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Flexural and impact properties of all-cellulose composite laminates

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ABSTRACT

All-cellulose composites (ACCs) represent a class of biocomposite that are entirely synthesised from cellulose, resulting in a matrix and reinforcing phase that are chemically identical. The flexural strength, puncture impact strength and unnotched Charpy impact strength of ACC laminates are reported for the first time and compared with conventional biocomposites. In this study, the flexural and impact properties of ACC laminates based solely on a rayon textile were investigated. It is observed that all-cellulose composite laminates exceed the impact properties of most conventional biocomposites. A high level of fibre–matrix adhesion was observed to hinder interlaminar failure. The unique combination of high flexural and impact strength of ACC laminates demonstrates the potential of ACC laminates as a new class of biocomposite.

1. Introduction

Elementary cellulose fibrils have the highest specific stiffness of all natural materials and their specific tensile strength also ranks above most alternatives [1]. Hence, cellulosic materials have the potential to play an important role in the future development of sustainable alternatives to commonly used petroleum-based materials used in conventional composite materials [2]. However, the high properties of cellulose are not fully exploited in many cellulose-containing biocomposites due to poor bonding between the cellulosic fibre and polymer matrix [3]. Strong fibre–matrix adhesion allows an improved load transfer throughout the composite and will largely determine the mechanical efficiency of the composite [4]. Typically, biocomposites utilise chemically different materials for the reinforcement (hydrophilic natural fibres) and matrix (petrochemical-derived thermoplastic or thermosetting polymers).

All-cellulose composites (ACCs) represent a relatively new class of materials that unlike other biocomposites are made entirely from cellulosic materials, leading to chemically identical matrix and reinforcing phases [5,6]. Two processing pathways are described for the synthesis of an ACC: (i) complete dissolution of a portion of cellulose followed by mixing this portion with additional reinforcing cellulosic material [7], and (ii) partial dissolution of cellulosic material to form a matrix phase *in situ* around the remaining fibre core [6]. Various sources of cellulose have been examined for the production of ACCs including microcrystalline cellulose [8], cotton linters [9], wood fibre [6], ramie fibre [10], hemp fibre [11], filter paper [12], and man-made cellulose fibres such as Lyocell and Bocell [13,14]. Common solvent systems for the synthesis of ACCs include LiCL/DMAc [15] or NMMO [16]. Recently, ionic liquids (ILs) have been identified as attractive solvent systems for the processing of cellulose [17]. ILs are organic salts that exist in the liquid phase below 100 °C. Several IL cation and anion combinations have been reported to exhibit a high solvency for cellulose, recyclability and a very low vapour pressure resulting in easier handling compared to other solvent systems of cellulose. The dissolution of cellulose *via* ILs has been recently reviewed by Pinkert et al. [18]. The solvent is removed by the introduction of a coagulant such as water or ethanol; this solvent exchange results in the *regeneration* of solid phase cellulose. Consequently, the chemical similarity of the matrix and reinforcement phases in ACCs is hypothesised to create a composite material that is devoid of interfaces between reinforcement and matrix, or an *interfaceless* composite [5]. The end result of such an approach is the possible optimisation of fibre–matrix adhesion, making additional pre-treatment of the fibres or addition of a coupling agent redundant. Studies have shown ACCs to exhibit tensile strengths and Young's moduli as high as 910 MPa [13] and 26 GPa [19], respectively. The remarkable properties of ACCs compared with conventional biocomposites support the assumption that the interfacial bonding between reinforcement and matrix is improved in these single-polymer composite materials.

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The use of natural fibres such as hemp, flax, ramie, sisal or wood in conventional biocomposites can lead to sufficient tensile strengths and moduli for semi-structural industrial applications [20]. However, conventional biocomposites often fail to meet specifications in terms of the impact resistance [21]. Attempts to improve the impact resistance have been based on using polymer matrices with intrinsically high impact properties [22] or *via* the utilisation of high strain regenerated cellulose fibres such as Lyocell [23]. Presently, the impact and flexural resistance of ACCs is largely unknown. Therefore, the present study will focus on the impact and flexural properties of ACC laminates based on regenerated fibres using 3-point bending, puncture impact and Charpy impact testing for comparison with conventional biocomposites. A secondary objective of this work is explore the concept of an interfaceless composite in the framework of ACCs. This is explored for what could be deemed a "simpler" system since the ACCs presented here will be composed of reinforcement and matrix phases that are both cellulose II and thus possibly very similar chemically and structurally.

2. Experimental procedures

2.1. Experimental materials

The ionic liquid 1-butyl-3-methylimidazolium acetate (BmimAc) (BASIONIC BC 02™, Sigma–Aldrich, St. Louis, USA) was dried in a vacuum furnace (Binder GmbH, Tutlingen, Germany) for 5 days at 80 °C before use. The rayon textile used in this work (Cordenka™ K2/2 twill weave, surface mass = 450 g/m^2, Cordenka GmbH, Obernburg, Germany) is composed of regenerated cellulose in the form of cellulose II (crystallinity ≈ 45%). A single fibre of the Cordenka yarn has been reported to have a diameter of 12 μm, tensile strength of 830 MPa, Young's modulus of 20 GPa and elongation at break of 13% [24]. The Cordenka textiles were dried in a vacuum furnace for 24 h at 80 °C before processing.

2.2. Laminate processing

A detailed description of the process used to manufacture the ACC laminates is found elsewhere [25]. Briefly, a process termed solvent infusion processing (SIP) was used to fabricate an ACC laminate consisting of 5 layers of the Cordenka textile (130 × 130 mm). The textile layers were vacuum-infused with approximately 40 g of IL. The IL showed flow characteristics similar to synthetic oil during infusion. A hot press (Gibitre Instruments, Bergamo, Italy) was used to apply 0.2 MPa pressure for 60 min at 100 °C to achieve partial dissolution of the textiles, followed by vacuum infusion with approximately 250 ml of distilled water to remove the IL to regenerate the dissolved portion of cellulose. A vacuum pump (Laboport, KNF NEUBERGER, INC., Trenton, NJ, USA) was used to deliver a constant vacuum pressure of 0.1 MPa to achieve a high level of infusion through the textiles. Subsequently, the ACCs were washed thoroughly in distilled water to completely remove the IL. Finally, the ACCs were dried in the hot press under a pressure of 0.02 MPa for 4 h at 90 °C.

2.3. Mechanical testing and fractography

Puncture impact tests were performed in accordance with EN ISO 6603-2:2000 using an Imatek IM10 drop weight impact tester (Imatek Ltd., Old Knebworth, UK). A 20 mm hemispherical striker was used from a falling height of 1 m. The total striking mass was 9.54 kg and the impact velocity was 4.43 m/s, resulting in a total impact energy of 94 J. Five samples of 60 mm × 60 mm were cut from the laminates using a band saw and conditioned prior to testing at 23 ± 1 °C and 50 ± 1% R.H. for 24 h. Samples of 2 ± 0.05 mm in thickness were clamped within a 40 mm diameter support ring.

The unnotched Charpy impact strength was determined in accordance with DIN EN ISO 179/1eU. 12 samples of 80 × 10 × 3 mm were tested in flatwise impact direction using a 4 J pendulum. The samples were conditioned prior to testing at 23 ± 1 °C and 50 ± 1% R.H. for 24 h.

3-Point bending tests were conducted according to ASTM D790 on a MTS 858 tabletop system (MTS, Eden Prairie, MN, USA) equipped with a 2.5 kN load cell. Samples of 2 mm thickness, 10–11 mm in width and a length of 45 mm were tested at a crosshead speed of 2 mm/min. A span of 35 mm was used between the sample supports. Eight samples were tested after conditioning at 23 ± 2 °C and 50 ± 2% R.H. for 48 h.

Samples of approximately 3 mm length and 1 mm width were cut from the fracture surfaces of the impact and bending samples using a diamond saw (Allied High Tech Products, Inc., Rancho Dominguez, California, USA). The samples were sputter coated using an Emitech K975X coater (Quorum Technologies Ltd., East Grinstead, United Kingdom) with a gold target for 120 s. Secondary electron images were obtained with a JEOL 7000F FE-SEM (JEOL Ltd., Tokyo, Japan) using an acceleration voltage of 5 kV and probe current of 7 mA.

3. Results and discussion

3.1. Fracture behaviour of all-cellulose composite laminates during impact loading

Typically, there are four failure modes observed during puncture impact testing: (i) matrix failure, observed as cracking of the matrix phase parallel to the fibres; (ii) delamination of the laminate layers due to interlaminar stresses; (iii) fibre failure such as fibre breakage and fibre buckling; and (iv) full penetration of the laminate [25]. The fraction of matrix phase in ACC laminates is relatively low compared with most conventional polymer matrix composites; in particular, ACCs processed *via* partial fibre dissolution may have a fibre volume fraction as high as 90% [5] and in fact ACCs processed *via* SIP show a fibre volume fraction of 92% [27] while achieving an even matrix distribution as seen in a cross-section of an untested sample (Fig. 1). Hence, matrix failure is not expected to be the dominant failure mode.

A typical plot of the puncture impact load as a function of the striker displacement was observed to be broadly divided into 4

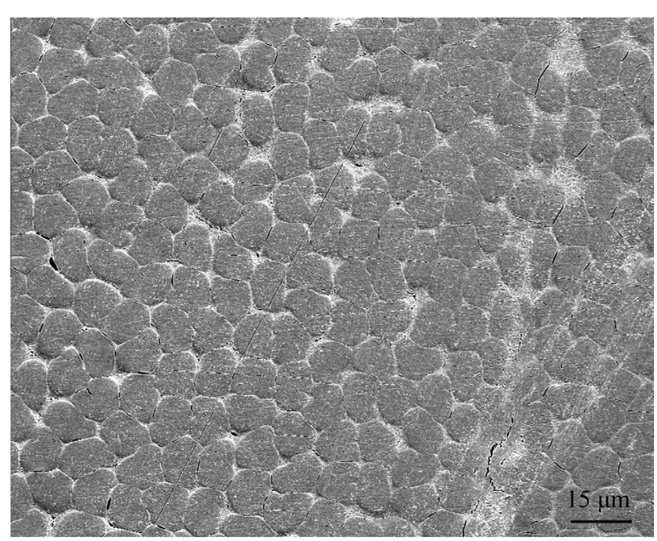

Fig. 1. Scanning electron micrographs of the cross-section of an untested sample of the processed ACCs showing individual rayon fibres surrounded by a very thin layer of matrix phase.