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Stress transfer in microfibrillated cellulose reinforced poly(vinyl alcohol) composites

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ABSTRACT

Combined homogenisation and sonication treatments of micron-sized lyocell fibres were used to generate microfibrillated cellulose (MFC) with fibril diameters of ~350 nm. No further reduction in fibril diameter was observed after 30 min treatment. Poly(vinyl alcohol) (PVA) composites reinforced with these fibrils were fabricated using solvent casting and physical and mechanical properties were investigated. The presence of MFC in PVA increased the thermal degradation of the polymer. An increase in both the tensile strength and modulus of the composites was observed for up to 3 wt.% of fibrils; beyond this point no significant increases were observed. An estimate of ~39 GPa is made for the fibril modulus based on this increase. Stress-transfer between the polymer resin and the fibrils was investigated using Raman spectroscopy. Stress transfer in the composite is shown to be greater than that of a pure network of fibres, indicating a good fibre–matrix bond.

1. Introduction

The term microfibrillated cellulose (MFC), was introduced in 1983 by Herrick et al. [1] and Turbak et al. [2] to describe high aspect ratio cellulosic fibrils with diameters of 10–100 nm and lengths of several tens of microns obtained by high-pressure homogenisation of wood pulp suspensions [1–3]. It has subsequently been established that MFC can be readily prepared using a range of mechanical treatments including grinding, microfluidising, sonication and homogenisation [1,3–9]. Interest in the use of MFC to reinforce a polymer composite has grown over the last decade due to the fibres' high aspect ratio, crystallinity, stiffness and specific surface area [3,10].

The crystal modulus of cellulose has been measured as about 138 GPa using an X-ray diffraction method [11,12]. A similar value of 143 GPa for the modulus of highly crystalline tunicate cellulose nanowhiskers, obtained using Raman spectroscopy, has also been reported [13]. Values in the range 29–180 GPa have been reported for cellulose fibrils produced from a variety of sources including wood fibres [14,15], bacterial cellulose [16,17], tunicates [18] and regenerated cellulose [14]. A recent modelling study has placed the modulus of MFC fibrils as low as 65 GPa [19], and some estimates, using Raman spectroscopic methods give values lower still at 29 GPa [15]. MFC has been previously used to prepare composite materials with a large number of polymers such as poly(lactic acid) (PLA) [7,10], poly(vinyl alcohol) (PVA) [8,20,21], polypropylene [20], polyurethane [22], phenol formaldehyde resin [23] and acrylic resin [24,25].

The effect of MFC on the mechanical properties of composites has been previously studied. The strength and stiffness of a 16.5 wt.% MFC/polyurethane composite was found to be greater than that of the pure polymer by factors of 5 and 30 respectively [22]. Similarly, Lu et al. [8] found that MFC reinforced PVA composites showed enhanced mechanical properties compared to the pure resin. The strength of MFC reinforced phenol formaldehyde resin composites was found to increase by ~50% compared to the pure resin [23]. Suryanegara et al. [10] compared the tensile strength and Young's modulus of PLA reinforced with 10 wt.% MFC with those of the pure PLA; although tensile strength increased by only about 10%, the Young's modulus increased by almost 30%. In part, these increases were also due to an increase in the degree of crystallinity of the composite, since MFC acts as a nucleating agent for crystal growth.

Raman spectroscopy has been used to better understand the interfaces between cellulose nanofibres and polymer matrices [4,26,27]. The position of a Raman band initially located at

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~1095 cm^{-1}, corresponding to C–O and C–C stretching modes along the cellulose polymer backbone [28], has been monitored during tensile deformation. The stress-transfer mechanisms of polymers reinforced with MFC [4,27], bacterial cellulose [26], cellulose nanowhiskers [29–31] have been previously reported.

The interfacial bonding between MFC and PVA should be good compared to hydrophobic matrices, since both materials exhibit hydrophilicity. In the present work MFC fibrils were prepared using combined homogeniser and sonicator treatments. PVA/MFC composites were then fabricated using a solvent casting method. We report also the use of Raman spectroscopy to investigate the stress-transfer process in the composites at the interface between the cellulose and the matrix polymer. Although several studies of MFC reinforced PVA composites have been published, to the authors' knowledge, none study the stress transfer process in these composites using Raman spectroscopy. Further, whereas previous studies report results for native (cellulose-I) fibrils, here, we use cellulose-II fibrils extracted from lyocell, which has been shown to produce nanofibrils with a potential axial tensile modulus of ~90 GPa [14].

2. Experimental

2.1. Materials

Chopped regenerated cellulose fibres of length of ~10 mm produced using a draw ratio of 8.9 (trade name Tencel®), provided by Lenzing AG, Austria, were used as the raw material to prepare MFC fibrils. Poly(vinyl alcohol) (PVA) with an average molecular weight of 85,000–124,000 g mol^{-1}, purchased from Sigma–Aldrich, was used as a matrix for the preparation of composites.

2.2. MFC preparation

Lyocell fibres were soaked in distilled water for 24 h before mechanical treatment. The suspension was mechanically treated using a homogeniser (ULTRA-TURRAX TP 18/2 K, Janke & Kunkel, Staufen) at 20,000 rpm for a range of times between 10 and 60 min, and then sonicated using a high intensity sonifier (BRANSON MODEL 250, 20 kHz) at 200 W for 30 min. The MFC suspension was poured into a Petri dish, and was subsequently kept in a controlled room at a temperature of 23 ± 2 °C and relative humidity of 50 ± 2% for at least a week until MFC networks were formed upon evaporation of the liquid phase. The networks were then dried in an oven at 50 °C for 7 days. The pure MFC network had a thickness of ~110 μm.

2.3. Composite preparation

MFC reinforced PVA composites were manufactured by first preparing a 10 wt.% solution of PVA in distilled water. Different weight fractions (1, 2, 3 and 4 wt.%) of the fibrils obtained after a 30 min mechanical treatment were mixed into the PVA solution for 4 h, and were subsequently sonicated for 10 min to optimise dispersion. These mixtures were poured into a Petri dish to cast into a film, and were kept in a controlled humidity and temperature room until the films had formed. These composite films were then fully dried in an oven at 50 °C for 6 h. The thickness of the composite films measured using a micrometer was ~170 μm.

2.4. Thermogravimetric analysis

The degradation temperature of MFC reinforced PVA composites, neat PVA and 60 min treated MFC was investigated using a NETZSCH Simultaneous thermogravimetic analysis (STA) 449C instrument. Samples with a mass of 5.0 ± 0.5 mg were placed in an aluminium crucible, and then were heated in the range 30–500 °C at 10 °C min^{-1} under a 50 ml min^{-1} nitrogen purge gas flow. At least three measurements were repeated to ensure reliability of the results.

2.5. Mechanical testing

Tensile properties of the PVA composites reinforced with MFC fibrils and neat PVA resin were measured using an Instron 1121 universal testing machine equipped with a 500 N load cell. Specimens with a gauge length of 10 mm and a width of 2 mm prepared using a razor blade were tested at a crosshead speed of 5 mm min^{-1}. Before testing, all specimens were kept in a controlled room at 23 ± 2 °C and 50 ± 2% relative humidity for 48 h. At least 7 samples were tested for each material.

2.6. Raman spectroscopy

Micromechanical deformation of the PVA composites reinforced with 4 wt.% MFC and MFC networks were studied using a Renishaw system 1000 Raman spectrometer coupled to a 25 mW 785 nm near-infrared laser. A 50× objective lens and an Olympus microscope system were used to focus the laser on the samples' surfaces with a spot size ~2 μm and intensity of ~1 mW. The samples were deformed using a customised deformation rig equipped with a 2 kN load cell (Deben Microtest, Deben, Bury St Edmonds, UK). Raman spectra were recorded in the range of 1050–1150 cm^{-1} using an exposure time of 50 s (consisting of an exposure time of 10 s and five accumulations) at strain increments of 0.1%. A combined Gaussian/ Lorentzian distribution was used to determine the peak position of a Raman band initially located at ~1095 cm^{-1} using a least-squares fitting method. At least three samples were tested for each set of materials.

3. Results and discussion

3.1. Morphology of MFC fibrils

Fig. 1 shows 1% (w/w) aqueous suspensions of lyocell fibres and MFC with different mechanical treatment times (10, 20, 30, 40, 50 and 60 min). No appreciable sedimentation can be observed for MFC fibrils, even after 24 h. This lack of sedimentation is due to an increase of the degree of fibrillation, an increase in the aspect ratio and the surface area of MFC fibrils. Our observations are

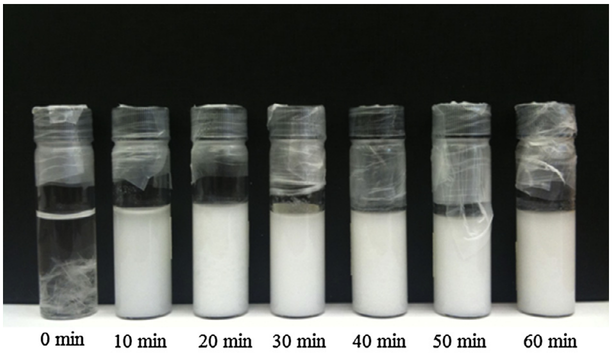

Fig. 1. Aqueous suspensions of lyocell fibres (0 min) and MFC fibrils after mechanical treatment for specific times (10–60 min). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)