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Superhydrophobic, superoleophobic coatings for the protection of silk textiles

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ABSTRACT

The fabrication of protective coatings on silk with special properties is presented. A water soluble siloxane emulsion enriched with silica nanoparticles (7 nm) is sprayed on silk, without the use of any organic solvent. By adjusting the nanoparticle concentration, treated silk obtains (i) superhydrophobic and superoleophobic properties, as evidenced by the high static contact angles of water and oil droplets (>150°) and (ii) water and oil repellent properties, as supported by the corresponding low tilt contact angles (<7°). SEM images show that nanoparticles lead to the formation of microscale clusters with nanostructures, which in turn induce a surface roughness at the micrometer and nanometer scale. The produced coatings have practically no effect on the aesthetic appearance of silk dyed with natural dyes such as indigo, weld, turmeric, and cochineal. Finally, it is shown that the applied coatings can be totally removed from the silk substrate using compressed carbon dioxide, either in supercritical or liquid state, mixed with a small amount of methanol. Consequently, the suggested method is reversible and therefore it has the potential to be used for the protection of modern as well as historic textiles.

1. Introduction

In the last two decades bioinspired surfaces of special wetting properties have attracted considerable attention e.g. [1,2]. Superhydrophobicity, accompanied by water repellency, is usually achieved by developing the special hierarchical micrometer and nanometer sized structure of the lotus leaf [3] on the surface of interest and applying low surface energy agents [4]. On the basis of these principles, and in relation to the final product application, several methods have been developed to fabricate superhydrophobic surfaces including, for instance, lithographic patterning [5,6], sol gel [7,8], layer by layer deposition [9], chemical vapor deposition [10], plasma etching [11] and nanoparticle deposition [12–16]. Moreover, green methods were developed using supercritical carbon dioxide for the fabrication of fluoropolymer nanoparticles [17] which were then used to produce superhydrophobic coatings [18,19].

Superomniphobic surfaces repel not only water, but virtually any liquid thrown on them. For practical applications, however, attention is mainly focused on oil and water repellency. The development of strategies to produce superomniphobic surfaces can be considered as the natural sequence of more than twenty years of research on superhydrophobic surfaces. Likewise with syperhydrophobicity, superomniphobicity is achieved by affecting appropriately both the surface geometry and surface chemical composition [20]. Consequently, the same techniques described above to achieve superhydrophobicity are roughly used to produce superoleophobic and superomniphobic materials and are, for instance, plasma treatment, self assembly, electrochemical deposition, magnetron sputtering deposition, chemical vapor deposition and polymer-nanoparticle coatings [21–35].

The textile industry has a special interest on superhydrophobic and superoleophobic materials as they can have an enormous impact on clothing and other textile products. Leng at al. [36] deposited charged micro- and nano-particles on cotton thus inducing a hierarchical structure. After the application of a perfluorodecyltrichlorosilane, the treated cotton obtained superhydrophobic properties [36]. Liu et al. produced superhydrophobic cotton using silica (SiO_2) nanoparticles and octadecyltrichlorosilane, as a low surface energy agent [37]. Hoefnagels et al. used also nanoparticles on cotton fibers to generate a dual-size sur-

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face roughness, while superhydrophobization was achieved using PDMS [38]. Artus et al. fabricated a superoleophobic polyester fabric coated with silicone nanofilaments and subsequent plasma fluorination [39]. Other researchers achieved the fabrication of superhydrophobic/superoleophobic textiles by layer by layer assembly [40], plasma treatment [39], sol-gel [41,42], chemical vapor phase deposition [43] and other methods [44–46].

In this work we present a simple, cost effective and green chemical method for the production of a coating on silk which shows both superhydrophobicity and superoleophocity accompanied by water and oil repellency. A water based emulsion of silane, siloxane and organic polymer is used and sprayed on silk. The resulting siloxane coating shows weak performance corresponding to relatively low/high static/tilt contact angles of water and oil droplets. However, the properties of the coating material are tuned by adding SiO_2 nanoparticles in the emulsion which enhance drastically both the hydrophobic and oleophobic character of the produced coating, increasing (>150°) and decreasing (<7°) the static and tilt contact angles, respectively, of both water and oil drops on treated silk. Dodecane droplets on treated silk are also studied to strengthen the reported observations. Furthermore, it is shown that the applied coatings can have negligible effects on the aesthetic appearance of dyed silk. The suggested method is designed to have the potential to be used for the protection of historic silk textiles of the cultural heritage. In 1963 Bradni published "La theoria del restauro" [47], where the basic principles of conservation science were introduced including reversibility which implies that any intervention on an object of the cultural heritage should be removable. We demonstrate that compressed carbon dioxide (CO_2), either in the supercritical or liquid state, mixed with a small amount of methanol (MeOH) is an effective solvent mixture which can remove the protective coatings from the silk substrate.

According to the above, the coating produced herein, (i) induces superhydrophobicity/superoleophocity accompanied by water/oil repellency on silk, (ii) is applied without using organic solvents, (iii) has practically no effect on the aesthetic appearance of dyed silk and (iv) can be removed by compressed CO_2. To the best of our knowledge, this is the first report where all these properties are combined in one product, designed for textile protection and conservation.

2. Materials and methods

Silres BS29A, a water soluble emulsion of silane, siloxane and organic polymer, was diluted in distilled water to prepare a stock solution of 7% wt. Silica (SiO_2) nanoparticles of 7 nm in mean diameter (Aldrich) were dispersed in the stock solution in various concentrations, that are 0.5%, 1%, 2%, 3%, 4% and 5% w/w. Dispersions were stirred vigorously for 30 min and sprayed onto clean 4 cm × 5 cm silk specimens, purchased from the local market. For comparison, pure Silres BS29A solution (without nanoparticles) was also sprayed on silk as well as clean glass slides. An airbrush system (Paasche Airbrush) with a nozzle of 660 μm diameter was used for the deposition of the dispersions and the solution. Each coating was produced by depositing 1 ml of the dispersion/solution while the airbrush was held at a distance of 20 cm from the silk surface (Fig. 1). Treated silk specimens were annealed at 40 °C overnight to remove residual solvent (water) and kept at room temperature for 2–3 days. It is noted that dispersions with nanoparticle concentration >5% w/w were too viscous and could not be deposited using the aforementioned Paasche airbrush system.

Static and tilt contact angles were measured on the surfaces of the treated silk specimens using an optical tensiometer apparatus (Attension Theta) and droplets of distilled water, olive oil (purchased from local market) and dodecane (Merck). Furthermore, contact angles of droplets, prepared using distilled water and hydrochloric acid (HCl) or sodium hydroxide (NaOH), corresponding to a pH range from 0.38 to 13.79, were measured. The reported contact angles are averages of five measurements. Variations are provided as error bars. The volume of the droplets was 8 μl.

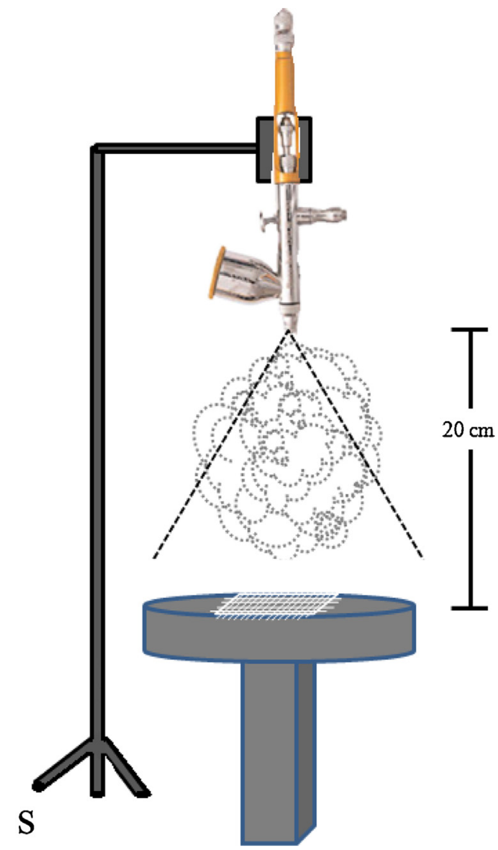

Fig. 1. Scheme of the experimental set up.

Scanning electron microscopy (SEM; JEOL, JSM-6510) was employed to study the surface structures of the treated silk specimens, which were coated with a thin layer of carbon. Colourimetric measurements were carried out using a Miniscan XE Plus spectrophotometer from Hunter Associates Laboratory Inc. and the results were evaluated using the $L^* a^* b^*$ coordinates of the CIE 1976 scale. The reported results are averages of three measurements. Colourimetric measurements were carried out on silk samples dyed with natural dyes such as indigo, weld, turmeric, and cochineal, as described in the Supplementary file.

Coated silk specimens were treated with carbon dioxide (CO_2), in supercritical (200 bar and 40 °C) and liquid (200 bar and 25 °C) state, to evaluate its efficacy to remove the applied coatings from silk. Small amounts of methanol (MeOH) were added in the solvent mixture. The experimental high pressure apparatus is described in detail elsewhere [48–50]. Briefly, a syringe pump (ISCO 100DX) compresses CO_2 and transfers it inside a high-pressure cell (volume of 40 ml). A perforated metallic support, which holds the sample, is positioned inside the cell. Once the sample is set inside the cell, the cell is sealed, carbon dioxide is admitted inside the cell and the pressure rises, up to the desired point. Once the cleaning is completed, decompression takes place and the sample is removed from the cell. The cleaning results are evaluated by weight loss measurements using a Sartorius balance (model B120) with an accuracy of 0.0001 g. After decompression, some treated silk specimens were blown with compressed (1.5 bar) air for 2 min to achieve total removal of the coatings from the silk substrate.