Inkjet Printing of Fluorine-free Hydrophobic, Breathable Textile Coatings

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Abstract

We report an alternative method of creating hydrophobic and breathable fibers using organic fluoro-free materials causing structural changes on the surface of the fibers without affecting its texture. Crosslinked hydroxyl functional styrene nanoparticles were prepared by emulsion polymerization and deposited onto cotton either manually or via inkjet printing and the final sample was assessed for the durability of hydrophobicity and breathability after mechanical stressing and wash cycles.

Introduction

Hydrophobic textiles are used in numerous application including outdoor furniture clothing for leisure activities and uniforms for professionals such as surgeons. In garment related applications not only a high level of water repellency is required but also the textiles should be breathable allowing water vapor to pass through providing the wearer with greater level of comfort.

In nature there are examples of plants with superhydrophobic leaves [1], which prevent the water drop from spreading, achieving contact angle values in the vicinity of 140º. SEM analysis of these leaves revealed that their surface consists of numerous hydrophobic micro-protrusions resembling a bed of nails, which minimize the contact area between water droplet and the surface. This phenomenon, referred to as the "Lotus Effect", suggests that hydrophobicity is synergistic effect of both low surface energy and rough surface topography [1], [2]

Reproducing the Lotus effect in the lab has been a very versatile field of research and several different approaches have been explored.

- Luzinov et al [3] have reported the deposition of an immiscible polymer blend on PET fabric followed by selective etching of one phase leaving behind a hydrophobic porous coating with contact angle beyond the ultrahydrophobic boundary (150º).
- Organic/inorganic hybrid nanoparticles (using silica [4],[5],or silver [3] as core) functionalized with long hydrophobic hydrocarbons chemically bound to the textile surface are another example.
- Layer by layer deposition [6] of hydrogen bonded complexes of polymers and sol gel [7] processes followed by pyrolysis have also been reported as successful methods of preparation of superhydrophobic surfaces

Here we report the use of functionalized organic nanoparticles which are capable of being inkjet deposited onto textiles and covalently attached to yield a hydrophobic breathable coating. It is shown that coating the nanoparticles on cotton improves its ability to repel water, property which was retained after applying mechanical stresses such as stretching and friction.

The functionalized nanoparticles are crosslinked polystyrene emulsion particles, dispersed in water, having a particle size 41 nm. They are functionalized with glycidyl methacrylate, which is subsequently hydrolysed to give hydroxyl functionality capable of being crosslinked using melamine-formaldehyde resins.

Experimental

Materials

Styrene (St), divinylbenzene (DVB), glycidyl methacrylate (GMA), sodium dodecyl sulfate (SDS), ammonium persulfate, glycerol, melamine formaldehyde, para toluene sulfonic acid (PTSA) and polystyrene (PS) Mn = 340 kDa were purchased from Aldrich and used as received. Neodol 91-5 non ionic surfactant was provided by Shell. The experiments took place on cotton provided by Ten Cate.

Nanoparticle Synthesis

250 ml of deionised water were added to a 500 ml flange flask fitted with condenser, nitrogen flow, mechanical stirrer, a 5 blade impeller and a thermometer. 20 ml of 2.5% (w/w) solution of SDS (3.38 mmol) in deionised water were added along with the St (21 g, 216 mmol), DVB (2.1 g, 16.1 mmol) and GMA (3.0 g, 21.1 mmol). This mixture was stirred at 600 rpm while being degassed for an hour and heated to 80 °C. Once at temperature 1.0 g of the initiator ammonium persulfate (11.6 mmol) was dissolved in 10 ml of deionised water, degassed for 30 min and then added to the solution. The polymerisation proceeded for 24 h until completion, and the resultant suspension was passed through a 50 μm nylon gauze to remove any coagulum. Any unreacted material was removed via dialysis using deionised water for 1 week and the nanoparticle dispersion was used without further treatment. The solid content of the synthesized dispersion was measured adding 1.5 g of the dispersion in a preweighed container, allowing the solvent to evaporate and weighing the remaining solid. The particles produced had 11.49% GMA functionality by weight of total monomers, giving a suspension of 8.07 ± 0.45 wt-% solid content. The particle size was 41 nm (measured by Light scattering, Nano Z-Series, Malvern Instruments).

Instrumentation

Ink viscosities were measured using an Anton Parr AMVn automated micro-viscometer which is based on the rolling/falling ball principle (DIN 53015 and ISO 12058). Using a 1.8mm diameter capillary at 25 +/- 0.5 ^{o}C and an angle of 70^{o}, times were determined as the average of 4 determinations (+/- 0.2 cP). A KRUSS tensiometer (Drop Shape Analyzer DSA100, KRUSS GmbH, Hamburg, Germany) equipped with image analysis software was used to determine the surface tension of the inks and

equilibrium fluid contact angles on a substrate at 25 °C using the pendant and sessile drop methods respectively.

A Dimatix DMP-2800 inkjet printer (Fujifilm Dimatix, Inc., Santa Clara, USA) was used in the study using a disposable piezo "ink jet" cartridge. This printer can create and define patterns over an area of about 200 x 300 mm and handle substrates up to 25 mm thick being adjustable in the Z direction

Results and Discussion

Figure 1 show a SEM image of cotton before and after deposition of the polystyrene nanoparticles showing the development of a textures surface.

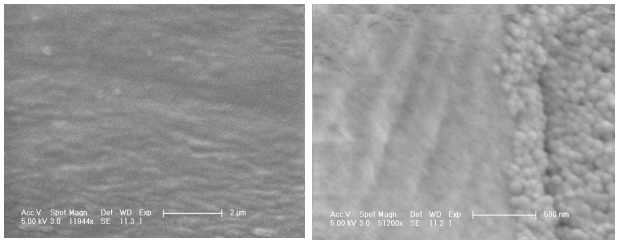


***Figure 1**: SEM images, cotton only left (2 µm scale) and cotton coated with the PS nanoparticles right (500 nm scale)*

The hydrophobicity of these textures surfaces were assessed by measuring the contact angle of a drop of deionised water immediately after the drop was formed and following the change of contact angle with time (Figure 2). Simple deposition of PS nanoparticles on cotton using a 1mm nozzle syringe followed by drying at 130 °C for 60 mins led to a hydrophobic substrate (♦) with contact angle 127° which remains unchanged for over 16 min. The apparent reduction of contact angle after 1000s (16 min) is due to water evaporation and the decrease of the drop size. Stretching the sample towards both planar directions or rubbing the surface with another piece of textile did not affect the CA vs time profile of the sample.

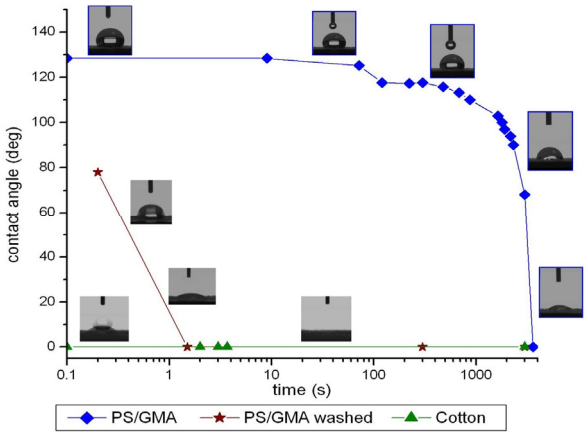


***Figure 2**: Contact angle vs time of PS nanoparticles on cotton*

The Van der Waals interactions between the nanoparticles and the substrate are strong enough to keep them in position when light mechanical stress is applied. However after washing the sample in a water/detergent bath, the contact angle versus time profile of the washed sample (★) is practically the same as the untreated cotton (▲).

Melamine formaldehyde crosslinking was used to covalently attach the hydroxyl nanoparticles to the hydroxyl rich cotton surface as a proof of concept [8],[9],[10]. A 50% w/w solution of MF in methanol was mixed with 2% w/w solution of PTSA in methanol in weight ratio 1:5 respectively. The mixture was stirred for 5 min, applied directly on cotton and allowed to react at 130ºC for 60 min prior to deposition of the nanoparticles and further reaction at 130 ºC for 60 min. Allowing the crosslinker to react with the substrate prior to deposition of the nanoparticles was found to be critical to retain the hydrophobic properties after washing with soap. The chemical binding of the nanoparticles on the cotton significantly improved the contact angle vs time profile of the sample (Figure 3 ■). Contact angle of 130º was achieved which remained for about 16 min before starting decreasing due to water evaporation. Application of mechanical stresses such as stretching and friction did not affect the behavior of the substrate. Hydrophobicity was retained after washing the crosslinking sample (Figure 3 ●) however its durability was significantly compromised, possibly due to partial hydrolysis of the formed bonds or incomplete covalent attachment.

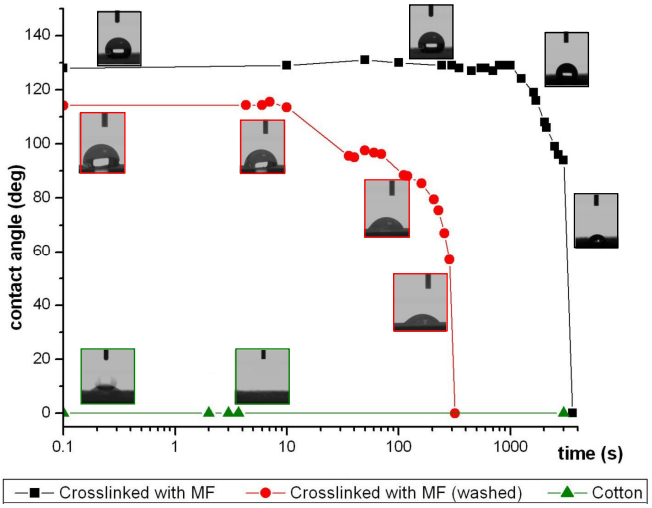


***Figure 3**: Contact angle vs time of crosslinked PS nanoparticles on cotton*

The texture of the cotton is not affected by the deposition of the nanoparticles or the crosslinking with MF and it remains soft and flexible. However prolonged polymerization of MF changes the feel of the substrate making it brittle and stiff. As control the deposition of a solution of PS 340 kDa in THF leads to a brittle and stiff coating with a contact angle of 99º.

Comparing the rate of water evaporation from a vial covered with different samples, showed that the addition of the nanoparticles, did not affect the evaporation process (Figure 4).
The evaporation of the water is a linear function of time, and the slope is the same for plain or treated cotton. The continuous increase of the mass of the evaporated water suggests that the samples do not get saturated with vapor but allow it through continuously

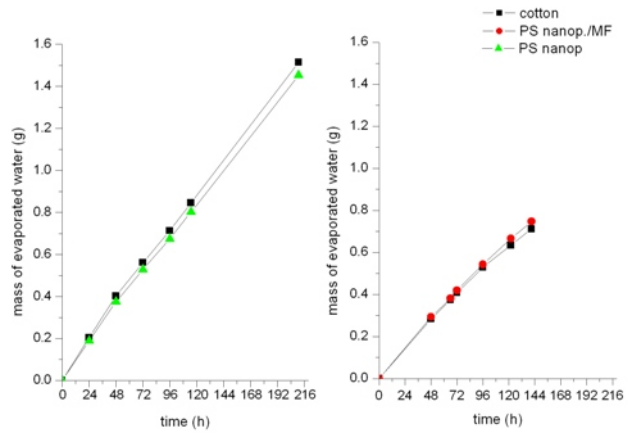
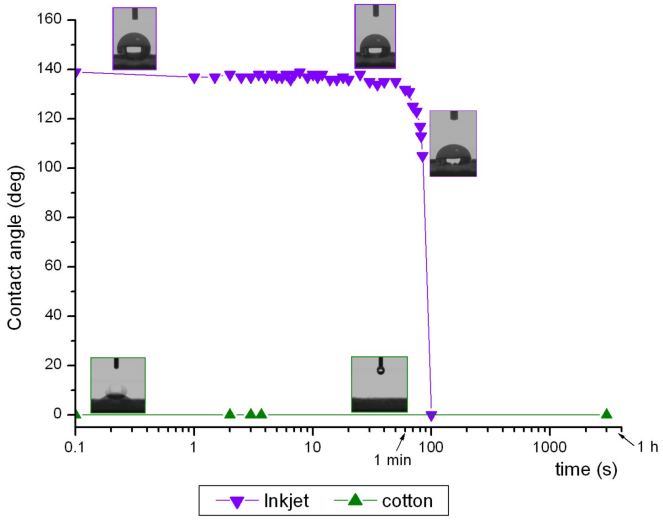


***Figure 4**: Breathability results*

Candidate inkjet inks were formulated using glycerol to increase the viscosity of the dispersion and non ionic surfactant (Neodol) to reduce the surface tension. Ink was filtered with 0.45 µm filter to remove any impurities and large particles that could block the nozzle. Printing took place at 18V and 5kHz, and the pulse parameters were tailored so that drop formation was stable, consistent without ligaments.

The effect of the number of inkjet printed layers deposited on the cotton was assessed. After 12 passes and subsequent crosslinking, hydrophobic behavior was observed but currently inferior to the drop cast samples, the high number of passes being necessary to deposit sufficient materials per unit area using the Dimatix printer (Figure 5 ▼).

***Figure 5**: Contact angle versus time on cotton for inkjet printed crosslinked nanoparticles after 12 passes*



Conclusions

Cotton hydrophobicity was improved by depositing crosslinked hydroxyl functional styrene nanoparticles prepared by emulsion polymerization. Simple deposition of the nanoparticles on cotton gives water contact angles of 127º without affecting their texture or their breathability properties, which can sustain mechanical stress and friction but not washing cycles. Covalent attachment of the nanoparticles on the cotton using MF as a crosslinking agent improved the water contact angle and its sustainability during washing. Preliminary inkjet data is reported but further work is required to optimize the deposition process in order to get sufficient material coverage

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The author completed her PhD research on "Synthesis of polymers of intrinsic microporosity and their application in inkjet printing and catalysis" under the supervision of Dr P.M.Budd in June 2009 in Manchester. She joined the group of Prof S.G.Yeates in Manchester in July 2009 working on the physical characterization of complex colloidal formulations for a range of applications. The focus of her current work is on inkjet printing of hydrophobic and breathable coatings on textiles.