“Mist Polymerization” Method for Fabricating Superhydrophobic Cotton Fabrics

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Abstract. Recently, our group developed a surface modification technology using “mist polymerization” to fabricate functional cotton fabrics. The “mist polymerization” method have both the advantages of liquid-phase and gas-phase reactions: less damages on the structure of the matrix material, very fine and controllable layer, wide applicable monomer range, and small monomer dosage. Here, I summarize recent works on the application of the “mist polymerization” method to fabricate superhydrophobic fabrics.

1. Introduction
Surface properties are a most important factor for many functional materials such as biomedical materials, catalytic materials, photoelectric materials and adsorption materials to realize their functions [1, 2]. Introduction of a special coating by chemical reaction or physical adsorption can change the surface characteristics of the substrate materials and thus endow them with new functions. More attention has been paid to the preparation of stable, durable and controllable surface coatings by chemical reaction. Basing on the phase state of the precursors, surface chemical modification can be divided into two categories: liquid phase and gas phase approaches (figure 1).

Figure 1. Liquid phase and gas phase approaches for surface modification.
As shown in figure 1a, the surface reactions in liquid form, such as electrochemical deposition and chemical bath deposition, is widely used. The merits for liquid phase method are simple equipment, wide precursor range, low reaction temperature and short surface treatment time. However, there are also several demerits for the approach, for example, serious damages on the substrate material, uncontrollable coating thickness and morphology, and a lot of side reactions. Until now, most graft copolymerizations are carried out in a liquid medium. Despite of living radical polymerization methods have been applied to graft polymerization, but the damages caused by organic solvents on the substrate structures are still unresolved [3, 4].

Surface modification using gas phase precursor includes ALD, MLD and CVD [5-7]. As shown in figure 1b, the conversion of precursor compounds into gases often requires high temperature and vacuum conditions, and the applicable range for precursors is very narrow. These technologies have been mostly used in the surface modification of inorganic materials, but recently have extended to the polymer materials. For example, MLD technology can prepare polymer deposition films with only a thickness of few angstroms, and CVD technology can give a layer with several nanometers thick [8-13]. However, many problems have also been exposed in such gas phase modification technology. The big issues include that gasifiable, adsorbable and reactive monomers are really rare, the high temperature and vacuum conditions generally need complex devices, the very low concentration of the gasified monomers lead to a considerably long reaction time.

Between liquid phase and gas phase, the reactions in aerosol state have attracted much attention. Some scholars tried to atomize precursor solutions into very small droplets and disperse them in gas medium to react on the surface of a substrate. The droplet size of a mist (aerosol with liquid dispersed phase) is generally small, which is quite different from that of the large droplets made from spray in terms of fluidity and adhesion. The surface chemical modification of precursors in aerosol state has obvious characteristics when compared with the approaches in liquid or gas phase. A number of studies have been published to improve inorganic functional materials such as semiconductors [14-17].

Recently, our group developed a surface modification technology using “mist polymerization” to fabricate functional cotton fabrics. We atomized organic monomer solutions into fine mist and transport it to the surface of cotton fabric for a graft polymerization. By using the “mist polymerization” strategy, we successfully impacted cotton fabrics with a variation of functionalities such as superhydrophobicity, antibacterial effect and self-clean power via a polymer surface layer in hundreds of nano-meters thick. As mentioned above, the “mist polymerization” method has both the advantages of liquid-phase and gas-phase reactions. For example, the structure of the matrix material is of less damages, very fine layer can be obtained, vacuum and high temperature conditions are unnecessary, the applicable monomer range is wide as the liquid approaches, and the dosages of monomer and solvent are very small. Compared with the liquid-phase and vapor-phase surface graft copolymerization methods, the “mist polymerization” approach is considered to have more potential application value. Here, I introduce several works on the application of the “mist polymerization” method to fabricate superhydrophobic fabrics [18-23].

2. Mechanism of the “Mist Polymerization”

In a previous work, we discussed the effect of solvents on the surface morphology of polymer films during the “mist polymerization” [22]. The organic solvents used to dissolve the monomers have great influences on the surface morphology of the resulting polymer coating. The graft polymer layer forms very complex morphologies such as granular holes, chains and duck eggs on the surface due to the solvent type (figure 2). However, these relatively simple and isolated studies are far from forming a theoretical system to reflect the reaction mechanism of the “mist polymerization”. In order to lay the theoretical foundation of the “mist polymerization” and to apply the “mist polymerization” method flexibly, there are still many basic scientific problems have to solve.
The essence of the “mist polymerization” is a liquid phase polymerization in a liquid film that attached on the substrate surface (about tens to hundreds of nano-meters). Because the polymerization is carried out in a very small volume, it should be affected by the interface properties between the monomer solution and the substrate. The mass transferring and heat transferring must be in a different role from conventional liquid phase polymerization, whereas has some characteristics similar to the gas phase polymerization. We extrapolate that the whole process of the “mist polymerization” can be divided into six stages: monomer atomization, fine mist transport, adhesion and wetting of the mist droplets, in situ polymerization, polymer precipitation, and solvent volatilization (figure 3). There are multiple factors affecting the formation of polymer layer at each stage. These factors are interrelated and constitute a complex system. Therefore, it is necessary to systematically study the influence of some important factors on this complex system. For example, the wetting and spreading of droplets on the surface of the matrix, the physical properties and chemical reaction characteristics of the surface of the matrix material are the key factors in the process of constructing the functionalized surface.

Figure 2. The surfaces morphologies resulted by the mist polymerizations of HFBMA with different solvents: (a) i-butanol, (b) i-propanol, and (c) ethanol.

Figure 3. The main stages of the “mist polymerization”. 
3. “Mist Polymerization” Method for Coating Cotton Fabric with Superhydrophobic Layer

We have prepared a series of superhydrophobic coatings on a single side of cotton fabrics by applying the “mist polymerization” method without fluorine reagents. A series of LMA solutions were atomized to fine mist, and applied onto cotton fabrics for the mist polymerization (figure 4). We found that the resulting polymer layers have nano-scale hierarchical structures on the cotton surface. The results also indicated that the solvents used and the mist stream quantity applied onto fabric surface play very important roles on the surface morphology. As a result, a superhydrophobic layer was built on the single side surface of the cotton fabric without any additional nano-sized particles and fluorine reagents, while the structural damages on the fibers were insignificant. Washing-durable superhydrophobicity with a water contact angle of more than 150° has been successfully conferred on the treated fabric side, whereas the opposite side of the fabric inherits the pristine cotton hydrophilicity (figure 5). The resulting cotton fabrics show medium-level water-absorbing ability that is better than PET fabrics, as well as good vapor transmissibility similar to pristine cotton fabric [18].

![Figure 4. The surface modification on the cotton fabric.](image)

Further, a copolymerization approach for fabricating superhydrophobic cotton fabric was explored via the mist polymerization method. Three monomers, TFMA, IEM and DB were dissolved into a mixed solution, atomized to fine mist, and applied onto cotton fabrics for the mist polymerization (figure 6). Observation using FE-SEM indicated that there are nano-scale hierarchical structures in the polymeric layer. Similarly, surface characterization shows that superhydrophobic property is impacted on the modified surface, whereas the opposite side of the cotton fabric keeps the hydrophilic nature of cotton. Moreover, the water adsorptivity and vapor transmissibility of the modified cotton fabric were inherited as the original cotton fabric after the surface modification [19-21].

![Figure 5. Optical photos of the modified cotton fabric with superhydrophobic layer on single side of cotton fabrics: (a) dyed water droplets, (b) immersed in water, and (c) a variety of droplets.](image)
In a recent work, we successfully applied the mist polymerization strategy to a “grafting to” method to modify cotton fabric surface. A diblock copolymer, PMMA-b-PTFMA, was synthesized via RAFT polymerization (figure 7), dissolved using acetone, atomized to fine mist, and applied onto cotton fabrics to build superhydrophobic layer on the cotton fiber surfaces. The PMMA block in the copolymer was used to make covalent linkages with the fiber surface via transesterification reactions (figure 8), while the PTFMA block was designed as a functional part to confer cotton fabric with healable superhydrophobicity (figure 9). As a result, the modified cotton fabric are superhydrophobic, with a WCA above 160 °. The modified side of the fabric also showed excellent stability against washing and abrasion. Even after 60 laundering cycles or 2,000 abrasion cycles, the fabric still remained WCA of higher than 140 °. Moreover, this superhydrophobicity could be healed using the common dry-cleaning agent, PCE. This mist finishing process gave the cotton fabric with insignificant impacts, especially on flexibility, water absorptivity and vapor permeability [23]. By comparing with the SIP methods that have been widely applied to modify fabric surface, this “grafting to” method had the remarkable merits of having a small dosage of finishing reagents and causing insignificant damage to the properties of cotton fabric.

The combination of “grafting to” methodology and mist-surface modification is suitable for large-scale production of superhydrophobic cotton fabric. Furthermore, this approach may open new way for the construction of fine structures and additional functions onto textile surfaces.
4. Conclusion
We have designed and fabricated several functional coatings on cotton fabric surface to impact superhydrophobicity to cotton fabrics. The coating on the cotton fabric can be easily introduced via the “mist polymerization” method. The modified cotton fabrics exhibit asymmetrically superhydrophobicity, the modified side has washing-durable and mechanically stable superhydrophobicity, but the inherent hydrophilic nature of cotton can be kept on the opposite side. Surface observation indicates that the mist polymerization can form a very thin layer on the fiber surface and the layer can be tailored. Compared with the other ways to obtain superhydrophobic wettability, the desired cotton features can be largely preserved. The unique functionalities with the intrinsic properties of cotton fabrics made the mist surface modification method has potential for fabricating functional textiles and other industrial fabrics.

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Abbreviations
ALD, atomic layer deposition; MLD, molecular layer deposition; CVD, chemical vapor deposition; HFBMA, 2,2,3,4,4-hexafluorobutyl methacrylate; PET, polyethylene glycol terephthalate; LMA, lauryl methacrylate; TFMA, 2,2,2-trifluoroethyl methacrylate; IEM, 2-isocyanatoethyl methacrylate; DB, divinylbenzene; FE-SEM, field emission scanning electron microscope; PMMA-b-PTFMA, poly(methyl methacrylate)-b-poly(trifluoroethyl methacrylate); WCA, water contact angle; PCE, perchloroethylene; SIP, surface-initiated polymerization.

References
[1] Vilan A and Cahen D 2017 Chemical Reviews 117 (5) 4624-4666
[2] Hetemi D and Pinson J 2017 Chemical Society Reviews 46 (19) 5701-5713
[3] Zoppe J O, Ataman N C, Mocny P, Wang J, Moraes J and Klok H A 2017 Chemical Reviews 117 (3) 1105-1318
[4] Zhou T, Zhu Y, Li X, Liu X, Yeung K W K, Wu S, Wang X, Cui Z, Yang X and Chu P K 2016 Progress in Materials Science 83 191-235
[5] Van Bui H, Grillo F and Ommen J R V 2017 Chemical Communications 53 (1) 45-71
[6] Meng X 2017 Journal of Materials Chemistry A 5 (35) 18326-18378
[7] Ji Q, Zhang Y, Zhang Y and Liu Z 2015 Chemical Society Reviews 44 (9) 2587-2602
[8] Bergsman D S, Closser R G, Tassone C J, Clemens B M, Nordlund D and Bent S F 2017 Chemistry of Materials 29 (3) 1192-1203
[9] Park Y S, Choi S E, Kim H and Lee J S 2016 ACS Applied Materials & Interfaces 8 (18) 11788-11795
[10] Wang M, Wang X, Moni P, Liu A, Kim D H, Jo W J, Sojoudi H and Gleason K K 2017 Advanced Materials 29 (11) 1604606
[11] Chen N, Kim D H, Kovacik P, Sojoudi H, Wang M and Gleason K K 2016 Annual Review of Chemical and Biomolecular Engineering 7 373-393
[12] Suh H S, Kim D H, Moni P, Xiong S, Ocola L E, Zaluzec N J, Gleason K K and Nealey P F 2017 Nature Nanotechnology 12 (6) 575-583
[13] Feng J G, Sun M and Ye Y M 2017 Journal of Materials Chemistry A 5 (29) 14990-14995
[14] Knapp C E and Carmalt C J 2016 Chemical Society Reviews 45 (4) 1036-1064
[15] Potter D B, Powell M J, Parkin I P and Carmalt C J 2018 Journal of Materials Chemistry C 6 (3) 588-597
[16] Tedstone A A, Lewis E A, Savjani N, Zhong X L, Haigh SJ, O'Brien P, Lewis D J 2017 Chemistry of Materials 29 (9) 3858-3862
[17] Ozkan E, Crick C C, Taylor A, Allan E, Parkin I P 2016 Chemical Science 7 (8) 5126-5131
[18] Wang L, Xi G H, Wan S J, Zhao C H and Liu X D 2014 Cellulose 21 (4) 2983-2994
[19] Xi G H, Fan W C, Wang L, Liu X D and Endo T 2015 Journal of Polymer Science Part A: Polymer Chemistry 53 (16) 1862-1871
[20] Xi G H, Wang J, Luo G Y, Zhu Y H, Fan W C, Huang M Q, Wang H Q and Liu X D 2016 Cellulose 23 (1) 915-927
[21] Xu Q B, Xie L J, Diao H, Li F, Zhang Y Y, Fu F Y and Liu X D 2017 Carbohydrate Polymers 177 187-193
[22] Wan S J, Wang L, Xu X J, Zhao C H and Liu X D 2014 Soft Matter 10 (6) 903-910
[23] Xu Q B, Shen L W, Duan P P, Zhang L, Fu F Y and Liu X D 2020 Chemical Engineering Journal 379 122401