Positive size and scale effects of all-cellulose composite laminates

Jan W. Dormanns [a,b], Felix Weiler [c], Jeremias Schuermann [a,b], Jörg Müssig [c], Benoît J.C. Duchemin [d], Mark P. Staiger [a,b,*]

[a] Department of Mechanical Engineering, University of Canterbury, Private Bag 4800, 8140 Christchurch, New Zealand
[b] The MacDiarmid Institute for Advanced Materials and Nanotechnology, PO Box 600, Kelburn, Wellington 6140, New Zealand
[c] The Biological Materials Group, Department of Biomimetics, HSB – University of Applied Sciences, Neustadtswall 30, 28199 Bremen, Germany
[d] Laboratoire Ondes et Milieux Complexes, UMR 6294, CNRS-Université du Havre, Le Havre, France

ARTICLE INFO

ABSTRACT

Negative size effects are commonly reported for advanced composite materials where the strength of the material decreases with increasing volume of the test specimen. In this work, the effect of increasing specimen volume on the mechanical properties of all-cellulose composites is examined by varying the laminate thickness. A positive size effect is observed in all-cellulose composite laminates as demonstrated by a 32.8% increase in tensile strength as the laminate thickness is increased by 7 times. The damage evolution in all-cellulose composite laminates was examined as a function of the tensile strain. Enhanced damage tolerance concomitant with increasing specimen volume is associated with damage accumulation due to transverse cracking and strain delocalisation. A transition from low-strain failure to tough and high-strain failure is observed as the laminate thickness is increased. Simultaneously, scale effects lead to an increase in the void content and cellulose crystallinity at the core, with increasing laminate thickness.

1. Introduction

The use of natural fibres as reinforcement in bio-based composites has received much attention due to the availability, mechanical properties and biodegradability of cellulose [1–3]. An interesting subclass of bio-based composites are all-cellulose composites (ACCs) which are single-polymer composites where both the matrix and reinforcement are based on non-derivatized cellulose [4]. Single-polymer composites are purported to have improved interfacial compatibility between the reinforcement and matrix phases compared with conventional biobased-composites that utilise hydrophilic natural fibres to reinforce a hydrophobic polymer matrix [3,5,6]. Hence, the mechanical properties of ACCs are found to exceed most conventional biobased-composites [7] while remaining fully bio-based and biodegradable [8].

ACCs can be processed via one of two routes: (i) A cellulose reinforcement (fibres or particles) is mixed with a pre-dissolved cellulose solution that forms the matrix [4]; or (ii) cellulose is brought into contact with a solvent so as to partially dissolve the surface,

thereby creating a cellulose matrix in situ [9]. Most studies of ACCs are based on the processing and characterisation of thin films (<1 mm). More recently, the authors have reported on the manufacture of thicker laminates (2–4 mm) by compression moulding [10] and solvent infusion processing (SIP) [11], with the aim of increasing the range of possible industrial applications. The ability to manufacture laminates should also allow greater customisation of the mechanical properties of ACCs, as permitted in conventional multi-axial composite laminates. In SIP, vacuum pressure is used to infuse a cellulosic textile with a solvent, similar to conventional resin infusion processes. Partial dissolution of the cellulose fibres is then triggered by a change in the temperature of the solvent. A matrix phase of regenerated cellulose is then formed in situ upon removal of the solvent. Subsequent drying removes the anti-solvent and results in dimensionally stable laminates with a relatively high volume fraction of fibres (>90%) [11]. Hence, the thickness of an ACC laminate may be controlled by simply varying the number of textile layers in the laminate stack.

The term size effect in composite materials, and indeed other families of materials, refers to changes in the mechanical properties caused by changes in the volume of the test specimen. In general, composite materials exhibit a negative size effect such that strength decreases with increasing specimen dimensions, as described by the weakest link theory [12–15]. The weakest link

* Corresponding author at: Department of Mechanical Engineering, University of Canterbury, Private Bag 4800, 8140 Christchurch, New Zealand.
E-mail address: mark.staiger@canterbury.ac.nz (M.P. Staiger).

model is based on the assumption that the probability of a critical-sized, failure-inducing defect being present in a sample increases as the volume of the test specimen is increased [14,15]. The phenomenon of size effects in composite materials has been reviewed elsewhere [12–15].

As mentioned, SIP facilitates the fabrication of ACC laminates of varying thickness. However, the effect of upscaling the specimen dimensions on the mechanical and physical properties of ACC laminates is unknown. In the present study the manifestation of size and scale effects in ACC laminates is investigated by characterising ACCs of increasing laminate thickness by tensile testing, wide-angle X-ray diffraction (WAXD) and scanning electron microscopy (SEM). Furthermore, the evolution of damage with increasing strain is examined in a series of interrupted tensile tests followed by microstructural characterisation using SEM.

2. Experimental procedures

2.1. Materials

A regenerated cellulose fibre (Cordenka® 700, 1840 dtex, f 1000, Cordenka GmbH & Co. KG, Obernburg, Germany) in the form of a simple 2D textile (2/2 twill weave) was used as precursor for fabricating single- and multi-layered ACC laminates. The areal mass of the textile was $450\,g\,mm^{-2}$, while the yarn density was 13 and 10 yarns cm^{-1} in warp and weft direction, respectively. An ionic liquid (IL), 1-butyl-3-methylimidazolium acetate (BmimAc, $\geqslant 95\%$, BASF, Ludwigshafen, Germany) was used as the cellulose solvent. Prior to use, the textile and IL were dried under vacuum at 85 °C for at least 24 h and 5 days, respectively, in order to exclude the influence of adsorbed moisture on cellulose dissolution.

2.2. Fabrication of ACC laminates

A laminate stack with 1, 2, 4 or 8 laminae was infused with the IL using a rectilinear setup (Fig. 1a) as previously described elsewhere [11]. Briefly, ACC laminates (ca. $180 \times 350\,mm^2$) were fabricated with a symmetric layup, with laminae aligned such that the warp direction was parallel to the infusion direction. Infusion with BmimAc was carried out at an absolute pressure of 200 mbar. Partial dissolution of the cellulose precursor was carried out in a laboratory hot press (Gibitre Instruments, Bergamo, Italy) at 95 °C under an applied pressure of 1 MPa for 60 min. The application of equal infusion pressure and dissolution time ensured homogeneous solvent uptake and matrix creation by partial dissolution in all laminates. The partially dissolved textiles were then regener-

ated and washed in distilled water at room temperature (20 ± 2 °C) with two water changes per day until no further increase in conductivity of the water bath was measured, indicating complete removal of the solvent. For comparison, a single layer laminate required a washing time of 3 days, while that with 8 laminae required 10 days. The removal of BmimAc was confirmed by Fourier-transformed infrared spectroscopy (FTIR). The regenerated material was cut for field emission SEM and tensile testing using a sharp blade. The specimens were then dried between porous polytetrafluoroethylene (PTFE) sheets (2 mm thick, pore size 20 μm, DIA-Nielsen GmbH & Co. KG, Düren, Germany) at 60 °C under vacuum and an external pressure of 0.2 MPa until their mass was constant (Fig. 1a).

An unreinforced cellulose film was prepared by dissolving 10 wt.% rayon (fibres of ~2 mm length) in BmimAc at a temperature of 95 °C for 60 min while continuously stirring. The cellulose-BmimAc solution was centrifuged at 3000 rpm for 10 min so as to degas the solution and separate undissolved cellulose residues. Subsequently, the solution was cast into a rectangular mould consisting of a 3 mm thick polypropylene plate with a rectangular opening of 55 mm length and 35 mm width sandwiched between two sheets of porous PTFE. The mould was submerged in distilled water and vacuum was applied so as to infiltrate the porous PTFE with water. The film was left to regenerate over night, removed from the mould and subsequently washed and dried as described above.

2.3. Materials characterisation

The ACC laminates were tensile tested according to ASTM D 3039 on a universal testing machine (Criterion 43, MTS Systems Corporation, Eden Prairie, USA) with a 500 N, 2.5 kN or 10 kN load cell using a minimum of 6 replicates. Non-contact displacement measurement was carried out with a video extensometer (Genie 1400, Teledyne DALSA, Waterloo, Canada). Rectangular specimens with a width of 14 mm and gauge length of 65 mm were tested at a constant crosshead speed of 2 mm min^{-1}. The tensile load was applied parallel to the warp direction (Fig. 1b). The unreinforced cellulose film was tested as rectangular specimens with a width and gauge length of 4 mm and 15 mm, respectively. All tensile specimens were conditioned at 23 °C and 50% RH for a minimum of 24 h prior to testing.

Young's modulus was determined as tangent modulus between strains of 0.1% and 0.3%. The work to fracture was determined by numerically integrating the stress–strain curve. Results are given as the arithmetic mean ± standard deviation. The differences in the observed mechanical properties were tested for statistical
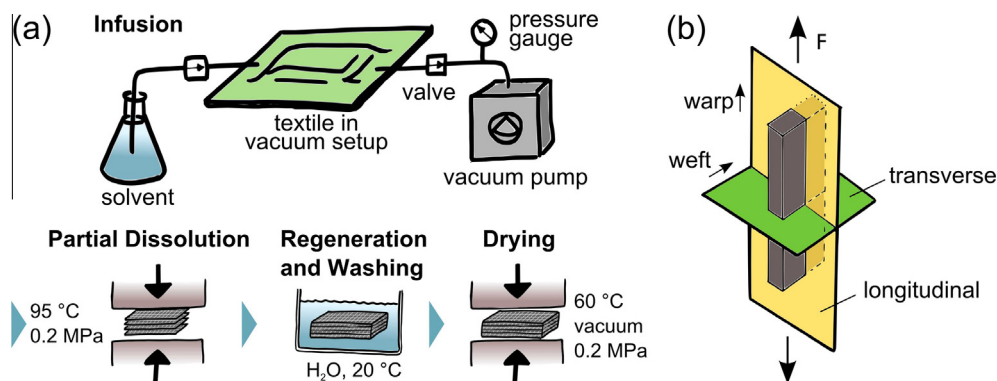
Fig. 1. Schematic of (a) solvent infusion processing of ACC laminates, and (b) the warp and weft directions in a laminate. The longitudinal (yellow) and transverse (green) planes describe the cross sections observed in microstructural analysis. Arrows indicate the direction of the tensile load (F) applied during testing. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)