

GREEN HIERARCHICAL COMPOSITES: THE BOTTOM-UP APPROACH

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SUMMARY

In this work, we present two new novel routes to manufacture composites with improved properties; grafting nano-cellulose onto the surface of natural fibres and surface functionalisation of bacterial cellulose. Both nano-cellulose grafted natural fibre composites and surface functionalised bacterial cellulose nanocomposites showed significant improvement in their mechanical properties.

Keywords: Bacterial cellulose, nanocomposites, esterification, polylactide, hierarchical composites

INTRODUCTION

Natural fibres have gained a lot of interests as reinforcement for the production of composite materials due to their attractive features of abundance, low cost, lightweight, renewability, and biodegradability. These qualities make them superior to glass fibre. Natural fibres are claimed to be capable of being part of everything from cars to golf clubs [1]. Now virtually all major car manufacturers in Germany use natural plant fibre-reinforced composites in applications such as rear storage shelves, door panels, pillar cover panels and boot lining [2]. Beside all the advantages, plant fibres however have drawbacks such as their incompatibility with non-polar polymers, their inconsistency in quality and inferiority to synthetic fibres, and their low resistance to water, bacteria and fungi.

Another green nano-filler in composites, which is now receiving much attention, is bacterial cellulose. Currently bacterial cellulose is used in food, specialty paper, speaker membrane and biomedical applications, such as wound dressings and artificial skin [3]. Bacterial cellulose has remarkable properties. It is a ribbon-shaped fibril, less than 100 nm wide, which is composed of a bundle of much finer microfibrils of 2 to 4 nm in diameter [4]. Its single fibre elastic modulus was recently measured to be 114 GPa [5]. It is

chemically the same as plant cellulose [6]. In addition, it has high degree of crystallinity (of up to 84-89%) and a high degree of polymerisation and high purity [7, 8].

Here we propose two routes to design truly green composites. The first route introduces the concept of hierarchical composites. A hierarchical structure within a composite is created by introducing nano-size bacterial cellulose onto the surface of natural plant fibre, which can be achieved by cultivating cellulose-producing strain of bacteria, *Gluconacetobacter xylinus*, in presence of natural fibres. The nanocellulose decorated natural fibre is then incorporated into a renewable polymer matrix to obtain hierarchical truly green composites. The whole process is environmentally friendly and the composites are entirely made from renewable and are biodegradable. In the second route, nanocomposites were produced using bacterial cellulose as the nano-reinforcement. The surface of bacterial cellulose nanofibrils was rendered hydrophobic via lauric acid esterification reaction. By modifying only the surface of bacterial cellulose nanofibrils, the highly crystalline structure (high Young's modulus) of bacterial cellulose nanofibrils can be retained whilst the surface is modified to become hydrophobic. The surface hydrophobisation of bacterial cellulose will enhance the interface between bacterial cellulose and hydrophobic polymer matrices. This will improve the stress transfer from the matrix to the nano-reinforcement, thereby improving the overall properties of the nanocomposites. The mechanical properties of the fabricated hierarchical composites and nanocomposites were assessed in this work.

MATERIALS AND METHODS

Hemp and sisal fibres were kindly supplied by Wingham Wool Work (Rotherham, UK) and Wigglesworth & Co. Limited (London, UK). Cellulose acetate butyrate (CAB-500-5, 51% butyryl content, 4% acetyl content, 1% hydroxyl content, $M_w = 57000$ g/mol, 1.14-1.28 g/cm³) was supplied by Eastman Chemical Co. (Kingsport, Tennessee, USA). Poly-L-lactic acid (PLLA L9000, $M_w > 150000$ g/mol, 1.25 g/cm³) was supplied by Biomer (Krailling, Germany). The fibres and polymers were vacuum dried at 60°C for 24 h prior to use. 1,4-Dioxane (Sigma-Aldrich ACS Reagent, $\geq 99\%$ purity) was used as the solvent for PLLA. Pyridine (analaR NORMAPUR, purity $\geq 99.7\%$) and ethanol (GPR, purity $\geq 99.7\%$) were purchased from VWR. Lauric acid (Aldrich, $\geq 98\%$ purity), dimethyl carbonate (Aldrich Reagent Plus, purity $\geq 99\%$) and *p*-toluenesulfonyl chloride (Aldrich, $\geq 99\%$ purity) were purchased from Sigma-Aldrich. All the materials were used as received without further purification.

To deposit bacterial cellulose onto the surface of natural fibres, the bacteria *Gluconacetobacter xylinus* strain BPR 2001 (ATCC® 700178) was used. The bacterium was extracted from a pool of *Acetobacter xylinum* by Toyosaki et al. [9] and it was chosen due to its reported high cellulose productivity. The bacteria strain was obtained from LGC Promochem (Middlesex, UK). The culture media comprised (per litre of deionised water); 50 g D - Fructose (Sigma-Aldrich), 5 g yeast extract (Sigma-Aldrich), 5 g peptone (Sigma-Aldrich), 2.7 g Na₂HPO₄ (Sigma-Aldrich), and 1.15 g citric acid (Fluka). In addition to this,

bacterial cellulose was also extracted from the commercially available *Nata-de-coco* (CHAOKOH coconut gel in syrup, Ampol Food Processing Ltd, Nakorn Pathom, Thailand). This batch of bacterial cellulose was used in the esterification reaction and used as the nano-reinforcement in the fabrication of nanocomposites.

Extraction and purification of bacterial cellulose from *Nata-de-Coco*

Bacterial cellulose was extracted from 5 jars of *Nata-de-Coco*. Firstly, the coconut gels were rinsed three times with de-ionised water and blended for 1 min using a laboratory blender (Waring Blender LB20EG, Christison Particle Technologies, Gateshead UK). The resulting blend of bacterial cellulose was then homogenised for 2 min using a homogeniser (Polytron PT 10-35 GT, Kinematica.CH, Switzerland) and centrifuged to remove the excess water. To further purify the bacterial cellulose, the centrifuged bacterial cellulose product was re-dispersed in 5 L of de-ionised water and boiled in 0.1 M sodium hydroxide solution at 80 °C for 20 min to remove any remaining microorganisms and soluble polysaccharides [9]. This purified bacterial cellulose was then successively centrifuged and homogenised to neutral pH.

Modification of Hemp and Sisal Fibres: Attaching Bacterial Cellulose in culture medium

The natural fibres were modified by attaching bacterial cellulose to the fibre surface by culturing the bacteria in presence of the natural fibres. The culture procedure was explained elsewhere [10]. Briefly, the fibres were added to the culture media in flasks. The bacterial broth was then aseptically inoculated into the flasks. After 1 week of incubation at 30°C, the modified fibres were purified in 0.1 M NaOH at 80°C for 20 min. Finally, the fibres were washed in deionised water until neutral pH.

Modification of bacterial cellulose (*Nata-de-Coco*) via lauric acid esterification reaction

2 g (dry weight) of the extracted and purified bacterial cellulose (*Nata-de-Coco*) was solvent exchanged from water through methanol into pyridine at a concentration of 0.3% (g mL⁻¹). The mixture was homogenised at 20,000 rpm for at least 1 min at each stage to completely disperse the bacterial cellulose in the solvent. Bacterial cellulose was retained through centrifugation at 14,000G for 15 min before re-dispersing it again in the subsequent solvent. In the final solvent exchange step, the concentration of bacterial cellulose in pyridine was adjusted to 0.5% (g mL⁻¹). The bacterial cellulose-pyridine mixture was then poured into a 1 L 3-neck round bottom flask and stirred using a magnetic stirrer. 92 g of *p*-toluenesulfonyl chloride was added into this mixture and an equimolar amount of lauric acid was added after the addition of *p*-toluenesulfonyl chloride. The reaction was conducted at 50°C for 2 h under nitrogen atmosphere and it was subsequently quenched with 1.5 L of ethanol. The product was solvent exchanged from ethanol to water using the previously

described centrifugation-homogenisation steps. In order to use the bacterial cellulose in later stages, the neat and modified bacterial cellulose were dispersed in water and dimethyl carbonate respectively at a concentration of 0.4% (g mL⁻¹) and subsequently freeze dried (Edwards modulyo freeze dryer, West Sussex UK).

Fabrication of bacterial cellulose grafted natural fibres reinforced hierarchical composites

Unidirectional long natural fibre reinforced composites were prepared with fibres aligned at 0° and 90° to the test direction. The fibres were impregnated by polymer powder using a dusting sieve. The impregnated fibres were then clamped at both ends of a metal mould prior to compression moulding, to ensure a high degree of alignment in the final composite tape. The fibre content of the composites was adjusted to 34% by weight. The clamped impregnated fibres were then compression-moulded in a hot press (George E Moore & Sons, Birmingham, UK) at 195°C (for CAB) and 220°C (for PLLA) and 1.8 MPa for 5 min, and left to cool down under load at a rate of approximately 4°C/min. The 0° composite tapes had dimensions 150 x 12.5 x 1 mm whilst the 90° composite tapes were 100 x 120 x 1 mm.

Fabrication of bacterial cellulose reinforced nanocomposites

In order to ease the processing of BACTERIAL CELLULOSE and PLLA in an extruder, a method based on thermally induced phase separation (TIPS) to produce porous composite microspheres in the absence of water was adopted from literature [11]. Such microspheres can be fed directly into the extruder. 395 mg of freeze-dried cellulose was added into 90 mL of 1,4-dioxane and homogenised at 20,000 rpm to disperse the cellulose in the solvent. 7.5 g of PLLA was then added into this mixture (1:12 g mL⁻¹) and the polymer was left to dissolve overnight at 60°C under magnetic stirring. The resulting mixture was then poured into a 50 mL syringe and added drop wise into a bath of liquid nitrogen to rapidly induce phase separation. The frozen microspheres were then transferred into a 500 mL one-neck round bottom flask and subsequently freeze-dried to remove the solvent and produce porous composite microspheres. 5.6 g of microspheres were fed into a 5 cm³ twin screw micro-extruder (DSM Research BV, The Netherlands) kept at a melt temperature of 180 °C and rotating at 10 rpm. After all the microspheres had been fed into the micro-extruder, the screw rotation speed was increased to 40 rpm for 30 min to promote mixing of cellulose in the polymer melt. The polymer melt was then extruded at a screw rotational speed of 20 rpm. These extruded products were pelletized and compression moulded into films in a hot press (George E Moore and Sons, Birmingham UK) at 180 °C and 2 t for 2 min. The resulting film was then left to cool down to room temperature naturally.

Tensile testing of composite films

In order to perform mechanical tests, the composite films were cut into dog-bone shaped specimens using a Zwick cutter (Zwick GmbH and Co. KG, Ulm, Germany). These dog-bone shaped specimens had an overall length of 75 mm, a gauge length of 30 mm and the narrowest part of the specimen was 4 mm. All the tensile tests were conducted in accordance to BS EN ISO 527: 1996 using an Instron universal material testing machine (Instron 4502, Instron Corporation, Massachusetts, USA). The testing speed and load cell used were 1 mm min^{-1} and 1 kN, respectively. At least five specimens were tested for each sample.

Scanning electron microscopy (SEM)

SEM was conducted using a high resolution field emission gun scanning electron microscope (LEO Gemini 1525 FEG-SEM, Carl Zeiss NTS GmbH) and used to characterise the bacterial cellulose grafted natural fibres. The accelerating voltage used was 5 kV. All the samples were fixed onto the SEM stubs using carbon tabs. Prior to the SEM, the fibres were coated with chromium for 1 minute at 75 mA.

RESULTS AND DISCUSSIONS

Morphology of bacterial cellulose modified natural fibres

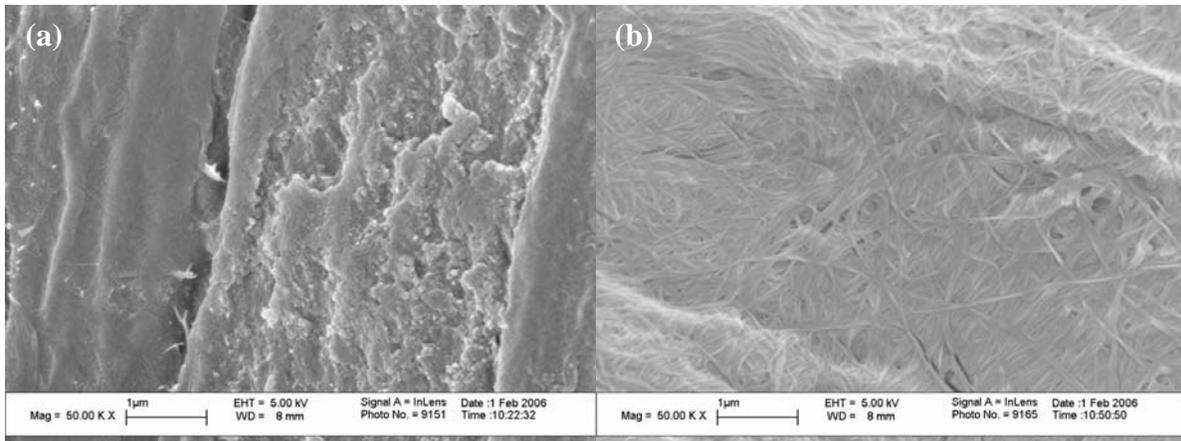


Figure 1: Scanning electron micrographs showing the surface of natural fibres. (a) Without bacterial cellulose (b) Grafted with bacterial cellulose

SEM micrographs of the surfaces of hemp fibres before and after the bacterial surface modification (figure 1) clearly show that bacterial cellulose nanofibrils of 50 to 100 nm in diameter almost completely cover the rather smooth natural fibre surface in a random orientation. The high extent of bacterial cellulose coverage of the fibre points to the strong interaction between bacterial cellulose and the fibre surface; this could be because of the

high self-affinity of cellulosic materials [6]. The large number of hydroxyl groups at the surfaces of the substrate and of the bacterial cellulose will help promoting hydrogen bonding between them. It is also possible that the bacterial cellulose fibril could root through the porous natural fibre.

With the modified natural fibres, the adhesion between the fibres and CAB/PLLA matrices, as measured in the form of the interfacial shear strength (IFSS), can be increased by up to 240% without much effect on the tensile properties of the natural fibres [12, 13]. The improved adhesion between the fibre and the matrix should enhance the stress transfer efficiency between them, which should result in an improvement in composite performance.

Mechanical properties of hierarchical composites

It can be observed that in the case of hemp reinforced composites, the modification procedure slightly degraded the tensile properties of composites with both CAB and PLLA matrices in both test directions (table 1 and 2). The exposure of hemp fibres to the aqueous medium used for the culturing of the bacteria and the NaOH treatment had some degrading effects on individual hemp fibres [12]. It was observed that after the modifications, hemp fibres became curly and had lighter colour. However, despite the likely loss of mechanical properties, the strength of the hemp fibre composites was only marginally affected. Thus the bacterial cellulose coating must have a positive impact on the composite properties.

In the case of sisal, no obvious changes of the modified technical sisal fibres were observed after the modification procedure [12]. In this case, the positive contribution of the nano-cellulose could produce a higher gain in composite performance. The parallel tensile strength of the modified sisal fibre reinforced composites increased significantly in both CAB and PLLA matrices. In all cases, the measured off-axis tensile strengths were much lower than those of pure polymers, suggesting that the composites still had weak interfaces. However, all measured tensile moduli of composites were on the contrary, indicating that there are some interactions between fibres.

It can be observed that in the case of hemp, the nano-cellulose fibrils attached to the hemp fibres sometimes “glued” the primary fibres together, which led to the formation of fibre bundles. The dense bacterial cellulose network then prevented the polymer from penetrating easily into this fibre bundle. These fibre bundles caused stress concentration and acted as weak points in the composite. Sisal seemed less susceptible to these problems than hemp. Sisal is also easier to process, due to its greater stiffness which reduces the tendency to produce fibre entanglements. The observed increase in the mechanical properties was more pronounced when using a PLLA matrix rather than CAB. PLLA contains more polar functional groups that have the potential to form hydrogen bonds with the hydroxyl groups of the bacterial cellulose attached to the surfaces of the natural fibres;

therefore, a much stronger interfacial adhesion can be expected. In any case, PLLA also has superior tensile properties to CAB, making it a more attractive candidate for reinforcement.

Table 1: Parallel (0°) tensile strength σ and Young's modulus E of original and bacterial cellulose modified hemp and sisal reinforced CAB and PLLA [10].

	σ / MPa	E / GPa	σ / MPa	E / GPa
Fibre	CAB/Hemp		CAB/Sisal	
Unmodified	98.1±12.7	8.5±1.3	92.9±9.3	5.6±0.5
Modified	86.7±13.6	5.8±0.5	100.4±7.0	8.81±1.4
	PLLA/Hemp		PLLA/Sisal	
Unmodified	110.5±27.2	11.8±4.2	78.9±14.7	7.9±1.3
Modified	104.8±9.1	7.9±1.2	113.8±14.0	11.2±1.2

Table 2: Off-axis (90°) tensile strength σ and Young's modulus E of original and bacterial cellulose modified hemp and sisal reinforced CAB and PLLA [10].

	σ / MPa	E / GPa	σ / MPa	E / GPa
Fibre	CAB/Hemp		CAB/Sisal	
Unmodified	15.8±2.2	1.9±0.1	10.9±1.7	1.6±0.1
Modified	13.4±1.4	0.6±0.1	14.4±3.7	1.8±0.3
	PLLA/Hemp		PLLA/Sisal	
Unmodified	13.4 ± 3.6	3.2±0.2	10.0 ± 3.1	2.1±0.1
Modified	13.3 ± 2.5	2.3±0.3	16.8 ± 4.1	3.1±0.2

Mechanical properties of cellulose nanocomposites

The mechanical properties of neat PLLA and cellulose reinforced PLLA nanocomposites are shown in table 3. It can be seen that both the tensile modulus and tensile strength of the nanocomposites increased when compared to neat PLLA. The tensile modulus of the bacterial cellulose reinforced nanocomposites increased by 40% but the tensile strength remained constant. On the other hand, the tensile modulus and tensile strength of lauric acid modified bacterial cellulose (C₁₂BC) reinforced nanocomposites improved by 50% and 15% respectively.

The improvement seen in the tensile modulus of the nanocomposites can be explained by the rule of mixture of nanocomposites materials. Cox's model [14] can be used to calculate the Young's modulus of the nanocomposites. It can be deduced from this equation that as

the reinforcing phase's volume fraction increases, the tensile modulus of the nanocomposites will no doubt increase. At first glance, the tensile strength of PLLA/BC seemed to improve compared to pure PLLA. However, when the errors from the tensile strength measurements are taken into account, the tensile strength between neat PLLA and PLLA/BC are the same. Even though the tensile strengths are the same, the increment in the tensile modulus of PLLA/BC nanocomposites is enough to justify the improvement in its mechanical properties. It can also be seen from table 3 that the PLLA/C₁₂BC nanocomposites showed significant improvement in both tensile strength and modulus. This improvement can be attributed to the improved interaction between modified bacterial cellulose and PLLA. In addition to this, the surface modification of the bacterial cellulose retains its highly crystalline structure and this contributed to the increment in mechanical properties of the nanocomposites as well.

Table 3: Tensile properties of cellulose/modified cellulose reinforced PLLA nanocomposites

Polymer/Cellulose (wt %)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
Neat PLLA	1.35 ± 0.10	60.3 ± 1.9	3.6 ± 0.2
PLLA/BC (5 wt%)	1.87 ± 0.04	61.3 ± 0.6	2.5 ± 0.1
PLLA/C ₁₂ BC (5 wt%)	1.98 ± 0.04	68.5 ± 1.5	2.7 ± 0.1

CONCLUSIONS

Two novel methods have been developed to improve the mechanical properties of composite materials; grafting of bacterial cellulose onto natural fibres, thereby creating hierarchical composites and surface functionalisation of bacterial cellulose nanofibrils to create nanocomposites. It was found that the bacterial cellulose adhere strongly to the surface of natural fibres. The resulting hierarchical composites showed significant improvements in terms of its mechanical properties. The tensile strengths and tensile moduli improved by 44% and 42%, respectively in the parallel direction, 68% and 48% respectively in the off-axis direction. This improvement can be attributed to the roughened fibre surface and the presence of cellulose hydroxyl groups attached to the fibre surface. The surface functionalisation of bacterial cellulose with lauric acid via esterification reaction rendered the surface hydrophobic. This improved the compatibility between bacterial cellulose and hydrophobic PLLA. As a result of improved compatibility, the tensile strength and tensile modulus increased by 50% and 15%, respectively even at a loading fraction of 5 wt%. This can be attributed to the improved stress transfer as a result of the enhanced interface due to the surface hydrophobisation of bacterial cellulose. Therefore, it can be concluded that truly green composite materials can be achieved through the fabrication of hierarchical composites or surface hydrophobisation of bacterial cellulose nanofibrils.

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