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Multifunctional coatings crafted via layer-by-layer spraying method

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ABSTRACT

In this study, a continuous layer-by-layer (LBL) spraying technique was proposed for fabricating multifunctional coatings on cotton fabrics and leather surfaces, separately. This coating could be crafted simply by depositing polyacrylate emulsion, ethanol solution of fragrance, SiO_2 dispersion and chitosan solution on substrates via spraying approach. In this designed coating, polyacrylate emulsion was used in the base coat, SiO_2 particles in the middle layer served as a reinforcing agent. Chitosan was employed as the topcoat, thus giving effective antibacterial action, while vanillin layer was covered by SiO_2 layer and chitosan layer which set double barriers for vanillin diffusion. The coated fabrics and leather samples both exhibited obvious long-term antibacterial performance and sustained fragrance release behaviors, as well as good wear-resistance. All the results suggest that this LBL spraying method hold much promise in designing of multifunctional coatings for industrial use due to its simple operation and versatility.

1. Introduction

Coating technology has emerged as a promising approach to modify surface or matrix in a simple way [1–4]. Up to now, attractive performances, such as UV-proof, water-resistance, antibacterial property, and so forth, have been obtained via coating technology in food, textile, paper packaging and other relative fields [5–9]. Nowadays, by advantageous attributes of skin-friendly nature, breath-ability, and flexibility, cotton fabrics or leather are extensively used in making garments, home furnishings and other industrial products. However, a vital drawback of these products lies in their high sensitivity regarding bacterial infections and external wear due to the natural texture [10–16]. This, indeed, calls for a suitable coating technology that endows fabric and leather surfaces with antimicrobial and wear resistant properties.

Today, consumers' concern towards fashion and active life style is creating new challenges in clothing and household items. Recently, aromatic fabrics have attracted extensive attention because of their pleasant smell and special experience for consumers [17–21]. Vanillin (4-hydroxy-3-ethoxybenzaldehyde), a most popular flavor and fragrance compound, is widely used as flavoring agent in foods, pharmaceuticals, and textiles [22–25]. However, sustained release of vanillin is still a challenge. Approaches addressing to this problem often involves encapsulation technologies, which may entail the high cost and complicated operations. Consequently, a facile method for designing sustained aromatic products is badly in need for wide industrialization.

Routes to craft functional fabrics or leather products always involve severe reaction conditions or complicated chemical reactions, which restrict their use [18,26–28]. Furthermore, the intrinsic characteristics of fabrics or leather products are more likely to be distorted during such unamiable processing. Layer-by-layer (LBL) spraying technique is a powerful coating method, its simplicity and tailor ability of coatings are spurring it for making flame retarded fabric, antibacterial fabric and other functional fabrics. LBL spraying technique constructs functional coatings on the basis of one or more interactions (usually, electrostatic or covalent interactions) taking place between the selected reagents [29,30]. In Grunlan's group, various flame retarded coatings fabricated on the surface of fabrics, PU foams and papers via LBL spraying technique [30–32]. In our previous work, superhydrophobic coatings on leather surface were fabricated via LBL spraying method, and this method was also proved universal on cotton fabric and paper [9].

Polyacrylate, which can form continuous and uniform film, has been widely used in leather finishing, printing, and fabric treatment, etc. due to its highly adhesion [9,33]. Besides, recently, several natural film-formers have also been investigated in designing functional coatings. Among them, chitosan, an abundant aminopolysaccharide derived from *N*-deacetylation of chitin, has been recognized as a suitable material for crafting antibacterial coatings [34]. To endow film-former with strong

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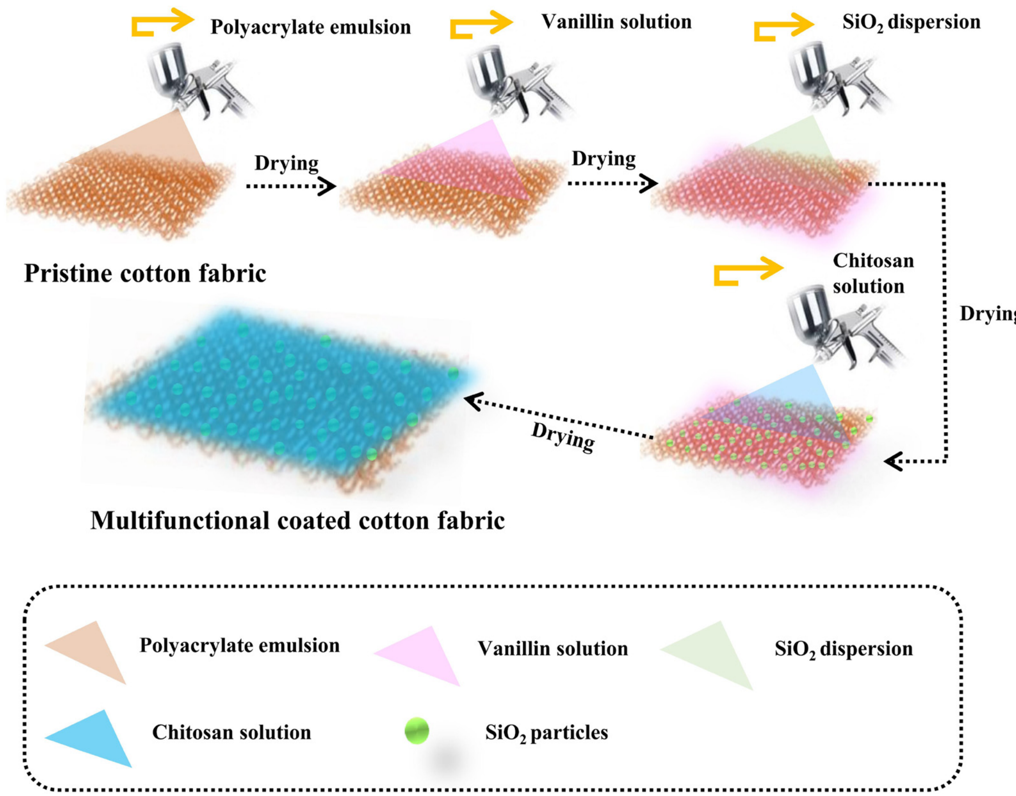

Scheme 1. Illustration for fabrication of the multifunctional coatings on cotton fabrics.

wear-resistance, inorganic particles are always introduced into polymer matrix, thus forming hybrid composite film-former. Ye et al. [35] introduced SiO_2 nanoparticles into hydroxyl acrylic resin and found that wear resistance of the hybrid coating was improved. In our previous work, it was also observed that SiO_2 particles facilitated the enhancement of mechanical strength for polyacrylate based hybrid coatings [36].

On this basis, in this work, LBL spraying method was employed to fabricate multifunctional coatings on cotton fabric and leather surfaces to endow them with fragrant sustained releasing behavior, antibacterial property, as well as desired wear-resistance in a facile and benign way. As is shown in Scheme 1 (taking cotton fabric for example), in the coating process, polyacrylate emulsion was used in the base layer to connect the substrate and coating together by virtue of its strong adhesion. After that, vanillin was used as model fragrance, and covered by commercially available SiO_2 particles in the middle layer, where SiO_2 particles also served as a reinforcing agent. Chitosan was employed as the topcoat where it served as a film-former as well as an antibacterial agent. In this spraying order, vanillin was covered by SiO_2 layer and chitosan layer which set double barriers for its diffusion, thus giving slow release behavior. Chitosan on the top layer may make its antibacterial action more effective, while SiO_2 particles embedded under chitosan layer may enhance wear-resistance of the coating. Accordingly, this method was also applied on coating leather surface to investigate its feasibility. Simple operation and versatility will make this LBL spraying approach hold much promise in various industrialized applications.

2. Material and methods

2.1. Material

Cotton fabrics were supplied by Shaoxing Qidong Textile Co., Ltd. (60 ends/cm, 30 picks/cm, 0.42 mm thickness, 120 g/m^2 weight, 35.2 m^2/g specific surface area). Chitosan (M_W = 20 kDa, 95% deacetylation) was obtained from Qingdao Yunzhou Biochemistry Co., Ltd. Polyacrylate emulsion was supplied by Y&B International Guangzhou Co., Ltd, the feature of this polyacrylate [poly (MMA-*co*-BA-*co*-AA)] emulsion: 35 wt% solid content, pH = 7.0. SiO_2 powder (10 μm) was provided by Henan Nano Materials Engineering Technology Research Center. Vanillin was purchased from Sigma Aldrich. Ethanol (99.7%) and acetic acid (99%) were obtained from Tianjin Kemiou Co. Ltd. All the chemicals were used without further treatment.

2.2. Fabrication of multifunctional coatings on cotton fabrics and leather surface

Substrate surface pretreating: Cotton fabrics were washed with deionized water to remove the impurities on surface before coating. In the case of leather, its surface was cleaned with cleaning solution (H_2O/99.7 wt% C_2H_5OH/28 wt% NH_4OH, 85/10/5, v/v/v) to remove the impurities.

Coating: Polyacrylate emulsion was diluted into 2.5 wt% with water and sprayed on the fabric surface. After drying, the fabric was sprayed with vanillin ethanol solution. Meanwhile, SiO_2 particles dispersed in ethanol after vigorous sonication for 1 h were sprayed on vanillin coated fabric. After that, an aqueous chitosan solution prepared by dissolving chitosan in 1 wt% acetic acid solution at 50 °C for 24 h was sprayed on the fabric. Finally, the coated fabric was dried out at room temperature. As for LBL coating on leather surface, the processing is the same as that described above for cotton fabric, thus multifunctional cotton fabrics and leather were obtained.

Working pressure of the spray gun was 4–6 kPa, and distance between the spray gun and the fabric (or leather) surface was kept about 15 cm A room-temperature drying process was conducted after each time of spraying. Usage and the solid content of polyacrylate emulsion, vanillin ethanol solution, SiO_2 ethanol dispersion and chitosan solution sprayed on the fabric or leather surface were listed in Table 1.