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Discrimination of matrix–fibre interactions in all-cellulose nanocomposites

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ABSTRACT

All-cellulose nanocomposites are produced using dissolved microcrystalline cellulose (MCC) as the matrix and cellulose nanowhiskers (CNWs), produced by acid hydrolysis, as the reinforcement. These nanocomposites are then characterised using X-ray diffraction to determine their crystallinity, and Raman spectroscopy to discriminate the reinforcing phase (cellulose I) from the CNWs and the matrix phase (cellulose II) from the dissolved MCC. Mechanical testing of the composites shows that there is a significant systematic reinforcement of the matrix material with the addition of CNWs. Furthermore, Raman spectroscopy is used to show that distinct spectroscopic bands for each phase within the composite spectrum can be used to discriminate the effects of both reinforcement and matrix. It is shown that a Raman band located approximately at 1095 cm^{-1} can be used to follow the micromechanical deformation of the CNWs and matrix, whereas another band located at 895 cm^{-1} arises purely from the matrix. This spectroscopic fingerprint is used to gain insights into the complex interactions occurring in these potentially recyclable composite materials, and offers a way forward to optimising their properties.

1. Introduction

Cellulose is an abundant and cheap resource that can be used for a wide variety of applications; traditionally in the timber industry for construction, papermaking and for textiles. In recent times cellulose fibres have been widely reported as a possible replacement for glass fibres in composite materials, due to their comparatively lower weight, cost and for the fact that they are easier to process [1]. The mechanical properties of cellulose fibres (typically extracted from plant material, either by chemical and/or mechanical means) are known to be variable, due to growing conditions, the environment in which they are tested and damage that can occur during extraction [2]. In particular, the defects that occur in the cell walls of plant fibres are known to be sources of local stress concentrations, which can lead to premature failure and low fracture toughness of natural fibre composites [3,4]. In recent times, cellulose nanofibres (in the form of whiskers, fibrils, etc.) have been reported as possible ways to overcome the natural variability of plant fibres [5,6]. The concept is that the plant fibres can be broken down into nanosized constituent fibrous components, either by mechanical or chemical treatment. Nanofibres of cellulose that are generated by mechanical means are usually referred to as Microfibrillated Cellulose (MFC), a term that was originally coined by Turbak et al. [7]. They are generally long fibrils of cellulose and have been studied widely in terms of their reinforcement capability [8,9]. Chemical hydrolysis of plant cellulose can produce whiskers of material (sometimes called cellulose nanocrystals but herein referred to as cellulose nanowhiskers (CNWs)). These CNWs were first discovered by Ranby and Noe [10], and subsequently Revol et al. [11] showed how they could undergo chiral nematic ordering in suspension. A form of CNWs can be extracted from the tunicate sea squirt (*Halocynthia roretzi*) [12], and have also been reported to be efficient reinforcement materials in nanocomposites owing to their ability to form percolated networks [13–15].

Most cellulose fibre-based composites comprise two dissimilar phases; namely the reinforcement (fibre) and matrix phases. Typically the latter is a synthetic polymer; which raises issues when it comes to end-of-life use, particularly if recycling of the material is required. In recent times a new form of composite has been developed, whereby the matrix is reinforced with a fibre of the same material, thereby overcoming recycling issues. These all-polymer composites were initially developed through the pioneering work of Ward and colleagues at the University of Leeds, who first reported a method of hot-compacting polyethylene fibres into a single-phase composite [16]. Subsequently a large body of work has been completed in this area by this group and others, resulting in many commercial products; a review of which is beyond the scope of this article. A forerunner to the development of all-cellulose composites was the work of Glasser et al. [17–19], who reinforced a cellulose ester (cellulose acetate butyrate) matrix using regenerated cellulose fibres. Subsequently Gindl and Keckes [20] reported the reinforcement of a cellulose acetate butyrate matrix using bacterial cellulose. It was, however, Nishino et al. [21] who first used the expression “all-cellulose composite” when they reported

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remarkable reinforcement upon incorporating ramie fibres in a dissolved cellulose matrix material derived from Kraft pulp (dissolved in a solvent of LiCl/DMAc – lithium chloride and dimethylacetamide). Subsequently, Gindl and Keckes showed self-reinforcement in a composite material using partially dissolved microcrystalline cellulose [22]. After this pioneering work, a large number of papers have been published on all-cellulose composites [21–31], typically produced by dispersing fibres into dissolved matrix materials derived from a variety of sources. Some fundamental work has been undertaken on the interaction between the matrix and fibre phases in all-cellulose composites using synchrotron X-ray diffraction, whereby the crystallographic orientation of the reinforcing fibre phase could be followed, as distinct from the matrix [23].

In this study, we report the use of a Raman spectroscopic technique to follow the local deformation of an all-cellulose nanocomposite. Raman spectroscopy is a technique that has been used to map the local stress state in a variety of fibre reinforced composites [32]. The technique relies on obtaining a clear and distinct spectrum of an embedded reinforcing phase, typically using a composite with an optically transparent matrix. The position of Raman peaks within this spectrum are found to shift upon the external application of strain to the composite, this shift being related to the direct molecular or structural deformation of the reinforcing fibre. By using a variety of composite geometries, and model fits to data obtained by this approach, a picture of the interfacial behaviour between the reinforcing phase and matrix can be obtained [33–35]. The technique has been applied to cellulose fibre-based composites [36–38] and more recently cellulose nanocomposites [39–41]. We report, for the first time, the use of a Raman spectroscopic technique to discriminate between the deformation behaviour of CNW reinforcement within a cellulose matrix composite.

2. Experimental

2.1. Materials and sample preparation

Microcrystalline cellulose (MCC) (Avicel, PH-101, Sigma–Aldrich, UK; particle size ~50 μm) was used as the source of the matrix material. The solvent used to dissolve the MCC was lithium chloride (LiCl) (Sigma–Aldrich, UK; anhydrous, ⩾99.0%) and N,N-dimethylacetamide (DMAc) (Sigma–Aldrich, UK). Cellulose nanowhiskers (CNWs) were produced by acid hydrolysis of cotton linters (Whatman filter grade, Whatman).

The MCC was activated for 5 h in distilled water at room temperature to swell the material ready for dissolution. This swollen material was then sequentially dehydrated in acetone and DMAc for 5 h and 4 h, respectively, before the DMAc was decanted from the dehydrated cellulose. A solution of 8 wt.% of LiCl in DMAc was then prepared, and stirred at a temperature of 120 °C for 30 min until the LiCl completely dissolved. Then the activated MCC (2 g) was dissolved in the LiCl/DMAc solution by magnetic stirring at room temperature for 5 min. In order to prepare fully amorphous cellulose, the solution of activated MCC/LiCl/DMAc was stored in a sealed bottle for 1 week to allow full dissolvation.

CNWs were produced from cotton linters using the following process, which has been described elsewhere [40]. The cotton linters (40 g) were reacted with sulphuric acid (64 wt.%, 700 ml) at 45 °C for 45 min, after which the reaction was quenched using a fivefold dilution. The reaction media was then concentrated and rinsed by centrifugation (6000 rpm, 10 min) followed by dialysation against water until neutral pH conditions were obtained. The suspension was then sonicated, treated with mixed bed ion-exchange resin and filtered using glass microfiber filters (Whatman). The concentration of the final suspension was 2.0 ± 0.2 wt.%. To generate CNWs reinforced composite films, either 0.5 g or 1 g (to make either a 0.5% or 1% volume fraction composite, respectively) of freeze-dried CNWs were added to the dissolved MCC solution, and then dispersed using ultrasonification. The resultant viscous solution was then poured into a Petri dish and left under ambient conditions for 8 h. After a transparent gel film had formed, this was washed in distilled water, and then dried at 40 °C for 4 h.

2.2. X-ray diffraction and Raman spectroscopy

A powder X-ray diffractometer (Philips X'Pert-MPD) was used to determine the crystallinity of the composite and control samples. Activated MCC powder, CNWs and the composite samples were analysed using Cu Kα radiation, with a step size of 0.05° over a 2θ range of 5–40°. Crystallinity of the samples was determined using Segal's method [42].

Raman spectroscopy was carried out using a Renishaw System 1000 spectrometer coupled to an Olympus BH-1 microscope fitted with a 50× lens to focus the output from a 785 nm near-infrared laser to a 1–2 μm spot on the surface of the samples. The power on the sample was recorded and found to be 1 mW. Spectra were obtained using an exposure time of 600 s.

2.3. Mechanical testing of composites

Tensile testing of thin films of the cellulose nanocomposites was performed using an Instron 1121 universal testing machine. A gauge length of 50 mm and a nominal width of 5 mm was used for the dimensions of the specimens. Actual specimen dimensions (width and thickness) used to calculate stress were measured using a micrometer. All specimens were equilibrated (for 48 h prior to testing) and tested under standard conditions of 23 ± 1 °C and 50 ± 5% relative humidity. Samples were deformed in tension using a cross-head displacement rate of 1 mm min^{-1} and a 500 N (full scale) load cell was used to record the load.

2.4. Micromechanical deformation of composites using Raman spectroscopy

Raman micromechanical deformation studies were performed on individual nanocomposite samples, with gauge lengths of 50 mm, fixed onto a customised deformation rig (Deben, MICROTEST). Spectra were obtained from the nanocomposites during incremental tensile testing on this deformation rig, which fitted directly onto the microscope stage of the Raman spectrometer. The laser beam was polarised parallel to the nanocomposite sample's axis, and an exposure time of 60 s with two accumulations (total time = 120 s), was used to obtain a spectrum at each strain increment (0.1%). All samples were deformed until fracture occurred.

3. Results and discussion

3.1. Crystallinity and molecular composition of all-cellulose nanocomposites

Typical X-ray diffraction patterns for pure CNWs, a nanocomposite of CNWs and MCC dissolved in LiCl/DMAc and a pure matrix of MCC dissolved in LiCl/DMAc are reported in Fig. 1. All peaks present for the CNWs are consistent with a cellulose I structure, apart from a peak at 12°. The origin of this peak is unknown. Crystallinities for each of these samples are reported in Table 1. It is clear that the CNWs are highly crystalline (~85%). However, the matrix material of MCC dissolved in LiCl/DMAc exhibits low crystallinity (~26%). The addition of CNWs to this matrix material in-