Carbohydrate Polymers 90 (2012) 730–733

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Short communication

Solvent infusion processing of all-cellulose composite materials

Tim Huber[a], Simon Bickerton[b], Jörg Müssig[c], Shusheng Pang[d], Mark P. Staiger[a,*]

[a] Department of Mechanical Engineering, University of Canterbury, Private Bag 4800, 8140 Christchurch, New Zealand
[b] Department of Mechanical Engineering, University of Auckland, 20 Symonds Street, Auckland, New Zealand
[c] Department for Biomimetics, University of Applied Sciences Bremen, Neustadswall 30, 28199 Bremen, Germany
[d] Department of Chemical and Process Engineering, University of Canterbury, Private Bag 4800, 8140 Christchurch, New Zealand

ARTICLE INFO

Article history:
Received 4 March 2012
Received in revised form 13 April 2012
Accepted 17 May 2012
Available online 24 May 2012

Keywords:
Cellulose
Textile composites (A)
Fibre/matrix bond (B)

ABSTRACT

Continuous fibre-reinforced all-cellulose composite (ACC) laminates were produced in the form of a dimensionally thick (>1 mm) laminate using an easy-to-use processing pathway termed solvent infusion processing (SIP) from a rayon (Cordenka™) textile using the ionic liquid 1-butyl-3-methylimidazolium acetate. SIP facilitates the infusion of a solvent through a dry cellulose fibre preform with the aim of partially dissolving the outer surface of the cellulose fibres. The dissolved cellulose is then regenerated by solvent exchange to form a matrix phase *in situ* that acts to bond together the undissolved portion of the fibres. SIP is capable of producing thick, dimensionally stable ACC laminates with high volume fractions of continuous fibres (>70 vol.%) due to the combination of two factors: (i) homogeneous and controlled partial dissolution of the fibres and (ii) the application of pressure *during* regeneration and drying that provides a high level of fibre compaction, thereby overcoming void formation associated with material shrinkage. The effect of inlet and outlet positioning, and applied pressure on the macro- and microstructure of all-cellulose composites is examined. Finally, SIP expands the applications for ACCs by enabling the production of thick ACC laminates to overcome the limitations of conventional thin-film ACCs.

1. Introduction

The high specific strength and stiffness, low cost and sustainability of cellulose fibres have led to intensive interest in the development of natural fibre-reinforced polymer matrix biocomposites (Graupner & Mussig, 2010; Jacob John & Thomas, 2008). Unfortunately, achieving robust interfacial adhesion between cellulosic fibre and, particularly, a thermoplastic matrix remains a major challenge for biocomposites in spite of the use of fibre pre-treatments and chemical coupling agents (George, Sreekala, & Thomas, 2001). However, strong interfacial bonding, and hence efficient stress transfer, between the reinforcing and matrix phases is required for maximising the load-bearing capability (Drzal & Madhukar, 1993).

A new class of monocomponent (or single polymer) biocomposites known as all-cellulose composites (ACCs) has emerged through the pioneering work of Nishino (Nishino, Matsuda, & Hirao, 2004). Both, the reinforcement and matrix of an ACC are based on non-derivatised cellulose, ideally leading to an *interfaceless* composite. The concept of monocomponent or single polymer composites was originally applied to thermoplastic systems to simplify the recycling process rather than manipulate the interfacial properties *per se* (Matabola, De Vries, Moolman, & Luyt, 2009). Yet, the use of cellulose for both the reinforcing and matrix phases can lead to outstanding mechanical properties compared with conventional biocomposites depending on the used fibre types (Huber et al., 2012).

Cellulose is not amenable to melt-processing due to extensive intra- and inter-chain hydrogen bonding. However, cellulose can be dissolved with a suitable solvent and then re-solidified (or *regenerated*) by the removal of the solvent. An ACC is either synthesised from (i) completely dissolved cellulose combined with undissolved cellulose and subsequent regeneration to form the matrix phase (Nishino et al., 2004) or (ii) partial dissolved cellulose in which the partially dissolved portion is regenerated *in situ* to form a matrix adjacent to the undissolved portion (Gindl & Keckes, 2005). Regeneration is achieved *via* solvent exchange with an anti-solvent, such as water or alcohol (Pinkert, Marsh, Pang, & Staiger, 2009). The various processing routes for ACCs and the effect on their properties have been recently reviewed in detail by Huber et al. (2012).

ACCs reported in the literature are invariably in the form of a thin film (<1 mm thickness). However, the use of ACCs in the form of a thin film limits the applications of ACCs particularly since their mechanical properties have potential in structural applications. Additionally to structural limitations, Duchemin reported

* Corresponding author. Tel.: +64 33642987; fax: +64 33642078.
E-mail address: mark.staiger@canterbury.ac.nz (M.P. Staiger).

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http://dx.doi.org/10.1016/j.carbpol.2012.05.047

problems with differential shrinkage and resulting lateral shear stresses in the films. The shrinkage is the result of water diffusion processes during composite processing and a high water uptake of the strongly hydrophilic cellulosic material (Duchemin, 2008). In the present work, a new approach to the synthesis of ACCs termed solvent infusion processing (SIP) is developed with the aim of producing thick (>1 mm), continuous rayon fibre-reinforced ACC laminates for the first time. Conceptually, SIP is similar to vacuum-assisted resin transfer moulding (VARTM) (Williams, Summerscales, & Grove, 1996).

2. Experimental procedures

2.1. Experimental materials

1-Butyl-3-methylimidazolium acetate (BmimAc) (BASIONIC BC 02^{TM}, Sigma–Aldrich) was dried in a vacuum oven at 80 °C for 5 days prior to use to remove residual moisture. An experimental textile based on rayon fibre (Cordenka^{TM} K2/2 twill weave, surface mass = 450 g/m^2, thickness approx. 0.55 mm) composed of regenerated cellulose in the form of cellulose II (crystallinity ≈ 45%) was used as the *sole* precursor material for synthesising the ACCs. The textile was based on a multifilament yarn (Cordenka 700, 1840 dtex, f 1000) with a filament diameter of 12 μm. A single filament of the Cordenka fibre is reported to have a tensile strength of 830 MPa, a Young's modulus of 20 GPa and a strain to failure of 13% (Wunderlich & Zimmerer, 2011). The textile was dried in a vacuum oven at 80 °C for 24 h prior to processing. Four layers of the textile were used to prepare ACC laminate samples of ~120 mm × 120 mm.

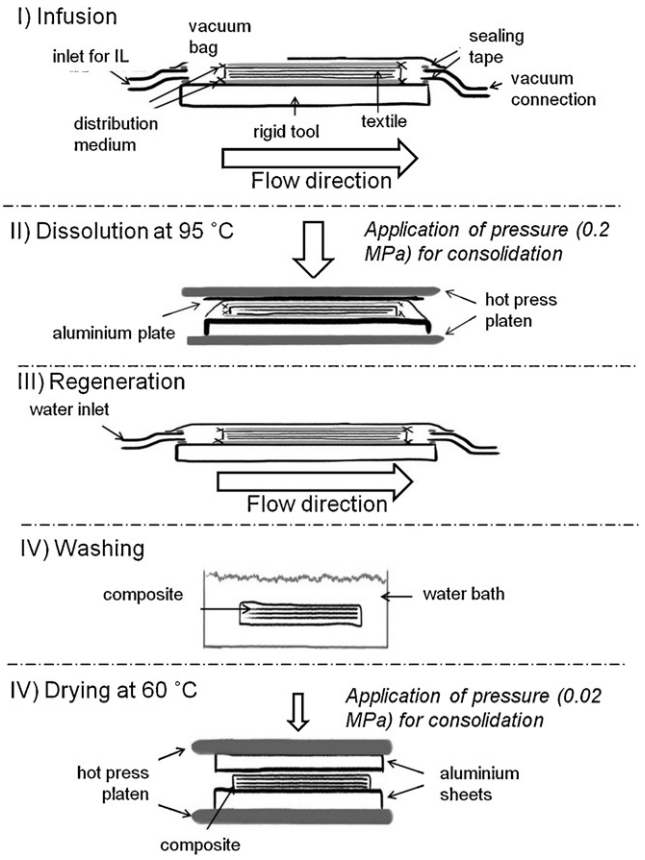

Fig. 1. Schematic of the apparatus and 5 stages of SIP.

2.2. Solvent infusion processing

Solvent infusion processing of ACC laminates involves five distinct stages shown schematically in Fig. 1. The textile layers were placed between two sheets of perforated plastic film to (i) improve the distribution of the IL and water and (ii) prevent migration of the cellulose–IL solution, following the IL infusion. Distribution media was used to enhance the flow of the IL across the textile layers (Fig. 2). A vacuum pump maintained a constant pressure differential of 0.1 MPa during the solvent infusion. The textile layers were partially dissolved by holding at a temperature of 95 °C for 60 min after the infusion. The partially dissolved assembly of layers was then infused with distilled water to regenerate the dissolved cellulose. A mixture of water and IL was removed from the mould and collected in a vacuum trap. The regenerated laminate was then removed from the mould and washed in a 1:1 mixture of ethanol and water for 12 h. Finally, the laminate was press-dried in a hot press at 60 °C and 0.02 MPa for 8 h. Collection of the water–IL mixture followed by evaporation of the water allows the recovery of the used IL.

The effect of the inlet and vent positioning on solvent flow during infusion, and thus the efficiency of the dissolution process, was investigated using either a radial or rectilinear infusion set-up (Fig. 2). Three variants of the infusion procedure were examined: (i) radial infusion followed by sealing the mould (inlet and vent), placing the assembly in an oven at 95 °C for 60 min, and regenerating with an infusion of 500 ml of distilled water (L1); (ii) as for (i) except the vacuum pressure (0.1 MPa) was reapplied every 30 min for 10 min with a total dissolution time of 90 min in the oven (L2); and (iii) rectilinear infusion followed by the assembly being placed in the hot press at 95 °C and 0.2 MPa for 60 min, and regenerating in a 2 l bowl of distilled water (L3).

2.3. Microstructural characterisation

Samples were prepared for scanning electron microscopy (SEM) by drying in a vacuum oven at 80 °C for 24 h, and then placing the samples on carbon tabs and gold coating them for 180 s at 25 mA. SEM was performed with a JEOL7000F FE-SEM using an accelerating voltage of 10 kV.

2.4. Tensile testing

Six samples each with dimensions of 110 mm (length) × 10 mm (width) × 1.6–2.3 mm (thickness) were cut from the laminates using a diamond saw. The samples were tensile tested with an MTS 858 tabletop system with a 2.5 kN load cell at a cross-head speed of 2 mm/min and the cross-head displacement was used to calculate strain values. The gauge length was 40 mm. The samples were conditioned at 23 °C at a relative humidity of 50% for 24 h prior to testing.

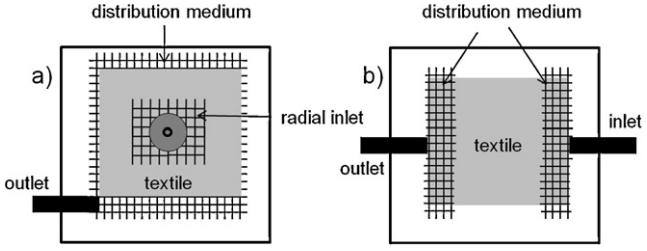

Fig. 2. Top view schematics of the (a) radial infusion and (b) rectilinear infusion set-ups used in SIP. The perforated plastic film is not shown in the schematics.

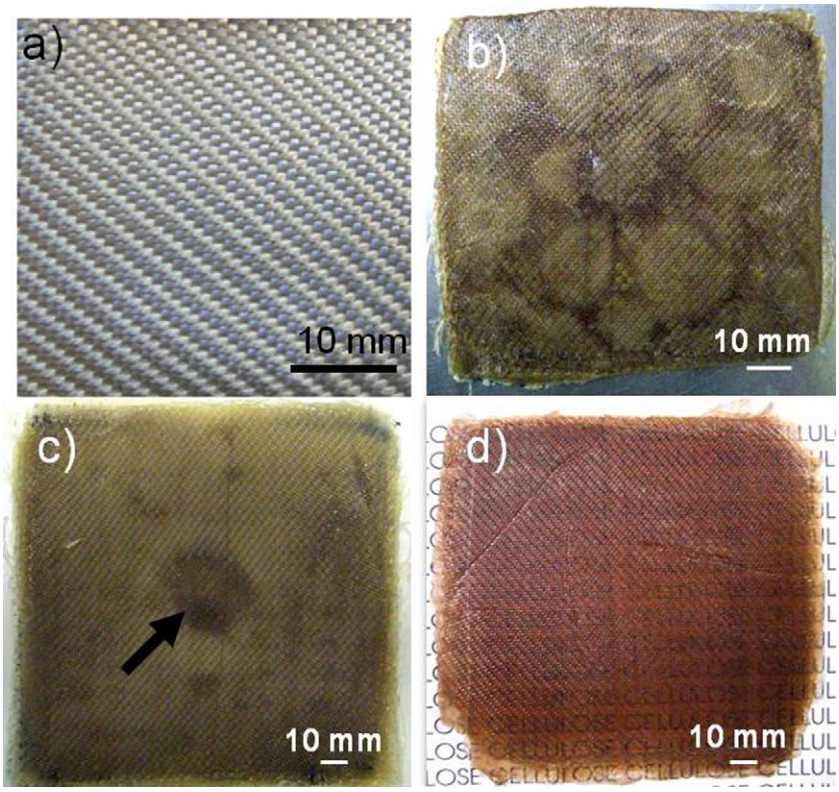

Fig. 3. Photographs of the original textile (a) and laminates L1 (b), L2 (c) and L3 (d). The arrow indicates an imprint left at the site of the infusion inlet for L2.

3. Results and discussion

SIP was observed to be a facile method for producing strong cellulose-based laminates that are more than three times thicker than the thickness of ACC films reported in the literature. The process could easily be extended to the production of ACC laminates that are several millimetres thick by simply increasing the number of textile layers used during SIP. No dimensional shrinkage or warpage was observed for the ACCs processed in this work. Hence, SIP provides a viable route for upscaled production of thick ACC laminates in a commercial setting. A similar approach describing the formation of open networks of biopolymer fibres from natural fibre textiles has been recently illustrated by Haverhals, Reichert, De Long, & Trulove (2010).

All of the set-ups successfully produced consolidated ACC laminates based on 4 layers of the textile. However, significant differences in their consolidation behaviour and final thickness could be observed depending on the processing conditions. The final thickness of ACC laminates is a strong function of the applied pressure, reducing the average thickness of the laminates by 5% to 2.28 ± 0.06 mm for L1, by 21.25% to 1.89 ± 0.06 mm for L2 and by 31.5% to 1.66 ± 0.04 mm for L3.

The distribution medium and inlet used in the radial set-up were pressed into the dissolved and malleable portion of the cellulosic textile during the pressure application of L2, leaving a distinct imprint in the centre of the panel (Fig. 3c). Thus, the distribution medium was placed only on the sides of the textile layers for the rectilinear infusion set-up.

In this work, a process was developed to produce ACC laminates with extensive inter- and intralaminar bonding and minimal void formation during regeneration and drying. All of the ACC laminates exhibited extensive inter- and intralaminar bonding. However, L1 exhibited large interlaminar (Fig. 4a) and intralaminar (Fig. 4d) voids, while smaller interlaminar voids were visible for L2 (Fig. 4b). Overall L2 exhibited improved compaction and interlaminar bonding compared with L1 while L3 exhibited the greatest interlaminar bonding with only few voids being present (Fig. 4c). Interestingly, additional to intralaminar voids, the interlaminar voids present in L1 (Fig. 4d) were only observed to a very small extent in L2 (Fig. 4e) and were completely negligible in L3 (Fig. 4f) showing that increasing the applied pressure *during* dissolution appears to improve the interlaminar adhesion. The presence of interlaminar and intralaminar bonding in L1 demonstrates that the locally dissolved cellulose remains close to the fibre core in the absence of applied pressure. On the contrary, fluctuations in the applied pressure in L2 cause a change in the capillary "ebb-and-flow" movement of the dissolved cellulose through the assembly, with backflow occurring if the pressure is released probably causing the interlaminar voids. The constant pressure applied during dissolution of L3 resulted in a more effective distribution of the dissolved cellulose filling any present voids.

The improvement of interfacial bonding as a result of applied pressure is reflected in the tensile properties of the three composites, with L3 showing the highest tensile strength of 91.12 MPa and Young's modulus of 4.1 GPa compared to L1 (64.99 MPa, 1.08 GPa) and L2 (71.61 MPa, 2.71 GPa) (Fig. 5). Although the herein achieved properties are lower than of several other ACCs described in the literature (*cf.* Huber et al., 2012), the described process could be easily extended to unidirectional textiles and/or stronger fibres to improve the tensile properties. The observed relationship between microstructure and tensile properties clarifies the critically important role of applied pressure *during* both the dissolution and regeneration of the cellulose source to the final quality of the ACC laminate.

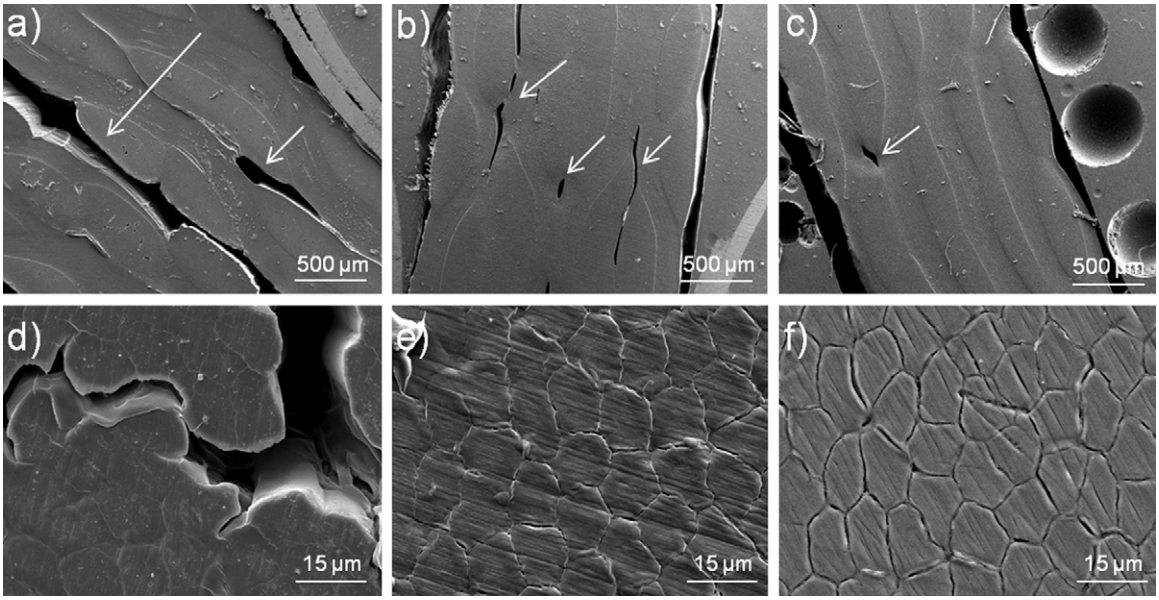

Fig. 4. Scanning electron micrographs of the as-processed microstructure of ACC laminates: L1 (a and d), L2 (b and e) and L3 (c and e) at 50× (top row) and 1500× (bottom row) magnification. Arrows indicate the presence of interlaminar voids. Image (d) shows the big intralaminar voids present in L1.

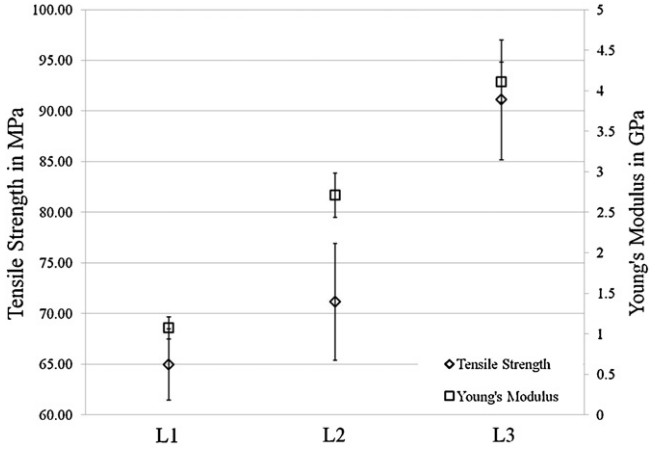

Fig. 5. Tensile strength and Young's modulus of the three produced laminates L1, L2 and L3.

4. Conclusions

- A facile method, termed solvent infusion processing (SIP) and based on a partial dissolution approach, has been developed for the manufacture of thick ACC laminates based on simple 2D cellulosic textiles showing no dimensional shrinkage.
- Applied pressure *during* cellulose dissolution is necessary to achieve high levels of compaction in the final ACC laminate, which in turn significantly affects the tensile properties of the laminate and prohibits warpage of the laminates.
- The more uniform application of pressure of the rectilinear infusion set-up results in a better fibre–matrix interface and improved tensile properties.

Acknowledgements

The authors acknowledge the financial support of the New Zealand Foundation for Research, Science, and Technology. The authors are grateful to Cordenka™ (Obernburg, Germany) for kindly providing the Cordenka™ textiles used in this study. The authors thank Mr. M. Flaws for technical assistance.

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