BACTERIAL CELLULOSE "GRAFTING" – A BOOST TO PLANT FIBRE-POLYMER MATRIX ADHESION IN GREEN COMPOSITES

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Abstract

Natural fibres have poor compatibility with polymers, which poses a problem when using them as reinforcement in green composites. We have successfully overcome this problem by attaching nano-size bacterial cellulose to the fibre surface using a strain of cellulose-producing bacteria, Gluconacetobacter xylinus. Natural fibre surfaces can be well covered by network of bacterial cellulose with our technique, which has changed the nature of the fibre surface and leads to an improvement in the interfacial shear strength (IFSS) between the fibres and the polymer.

The potential of this novel technique in green composite fabrication was further investigated by incorporating the modified fibres into cellulose acetate butyrate (CAB) and poly-L-lactic acid (PLLA) matrices. Composites were manufactured and tested for tensile properties. The tensile strengths of the composites were found to increase significantly. Scanning electron microscopy (SEM) also confirmed the improved interaction between the fibre and the polymer matrix.

1 Introduction

The composites industry is now confronted with a major challenge in the coming years: How to deal with production and end-of-life waste? So far, end-of-life composite waste has generally been regarded as non-recyclable due to its multi-component nature. The European Union (EU) end-of-life vehicles directive, applying to all passenger cars and light commercial motor vehicles, will enforce a reuse and recovery target of 95% of the vehicle weight by January 1st, 2015 [1]. Now virtually all major car manufacturers in Germany (i.e., DaimlerChrysler, Volkswagen Audi Group, BMW, Ford and Opel) have turned to more environmental-friendly materials, such as natural fibre-reinforced composites, in applications such as seat backs, door panels, pillar cover panels and boot linings [2]. Automobile applications represent one of the best opportunities for natural fibre filled thermoplastics due to some distinctive advantages over glass fibre composites [3]. Another EU directive that enforces reuse or recycle targets upon the composite manufacturers is the EU directive on waste electrical and electronic equipment (WEEE) [4].

Natural fibres have many attractive features for the composite industry. On a per weight basis, they have comparable strengths, and in some cases even higher stiffness, than E-glass fibres [5-7]. They are also abundant, renewable, non abrasive to processing equipment, can be incinerated, and are CO_2 neutral when burned [8]; their hollow tubular or cellular nature reduces their bulk density, making them lightweight [7], as well as improving acoustic and thermal insulation performances. However, natural fibres also have some major drawbacks, including poor compatibility with non-polar polymers, poor moisture resistance, and inconsistent or variable properties [9].

In this work, bacterial cellulose is used to enhance the adhesion between natural fibres and bio-based polymers. Nano-sized bacterial cellulose is attached onto the fibre surface by culturing

cellulose-producing bacteria (Gluconacetobacter *xylinus*) in presence of natural fibres. This modification was found to promote the adhesion between the fibres and the polymer matrix in composites since the fibre surface will be roughened and full of hydroxyl groups which have potential to form chemical bonding to functional groups in polymers [10]. The improved adhesion will enhance the stress transfer efficiency between the two phases, in turn resulting in an improvement in actual composite performance. To explore whether this expectation is fulfilled, we incorporate bacterial cellulose modified hemp and sisal fibres into the renewable polymers cellulose acetate butyrate (CAB) and poly-L-lactic acid (PLLA), in order to create truly green, i.e. fully renewable and biodegradable, composites. The mechanical properties of the resulting composites were assessed in terms of the tensile properties. The fracture surfaces of the composites were investigated by scanning electron microscopy (SEM) to characterise the interface between the fibre and the matrix.

2 Experimental

2.1 Materials

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/cm^3) was supplied by Eastman Chemical Co. (Kingsport, Tennessee, USA). The fibres and polymers were vacuum dried at 60°C for 24 h prior to use.

The bacteria Gluconacetobacter *xylinus* strain BPR 2001 (ATCC® 700178), which was extracted from a pool of Acetobacter *xylinum* by Toyosaki et al. [11] 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 Na_2HPO_4 (Sigma-Aldrich), and 1.15 g citric acid (Fluka).

2.2 Modification of Hemp and Sisal Fibres: Attaching Bacterial Cellulose

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]. In shorts, the fibres were added to the culture media in flasks. The bacterial broth was then aseptically inoculated into the flask. 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. These modified fibres will be referred to as ‘grafted hemp’ and ‘grafted sisal’.

2.3 Fabrication of Composites

Randomly oriented natural fibre composites were prepared by polymer solution impregnation followed by solvent evaporation method. Unmodified and grafted hemp fibres were used in comparison to unmodified and grafted sisal. CAB was used as a matrix polymer. The fibres were chopped into 0.5-1 cm length and added to the 4 wt.-% CAB acetone solution. The content of the chopped fibres were adjusted to achieve a fibre weight content (FWC) of 20%-50%. The solvent was initially removed by vacuum drying in an oven at 80 °C for at least 48 h. The dried mixture was then compression-moulded in a hot press (George E Moore & Sons, Birmingham, UK) at 195 °C and 1.8 MPa for 5 min and left to cool down under applied pressure. The average thickness of the composite film is 1 mm.

2.4 Tensile Testing of Composites

The composite sheet was cut using a Zwick cutter (Zwick GmbH & Co. KG, Ulm, Germany) into dog-bone specimens for tensile testing. The samples had an overall length of 80 mm, a width at the grip end was 15 mm, the gauge length was 10 mm, and the width at the narrowest part was 10 mm. The tests were conducted according to the industrial standard ASTM D3039, at a testing speed of 2 mm/min. All specimens were preconditioned at 20°C in 54% relative humidity in a desiccator containing a saturated solution of $Mg(NO_3)_2$, for at least 48 h prior to testing. The tensile tests were conducted using an Instron universal material testing machine (Instron 4502, Instron Corporation, Massachusetts, USA) equipped with a 1 kN load cell. At least 5 specimens were tested per sample.

2.5 Scanning Electron Microscopy (SEM)

SEM (LEO 1525) was used to study the surface morphology of the dried fibres with 5kV accelerating voltage while the cryogenically-fractured composite samples were observed using 30 kV accelerating voltage in a JEOL JSM-5300 Scanning Electron Microscope (Jeol Ltd., Tokyo, Japan) to visualise the interface between the reinforcing fibre and the matrix. All samples were

fixed to aluminium stubs with carbon tape. Prior to SEM, the fibre and composite samples were gold coated for 2 min at 20 mA (Emitech Ltd K550, Ashford, UK) to ensure sufficient electrical conductivity. The gold particle size was approximately 10 nm.

3 Results and Discussion

3.1 Surface of Bacterial Cellulose "Grafted" Fibres

SEM micrographs of the surfaces of hemp fibres before (Fig. 1a) and after the bacterial surface modification (Fig. 1b) clearly show that bacterial cellulose nanofibres of 50 to 100 nm in diameter almost completely cover the rather smooth natural fibre surface in a random orientation. This has roughened the fibre surface, which might lead to a stronger interface with polymers. Bacterial cellulose is an attractive reinforcement in composite making. It has features of small size, green credentials and excellent intrinsic properties. It is highly crystalline (up to 84-89%) [12] and has a relatively high elastic modulus of 78 GPa [13]. This modulus is comparable to that of standard glass fibres. Therefore attaching bacterial cellulose to natural fibres and its simultaneous incorporation into composites should lead to better performance composite materials.

Using the modified natural fibres the interfacial shear strength (IFSS), as a measure of the adhesion between the fibres and CAB, can be increased by up to 240% without much effect on the tensile properties of the natural fibres [14]. 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.

3.2 Tensile Properties of Composites

The measured tensile properties of randomly oriented hemp and sisal reinforced CAB composites with FWC of 20% to 50% are summarised in Table 1. A comparison is made between unmodified fibres and grafted fibres. Composites with a FWC ranging from 20% to 50% reinforced with the original untreated fibres were fabricated, whilst the composites reinforced with modified fibres were fabricated with FWC of 20% and 30%. Note that at FWCs exceeding 40%, voids, i.e. none-impregnated fibres, became visible within the composite, which indicated that there was not enough polymer to wet out all the fibres completely. For that reason we only fabricated grafted fibre/CAB composites with FWC of 20% and 30%.

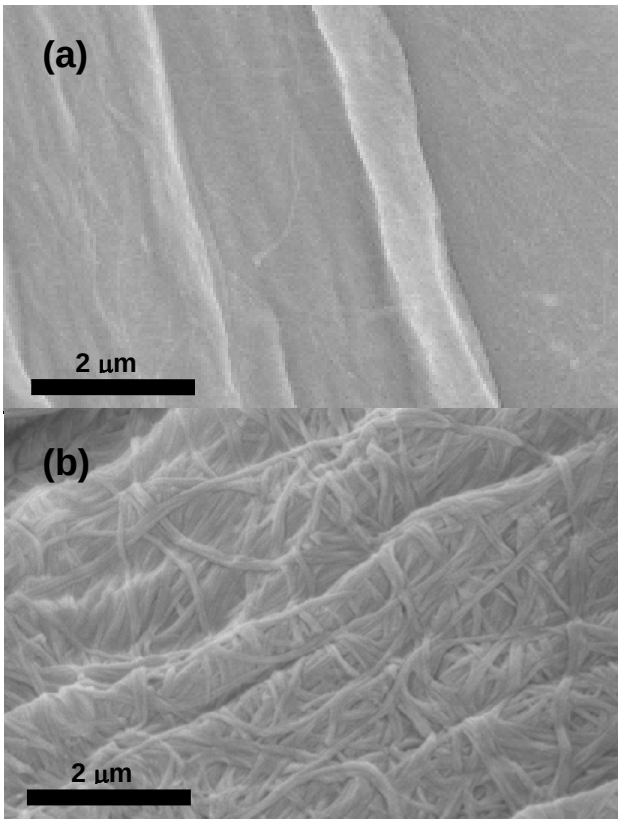


Fig. 1. SEM micrographs of surfaces of (a) unmodified hemp fibre and (b) hemp after grafted with bacterial cellulose

The measured tensile properties show that incorporating unmodified hemp or sisal fibres into CAB leads to a small but recognizable reduction of the tensile strength of the composites. The same was also reported by some other research groups for randomly-oriented natural fibres reinforced composites [15-20]. It could be because the well-known poor adhesion between the polar natural fibres and rather non-polar polymers obstructed the stress transfer between them. And this will build up the stress concentration at the interface, leading to poor tensile properties. However, the Young's modulus increases significantly by the addition of the natural fibres, since the fibres will restrict the elongation of the composite.

Table 1. Tensile properties of CAB reinforced with original and grafted hemp and sisal fibres

Fibre		Hemp/CAB		Sisal/CAB	
	FWC / %	σ / MPa	E / GPa	σ / MPa	E / GPa
	0	33.1± 1.2	0.24 ± 0.01	33.1± 1.2	0.24 ± 0.01
Unmodified	20	27.0 ± 4.0	1.36 ± 0.25	28.8 ± 5.6	0.83 ± 0.13
Grafted		23.0 ± 2.8	0.63 ± 0.04	26.7 ± 2.9	1.32 ± 0.04
Unmodified	30	20.9 ± 3.3	1.27 ± 0.10	27.7 ± 7.9	1.35 ± 0.32
Grafted		23.7 ± 3.2	0.81 ± 0.05	16.3 ± 4.7	1.33 ± 0.23
Unmodified	40	23.4 ± 5.8	1.76 ± 0.32	24.7 ± 7.9	1.49 ± 0.42
Unmodified	50	28.5 ± 5.7	0.92 ± 0.14	20.6 ± 8.2	0.63 ± 0.14

The results obtained for grafted fibre reinforced composite was even more disappointing, suggesting that the modified fibres incorporated into the CAB matrix actually worsen the tensile properties of the composite in comparison to the original fibres, in spite of the improved interfacial shear strength in the CAB matrix [14]. This inefficiency of the grafted fibres to yield improved composite properties is most likely because the grafted fibres are "glued" together. One of the problems of our bacterial cellulose-modification procedure is that the bacterial cellulose sometimes grows around the natural fibres too well, specifically for hemp. This bacterial cellulose will forms strong network, binding neighbouring fibres together firmly. When this "glued" bundle of fibres is processed in composite making, the polymer cannot penetrate into the bundle. This therefore creates stress concentration around it when the composite is subjected to load, and becomes the weak point of the composite. However sisal does not have as much problem as hemp. Sisal is also easier to process than hemp since it is much stiffer than hemp and does not curl up and form knots like hemp.

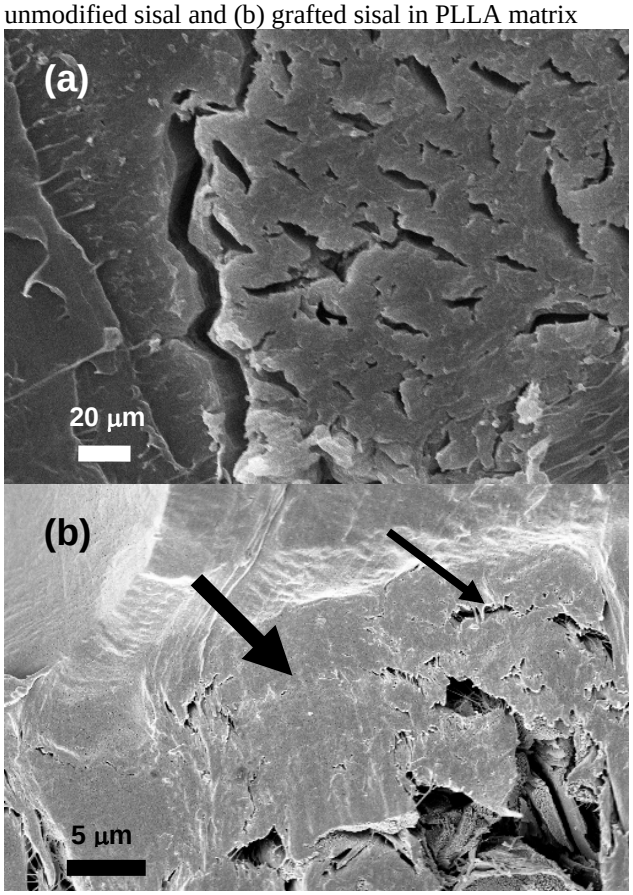
Despite the results in random-oriented fibre reinforced CAB, in our former publication [10], an improvement in tensile properties was observed in unidirectional sisal reinforced PLLA. With grafted sisal, the tensile strength of PLLA composites with 34% FWC sisal aligned parallel to the test direction improved from 79 MPa to 114 MPa, while the Young's Modulus improved from 7.9 GPa to 11.2 GPa [10]. The improvements were also observed with sisal fibre aligned perpendicular to the test direction, in which the tensile strength improved from 10 MPa to 17 MPa, and the Young's Modulus improved from 2.1 GPa to 3.1 GPa [10]. Therefore in this case it can be concluded that our bacterial cellulose modification can enhance the result tensile properties of the composites.

Comparing CAB to PLLA, the improvements of the tensile properties were more pronounced when using PLLA rather than CAB [10]. 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 and a much better mechanical properties of the result composites can be expected.

3.3 Analysis of Fracture Surfaces of Composites

Figure 2 shows the interface of composites fabricated with unmodified (Fig. 2a) and grafted sisal (Fig. 2b) in PLLA matrix. The SEM micrographs show some significant differences. In case of the unmodified fibres, there was a gap between the fibre and the matrix, indicating the poor adhesion at the interface. However, in the case of modified fibres we can observe matrix adhering to or wetting the fibres (big arrow in Fig. 2b) after fractured. This improved adhesion will enhance the stress transfer from the matrix to the fibre and will hence improve the tensile properties of the composites. There is also a gap between the fibres and the matrix (small arrow in Fig. 2b), which suggests either that the fibres are not completely covered by a dense layer of bacterial cellulose or that the interface between the bacterial cellulose and the fibres is not as strong as the interface between the cellulose and the matrix.

Figure 2. The interface of composites fabricated with (a) unmodified sisal and (b) grafted sisal in PLLA matrix



4 Conclusion

We have successfully modified natural fibres by attaching bacterial cellulose to their surfaces. The fibre surface changed after the modification leading to an improvement in IFSS between the fibre and the polymer matrix. The improvement can be attributed to enhancement of the interfacial performance, which is due to the roughened fibre surface and the presence of cellulose hydroxyl groups attached to the fibre surface. However, despite an improvement in the tensile properties of unidirectional sisal reinforced PLLA composites [10], in the case of the randomly-oriented fibre reinforced composites, we have no improvement in tensile properties. This is due to 'fibre gluing' after the modification.

The modification process needs to be optimised; the "grafting" content of nanocellulose should be maximised whilst avoiding excessive bonding of neighbouring fibres. In the future, we will fabricate the short fibre composites with a polymer mixer, which are much closer to current industrial materials.

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