IMPACT AND FLEXURAL STRENGTH OF RAYON BASED ALL-CELLULOSE COMPOSITE LAMINATES

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1 General Introduction

Cellulose is the most abundant biopolymer on earth, providing a sustainable and biodegradable source of polymeric material. The specific strength of cellulose has been ranked as the highest among all natural materials although the mechanical properties of cellulose-reinforced polymer composites often fall short of expectations due to insufficient bonding between the cellulose and polymer matrix. Especially the low impact properties of many natural fibre reinforced composites reduce their potential for a substitution of non-sustainable materials in industrial applications [1, 2].

In a new type of monocomponent composite, so-called all-cellulose composites (ACCs), interfacial bonding problems are negated by using cellulose for both the reinforcement and the matrix. Strong hydrogen bonds are hypothesised to yield strong adhesion between the cellulosic matrix and fibres, thereby improving the mechanical properties and providing an “interfaceless” composite material [3]. A good fibre-matrix adhesion allows an improved load transfer throughout the composite and will determine its mechanical properties [4]. So far produced ACCs showed outstanding values for tensile strength and stiffness reaching values up to 910 MPa [5] and 26 GPa [6], respectively, supporting the idea of a superior interface leading to good mechanical properties.

Cellulose requires dissolution in an appropriate solvent as it is not amenable to melt-processing. Following the dissolution, the solvent has to be removed by the introduction of an anti-solvent such as water or ethanol; this usually results in a solidification of the cellulose, commonly referred to as regeneration. In recent years ionic liquids (ILs) have become an attractive alternative, first reported by Swatloski et al. in 2002 [7]. Ils are organic salts that persist in the molten state below 100 °C. Several IL cation and anion combinations have been reported to exhibit high cellulose dissolution capacity, recyclability and low vapour pressure compared to other solvent systems of cellulose [8].

Two different ways have been described to form an ACC using a solvent system; (i) complete dissolution of a portion of cellulose followed by mixing this portion with additional reinforcing cellulosic material [9] and (ii) partial dissolution of a cellulosic fibre to form a matrix phase in situ around the remaining fibre core [3].

However, the production of ACCs has been limited to labour-intensive, small quantities of thin films produced in laboratory experiments. Until now, neither flexural nor impact properties of ACCs have been reported. Therefore, we will present impact and flexural data of thick ACC laminate made from a rayon textile in this paper.

2 Materials and Methods

2.1 Materials

The ionic IL 1-Butyl-3-methylimidazolium acetate (BmimAc) (BASIONIC BC 02™, Sigma-Aldrich) was used as a cellulose solvent. As a cellulose source, a rayon textile was used (CordenkaTM K2/2 twill weave, surface mass=450 g/m^2), composed of regenerated cellulose in the form of cellulose II (crystallinity ≈ 45%).

2.2 Processing

To produce one ACC laminate, five layers of the Cordenka textile (130 mm x 130 mm) were infused with approximately 40 grams of the IL. A hot press (Gibitre Instruments, Bergamo, Italy) was used to apply 2 bar pressure for 60 min during the dissolution process at 100 ˚C, followed by an infusion with approximately 250 ml of distilled water to remove the IL and 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 for all the infusion processes. Afterwards the composites were dried under light pressure of 0.2 bar for 4 hours at 90 ˚C.

2.3 Experimental Methods

3-point bending tests were conducted on a 581 tabletop system (MTS, Eden Prairie, MN USA) with a 2.5 kN load cell according to ASTM D790 to determine the flexural strength of the ACCs.
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.
Additional impact tests were executed in accordance with DIN EN ISO 179 to determine the unnotched Charpy impact strength. 12 samples of 80 x 10 x 3 mm were tested in parallel impact direction using a 4 J pendulum.
The fracture surface of tested samples were sputter coated using an Emitech K975X coater (Quorum Technologies Ltd, East Grinstead, United Kingdom) with a gold target for 120 seconds. SEM analysis was performed using a JEOL 7000F FE-SEM (JEOL Ltd, Tokyo, Japan) using an acceleration voltage of 5 kV.

3 Results and Discussion

3.1 Impact testing

The ACCs showed a good impact response with a combination of different failure modes such as fibre fracture and delamination shown in Figure 2b & 2e. The four typical failure modes have been identified as (i) matrix failure, meaning 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) penetration [10]. The four failure modes mentioned above can be identified in Figure 1 showing the plot of force vs. displacement for one puncture impact sample. The matrix phase will transfer the applied load to the fibre, resulting in fibre fracture, while the fibres stay connected. The intact matrix phase between individual fibres can be seen in Figure 2 d & 2f. In contrast, in the case of delamination, less of the fibre might have been dissolved resulting in areas of weak adhesion and therefore delamination (cf. Figure 2c).
While both failure modes contribute to the high impact strength of the ACCs, large amounts of the impact energy will be dissipated by breaking up the strong hydrogen-bonding network connecting the individual fibres, or fracturing the small amounts of matrix present between all fibres. Furthermore, the high elongation of the used rayon fibre does also improve the impact behaviour, as it has been shown that the impact strength of a natural fibre composite can be enhanced by the addition of high strain fibres [11].
The average unnotched Charpy impact strength of the four tested samples was 41.54 kJ/m^2 (±4.44 kJ/m^2). All samples showed hinge break behaviour, meaning an incomplete break such that both parts of the specimen are held together only by a thin peripheral layer in the form of a hinge having low residual stiffness. The reported values for Charpy impact strength support the assumption of a good impact behaviour, compared to other biocomposites using jute fibre and polyester resin (31.87 kJ/m^2 [12], 29 kJ/m^2 and 27 kJ/m^2[13]).

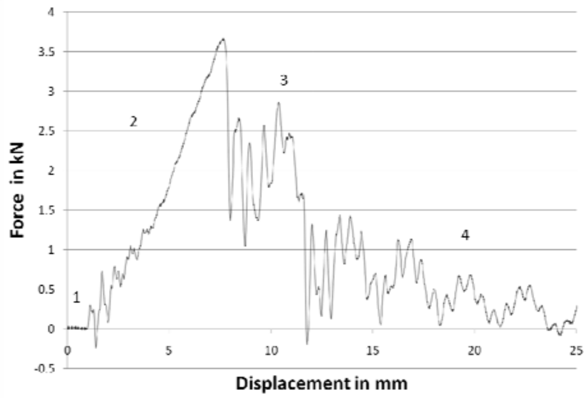

Fig.1. Plot of force vs. displacement for a drop-impacted tested ACC laminate sample. Typical failure modes are indicated by the numbers 1-4.

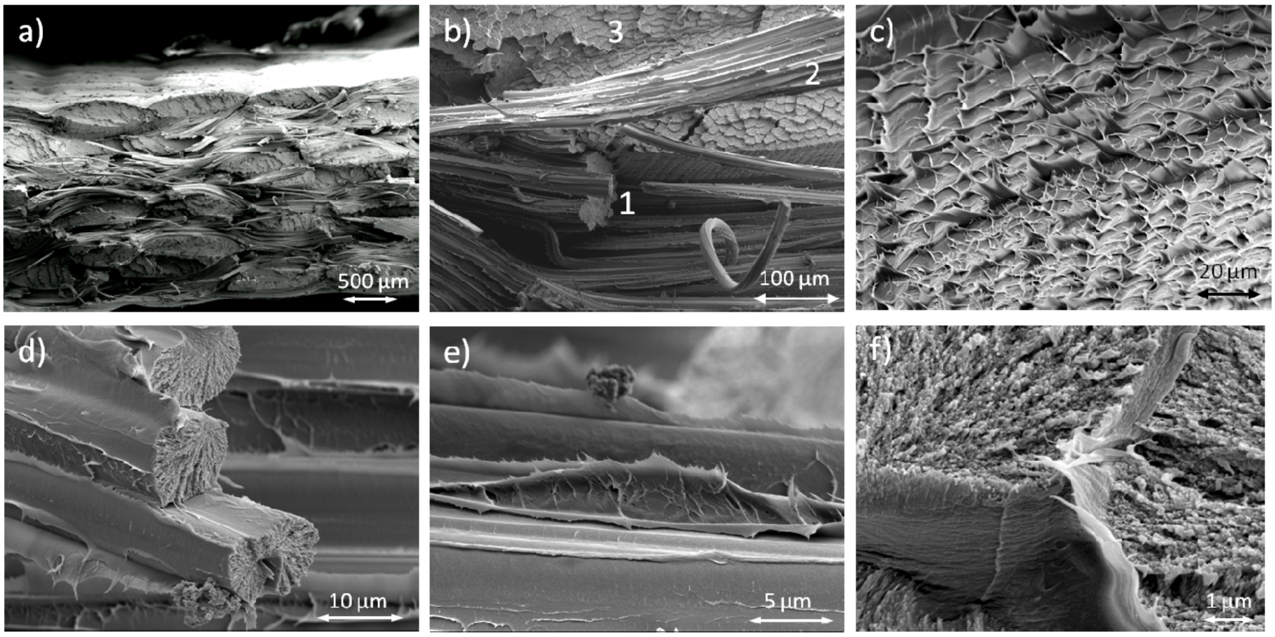

Fig. 2. SEM images of the fracture surface of an impacted tested ACC laminate. 3 a) shows an overview of the cross-section, 3 b) shows occurring failure modes with (1) fibre fracture, (2) fibre delamination, (3) fracture of a complete yarn. 3 c) shows the delamination of a yarn, 3 d) fractured fibres, 3 e) delaminated fibres and 3 f) the fracture surface of two single fibres.

3.2 Flexural testing

The average flexural strength of the tested samples was 135.24 MPa (± 11.16 MPa); the average flexural modulus was 3.72 GPa (±0.34 GPa). A step-wise decrease in stress after reaching the maximum before actual sample break was observed in all samples, indicating failure within the sample. The failed sample, however, does not show signs of clear interlaminar failure, as can be seen in Figure 3. It seems possible that in a mode similar to the impact sample, a delamination of collectives of fibres and individual fibres occur before the sample cracks. The gradual decrease in strength before complete failure does support this assumption.

The strong interface between individual fibres and matrix phase results in composite laminates with high flexural strength [4]. However, the failure mode does indicate a separation between fibre and matrix, therefore the composites cannot be classified as truly “interfaceless”. This can be explained by the structural changes of the cellulose crystals during dissolution and regeneration.

Zhao et al. reported that cellulose I or native cellulose, when dissolved in the IL 1-Butyl-3-methylimidazolium chloride and regenerated transforms into cellulose II [14]. It is not known if similar structural changes occur when cellulose II is used as a starting material and dissolved and renerated in an IL. However, structural changes from cellulose II to cellulose IV_2 can occur under certain conditions [15, 16]. Thus, crystalline differences between matrix and reinforcing phase cannot be ruled out. Nishino et al. and Soykeabkaew *et al.* observed an overall decrease in crystallinity of dissolved and regenerated cellulose [5, 17]. Furthermore, Duchemin *et al.* found that dissolved and undissolved portions of cellulose will swell by different amounts which upon regeneration again can cause differential shrinkage during regeneration, leading to the formation of voids at the fibre-matrix interface [18]. It can therefore be assumed that in spite of being chemically identical, structural changes between matrix and reinforcing phase inhibit the formation of an interfaceless composite.

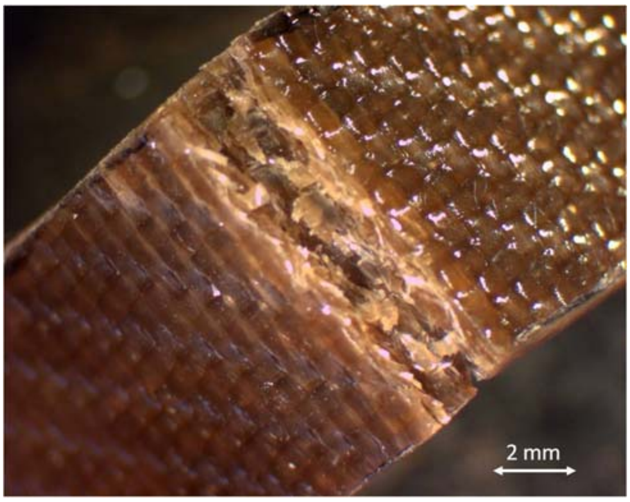

Fig. 3. Fracture of a tested 3-point bending ACC laminate sample.

Conclusions

It has been demonstrated that all-cellulose composite made from a rayon textile have a high impact strength. The ACC response to punctural impact shows two different modes (i) fibre failure and (ii) fibre delamination. As a result of the manufacturing process, all fibres in the composite are surrounded by the cellulosic matrix phase. The strong fibre-matrix interface is likely to dissipate large amounts of the impact energy in the process of breaking the hydrogen bond network present between fibre and matrix causing crack propagation through the matrix phase before fracturing the fibres. In combination with the high strain of the Cordenka fibre compared to often used bast fibres, this leads to a higher impact strength. This assumption could be supported by the high Charpy impact strength of the tested composites.

The flexural strength of the ACC laminates has been shown to be superior to many other biocomposites, and this also results from the strong interfacial adhesion present in these materials. Especially the combination of high flexural and impact strength can unusually not be found in the more common bast fibre reinforced composite, showing the high potential of this new class of composites.

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