Renewable nanocomposite polymer foams synthesized from Pickering emulsion templates

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Received 21st May 2009, Accepted 9th July 2009
First published as an Advance Article on the web 23rd July 2009
DOI: 10.1039/b913740h

Fully renewable macroporous thermosetting and UV-cured cellulose nanocomposites have been synthesized from medium and high internal phase water-in-acrylated soybean oil emulsions stabilized solely by hydrophobized bacterial cellulose nano-fibrils.

Research efforts are being focused on the development of environmentally friendly renewable highly porous nanocomposite foams in the desire to seek alternatives to petroleum-based materials. Emulsion templating has emerged as an effective route to prepare porous polymer foams with a well-defined morphology since the latter is defined by the structure of the emulsion template at the gel-point of the polymerization.[1] Commonly, water-in-oil (w/o) emulsions are stabilized against droplet coalescence by large amounts (5–50 vol.%) of suitable but structurally parasitic (mainly non-ionic) surfactants,[2,3] which must be removed during post-processing. Pickering emulsions are emulsions that are solely stabilized by small particles.[4,5] These emulsions are extremely stable due to the irreversible adsorption of particles at the interface between the dispersed and continuous phase.[6] Bacterial cellulose is attractive as a source of renewable nano-fibrils because unlike plant-based cellulose it has the advantage of being free from lignin, hemicellulose and pectin.[7] Whilst cotton is relatively free from these components it does have a wax layer between the cellulose micro-fibrils, which must be removed by extraction. Bacterial cellulose has widths already in the nanometre size range and possesses a high Young's modulus, reported at 114 GPa.[8] It is highly hydrophilic and therefore, lacks compatibility with many polymers. However, the nano-fibrils can be modified in order to tune their surface chemistry and wettability.

Plant oils, such as soybean oil, castor oil and linseed oil are important natural resources, consisting predominantly of triglycerides, which are themselves composed of three fatty acids by a glycerol centre through ester linkages. The fatty acids range in length from 14–22 carbon atoms with 0–3 double bonds per fatty acid.[9,10] Triglycerides with acrylate functionality have been prepared through various active sites within the triglyceride structure.[11–14] These functionalized triglycerides can be polymerized to high molecular weights and high cross-linking densities. The mechanical properties of soybean-, linseed- and castor-oil-based thermosetting polymers have been shown to be comparable to petroleum based unsaturated polyester resins.[10,11,15] Flexural moduli and strengths for these bio-based polymers have been reported in the range of 0.8–2.5 GPa and 32–112 MPa, respectively, with glass transition temperatures ranging from 72 to 152 °C.[15] However, at high cross-link density these polymers suffer from embrittlement and low fracture toughness due to reduced mobility of the fatty acid chains. To counter this, the addition of low amounts of nano-clays fillers (<5 wt.%) has been reported to double the fracture toughness with no trade off with other thermal or mechanical properties.[12] The processing of fibre reinforced soy-epoxy composites by pultrusion[16] and the foaming of acrylated epoxidized soybean oil using blowing agents has been investigated.[17] In this work we have selected acrylated epoxidized soybean oil (AESO) as it is one of the more widely characterized functionalized natural oil monomers.[9,10,12,13,15,18]

Here we provide evidence that it is possible to stabilize Pickering medium internal phase emulsions (Pickering-MIPEs) containing modified soybean oils within the continuous phase and having internal aqueous phase levels approaching 70 vol.% solely by hydrophobized bacterial cellulose nano-fibrils. Such emulsion templates can be used for the synthesis of polymer foams, so-called poly-Pickering-M/HIPEs (medium/high internal phase emulsions) if the components of the continuous phase are polymerizable.[19] MIPEs are defined as emulsions with internal phase volumes ranging from 30 to 70%.[20] Due to the hydrophilic nature of cellulose, water continuous phase (oil-in-water (o/w)) emulsions tend to be stabilized,[21] the nano-fibrils act to sterically hinder droplet coalescence. It has been shown that water-in-toluene (oil) (w/o) emulsions containing up to 50 vol.% of internal phase can be stabilized using hydrophobized microfibrillar cellulose.[22] More recently, a liquid–liquid dispersion technique has been described,[23] whereby the hydrophobic cellulose derivative hypromellose phthalate was dissolved in water-miscible solvents and sheared in aqueous media; micrometre sized cellulose particles were reported to form by solvent attrition and adsorbed onto water/air and w/o interfaces, resulting in foams or foam emulsions that were stable for months in the presence of circa 1 wt.% of the particles. We show that it is possible to synthesize renewable nanocomposite polymer foams using cellulose nano-fibril stabilized MIPE templates. Suitably hydrophobized bacterial cellulose nano-fibrils were used to stabilize oil phases ($\leq$ 50 vol.%) as the continuous phase through adsorption at the o/w interface.

Cellulose nano-fibrils were extracted and purified from *nata-de-coco* (coconut gel) and rendered hydrophobic *via* two separate methods, which are detailed in the experimental section: i) *via* silylation using the reagent chloro(dimethyl)isopropylsilane,[24] and ii) *via* a greener renewable acetic acid esterification modification.[25,26] The authors

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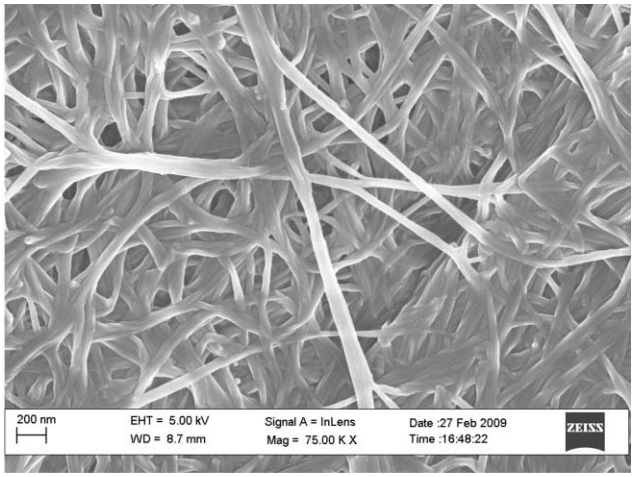
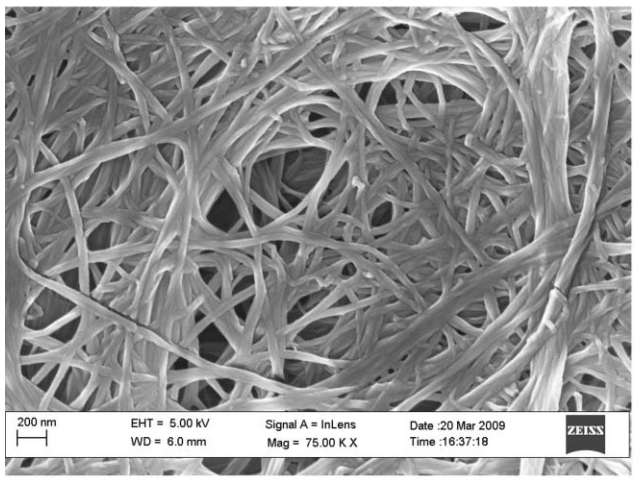
recognize that the silylation route involves the non-renewable reactant chloro(dimethyl)isopropylsilane, whereas the esterification may be regarded as greener since acetic acid is a renewable resource. However, both modification routes require harmful solvents, such as methanol, THF, toluene and pyridine, which may be recycled.[27] It is in fact possible to obviate the solvent exchange step (involving methanol), which is described in the methodology, by freeze-drying the bacterial cellulose after the extraction step.

FTIR spectroscopy (data not shown) confirmed the silylation of the cellulose, with characteristic peaks at 855 cm^{-1} (Si-C stretch), 833 cm^{-1} (Si-CH_3 stretching) and 777 cm^{-1} (Si-CH_3 rocking);[24] in the case of the acetic acid esterified samples the characteristic ester carbonyl band appears around 1735–1750 cm^{-1}.[25] SEM observations of the unmodified and esterified bacterial cellulose samples show no obvious changes in morphology, as shown in Fig. 1a,b. Water-in-air contact angle and Zeta (ζ)-potential measurements demonstrated the effect of the modification to the surface properties of the nano-fibrils, as shown in Table 1. Measuring contact angles on samples that are rough at the nano- and micrometre scale must be interpreted carefully due to Wenzel and Cassie-Baxter effects,[28] however, it is clear that the otherwise hydrophilic cellulose has been rendered significantly hydrophobic as the water forms stable droplets with a large contact angle on the modified cellulose nano-fibrils, whereas water almost immediately wicks into the unmodified cellulose and possesses a low contact angle. The real three-phase contact angle, AESO resin-in-water on silylated bacterial cellulose films was also measured. Contact angles were obtained by the sessile drop method (at 80 °C, which was the polymerization temperature later applied) to represent the three-phase contact angle in the emulsion. AESO-in-water contact angles (measured through water) were 134° ± 10° and 40° ± 9°, on silylated and unmodified bacterial cellulose films, respectively. The silylated bacterial cellulose is preferentially wet by the oil phase rather than the water phase. Contact angles of > 90° (measured through water) characterize hydrophobic particles, which allows them to be adsorbed at the interface, stabilising w/o emulsions; the converse is true if this angle is < 90°.[6] ζ-Potential analysis confirms successful modification as the plateau value is shifted to increasingly lower values and the isoelectric point shifts to higher pH values, indicative of a reduction in hydroxyl groups at the cellulosic surface.



(a)



(b)

Fig. 1 SEM micrographs of a bacterial cellulose film (a) and acetic acid esterified bacterial cellulose (b).

Preparation of water-in-AESO emulsions and macroporous polyAESO synthesized using silylated bacterial cellulose

Between 10–15 ml of AESO was added into Falcon™ tubes, containing 0.5–5 wt.% silylated bacterial cellulose with respect to the AESO phase. The mixtures were homogenized in an ice bath to prevent premature polymerization of the AESO at 20 000 rpm (using a Polytron PT10–35 GT batch homogenizer, Kinematica, Switzerland with a 9 mm rotor) for 1 min to disperse the cellulose nano-fibrils prior to drop-wise addition of the aqueous phase, which contained 0.3 M $CaCl_2{\cdot}2H_2O$. Homogenization was continued for a further minute after addition of the aqueous phase. Samples of the emulsions were then taken and dripped into water to determine the emulsion type. The emulsion stability index, which is the time dependent emulsion volume relative to the total volume of the water and oil phases, was assessed over a 3 day period. A summary of selected emulsion compositions, their character and stability is given in Table 2. Emulsions

Table 1 Results of electrokinetic and wettability characterization of unmodified and hydrophobized bacterial cellulose (BC) substrates

Sample	ζ-Potential (plateau value) [mV]	Iso-electric point [pH value]	Advancing contact angle [°]	Receding contact angle [°]
Unmodified BC	−7.1 ± 0.6	3.6 ± 0.1	11 ± 3	–[a]
Silylated BC	−24.0 ± 1.0	3.8 ± 0.1	105 ± 2	73 ± 2
Acetic acid esterified BC	−20.8 ± 0.7	3.8 ± 0.1	75 ± 3	35 ± 6

[a] Receding contact angle could not be obtained due to wicking.

Table 2 Composition of the emulsion templates stabilized by silylated bacterial cellulose

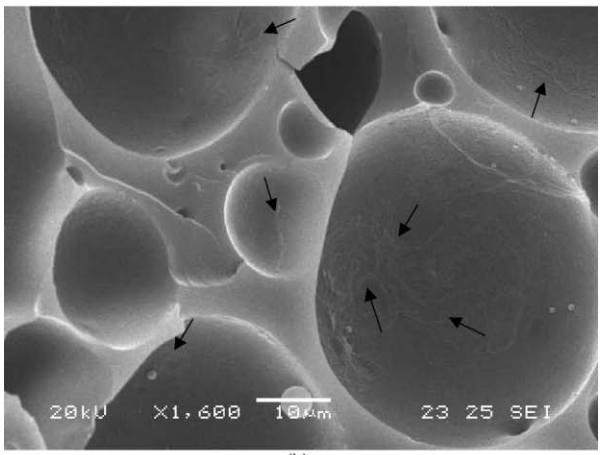
Sample ID	Organic phase[a] [vol.%]	Modified cellulose [wt.%][b]	Emulsion Character	Emulsion stability index [%][c] 0.5 h	3 days
A	50	0.5	w/o	100	98.5
B	50	1	w/o	100	95.6
C	50	2	w/o	100	95.4
D	40	0.5	w/o	100	99.7
E	40	2	w/o	97.5	96.8
F	30	1	o/w	57.6	54.5
G	30	2	o/w	68.4	63.2

[a] Volume of the organic phase (AESO) relative to the total volume of the emulsion. [b] wt.% of hydrophobized bacterial cellulose relative to the organic phase volume. [c] Volume of emulsified phase relative to the total volumes of monomer and aqueous phases.

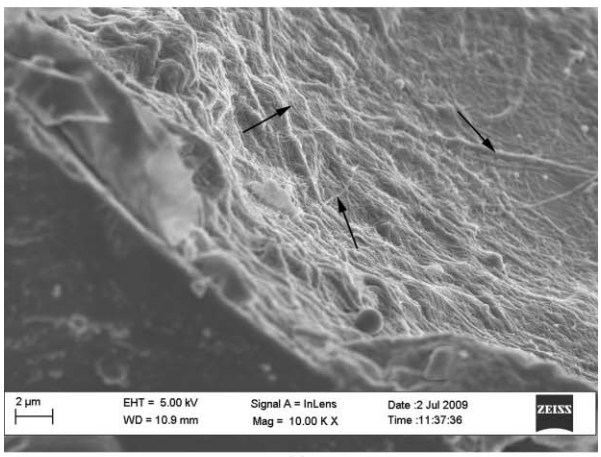
containing aqueous phase levels > 70 vol.% (Samples F and G) underwent catastrophic phase inversion from w/o to o/w emulsions, this type of inversion has been reported to occur for other Pickering emulsions at this volume fraction (0.7) as this is near the limit of sphere close packing.[29] Samples F and G, creamed into an o/w phase at the top, with a water phase at the bottom; increasing the cellulose loading increased the creamed volume and stability. Emulsions that undergo catastrophic phase inversion can be multiple emulsions (w/o/w for example), as described in the literature.[29] Whilst the density of AESO is 1.04 g cm^{-3} the creaming observed may be due to the entrapment of air, along side the formation of a multiple emulsion and due to the hydrophobic cellulose nano-fibrils favoring an air interface over a water interface, as has been observed during their centrifugation. A slight decrease in emulsion volume (< 2.5 vol.%) occurred in samples A–E during the first few hours and can be attributed to the ejection of little continuous phase; a separate oil phase was observed below the emulsion. It was not possible to prepare stable emulsions with > 4 wt.% hydrophobized bacterial cellulose loadings relative to the organic phase (with < 40 vol.% organic phase) due to flocking of cellulose fibrils and an inability to introduce enough shear during homogenization to disperse the fibrils effectively.

To polymerize the emulsion template, 3 wt.% of the initiator cumene hyperoxide (relative to the organic phase) was added to the AESO immediately prior to the preparation of the emulsion (the aqueous phase addition is described above). The Falcon™ tubes were then capped and placed in an oven at 80 °C for 24 h. The polymerized samples were then removed from the tubes and dried *in vacuo* at 80 °C for a further 24 h. The polymerization of the continuous phase of emulsions A–E (Table 2), containing 50 and 60 vol.% aqueous disperse phase, resulted in closed celled polymer foams (Fig. 2a–c). The silylated bacterial cellulose nano-fibrils can clearly be seen (arrowed) lining the pore walls in Fig. 2b,c, proving their adsorption at the former w/o interface. The smallest pores exhibiting these cellulose nano-fibril linings were > 7 μm in diameter (Fig. 2b), indicating a lower limit on the size of the stabilized emulsified drops; the majority of pores were in the range 10–300 μm diameter, with a mean of 80 μm.

(a)



(b)



(c)

Fig. 2 a. PolyPickering (MIPE) foam, formed from an emulsion stabilized by silylated bacterial cellulose (note the diameter of the sample was 23 mm). b. PolyPickering (MIPE) foam; silylated bacterial cellulose fibrils can be seen lining the pores (arrowed), in comparison to the smooth fracture surfaces of the pore walls, which did not appear to contain cellulose fibrils. c. Pore wall at high magnification showing silylated bacterial cellulose nano-fibrils (some arrowed) lining a pore wall in an AESO foam, note the smooth fracture surface of the pore wall (left corner of the image), where no fibrils are visible.

However, some larger pores several millimetres in diameter were also present. Polymerization of emulsions having aqueous phase levels > 70 vol.% resulted in the formation of a porous material consisting of fused solid spheres. Interestingly when 70 vol.% aqueous phase emulsions stabilized by 3 wt.% of hydrophobized cellulose were polymerized, fused hollow spheres were produced (Fig. 3; SEM of the sectioned sample inset). We hypothesize that a water-in-oil-in-water emulsion may have formed, leading to the development of hollow spheres after drying. The foam produced from the polymerized continuous phase of emulsion formulation B (polyMIPE B), which had an internal aqueous phase of 50 vol.% exhibited a porosity of 76 ± 1% which is likely to result from the presence of some air being beaten in during homogenization (causing some of the larger pores), and some ejection of the continuous phase. Porosity was determined using pycnometry as described in ref. 3.

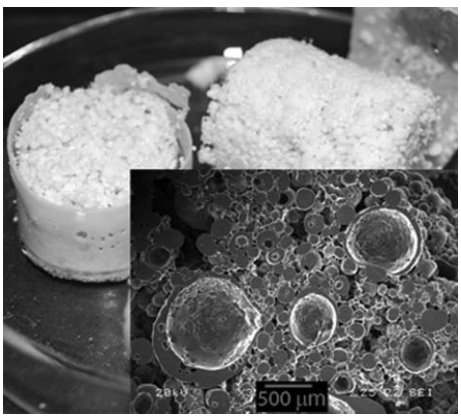
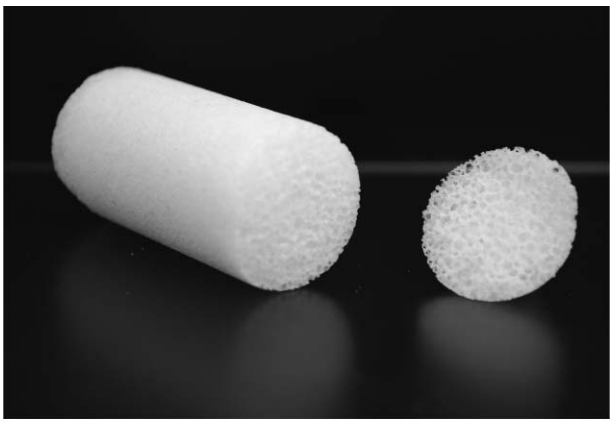


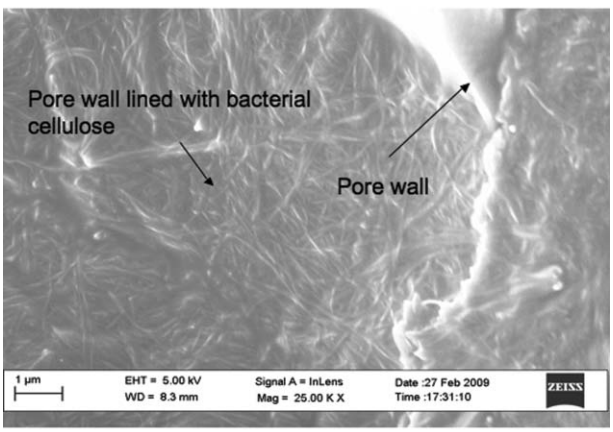
Fig. 3 Hollow spheres; note the diameter of the sample shown in the background image was 23 mm.

Production of water-in-AESO emulsions and foams using acetic acid modified bacterial cellulose

Water-in-AESO emulsions were prepared *via* an organic phase exchange method, described below. This method was used because the AESO phase was initially too viscous to prepare the emulsions. 20 ml water containing 0.5 wt.% acetic acid esterified bacterial cellulose were added into a 50 ml capacity Falcon™ tube and an equal volume of soybean oil (with a density of 0.9 g cm^{-3}) was added. The mixture was homogenized at 20 000 rpm for 1 min to disperse the cellulose nano-fibrils throughout the system. The mixture was then left overnight in the capped tube to allow the modified nano-fibrils to swell and migrate to the water-oil interface. Afterwards, the sample was shaken by hand for a period of 30 s, resulting in the formation of a water-in-oil emulsion. The emulsion was allowed to sediment to a stable volume; water droplets were observed to sediment to the bottom of the Falcon™ tube, reaching a stable level at circa 30 ml after several hours. The ejected oil phase was then removed using pipette from the top of the tube and an equal mass of soybean oil replaced by AESO, which was added at 80 °C to allow the otherwise viscous monomer to flow. The sample was then re-shaken by hand to reform the stable emulsion. This process of soybean oil removal and AESO addition was repeated (twice) until 18 ± 2 ml of the original soybean oil was replaced by AESO. Finally, 4 wt.% of a UV-photoinitiator (Darocure 1173, Ciba, Basel, Switzerland) was added with respect to the monomer phase.[18] The sample was then re-shaken to improve homogeneity of the emulsion. The sample was then capped and left in an oven at 80 °C to allow the water droplets to sediment until reaching a stable emulsion volume (30 ± 0.5 ml) and any further excess ejected phase was removed. The sample was then exposed to UV radiation using a 100 W mercury lamp (SB-100P flood lamp, Spectronics, NY, USA) with a wavelength > 280 nm to photopolymerize the AESO phase; the Falcon™ tube containing the sample was rotated on a stage in front of the lamp at 20 rpm to enable more homogeneous polymerization. The polymerized sample was then removed from the tubes and dried *in vacuo* at 80° C for 24 h. The resultant foam is shown (sectioned) in Fig. 4a; the heterogeneously esterified bacterial cellulose nano-fibrils can be seen lining the pore walls in the SEM (Fig. 4b), akin to the silylated nano-fibril example (Fig. 2c). The porosity of the sample shown in Fig. 4a was 69 ± 1%, consistent with the internal aqueous phase volume present prior to polymerization.



(a)



(b)

Fig. 4 a. Esterified bacterial cellulose/photopolymerized acrylated epoxidized soybean oil nano-composite foam (23 mm in diameter). b. Esterified cellulose nano-fibrils are shown to line a pore.

In conclusion, novel renewable nanocomposite foams made from AESO and hydrophobized bacterial cellulose nano-fibrils have been produced using Pickering emulsion templating.

Bacterial cellulose nano-fibrils hydrophobized either *via* silylation or acetic acid esterification (truly renewable) were able to stabilize water-in-modified natural oil emulsions. The organic acid esterification route is greener than the silylation route and is the focus of further investigation. This technique will expand the applications and processing options available for renewable foams to produce large composite structures and sandwich cores for composite applications, which can be formed *in situ*.

Materials

Bacterial cellulose was extracted from *nata-de-coco*, a commercially available product, CHAOKOH® coconut gel in syrup (Thep. Padung Porn Coconut Co. Ltd, Bangkok, Thailand). Soybean oil, acrylated epoxidized soybean oil (AESO), chloro(dimethyl)isopropylsilane (CDMIPS) (97%), imidazole (99%), toluene (99.8%), cumene hyperoxide solution (~80% in cumene), toluene (99.8%), methanol (99.8%), acetone (99.8%), tetrahydrofuran (99.9%) and *p*-toluenesulfonyl chloride (99%) were purchased from Sigma-Aldrich (Poole, UK). Pyridine (99.7%) and acetic acid (glacial, 100%) were obtained from VWR, UK. All reagents were used without further purification.

Preparation of hydrophobic cellulose nano-fibrils *via* silylation

Bacterial cellulose was extracted from *nata-de-coco*, by first rinsing the food product three times with dH_2O, the product was then sieved, homogenized and blended using a variable speed laboratory blender operated at maximum speed (Waring Laboratory, Essex, UK). The bacterial cellulose was then purified by boiling a mixture having a concentration of 0.6 w/v% in 0.1M NaOH at 80 °C for 2 h to remove any remaining microorganisms and soluble polysaccharides.[30] Bacterial cellulose was successively centrifuged, homogenized and rinsed to neutral pH. The cellulose was hydrophobized by adapting a protocol described in ref. 24, which was slightly modified to suit our application. Briefly, bacterial cellulose fibrils in aqueous suspension (0.3%, w/v) were solvent exchanged into acetone, through methanol to dry toluene. CDMIPS was added at a molar ratio of 4:1 with respect to the repeating glucose units of the bacterial cellulose. Imidazole was added equimolar to CDMIPS to drive the reaction and trap the HCl released. During the silylation procedure, the CDMIPS reacts with the hydroxyl groups of the cellulose resulting in hydrophobization of its surface. The reaction mixture was agitated using an orbital shaker (600 rpm) for 16 h prior to centrifugation (15 000 g) and decantation. Afterwards, a mix of methanol and THF (20:80, v/v) was added to dissolve the imidizolium chloride by-product and any disilylethers that may have formed, followed by centrifugation and decantation to obtain a modified cellulose plug. Dispersions of hydrophobized bacterial cellulose in AESO were obtained after rinsing twice with THF and successive centrifugation and re-dispersion operations to exchange the THF with toluene, and exchange of toluene with AESO.

Preparation of hydrophobic cellulose nano-fibrils *via* acetic acid esterification

Bacterial cellulose was extracted as previously described and solvent exchanged from water through methanol into pyridine at a concentration of 0.3% w/v. After each solvent exchange the mixture was homogenised at 20 000 rpm for 1 min to disperse the nano-filbrils, then centrifuged at 15 000 g prior to re-dispersion in the required solvent. Three solvent exchanges were performed for each solvent during the exchange. The cellulose was adjusted to a concentration of 0.5% w/v with respect to pyridine in a 3-neck round bottom flask and *p*-toluenesulfonyl chloride added at a ratio of 1:4 by weight with respect to the pyridine. Acetic acid was added equimolar with respect to the *p*-toluenesulfonyl chloride. Batches of 2 g equivalent dry weight of bacterial cellulose were modified using this route. The mixture was magnetically stirred and the reaction allowed to progress at 50 °C for 2 h under nitrogen. The reaction was subsequently quenched using 1.5 l of ethanol and the mixture then solvent exchanged from pyridine/ethanol through ethanol to water as previously described using successive centrifugation and homogenization steps. This was performed until the colour of the supernatant did not change.

Characterisation of the hydrophobised bacterial cellulose

Films of unmodified bacterial cellulose were formed by taking some centrifuged sample (circa 1 g equivalent dry weight), rolling and pressing this in between release film to remove the water. The films were near fully dried in a hot press (George E. Moore and Sons, Birmingham, UK) and then pressed at 100 °C and 50 kN for 5 min, then further dried in a vacuum oven over night. Films of the modified bacterial cellulose were made by dispersing the nano-fibrils in chloroform and then filtering this through PTFE membranes; the resultant films that formed on top of the membrane were then pressed. The degree of hydrophobization was assessed by advancing and receding sessile drop contact angle measurement. The wettability of cellulose films was determined by contact angle analysis using a Drop Shape Analyser (DSA 10 MK2, Krüss, Germany). Advancing and receding contact angles were measured by increasing the volume of water droplets placed on the cellulose films in the range 2 µl–20 µl at a rate of 6.32 µl min^{-1} and then decreasing the drop volume at the same rate, using a motorized syringe. At least six independent determinations at different sites for each sample were made. Zeta (ζ)-potential measurements (EKA, Anton Paar KG, Graz, Austria) in the streaming mode on films of the unmodified and modified bacterial cellulose, following the method previously described in ref. 31. The modification was characterised using ATR-FTIR (Spectrum 100, Perkin Elmer, Bucks UK) and morphology assessed by SEM. Scanning electron microscopy (LEO Gemini 1525 FEG-SEM, Carl Zeiss NTS GmBH) was conducted on chromium sputter coated samples (sputtered for 1 min at 75 mA), these conditions gave < 15 nm coating thickness.

Acknowledgements

The authors acknowledge Dr. Ryo Murakami (formerly of the PaCE group) for helpful discussions. This work was supported by the Challenging Engineering Programme (EP/E007538/1) of the UK Engineering Physical Science Research Council (EPSRC).

References

1 A. Menner, R. Verdejo, M. Shaffer and A. Bismarck, *Langmuir*, 2007, **23**, 2389–2403.
2 J. M. Williams and D. A. Wrobleski, *Langmuir*, 1988, **4**, 656–662.
3 A. Menner, R. Powell and A. Bismarck, *Macromolecules*, **39**, 2034–2035.
4 W. Ramsden, *Proc. Roy. Soc. London*, 1903, **72**, 156–162.
5 S. Pickering, *J. Chem. Soc.*, 1907, **91**, 2001–2020.
6 B. P. Binks and S. O. Lumsdon, *Langmuir*, 2000, **16**, 8622–8631.
7 (*a*) M. Iguchi, S. Yamanaka and A. Budhiono, *J. Mater. Sci.*, 2000, **35**, 261–270; (*b*) M. A. Hubbe, O. J. Rojas, L. A. Lucia and M. Sain, *BioResources*, 2008, **3**, 929–980.
8 Y. C. Hsieh, H. Yano, M. Nogi and S. J. Eichhorn, *Cellulose*, 2008, **15**, 507–513.
9 F. S. Güner, Y. Yağci and A. T. Erciyes, *Prog. Poly. Sci.*, 2006, **31**, 633–670.
10 J. Lu and R. P. Wool, *J. Appl. Polym. Sci.*, 2006, **99**, 2481–2488.
11 J. La Scala and R. P. Wool, *Polymer*, 2005, **46**, 61–69.
12 J. Lu and R. P. Wool, *Comp. Sci. Tech.*, 2008, **68**, 1025–1033.
13 R. Wool, S. Küsefoğlu, G. Palmese, S. Knot and R. Zhao, *US Pat.*, 6 121 398, 2000.
14 A. Campanella, M. Fahimian, R. P. Wool and J. Raghavan, *J. Biobased Materials and Bioenergy*, 2009, **3**, 91–99.
15 E. Can, R. P. Wool and S. Küsefoğlu, *J. Appl. Polym. Sci.*, 2006, **102**, 1497–1504.
16 S. Sundararaman, A. Shabeer, K. Chandrashekhara and T. Schuman, *J. Biobased Materials and Bioenergy*, 2008, **2**, 71–77.
17 S. P. Wu, M. Z. Rong, M. Q. Zhang, J. Hu and T. Czigany, *J. Biobased Materials and Bioenergy*, 2007, **1**, 469–471.
18 H. Pelletier, N. Belgacem and A. Gandini, *J. Appl. Polym. Sci.*, 2006, **99**, 3218–3221.
19 (*a*) V. O. Ikem, A. Menner and A. Bismarck, *Angewandte Chemie*, 2008, **120**, 8401–8403; (*b*) A. Menner, V. Ikem, M. Salgueiro, M. S. P. Shaffer and A. Bismarck, *Chem. Commun.*, 2007, 4274–4276.
20 K. J. Lissant, *J. Soc. Cosmet. Chem.*, 1970, **21**, 141–154.
21 H. Ougiya, K. Watanabe, Y. Moringaga and F. Yoshinaga, *Biosci. Biotech. Bichem.*, 1997, **61**, 1541–1545.
22 M. Andresen and P. Stenius, *J. Disp. Sci. Tech.*, 2007, **28**, 837–844.
23 H. A. Wege, S. Kim, V. N. Paunov, Q. X. Zhong and O. D. Velev, *Langmuir*, 2008, **24**, 9245–9253.
24 (*a*) L. Ladouce, E. Fleury, C. Gousee, R. Cantiani, H. Chanzy and G. Excoffier, *US Pat.*, 6 703 497 B1, 2004; (*b*) C. Goussé, H. Chanzy, G. Excoffier, L. Soubeyrand and E. Fleury, *Polymer*, 2002, **43**, 2645–2651; (*c*) M. Andresen, L.-S. Johansson, B. S. Tanem and P. Stenius, *Cellulose*, 2006, **13**, 665–677.
25 C. S. R. Freire, A.J. D. Silvestre, C. Pascoal Neto, N. Belgacem and A. Gandini, *J. Appl. Polym. Sci.*, 2006, **100**, 1093–1102.
26 P. Jandura, B. Riedl and B. V. Kokta, *Poly. Degrad. Stab.*, 2000, **70**, 387–394.
27 T. Heinze, in *Esterification of Polysaccharides*, Springer, New York, 2006, pp. 75–77.
28 C. Dorrer and J. Rühe, *Soft Matter*, 2009, **5**, 51–61.
29 B. P. Binks and S. O. Lumsdon, *Langmuir*, 2000, **16**, 2539–2547.
30 H. Toyosaki, T. Naritomi, A. Seto, M. Matsuoka, T. Tsuchida and F. Yoshinaga, *Biosci. Biotech. Biochem.*, 1995, **59**, 1498–1502.
31 L. Safinia, K. Wilson, A. Mantalaris and A. Bismarck, *Macromol. Biosci.*, 2007, **7**, 315–327.

