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Biodegradability of all-cellulose composite laminates

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ABSTRACT

The high mechanical properties of single-polymer composites based on degradable non-derivatised cellulose, *aka* all-cellulose composites, have recently captured the attention of researchers. All-cellulose composites possess the intriguing combination of high strength and biodegradability. However, the biodegradation behaviour of all-cellulose composites has so far not been reported. In this work, soil burial experiments were carried out to compare the biodegradation behaviour of all-cellulose composites with conventional biocomposites in order to investigate the end-of-life disposal of this relatively new class of bio-based composite materials. All-cellulose composites are characterised by exceptional biodegradability with mass losses of up to 73% following a soil burial time of 70 days. An investigation of the mechanisms of biodegradation of all-cellulose composites is undertaken for the first time.

1. Introduction

Cellulose is a biopolymer readily available in vast quantities, combining low density (1.53–1.89 g/cm^{-3} [1]) with relatively high tensile strength (17.8 GPa [2]) and Young's modulus (138 GPa [3]). The potential for high mechanical properties makes either natural or regenerated cellulose fibre an attractive option as a "green" reinforcement for composite materials [4–6]. The increasing use of natural or regenerated cellulose fibres over petrochemical-derived fibres improves the CO_2 balance due to sequestering of CO_2 during the cultivation of natural fibre [7].

Bio-based composites are a class of composite materials that are defined as having at least one of their component phases (*i.e.* matrix or reinforcement) derived from biomass [8,9]. Recent heightened activity in the development of bio-based composites is a reaction to the escalating problem of end-of-life disposal of plastic materials and reducing number of available landfill sites [10]. Mohanty et al. [5] reported in 2000 that 10 million tons per annum of waste plastic alone was generated in the US and European Union. Bio-based composites are now found in a wide variety of both short term (*e.g.* packaging) and long term (*e.g.* automotive, construction, *etc.*) applications [9]. Currently, the most commercially-important bio-based composites have matrices that are based on petrochemical-derived polymers such as polypropylene, polyethylene and epoxy resins, and reinforcement based on a variety of natural cellulosic fibres including wood pulp, flax and hemp [11].

The main disadvantages of current industrial bio-based composites are their (i) structural or chemical inhomogeneities due to natural variations during cultivation and post-harvest processing conditions of natural fibres; (ii) poor interfacial adhesion between the hydrophilic cellulosic reinforcement and hydrophobic matrix phases, resulting in inefficient transferral of load from the matrix to the reinforcement [9]; and (iii) problematic end-of-life disposal of the matrix phase, where non- or slowly-degrading petrochemical-derived thermoplastics or bio-based polymers are used. In general, regenerated cellulose fibres (*e.g.* Viscose, Modal, Lyocell, Cupro, *etc.*) offer greater consistency in terms of mechanical properties, fibre structure and fibre diameter when compared with natural fibres [12,13]. Hence, the use of man-made cellulose fibres in bio-based composites avoids many of the inhomogeneities that are introduced by natural fibres. Various physical and chemical treatments have been applied to increase fibre–matrix interfacial adhesion [14] although invariably these increase the processing steps and cost of producing bio-based composites [15–17]. Common commercially-important bio-based polymers such as the polylactides are found to degrade very slowly without elevated temperature composting conditions [18,19].

Single-polymer bio-based composites based solely on non-derivatised cellulose were investigated with the aim of improving the fibre–matrix interfacial bonding through the use of chemically identical reinforcing and matrix phases [20]. Nishino et al. coined the term "all-cellulose composites" for this new class of materials. In general, single-polymer composites have the advantage of ease of recyclability (either for reuse or end-of-life disposal) since the separation of chemically-identical reinforcing and matrix phases

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becomes unnecessary. Additionally, both the reinforcing and matrix phases should undergo biodegradation for the case of an all-cellulose composite. While the mechanical properties of all-cellulose composites are reasonably well known [21–23], there is no published work regarding the details of their biodegradation behaviour.

In the present study, the biodegradability of an all-cellulose composite (ACC) based on regenerated cellulose fibre is examined *via* soil burial experiments that simulate degradation in a biologically-active environment. The biodegradability of regenerated cellulose fibre-reinforced polylactides (PLA) composites was also examined so as to make comparisons with the ACC. The biodegradability of natural materials can also be controlled *via* additives such as fungicides [24]. Thus, the efficacy of a fungicide on hampering the biodegradation process in the ACC was also evaluated as means of controlling the onset of biodegradation during the practical application of ACCs.

2. Experimental procedures

2.1. Fabrication of all-cellulose composite laminates

ACCs were synthesised *via* solvent infusion processing (SIP) as described in detail by Huber et al. [25]. Briefly, four layers of rayon textile (Cordenka™ K2/2 twill weave, surface mass = 450 g/m^2, thickness approx. 0.55 mm; Cordenka GmbH, Obernburg, Germany) were used as a precursor for the synthesis of an ACC laminate. An ionic liquid (IL), 1-butyl-3-methylimidazolium acetate (BmimAc) (BASIONIC BC 02™, Sigma-Aldrich, St. Louis, USA), was selected as the solvent for cellulose. BmimAc was dried in a vacuum oven at 80 °C for at least 48 h prior to SIP. SIP was then used to partially dissolve the cellulose fibres [26]. Cellulose dissolution was undertaken within a hot press (Laboratory Press, Gibitre Instruments, Bergamo, Italy) by applying a pressure of approximately 1 MPa at a temperature of 100 °C for 1 h. The removal of BmimAc and regeneration of the cellulose was performed by washing with ethanol (97% purity, Thermo Fisher Scientific, Waltham, USA). Subsequent drying of the cellulose led to a fully consolidated ACC laminate. The regenerated cellulose fibre changes from a white to brownish coloration during production of the final ACC laminates due to some partial degradation of the cellulose by BmimAc [27].

An environmentally-safe fungicide (Mycostat, Damolin Hamburg GmbH, Germany) was also used to investigate its influence on the biodegradation behaviour of ACC laminates. 0.3 g of fungicide was applied manually to each side of the layers of rayon textile prior to SIP. The active ingredients of the fungicide and concentrations are propionic acid (2.8–2.9 mass%), ammonium propionate (0.1–1 mass%), sorbic acid (0.1–1 mass%). The fungicide-treated laminates are referred to as ACC-f, while the untreated laminates are referred to as ACC-u. The retention of the fungicide post-regeneration was also examined by simple immersion in ethanol. 2 g of the fungicide was placed in a Petri dish and equilibrated at 23 °C and 50% RH in a Vötsch VCL 4003 climate cabinet (Vötsch Industrietechnik GmbH, Balingen-Frommern, Germany) until the mass change (Kern Analytical balance ABT 120-5DM, Kern & Sohn GmbH, Balingen-Frommern, Germany, precision: 0.1 mg) was less than 0.1%. The fungicide was then completely immersed in 10 ml of ethanol for 24 h at ambient conditions during which time the ethanol was completely evaporated. The residual fungicide was then weighed after equilibrating for constant mass at 23 °C and 50% R.H.

2.2. Fabrication of rayon fibre-reinforced PLA composites

Cellulose fibre-reinforced polylactide (PLA) granules with a diameter in the range of 2.5–3.5 mm were produced by Cordenka GmbH (Obernburg, Germany). The granules were reinforced with 20 wt.% rayon fibre using "Composite Reinforcement (CR) fibres" developed by Cordenka. CR grade has been specifically developed for thermoplastic melt processing. The matrix polymer of the granules was a standard PLA injection moulding grade from NatureWorks LLC (Minnesota, USA) [28]. The rayon-PLA granules were dried for 3 h at 85 °C prior to injection moulding (Plus 250/50 injection moulding machine, Wittmann Battenfeld GmbH, Kottingbrunn, Austria). The composites were then injection moulded into a dog bone shape according to DIN EN ISO 527 by J.H. Tönnjes GmbH & Co. KG (Delmenhorst, Germany). The injection moulding temperature was kept below 190 °C to prevent thermal degradation of the rayon. The mould temperature was maintained in the range of 40–50 °C.

2.3. Biodegradation testing

Coupons were cut from the ACC laminates and rayon-PLA composites with a coupon size of 30 × 30 × 2 mm and 20 × 22 × 3 mm, respectively. The coupons were preconditioned by drying at 80 °C in a vacuum oven for at least 48 h. The initial dry mass of the coupons was recorded. Soil burial tests were performed using 10 replicates.

Biodegradation testing was conducted inside a controlled environment growth cabinet (Plant Growth Cat 620, Contherm Scientific Company, Lower Hutt, New Zealand). The ambient temperature (T1) in the cabinet was set to 22.5 °C (±0.41 °C) that gave a temperature of 20.83 °C° (±0.82 °C) in the soil. Soil burial testing was also performed at an elevated temperature (T2) using a cabinet temperature of 36.75 °C (±4.19 °C) that led to a soil temperature of 33.45 °C (±2.39 °C). The soil used in the experiments was a 1:1 mixture of mature leaf compost and soil taken from local flowerbeds (University of Canterbury, Christchurch, New Zealand). Coupons were buried in plant pots at a depth of at least 50 mm. The approximate moisture content of the soil-compost mixture for T1 and T2 was 51% and 28%, respectively. A sprinkler system was used to dispense approximately 300 ml of non-chlorinated tap water within the cabinets twice a day in order to maintain the moisture content of the soil. Additionally, cotton strips (25 × 100 mm) were buried in each plant pot to verify both the presence of cellulose degrading microorganisms and their relative activity. The cotton strips were completely decomposed following 6 weeks of burial, confirming the activity of the microorganisms.

The coupons were removed from the soil after 28, 42, 56 and 70 days, carefully washed and weighed in the wet state (Sartorius ED224S analytical lab balance, Sartorius, Göttingen, Germany, precision: 0.1 mg) in order to determine the mass loss. Three 5 × 10 mm samples were taken from one of the coupons after 56 days and mounted in Epofix cold-setting resin (Electron Microscopy Sciences, Hatfield, PA, USA). The mounted samples were then polished to a grain size of 1 μm according to ASTM E3-01 (2007) to observe the microstructure within the cross-section using electron microscopy. Sections of approximately 2 × 2 mm were also cut from the coupons and mounted on carbon tabs to analyse the surface of the composites. Samples were gold coated for 120 s at 25 mA using an Emitech K975X coater (Quorum Technologies Ltd., East Grinstead, United Kingdom) for analysis by scanning electron microscopy (JEOL 7000F FE-SEM, JEOL Ltd., Tokyo, Japan). An accelerating voltage of 5 kV was used during secondary electron imaging.

After 70 days all remaining samples were removed from the soil. The specimens were washed, weighed in the wet state, and then dried until no further mass change could be observed to determine the total loss in dry mass.