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Article

The effect of hydroxyl on the super-hydrophobicity of dodecyl methacrylate (LMA) coated fabrics through simple dipping-plasma crosslinked method

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Abstract: In order to obtain stable super-hydrophobicity, suitable hydrophobic treatment agent should be selected according to different materials. In this paper, cotton and poly (-ethylene terephthalate) (PET) fabric was respectively coated by dodecyl methacrylate (LMA) via argon combined capacitively coupled plasma (CCP), and the surface hydrophobicity and durability of treated cotton and polyester fabrics were also discussed. An interesting phenomenon was happened that LMA coated cotton fabric (Cotton-g-LMA) had better water repellency and mechanical durability than LMA coated PET fabric (PET-g-LMA), and LMA coated hydroxyl grafted PET fabrics (PET fabrics were successively coated with polyethylene glycol (PEG) and LMA, PET-g-PEG&LMA) had similar performance to those of cotton fabrics. The water contact angle (WCA) of Cotton-g-LMA, PET-g-LMA and PET-g-PEG&LMA was 156 °, 153 ° and 155 °, respectively, and after 45 washing cycles or 1000 rubbing cycles, the corresponding WCA was decreased to 145 °, 88 °, 134 °and 146 °, 127 °, 143 °, respectively. Also, thermoplastic polyurethane (TPU) and polyamides-6 (PA6) fabrics were all exhibited the same properties to PET fabric. Therefore, the grafting of hydroxyl can improve the hydrophobic effect of LMA coating and the binding property between LMA and fabrics effectively without changing the wearing comfort..

Keywords: Super-hydrophobic, Polyethylene glycol (PEG), Hydroxyl, Stable, lauryl methacrylate (LMA)

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1. Introduction

In 1997, Barthlott and Neinhuis [1] discovered the unique self-cleaning properties of lotus leaf, and electronic microscopy of the surface of louts leaves showed protruding nubs about 20-40μm covered with smaller scale roughness [2]. A lot of studies had confirmed that combination of nano- or micro-roughness, along with low surface energy could result to water contact angle (WCA) higher than 150 ° [3]. Surfaces with these properties called “super-hydrophobic”. Cotton and polyester fabric are all the most wildly used fabrics in our daily lives and industries. So an enormous amount of researches are interested in making the super-hydrophobic cotton or PET fabrics [4] incorporate in a vast numbers of applications such as clothing, moisture collection [5] and corrosion-resistance [6], etc.

With years of efforts, researchers had found ways to create super-hydrophobic surfaces by tailoring the surface topography and chemical composition by using various techniques such as layer by layer assembling [7], electrochemical deposition treatment [8], the sol-gel method [9], electrospinning [10]], dip-coating [11] and their combinations [12]. Nevertheless, the aforementioned methods usually rely on multi-step and time-consuming processes necessary for nanoparticle synthesis or functionalization. Furthermore, they share common disadvantages on involving many reactive chemicals, especially volatile organic compound (VOC) that may pose health risks. All these techniques to make super-hydrophobic surfaces can simply divided into two parts: to make a rough surface and to lower surface energy.

Recently, as one of the environmentally friendly process, plasma treatment has been more and more popular in modifying surface properties of polymers and textile materials. Compared with traditional methods, the reaction occurs in non-equilibrium plasma with high electron density and high-power density, the vaporized LMA substances are expected to suffer from molecular dissociation, excitation, and ionization caused by intense electron collision. It is possible that, the electron impact results in LMA chain scission producing smaller fragmented radicals. Also, the collision would create radicals at the polymer side chain due to methyl abstraction process. This permits the formation branching or networked structures. Another competing chemical process taking place simultaneously is the plasma polymerization, which combines those dissociated radicals and forms a disordered 3-D structure on the surface. Since the reactions are at relatively high energy and high entropy states, the subsequent structures are highly irregular with a high degree of roughness, favorable to super-hydrophobic properties [13]. Based on the above advantages, plasma treatment is totally fit to the definition of ecological textile manufacturing and be used to manufacture super-hydrophobic fabrics. Karaman M, et al. [14] presented the plasma polymerization of poly (hexafluorobutyl acrylate) (PHFBA) thin films on different substrates in an RF plasma reactor with an outer planar electrode, they observed that better hydrophobic was obtained at high plasma power with a WCA of 156° and they also confirmed that the monomer had the covalent bond linkages to the fabric surface. In our past research, we used LMA as the monomer via plasma enhanced chemical vapor deposition (PECVD) method [15-17] and immersion-plasma induced crosslinking method [18] respectively to successfully prepare durable super-hydrophobic cotton fabric. And it was found that the super-hydrophobicity of cotton fabric made by the immersion-plasma induced crosslinking method had better durability.

Therefore, in this paper, cotton, PET, TPU and PA6 fabrics were treated by LMA and low-voltage capacitively coupled discharge plasma (LP-CCP) via immersion-plasma induced crosslinking method, and the performances of cotton and PET fabrics were compared to probe the influence of the presence of hydroxyl groups on the properties of LMA coated fabrics.

2. Experimental Procedure

The knitted polyester fabrics (100%, 120 g/m2), double-knitted cotton fabrics (100%, 210.85 g/m^2), plain woven thermoplastic polyurethane fabrics (100%, 119 g/m2) and plain woven polyamides-6 fabrics (100%, 196 g/m2) were purchased from Miandu Textile Co., Ltd. (Zhejiang, China) used as samples. Polyethylene glycol (PEG-1000, CAS# 25322-68-3) and lauryl methacrylate (LMA, 97%, CAS# 142-09-6) were supplied by Alfa Aesar Tech. Co., Ltd. (Shanghai, China) as monomer. Detergent 209 and standard soapflake were purchased from Wangnilai Co., Ltd. (Guangzhou, China) and the China Textile Institute of Science and Technology (Beijing, China, respectively. Ethanol (AR, ≥99.7%) and argon gas were supplied by Changzhou Hongsheng Fine Detail Co., Ltd (Jiangsu, China) and Canghai industry Gas Co., Ltd. (Shanghai China), respectively.

All fabrics were washed to remove any possible dust or chemical residues, which can probably affect the surface treatment. For PET, TPU and PA6 fabrics, which were immersed into 2 g/l detergent 209 and 2 g/l sodium carbonate with the liquor ratio of 50:1 at a temperature of 40℃ in an ultrasonic bath for 40 min. And then washed repeatedly with deionized water and dried in an oven at a temperature of 70 ℃ for 2 hours. The preprocessing method for cotton fabrics and the solution impregnation and plasma treatment for super-hydrophobic fabrics have been described in the previous article [18].

Surface morphology was characterized by scanning electron microscope (SEM, Hitachi S-4800, Hitachi, Japan) and atomic force microscope (AFM, 5500AFM-SPM, Aglient, America). Surface

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chemical compositions of samples were analyzed by X-ray photoelectron spectroscopy (XPS, Kratos AXIS UltraDLD, Shimazu, Japan) and attenuated total reflectance flourier transform infrared spectrometer (ATR-FTIR, Nicolet 6700, America). The water repellency of control and treated PET fabrics was evaluated by static water contact angle at room temperature and ambient humidity on the DropMeter™ Professional A-200 instrument, equipped with a video camera, the volume of droplets was 5 μl. The washing and abrasion durability of samples was evaluated by the water contact angles after several washing (according to AATCC 61-2006. 2A, SW-8, Mebon Instrument Co. Ltd., China) or abrasion (according to ISO 105-X12:2001, dry friction mode, Y571N, Nantong Hongda Instrument co., China) cycles, respectively. Wearing comfort of fabric is determined by the water vapor transmission (GB/T 12704.2-2009, YG601H, Ningbo Textile Instrument Factory, Zhejiang China) and air permeability (GB/T5453-1997, YG461E, Wenzhou Fangyuan Instrument Co. Ltd. Zhejiang, China). The mechanical strength of the samples was determined on a YG026MB multi-function electronic fabric strength machine (according to GB/T3923.1-2013). The moisture regains and wicking property was used to measure the hydrophilicity of fabrics according to GB/T 6503-2017 and FZ/T 01071-2008, respectively. And all the samples were conditioned for 48 hours in atmospheric conditions of 20±2℃ temperature and 65±2 % relative humidity before tests were performed.

3. Results and discussion

3.1. Properties of LMA coated fabrics

In order to make sure the optimal monomer concentration of LMA, the fabrics were treated by plasma after being immersed in the monomer solution with different concentrations. The relationship between the surface water repellency of fabrics and the monomer concentration was as shown in Fig.1(a). After treatment fabrics were exhibit hydrophobicity with all monomer concentrations, indicating that the use of LMA can effectively improve the hydrophobicity of cotton and PET fabrics. the monomer concentration of 5 g/l and 35 g/l, cotton-g-LMA and PET-g-LMA fabrics got the best hydrophobicity (water contact angle (WCA) of 156.7° and 152.6°, respectively). Washing and rubbing stability was also discussed and the result was as shown in Fig. 1(b) and (c). It was found that the WCA of PET-g-LMA fabrics decreased rapidly (after 45 washing or 1000 rubbing cycles the WCA reduce to 88.5°and 136.3°). However, Cotton-g-LMA fabrics exhibited better durability, whose WCA decreased slowly and kept at 145.4 and 146.3°, after 45 washing or 1000 rubbing cycles, respectively. It was indicated that only adhered proper amount of monomer, fabrics could get the best water repellency after plasma treatment. And the performance of Cotton-g-LMA fabric was better than that of PET-g-LMA fabric.

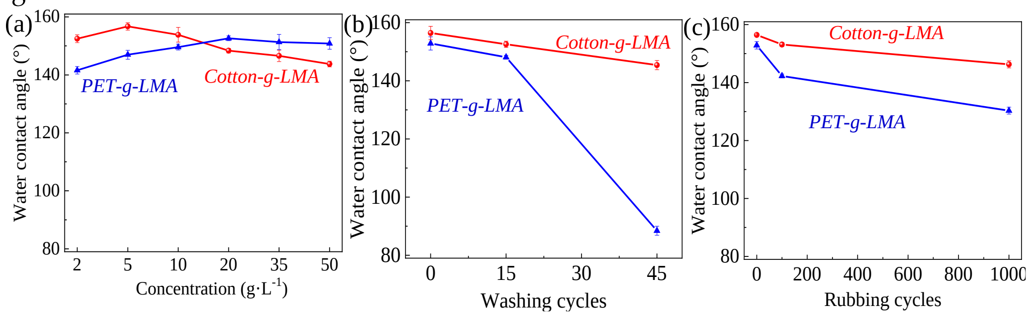

Figure 1. (a) Water repellency, (b) washing durability and (c) rubbing stability of Cotton-g-LMA and PET-g-LMA fabrics.

3.2. Hydrophilicity and chemical compositions of PET fabrics

Hydrophilicity and durability of plasma treated PET-g-PEG fabrics were measured. And as shown in Fig. 2(a), after PEG coated, the moisture regains and wicking performance of PET fabrics increased from 0.40% and 0 mm/30min to 0.91% and 95.30 mm/30min. What's more, even after 20 washing cycles the moisture regains and wicking performance of PET-g-PEG fabrics still retained at 0.86% and 73.50 mm/30min, respectively. According to the surface morphology of PET fabrics, PET-g-PEG fabrics and PET-g-PEG fabrics after 20 washing cycles in Fig 2(b) found that, PEG film had been completely covered on the PET fabric surface even after 20 washing cycles. To determine the effect of different treatments on the chemical composition of PET fabrics, ATR-FTIR was used and the result was as shown in Fig.2(c). It was found that, after PEG impregnated and plasma crosslinked, the stretching vibration peak of alcohol hydroxyl group in hydrogen bond association state at about 3471cm-1 in region I, and the symmetric and antisymmetric stretching vibration peaks of -CH2- at 3000~2800cm-1 in region II were all enhanced significantly, which were the characteristic peaks of PEG-1000 [19]. It was indicated that, after plasma treatment PET fabrics were successfully coated with PEG film and got excellent hydrophilicity and durability.

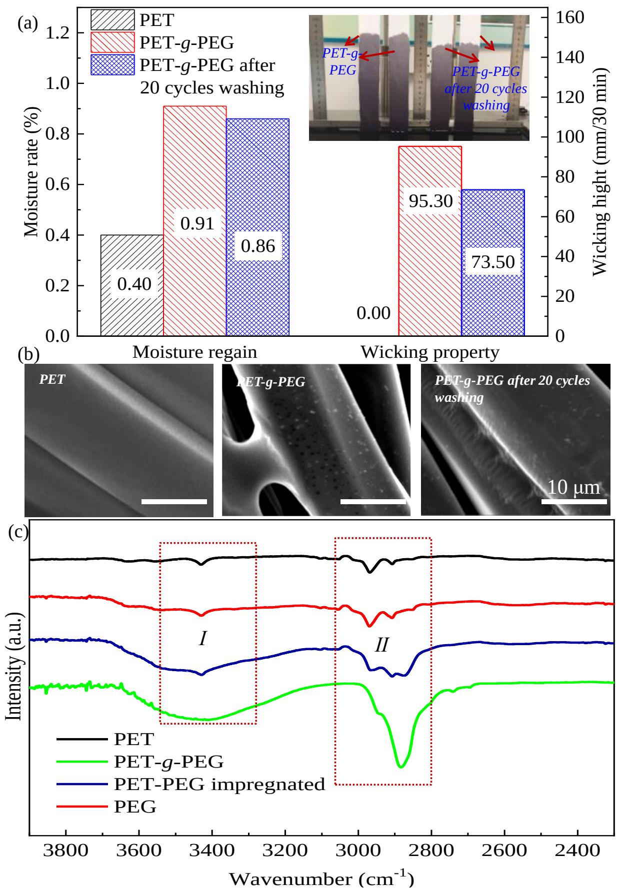

Figure 2. (a) The hydrophilicity, (b) surface morphology and (b) FTIR spectra of PET fabrics with different treatment.

3.3. Water repellency of PET fabrics

As shown in Fig. 3, water has different contact states with different PET fabrics. When PET fabric was in contact with water, it emerged the Wenzel state (Fig. 3(a)) and was suspended in water (Fig. 3(d)), which was caused by the hydrophobicity of PET fabric. After PEG impregnation or coating treatment, PET fabric was penetrated immediately by water (Fig. 3(b)) and completely immersed in water (Fig. 3(d)). However, in the PET-g-LMA and PET-g-PEG&LMA fabric surface the nano or micro rough structure can capture the stable air cushion to form a uniform and stable air shield on the surface, this makes it difficult for water molecules to get close to and adhere to the fabrics surface. Also, when PET-g-LMA and PET-g-PEG&LMA fabric was in contact with water, it emerged the Cassie state (Fig. 3(c)) [20]. The existence of the air shield on the super-hydrophobic structure also makes the fabric hanging on the deionized water surface. (Fig. 3(d)). It suggested the PET-g-LMA and PET-g-PEG&LMA fabric has strong water repellency.

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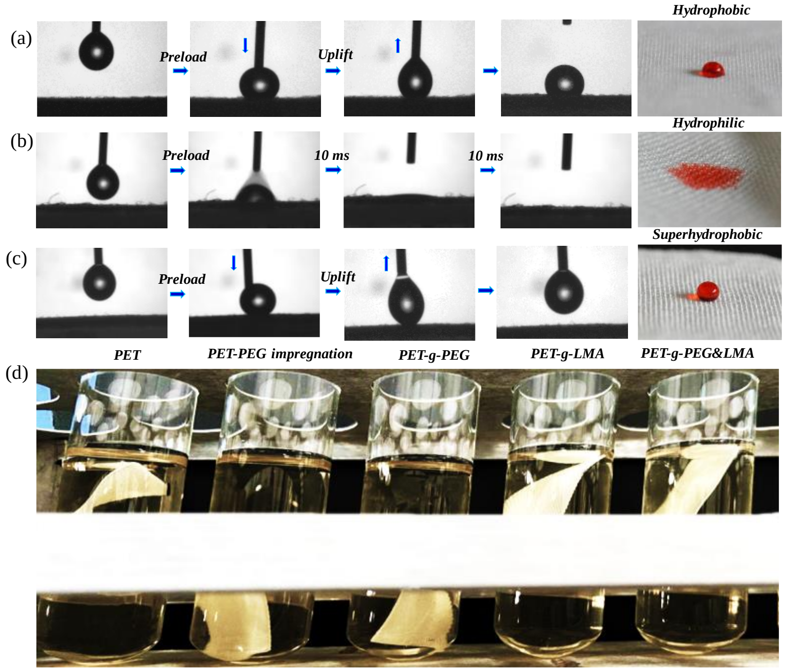
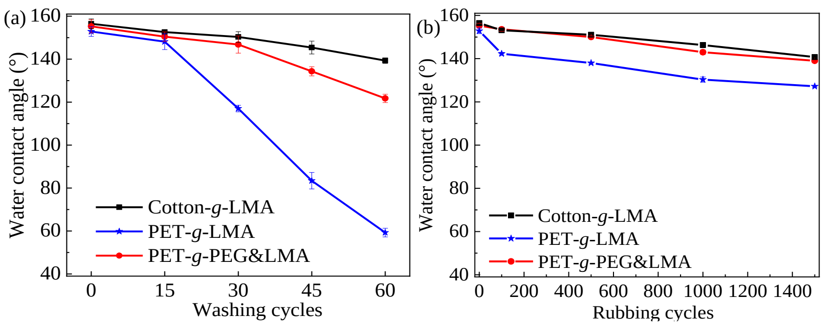


Figure 3. The contact states of water droplet with different PET fabrics surface: (a) PET, (b) PET-g-PEG, (c) PET-g-PEG&LMA (or PET-g-LMA) and (d) the state of different PET fabrics in deionized water.

3.4. Mechanical stability

Mechanical stability of superhydrophobic fabrics plays a vital role on their applications, as the surface micro or nano scale roughness, which is mechanical weak and readily abraded [21]. So, in this paper, the durability of washing and rubbing was evaluated. Fig.4 shows the water repellency (Fig.4 (a) and (b)), surface morphology (Fig.4 (c) and (d)) of different fabrics after different washing or rubbing cycles. And it can be seen from Fig. 4(a) and (b) that, PET-g-PEG&LMA fabrics had almost the same washing and rubbing stability to Cotton-g-LMA fabrics, which were much higher than that of PET-g-LMA fabrics. Combined with SEM analysis (Fig.4 (b-f) and Fig.S1), all the superhydrophobicity of plasma treated PET fabrics could be due to the drafting of the polymerized LMA film with chemical bonds under plasma process. Moreover, the uniform structure of the film can help it still maintain good hydrophobicity after 1500 rubbing cycles or 100 washing cycles. In addition, this paper also performed the same treatment of TPU and PA6 fabrics respectively, which further verified that the introduction of hydroxyl groups could effectively increase the hydrophobicity and mechanical stability of the immersion-plasma induced crosslinking LMA coated fabrics (Table S1).



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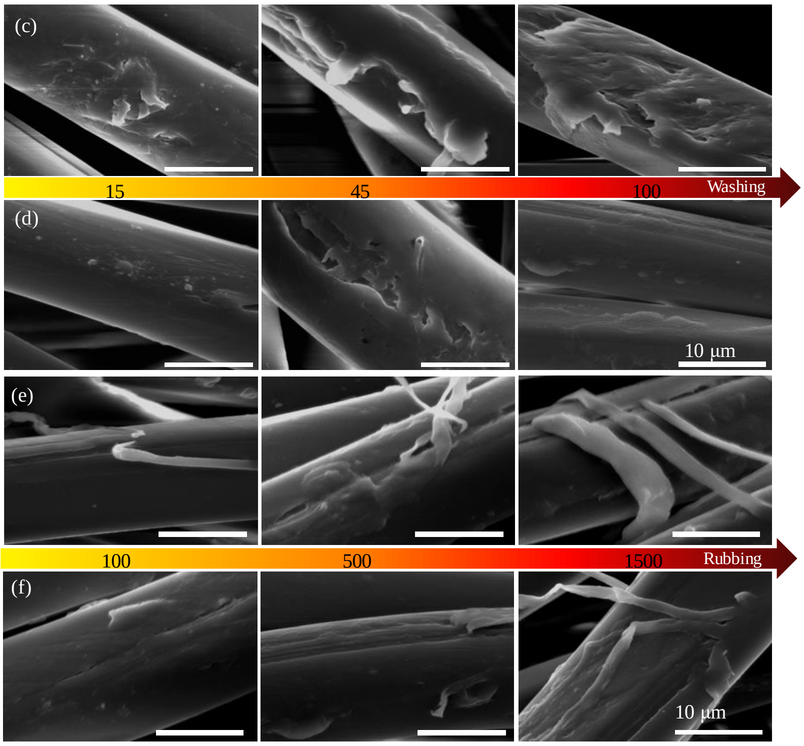

Figure 4. (a) The washing and (b) rubbing durability of PET fabrics and the corresponding surface morphology of (c, e) PET-g-LMA and (d, f) PET-g-PEG&LMA fabrics.

3.5. Wearing comfort

The pore size distribution and porosity of the fabric are the main factors affecting the air permeability and water-vapor transmission of fabrics, which are closely related to the wearing comfort. Therefore, we tested the air permeability and water-vapor transmission of different PET fabrics. As shown in Table 1, compared to PET fabrics, the air permeability and water-vapor transmission of PET-g-LMA and PET-g-PEG&LMA fabrics were reduced by 18.93%, 16.06% and 7.79%, 11.79%, respectively. It was due to the reduction of pore size and porosity of PET fabrics after coating treatment, and the adhesion of the hydrophobic LMA film also affected the absorption of water-vapor by the PET fibers and the transportation to the low vapor pressure side of capillary water through capillary action between pores. What's more, PET-g-PEG&LMA and PET-g-LMA fabrics had extremely the same wearing comfort, that was means, the grafting of hydroxyl groups on the surface of PET fabrics could effectively improve its water repellency and mechanical durability without changing the wearing comfort of the PET fabrics.

Table 1. The air permeability and water-vapor transmission of different PET fabrics.

Sample	Air permeability mm/s	Water-vapor transmission g/(m²·h)
PET	1026.61	48.41
PET-g-LMA	832.26	44.64
PET-g-PEG&LMA	861.69	42.70

4. Conclusion

In this paper, a superhydrophobic fabric was produced via immersion-plasma crosslinking method with monomer of LMA. And we also discussed the existence of hydroxyl and the water repellency and mechanical stability of LMA coated fabrics. It was found that, Cotton-g-LMA fabrics had similar water repellency and mechanical robust to PET-g-PEG&LMA fabrics, which much higher than PET-g-LMA fabrics. Combined with the SEM and TPU, PA6 fabrics treated result, the existence of hydroxyl could improve the hydrophobic effect of LMA coating and the binding property between LMA and fabrics effectively. Besides, super-hydrophobic treatment had little effect on the wearability of PET fabric. All above explained that the introduction of hydroxyl can effectively promote the formation of robust and comfortable LMA coated super-hydrophobic fabrics.

Supplementary Materials: Figure S1. The surface morphology of treated PET fabrics: (a) dipping PEG; (b) PET-g-PEG; (c) PET-g-LMA; (d) PET-g-PEG&LMA.

Table S1. Water repellency and washing stability of different fabrics.

Author Contributions: Ying Guo, Ruiyun Zhang, and Yue Shen contributed to the project management, Liyun Xu and Yu Zhang contributed to the experiment and characterization of fabrics; Liyun Xu, Jianjun Shi and Jianyong Yu contributed to the choice of materials.

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Conflicts of Interest: The authors declare no conflict of interest.

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