Superhydrophobic bio-fibre surfaces *via* tailored grafting architecture†

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Superhydrophobic bio-fibre surfaces with a micro-nano-binary surface structure have been achieved *via* the surface-confined grafting of glycidyl methacrylate, using a branched "graft-on-graft" architecture, followed by post-functionalisation to obtain fluorinated brushes.

The ability to fabricate superhydrophobic and self-cleaning surfaces, with a water contact angle (CA) above 150°, has attracted great interest due to their potential use in various applications.[1] Superhydrophobic surfaces are usually prepared by combining an appropriate surface roughness with a hydrophobic material, since the hydrophobicity of a surface is determined by its chemical composition and topography.[2]

Cellulose-based materials would greatly benefit from an increased hydrophobicity. Cellulose is an abundant, inexpensive, biodegradable and renewable biopolymer exhibiting very good mechanical properties but is also water-absorbing. Modification of cellulose is often required to alter and tailor its chemical and physical properties.[3] The use of cellulose-based materials could thus be extended to new areas by the incorporation of functional moieties onto the fibre surface. For example, water-repellent and self-cleaning materials could be obtained using the incorporation of hydrophobic groups to the cellulose surface.

Our group has focused on surface modification of cellulose by graft-copolymerisation *via* atom transfer radical polymerisation (ATRP).[4] ATRP is a controlled radical polymerisation technique that has proven useful for the synthesis of functional macromolecules with accurately controlled molecular weight, molecular weight distribution and chain ends.[5] ATRP has also been used for surface modification from a broad variety of substrates to yield well-defined grafts.[6] This is especially interesting in applications where surface properties are of utmost importance. In addition, the grafting architecture can be tailored to obtain specific surface properties in a material.[7]

In this communication, versatile routes to superhydrophobic and self-cleaning bio-fibre surfaces are reported. Filter paper was chosen as bio-fibre substrate due to its high surface roughness.

The first route was simply to react the hydroxyl groups on the cellulose substrate with pentadecafluorooctanoyl chloride. FT-IR analysis confirmed the success of the acylation reaction by the appearance of a carbonyl peak at 1800 cm^{-1}, not seen for unmodified cellulose, as shown in Fig. 1A–B.

Water contact angle measurements revealed a hydrophobic surface after modification. However, the exact CA is somewhat difficult to determine due to the inherent roughness of the cellulose surface. The modified surface first seemed to be superhydrophobic, as the obtained CA was around 150° (Fig. 2a). However, it was observed that the water droplet was partly adsorbed into the surface after a period of time, suggesting an insufficient surface-coverage. The CA had decreased to 128° after 20 minutes and after 50 minutes the CA was below 90°, indicating a hydrophilic character of the surface.

In order to improve the surface-coverage and thereby the hydrophobicity, a functional monomer could be grafted from the cellulose substrate to enable attachment of an increased amount of fluorine groups. Immobilisation of the initiator, 2-bromoisobutyryl bromide, on the cellulose substrate was performed as previously described by Carlmark and Malmström.[4a] The initiator-modified cellulose surfaces were grafted with glycidyl methacrylate (GMA) using ATRP conditions similar to those described by Fernandez-Garcia and co-workers (Scheme 1).[8]

The grafting of GMA from the cellulose substrate was confirmed from FT-IR analysis by the appearance of a carbonyl stretch at 1730 cm^{-1} (Fig. 1C). The pendant epoxide groups in PGMA were hydrolysed under acidic conditions and subsequently reacted with pentadecafluorooctanoyl chloride (Scheme 1). A second carbonyl stretch at 1800 cm^{-1} confirmed the attachment of fluorine groups as can be seen in Fig. 1C. A slight increase in CA for the fluorinated PGMA-grafted filter paper, compared to the fluorinated cellulose substrate, was observed (Fig. 2b). A CA reaching as high as 154° was obtained, proving the surface to be

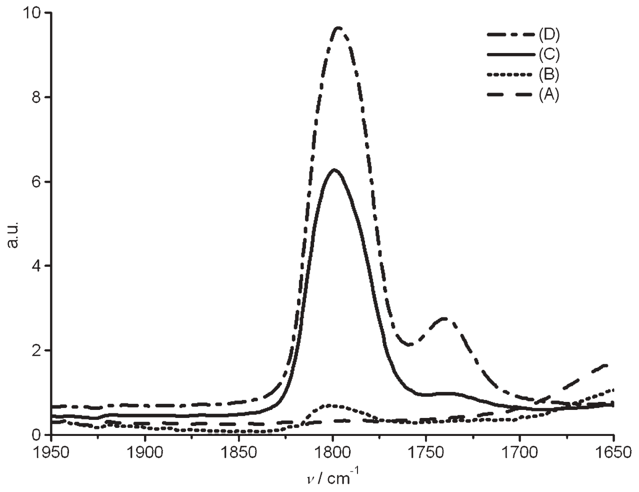

Fig. 1 FT-IR spectra of (A) unmodified filter paper, (B) fluorinated filter paper, (C) fluorinated PGMA-grafted filter paper and (D) fluorinated "graft-on-graft"-modified filter paper.

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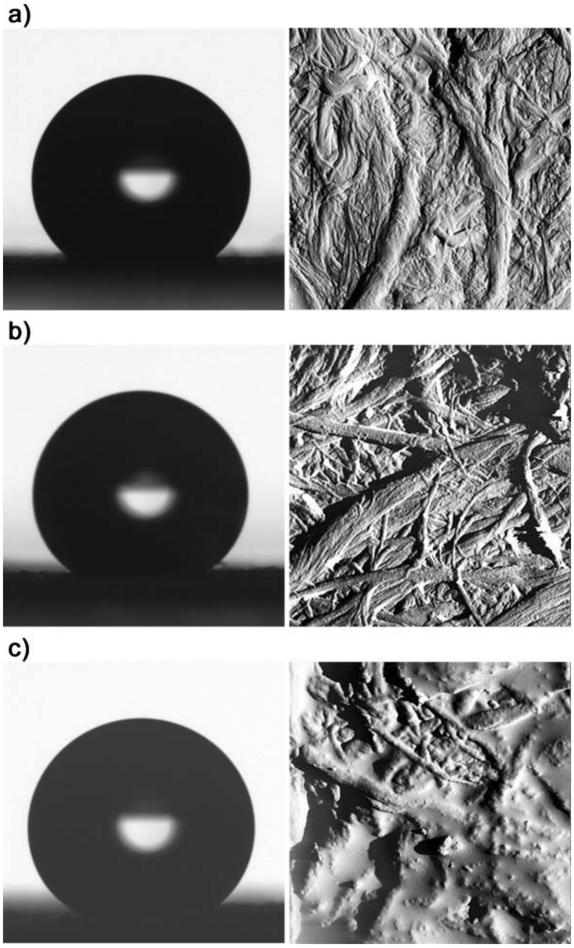

Fig. 2 (a) Fluorinated filter paper: Water contact angle 150° (left), and corresponding AFM amplitude image (5 × 5 μm) (right). (b) Fluorinated PGMA-grafted filter paper: Water contact angle 154° (left), and corresponding AFM amplitude image (5 × 5 μm) (right). (c) Fluorinated "graft-on-graft"-modified filter paper: Water contact angle 172° (left), and corresponding AFM amplitude image (5 × 5 μm) (right).

superhydrophobic. The improvement in CA is, however, small compared to the increase in the number of fluorine groups attached to the surface, as can be seen in the FT-IR spectra in Fig. 1A–C. The hydrophobicity of a surface is dependent on its chemical composition, but also on the topography. The surface roughness of the substrates prepared by the two modification routes was analyzed with AFM (Fig. 2a–b). The fibrillar structure resembling that of an unmodified surface can still be seen for both substrates. For the sample where the fluorine groups were attached directly, the surface appears more compact. When GMA was grafted from the substrate and subsequently ring-opened and fluorinated, the surface appears less dense. This might indicate that the grafting process affects the interfibrillar interactions giving rise to exposure of non-modified regions, which could explain the low increase in CA for this surface.

To further improve the superhydrophobicity, we decided to increase both the number of fluorine groups and the surface roughness of the fluorinated substrate. We believed that a branched "graft-on-graft" architecture of the grafts would fulfil both of these criteria. Hydrolysed epoxide groups in the PGMA-grafted substrate were reacted with 2-bromoisobutyryl bromide, to generate polymer grafts containing a multitude of initiator sites along the back-bone of each chain. A "graft-on-graft" architecture was obtained when GMA was polymerised from the initiating groups on each graft (Scheme 1). Post-functionalisation of the "graft-on-graft" polymers was carried out thereafter. The fluorinated "graft-on-graft" architecture showed an extremely high CA, around 170° (Fig. 2c). The applied water droplet was observed to almost hover above the surface. In the case of the lotus leaf, this phenomenon is explained by a low contact area between the water droplet and the surface of the leaf due to the binary surface structure.[9] Air is trapped between the water droplet and the voids at the surface resulting in high contact angles and low sliding angles. According to AFM analysis, the fluorinated "graft-on-graft"-modified substrates show a rough surface structure, as can be seen in Fig. 2c. The surface is clearly covered by the polymer; however, the fibrils are still visible providing a micro structure. Overlaying the fibrillar structure, nano-sized features are distinguished, demonstrating that the surface exhibits a micro-nano-binary structure analogous to that of the lotus leaf. The "graft-on graft" architecture enabled the addition of a very high number of fluorinated groups on the surface (Fig. 1D), and provided the observed nano-sized features. This unique architecture, combined with the inherent roughness of the substrate, gave a binary structure and therefore a truly superhydrophobic bio-fibre surface. The stability of the hydrophobic nature was also investigated by leaving a water droplet on the surface for a longer period of time. No significant decrease in the CA could be observed over time and the surface was still superhydrophobic, even after 50 minutes.

The self-cleaning ability of the modified cellulose substrates was also investigated. After contamination of the surface with carbon black powder, the water droplets applied to the surface collected the powder. The "dirt-containing" water droplets rolled off the surface as soon as the filter paper was tilted, leaving a clean surface, as can be seen in Fig. 3.

In conclusion, this work has demonstrated a straightforward approach to fabricate superhydrophobic cellulose surfaces. The cellulose substrate was modified by the ATRP of GMA, using a branched "graft-on-graft" architecture. Post-functionalisation using pentadecafluorooctanoyl chloride yielded a fluorinated surface with an extremely high CA of $> 170°$. It was evident from AFM characterisation that the surface possessed a micro-nano-binary structure. The micro structure was provided by the roughness of the bio-fibre substrate, and the grafting architecture provided the observed nano-sized features. The combination of the rough substrate and the grafting architecture rendered a truly superhydrophobic bio-fibre surface. Interestingly, the modified cellulose substrate was also found to be self-cleaning. We believe that our method, "graft-on-graft" and post-functionalisation, can be transferred to a variety of rough substrates to yield superhydrophobic surfaces in a simple manner.

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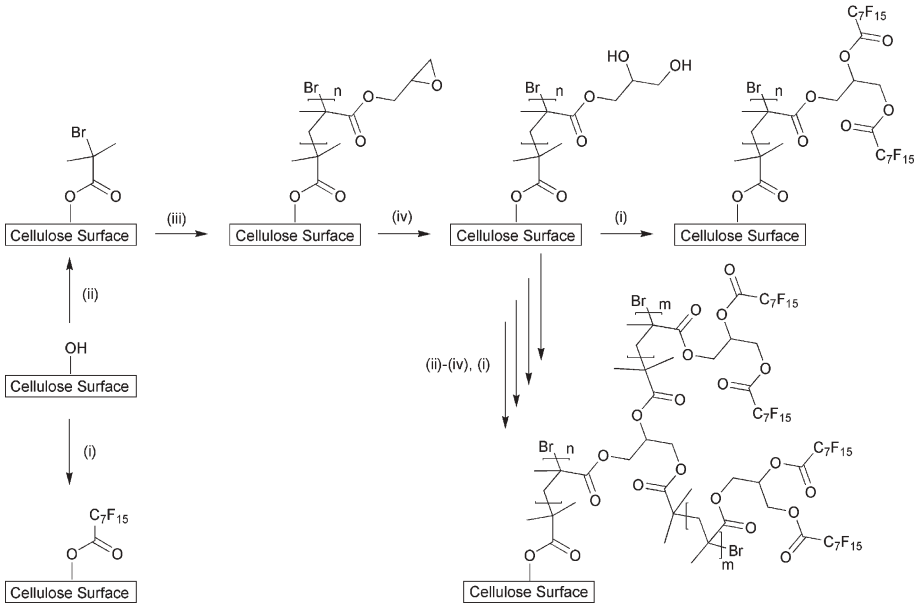

Scheme 1 Synthetic approach for functionalisation of cellulose substrate. *Conditions*: (i) pentadecafluorooctanoyl chloride, TEA, DMAP, DCM, room temperature (RT); (ii) 2-bromoisobutyryl bromide, TEA, DMAP, THF, RT; (iii) GMA, CuCl, $CuBr_2$, PMDETA, toluene, 30 °C; (iv) HCl(aq), THF, RT.

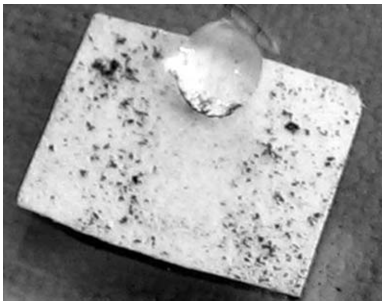

Fig. 3 Demonstration of self-cleaning ability by the removal of carbon black powder from the surface using a water droplet.

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