectively. Therefore, the existence of the CF₃, CF₂ and Si C groups could significantly reduce the surface energy of the PA-66 fabrics, and effectively improve the water and oil repellency [24].

Based on the analysis results of SEM, EDS and XPS, the superamphiphobic PA-66 fabrics surface was fabricated by combining micro-nano hierarchical rough structure and low-surface energy materials. Generally, water or oil droplets could be easily absorbed by pristine PA-66 fabrics due to the capillary effect of the textile structure. However, after being coated with the amphiphobic emulsion and MMT dispersion, the modified fabrics became superamphiphobic. As can be seen in Figure 4(a), the water (dyed with methylene blue) contact angle was 168.1 ± 1.3°, and the oil contact angles of hexadecane (dyed with Sudan red), soybean oil and glycerol were 150.2 ± 2.2, 163.5 ± 1.9 and 155.7 ± 1.8°, respectively. And their sliding angles were 1.9 ± 0.8, 10.7 ± 1.1, 2.3 ± 0.9 and 3.7 ± 0.9°, respectively. Moreover, the above four liquids droplets were nearly spherical on the fabrics surface (Figure 4(b)), confirming the excellent water and oil repellency.

In order to evaluate its self-cleaning performance, the superamphiphobic PA-66 fabric was placed in a watch glass with an inclination angle of 22°. Sudan red powders were selected as the contaminant and randomly scattered on the fabric surface, as shown in Figure 5(a). And then two or three water and soybean oil droplets were dripped using disposable droppers, respectively. As presented in Figure 5(b), the contaminants were easily removed from the fabric surface with both water and oil droplets rolling. Thus, it could be concluded that the superamphiphobic PA-66 fabrics exhibited excellent self-cleaning performance.

The mechanical durability of wear-resistant of superamphiphobic fabrics were tested according to Ren’s method and the results were shown in Figure 6 [25]. It was observed that contact angle values for water, soybean oil, glycerol and hexadecane decrease slightly with the increasing of abrasion cycles. Even after 50 abrasion cycles, the water contact angle still maintained 151.9 ± 1.3° and hexadecane contact angle maintained 135.7 ± 3.0°. The results demonstrated that the fabricated fabrics possessed excellent mechanical durability.
4 | CONCLUSION

In this work, we successfully prepared superamphiphobic PA-66 fabrics with wear-resistance performance by coating of the amphiphobic emulsion and MMT dispersion. The as-prepared fabrics showed superhydrophobicity, superoleophobicity, excellent mechanical durability and self-cleaning performance. The superamphiphobic PA-66 fabrics could be applied in the superantiwetting and other areas.

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