

BACTERIAL CELLULOSE AS THE BINDER FOR NATURAL FIBRE PREFORMS TO PRODUCE GREEN NANOCOMPOSITES

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Abstract

A novel robust non-woven sisal fibre preform was manufactured using a papermaking process utilising nanosized bacterial cellulose (BC) as binder for the sisal fibres. It was found that BC provides significant mechanical strength to the sisal fibre preforms. This can be attributed to the high stiffness and strength of the BC network. Truly green non-woven fibre preform reinforced hierarchical composites were prepared by infusing the fibre preforms with acrylated epoxidised soybean oil (AESO) using vacuum assisted resin infusion, followed by thermal curing. Both the tensile and flexural properties of the hierarchical composites showed significant improvements over polyAESO and neat sisal fibre preform reinforced polyAESO. These results were corroborated by the thermo-mechanical behaviour of the (hierarchical) composites, which showed an increased storage modulus and enhanced fibre-matrix stress transfer. By using BC as binder for short sisal fibres, added benefits such as the high Young's modulus of BC, enhanced fibre-fibre and fibre-matrix stress transfer can be utilised in the resulting hierarchical composites.

1 Introduction

Significant research effort has been poured into the manufacturing of sustainable materials due to public's growing demand for more environmentally friendly products, depletion of petroleum resources, the ever-growing problem of landfill of waste and heavy environmental legalisation [1]. Natural fibres have gained significant attention as potential replacement for glass fibres to produce greener composites. The advantages of natural fibres as reinforcement for polymers include low density, wide availability and biodegradability [2]. In addition to this, natural fibres possess decent mechanical properties [3]. However, natural fibres suffer from drawbacks such as poor compatibility with hydrophobic polymer matrices and its inherent variability in both fibre properties and dimensions, even within the same cultivation [4]. There is very little that can be done in terms of the variability of their properties and dimensions. However, significant research effort has been poured into modifying the fibres to enhance the fibre-matrix interface [5].

One method of modifying the fibre-matrix interface is to attach bacterial cellulose (BC) onto the surface of natural fibres [6-8]. BC is highly crystalline nano-sized cellulose (24-86 nm in diameter and several micrometres in length [9]) without impurities such as hemicellulose or lignin and possesses a degree of crystallinity of up to 90% [10]. The Young's modulus of a single BC nanofibre was reported to be 114 GPa [11], with theoretical cellulose crystal modulus being as high as 160 GPa [12]. In addition to this, BC also possesses a linear thermal coefficient of expansion (LTCE) of only $0.1 \times 10^{-6} \text{ K}^{-1}$ [13]. By culturing cellulose-producing bacteria, such as from the *Acetobacter* species [9], in the presence of natural fibres, BC is preferentially deposited *in-situ* onto the surface of natural fibres. The introduction of BC onto natural fibres provides a new means of controlling the interaction between natural fibres and polymer matrices. Coating of natural fibres with BC does not only facilitate good distribution of BC within the matrix, it also results in an improved interfacial adhesion between the fibres and the matrix. This enhances the interaction between natural fibres and a polymer matrix. In addition to culturing cellulose-producing bacteria in the presence of natural fibres to coat the fibres, a method based on slurry dipping was developed recently to coat the surface of sisal fibres with BC [14]. This method utilises the water absorbing capability of natural fibres to absorb the water in BC dispersion, drawing along the nanocellulose in the dispersion onto the surface of the fibres.

In this work, we extend our slurry dipping method to create non-woven sisal fibre preforms for thermosetting matrices. Natural fibres can be stitched or stapled together using polymer fibres to produce non-woven fibre preforms [15-18]. In addition to this, fibre preforms can also be produced by spraying a polymer solution onto the fibre mat followed by heat pressing to consolidate the polymer to bind the fibres together [19]. Natural fibres can be blended with a thermoplastic polymer and melt pressed to create the fibre preform [20]. To process them into composites, these polymeric binder based natural fibre preforms can then be impregnated with a thermosetting resin to produce natural fibre reinforced composites [19, 21, 22]. Natural fibre preform reinforced thermoplastic composites can also be produced using film stacking, whereby the fibre preforms are stacked between sheets of polymers in alternative sequence and consolidated [23, 24].

Our current study focuses on using BC as binder to produce novel non-woven short sisal fibre preforms, moving away from the conventional polymer binders such as polypropylene, polyesters and epoxies [25]. These natural fibre preforms are infused with epoxidised and acrylated soybean oil (AESO) using vacuum assisted resin infusion (VARI) and thermally cured to produce truly green hierarchical composites. Nature maximises the efficiency of structural materials by organising them hierarchically; the arrangement of the constituents at every level, from the molecular to the macroscopic level [26]. By applying this concept, composites that possess a hierarchical structure should have improved mechanical properties. Not only does the BC act as binder for the loose fibres, it also simultaneously acts as nanofiller to further enhance the mechanical properties of the hierarchical composites due to its high stiffness and strength. The mechanical properties, thermal degradation and thermo-mechanical behaviour of the hierarchical composites were studied.

2 Materials and methods

AESO (Aldrich, density = 1.04 g cm^{-3} , inhibited with 8500 ppm monomethyl ether hydroquinone) and *tert*-butyl peroxybenzoate, otherwise known as Luperox P (Aldrich, purity

$\geq 98\%$), were purchased from Sigma-Aldrich and used as the thermosetting monomer and thermal initiator, respectively, in this study. Loose sisal fibres were kindly supplied by Wigglesworth & Co. Ltd. (London, UK). These fibres were grown in East Africa. The harvested crop was left in the field for approximately 3 to 4 weeks for dew retting in order to allow the combined action of temperature, humidity and bacteria to loosen the fibres. After this retting process, the raw fibres were processed with a rudimentary tool to separate the fibres by hand. The fibres were afterwards washed with water and sun-dried for one day. BC was provided by fzmb GmbH as wet pellicle containing 94 wt.-% water. The synthesis of BC used in this study can be found in literature [27].

2.1 Manufacturing natural fibre preforms

The fibre preforms were manufactured using a papermaking process. Neat sisal fibre preforms were manufactured using 16 g of sisal fibres, cut to approximately 10 mm in length which were soaked in 2 L of de-ionised water overnight. This dispersion of short sisal fibres was then filtered under vacuum onto a 125 mm diameter filter paper (VWR, Lutterworth, UK) using a Büchner funnel. The filter cake was wet pressed twice under a weight of 1 t for 2 min. This wet pressed filter cake was then further dried in an oven at 60°C overnight under a weight of 10 kg. Short sisal fibres were used instead of long fibres because a more uniform dispersion of fibres in water can be obtained. The fibre preforms produced from short fibres were also more uniform.

In order to use BC as binder for the fibre preforms, 29.6 g of wet BC pellicles (equivalent dry mass of 1.78 g) were cut into small pieces and blended for 1 min using a blender (Breville BL18 glass jug blender, Pulse Home Products Ltd, Oldham, UK) and further homogenised (Polytron PT 10-35 GT, Kinematica, Lucerne, CH) for 2 min in 2 L of de-ionised water to produce a uniform dispersion of nanocellulose. 16 g of sisal fibres, cut to approximately 10 mm in length, were soaked in this nanocellulose dispersion overnight. The fibre preforms were then manufactured following the previously described wet pressing followed by drying method. The weight fraction of BC in these sisal fibre preforms was 10 wt.-%. Herein, fibre preforms with neat sisal fibres only and sisal fibres with BC binder are termed sisal fibre preforms and BC-sisal fibre preforms, respectively.

2.2 Manufacturing of natural fibre preform reinforced (hierarchical) composites

The (hierarchical) composites were manufactured using VARI. A schematic diagram of the VARI setup is shown in figure 1. A polyester porous flow medium (15087B, Newbury Engineer Textile, Berkshire, UK) was placed on top of the tooling side (a 460 mm x 920 mm heating plate equipped with a temperature control unit), which was covered by a layer of polyester film (Melinex PW 122-50-RL, PSG group, London, UK). The natural fibre preforms were sandwiched between two PTFE coated glass release fabrics (FF03PM, Aerovac, West Yorkshire, UK) and placed on top of the polyester porous flow medium. Another polyester porous flow medium was then placed on top of the PTFE glass release fabric. The whole setup was covered with a vacuum bagging film (Capran 519 heat stabilised Nylon 6 blown tubular film, Aerovac, West Yorkshire, UK) and sealed using vacuum sealant tape (SM5127, Aerovac, West Yorkshire, UK).

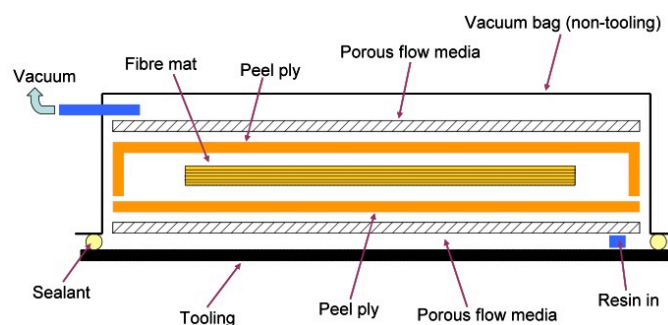


Figure 1. Schematic diagram of the VARI process

Prior to the infusion of the resin, the previously prepared fibre preforms were further dried by hot-pressing the preforms at 120°C and 0.25 t for 15 min. This also reduced the porosity of the fibre preforms, resulting in an increased fibre volume fraction of the final (hierarchical) composites. AESO was heated to 80°C to reduce its viscosity and 5 wt.-% of Luperox P relative to the weight of AESO was mixed into the resin. This mixture was then de-gassed at a reduced pressure of 100 kPa at 80°C for 30 min prior to the infusion step in order to remove all air bubbles entrapped during the mixing of the resin and the initiator. The infusion process starts with an air removal step, whereby vacuum was applied to the system via the tubing on the non-tooling side with the resin inlet tubing sealed off. When the maximum vacuum was achieved (~20 kPa), the VARI setup was left under vacuum for 2 h to ensure that there was no leakage in the setup by constantly monitoring the pressure in the vacuum bag. Once the system was determined to be leakage-free, the liquid resin was fed at the same temperature from the bottom of the polyester porous flow medium on the tooling side through the fibre preforms and exited via the tubing on the non-tooling side. Both the VARI setup and the resin were heated to 80°C in order to ensure a low enough viscosity of AESO such that it flows readily during the infusion process. The inlet and outlet of the setup were sealed off again once the resin fully penetrated the fibre preforms. The resin was heated to 110°C for 2 h using a heating rate of 5°C min⁻¹ to cure the resin, followed by a post-curing step at 130°C for 2 h. The VARI setup was cooled to room temperature prior to the removal of the manufactured (hierarchical) composites. The composites reinforced with sisal fibre preforms and BC-sisal fibre preforms are termed sisal-polyAESO and BC-sisal-polyAESO, respectively hereafter. Neat polymerised AESO was produced by pouring the resin into a mould with dimensions of 3 × 15 × 20 mm and polymerised using the same reduced pressure and curing cycle as previously described.

2.3 Density measurements of the fibre preforms and (hierarchical) composites

The density of the fibres, neat polyAESO and its (hierarchical) composites was measured using He pycnometry (AccuPyc 1330, Micromeritics Ltd, Dunstable, UK). The samples were weighed prior to placing them in the measuring chamber of the He pycnometer. As the pressure of He rises above the atmospheric value, it was expanded through a valve and this expanded volume was measured. Due to the expansion of He, the pressure inside the chamber will decrease to a steady-state value. With the mass of the sample known, the density ρ_m of the sample can then be calculated using the equation:

$$\rho_m = \frac{m_s}{V_c - \frac{V_E}{\frac{P_1}{P_2} - 1}} \quad (1)$$

where m_s is the sample mass, V_c is the volume of the chamber, V_E is the expanded volume of helium, P_1 and P_2 are the chamber's elevated pressure and steady-state pressure, respectively. The envelope density ρ_e of the fibre preforms was calculated from the mass and envelope volume of the preforms. The fibre volume fraction v_f of the (hierarchical) composites was calculated based on the densities of the fibre preforms and (hierarchical) composites, respectively.

2.4 Mechanical properties of (hierarchical) composites

The (hierarchical) composites were tested in tension and flexural (3-point bending) mode using an Instron universal material testing equipment (Instron 4505, Instron Corporation, MA, USA) in accordance to ASTM D 3039-00 and D638-03, respectively. The tensile test specimens possessed dimensions of $3 \times 15 \times 100$ mm, with a gauge length of 30 mm. Prior to the test, woven glass fibre reinforced polyester end tabs with a thickness of 1.6 mm were glued onto the samples using a two-part cold curing epoxy resin (Araldite 2011, Huntsman Advanced Materials, Cambridge, UK). The distance between the end tabs was set to be 60 mm. Strain gauges (FLA-2-11, Techni Measure, Studley, UK) were glued onto the middle portion of the test specimen using cyanoacrylate glue (EVERBUILD Building Products Ltd, Leeds, UK). Tensile tests were conducted using a crosshead speed and load cell of 1 mm min^{-1} and 10 kN, respectively. The flexural test specimens possessed dimensions of $3 \times 15 \times 80$ mm. The span-to-thickness ratio and crosshead speed used in flexural test were 20 and 1 mm min^{-1} , respectively. A total of 5 specimens were tested in each test for each type of samples.

3 Results and discussion

Both the tensile and flexural properties of neat polyAESO and its (hierarchical) composites are summarised in table 1. The fibre volume fractions of sisal-polyAESO and BC-sisal-polyAESO were found to be 40 vol.-%, implying that direct comparisons between sisal-polyAESO and BC-sisal-polyAESO can be made. When sisal fibres were used as reinforcement for polyAESO, the tensile modulus improved from 0.4 GPa for neat polyAESO to 3.2 GPa for 40 vol.-% sisal fibre reinforced polyAESO composites. A further improvement of the tensile modulus of the composites from 3.2 GPa to 5.6 GPa was achieved when BC was used as the binder for the natural fibre preform. This is thought to be due to the stiffening of polymer matrix when the fibre preform contained a hornified network of BC. It has been shown that the stiffness of a polymer matrix can be improved by as much as 40% when BC, which has an estimated Young's modulus of 114 GPa [11], at a loading fraction of only 5 wt.-% was used [28].

A similar trend was observed for the tensile strength of the (hierarchical) composites. Neat polyAESO had a tensile strength of only 4.1 MPa. When neat polyAESO was reinforced with 40 vol.-% sisal fibres the tensile strength increased to 18.4 MPa. A further improvement was achieved when 40 vol.-% of BC and sisal fibres in form of a preform, were used as reinforcement. The tensile strength of BC-sisal-polyAESO increased by 71% and nearly

700% when compared to sisal-polyAESO and neat polyAESO, respectively. This significant improvement when BC-sisal fibre preforms were used to create hierarchical composites can be attributed to (i) the enhanced fibre-matrix interaction (see DMTA section) and (ii) enhanced fibre-fibre stress transfer. The use of BC as binder for the fibres resulted in the formation of continuous but hornified BC network, encasing sisal fibres bonding them together. It is postulated that this enhances the fibre-fibre stress transfer compared to sisal fibre only preforms, where the fibres are mostly isolated. In addition to this, it has been shown that using BC as binder enhances the tensile properties (and, therefore, the handleability and robustness) of the BC-sisal fibre preforms compared to sisal fibre preforms. This translates to the improved tensile strength of the manufactured BC-sisal-polyAESO.

Table 1. Mechanical properties of neat polyAESO and its (hierarchical) composites. V_f , E_T , σ_T , E_F , σ_F denote the fibre volume fractions, tensile modulus, tensile strength, flexural modulus and flexural strength, respectively.

Sample	v_f (vol.-%)	E_T (GPa)	σ_T (MPa)	E_F (GPa)	σ_F (MPa)
Neat polyAESO	0	0.4 ± 0.1	4.1 ± 0.1	0.2 ± 0.1	9.0 ± 0.1
Sisal-polyAESO	40 ± 2	3.2 ± 0.2	18.4 ± 0.9	1.9 ± 0.2	28.9 ± 1.6
BC-Sisal-polyAESO	41 ± 3	5.6 ± 0.4	31.4 ± 0.5	4.6 ± 0.3	62.4 ± 3.0

The flexural modulus and strength of the (hierarchical) composites also increased when compared to neat polyAESO (see table 1). When BC-sisal fibre preforms were used as reinforcement to create hierarchical composites, improvements over sisal-polyAESO of 142% and 116% were observed in flexural modulus and strength, respectively. As aforementioned, the improvements in the flexural moduli of BC-sisal-polyAESO can be attributed to the inclusion of nano-sized BC, which is an effective stiffening agent, into the polymer matrix. This can be attributed to (i) enhanced mechanical performance of the BC-sisal preforms, (ii) rigid structure of BC and (iii) formation of a 3-dimensional network of rigid nanocellulose within the matrix [28].

4 Conclusions

A novel robust short sisal fibre preform was manufactured using BC as binder, moving away from commonly used polymer binders. PolyAESO reinforced with sisal fibre and BC-sisal fibre preforms was manufactured using VARI. The use of BC-sisal preforms improved both the tensile and flexural properties of BC-sisal-polyAESO when compared to sisal-polyAESO and neat polyAESO. The tensile modulus and strength of BC-sisal-polyAESO improved by 75% and 71%, respectively over sisal-polyAESO and 1300% and 600%, respectively over neat polyAESO. A similar trend was also observed for the flexural properties of the (hierarchical) composites. The flexural modulus and strength of BC-sisal-polyAESO improved by 142% and 116%, respectively over sisal-polyAESO and 2200% and 590%, respectively over neat polyAESO. These new types of natural fibre preform reinforced hierarchical composites offer promising alternative bio-based materials for the industry.

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