



Deformation micromechanics of all-cellulose nanocomposites: Comparing matrix and reinforcing components

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ABSTRACT

All-cellulose nanocomposites, comprising two different forms of cellulose nanowhiskers dispersed in two different matrix systems, are produced. Acid hydrolysis of both tunicate (T-CNWs) and cotton cellulose (CNWs) is carried out to produce the nanowhiskers. These nanowhiskers are then dispersed in a cellulose matrix material, produced using two dissolution methods; namely lithium chloride/*N,N*-dimethyl acetamide (LiCl/DMAc) and sodium hydroxide/urea (NaOH/urea). Crystallinity of both nanocomposite systems increases with the addition of nanowhiskers up to a volume fraction of 15 v/v%, after which a plateau is reached. Stress-transfer mechanisms, between the matrix and the nanowhiskers in both of these nanocomposites are reported. This is achieved by following both the mechanical deformation of the materials, and by following the molecular deformation of both the nanowhiskers and matrix phases using Raman spectroscopy. In order to carry out the latter of these analyses, two spectral peaks are used which correspond to different crystal allomorphs; cellulose-I for the nanowhiskers and cellulose-II for the matrix. It is shown that composites comprising a LiCl/DMAc based matrix perform better than NaOH/urea based systems, the T-CNWs provide better reinforcement than CNWs and that an optimum loading of nanowhiskers (at 15 v/v%) is required to obtain maximum tensile strength and modulus.

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1. Introduction

Cellulose is the most “common organic polymer” and utilized material in the world (Klemm, Heublein, Fink, & Bohn, 2005). In recent years the use of cellulose nanofibres has been extensively reported in the literature as potential reinforcements in composite materials (Eichhorn, 2011; Eichhorn et al., 2010; Klemm et al., 2011). With relevance to the present work cellulose nanowhiskers were first discovered by Bengt Rånby in 1949 (Rånby, 1949). Later it was shown that these colloidal rod-like particles of cellulose could form stable chiral nematic liquid crystalline phases (Dong, Kimura, Revol, & Gray, 1996; Revol, Bradford, Giasson, Marchessault, & Gray, 1992).

Favier et al. in 1995 (Favier, Chanzy, & Cavaille, 1995) were the first to show that cellulose nanowhiskers could reinforce a polymer matrix material. Cellulose nanowhiskers have subsequently been reported to reinforce composite matrices such as epoxy resin

(Tang & Weder, 2010), polyvinyl acetate (Rusli, Shanmuganathan, Rowan, Weder, & Eichhorn, 2010), polyurethane (Mendez et al., 2011) and polyesters (Goffin et al., 2011; Ten, Turtle, Bahr, Jiang, & Wolcott, 2010). Most recently they have been reported to reinforce hydrophobic polymers such as polypropylene (Pandey et al., 2012) and poly(styrene-co-butadiene) and polybutadiene (Dagnon, Shanmuganathan, Weder, & Rowan, 2012). In all of these nanocomposites, interfaces can occur between the nanowhiskers and the matrix, between the nanowhiskers themselves through hydrogen bonding in a paper-like network, or most probably via both mechanisms. Cellulose nanowhiskers and nanofibrils from tunicates are known to possess high stiffnesses; experimental values of ~140–150 GPa have been reported (Iwamoto, Kai, Isogai, & Iwata, 2009; Sturcova, Davies, & Eichhorn, 2005). This makes them ideal for reinforcement in composite matrices. It also is well-known that cellulose nanowhiskers can form percolated networks in nanocomposite materials above a certain volume fraction (Capadona, Shanmuganathan, Tyler, Rowan, & Weder, 2008; Capadona et al., 2007; Favier et al., 1995). It is these percolated networks that form the basis for much of the reinforcement observed in the nanocomposites, and disruption of the hydrogen bonding by water has shown that this effect can be “turned off”, leading to a flexible material (Capadona et al., 2008; Rusli et al., 2010).

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All-cellulose composites have been recently developed as an alternative to the conventional approach to natural fibre composites (Huber et al., 2012). They were first developed and called “all-cellulose” composites by Nishino et al. (Nishino, Matsuda, & Hirao, 2004). They can be made by combining cellulose fibres (in nano or micron sized form) with a dissolved matrix of the same material (Huber et al., 2012). This dissolved matrix can either be combined with the cellulose fibres (Qin, Soykeabkaew, Xiuyuan, & Peijs, 2008), or the outer perimeter of the fibres themselves can be selectively dissolved to form a matrix (Nishino & Arimoto, 2007; Soykeabkaew, Nishino, & Peijs, 2009a; Soykeabkaew, Sian, Gea, Nishino, & Peijs, 2009b). Nanosized fibres from bacterial (Soykeabkaew et al., 2009a,b), microcrystalline cellulose (Abbott & Bismarck, 2010; Gindl & Keckes, 2005) and cellulose nanowhiskers (Pullawan, Wilkinson, & Eichhorn, 2010; Qi, Cai, Zhang, & Kuga, 2009) have been reported as effective reinforcing agents for all-cellulose composites. In addition to this a number of cellulose dissolving solutions have been used to make the matrix component; these include lithium chloride/N,N-dimethyl acetamide (LiCl/DMAc) (Nishino et al., 2004), sodium hydroxide/urea (NaOH/urea) (Qi et al., 2009) and ionic liquids (Duchemin, Mathew, & Oksman, 2009; Ma, Zhou, Li, Li, & Ou, 2011; Ou et al., 2012; Yousefi, Nishino, Faezipour, Ebrahimi, & Shakeri, 2011; Zhao et al., 2009). Of these solvent systems, NaOH/urea has been recently reported as a promising approach for the dissolution of cellulose for a variety of applications, including all-cellulose composites (Cai & Zhang, 2005, 2006; Cai et al., 2007; Zhou & Zhang, 2000).

It has been reported that enhanced mechanical properties are obtained for all-cellulose composites compared to conventional natural plant fibre-based composites (Huber et al., 2012). It is therefore important to better understand the interfaces that lead to these enhanced effects seen in these so-called “interface-less” composites (Huber et al., 2012). Some work has already been carried out to monitor interfaces in all-cellulose composites, both using X-ray diffraction (Gindl, Martinschitz, Boesecke, & Keckes, 2006) and Raman spectroscopy (Pullawan et al., 2010; Pullawan, Wilkinson, & Eichhorn, 2012).

The Raman spectroscopic method for analysing interfaces in composites relies on the monitoring of a shift in the peak position of a characteristic Raman band. This band is typically associated with the main-chain or backbone moieties of the polymer as the material is deformed, either in tension or compression. The effect was first observed for cellulose in 1997 (Hamad & Eichhorn, 1997), and has subsequently been applied to a wide range of fibres (Eichhorn & Young, 2001; Eichhorn, Hughes, Snell, & Mott, 2000; Eichhorn, Sirichaisit, & Young, 2001a; Eichhorn, Young, & Yeh, 2001b; Gierlinger, Schwanninger, Reinecke, & Burgert, 2006; Hamad, Gurnagul, & Gulati, 2012; Peetla, Schenzel, & Diepenbrock, 2006), cellulose fibre reinforced composite materials (Eichhorn & Young, 2003, 2004; Mottershead & Eichhorn, 2007; Tze, O'Neill, Tripp, Gardner, & Shaler, 2007) and most recently cellulose nanofibres and composites (Rusli & Eichhorn, 2008, 2011; Rusli et al., 2010; Rusli, Shanmuganathan, Rowan, Weder, & Eichhorn, 2011).

In the present work we explore the influence of both the reinforcement type (cellulose nanowhiskers from tunicates and cotton) and the matrix type (dissolved cellulose using LiCl/DMAc and NaOH/urea) on the stress transfer properties of all-cellulose nanocomposites.

2. Experimental methods

2.1. Materials

Acetic acid, sodium hypochlorite solution (>4% chlorine) and sulphuric acid (98%) were all purchased from Fisher Scientific.

Lithium chloride (LiCl) and N,N-dimethylacetamide (DMAc) were purchased from Sigma–Aldrich. Microcrystalline cellulose (Avicell, PH-101, particle size ~50 µm) was also purchased from Sigma–Aldrich. Ion exchange resin (Amberlite MB 6113) was purchased from Fluka.

2.2. Production of cellulose nanowhiskers

Tunicate cellulose nanowhiskers (T-CNWs) were prepared by acid hydrolysis of tunicates (*Styela clava*) using sulphuric acid. The tunicates were first gutted and then heated in 3% (w/w) aqueous potassium hydroxide at 80 °C for 24 h in order to remove their outer walls, followed by mechanical agitation and scrubbing (van den Berg, Capadona, & Weder, 2007). Two more treatments with aqueous potassium hydroxide are then required, which is a slight modification of a procedure previously reported by Yuan, Nishiyama, Wada, & Kuga (2006). After neutralizing the tunicates with 3 L of water, 5 ml of acetic acid and 10 ml of sodium hypochlorite solution were added and heated up to 60 °C for 1 h. After this, 5 ml of acetic acid and 10 ml of sodium hypochlorite solution were added until the tunicate's colour changed to pure white. This bleaching procedure was repeated 2–3 times, depending on the particular batch of tunicates. These bleached de-proteinised walls were then washed with de-ionised water and disintegrated using a Waring blender to yield a fine cellulose pulp. Sulphate-functionalised tunicate nanowhiskers were then prepared by sulphuric acid hydrolysis of tunicates according to a modification of a method described by Elazzouzi-Hafraoui et al. (2008). The fine cellulose pulp was added to 48% sulphuric acid and subjected to vigorous mechanical stirring. The suspension was then heated to 55 °C for 13 h while continually stirring. The dispersion was then cooled, filtered and washed with de-ionised water until a neutral pH was reached. These nanowhiskers were then re-dispersed in 1 L of de-ionised water, sonicated overnight and freeze-dried.

Cotton cellulose nanowhiskers (CNWs) were prepared using a standard sulphuric acid hydrolysis of cotton linters as described by Revol et al. (1992). A graduated cylinder containing 64% (w/w) sulphuric acid was placed into a water bath at 45 °C. The cotton linters (40 g) were then added to the acid and stirred mechanically for 45 min. De-ionised water (2.5 L) was then used to dilute this suspension, which was then settled and rinsed by centrifugation for 4 cycles (Centrifugation Sigma U-16, Sci-Quip) at 6000 rpm, using 10 min for each cycle. This suspension was then dialysed against water until neutralized. After treatment with an ion-exchange resin it was filtered using Whatman microfibre filters. The suspension was then repeatedly sonicated (Branson Digital Sonifier) to produce a colloidal suspension of nanowhiskers. This suspension was then freeze-dried.

2.3. Production of all-cellulose nanocomposites

All-cellulose nanocomposite films were prepared using a matrix of cellulose derived using two different solvent systems; namely lithium chloride/N,N-dimethyl acetamide (LiCl/DMAc) and sodium hydroxide/urea (NaOH/urea). These two different matrices required two very different processing routes. For the LiCl/DMAc system the first stage microcrystalline cellulose was “activated” in de-ionised water for 5 h at room temperature. This step swells the cellulose in preparation for dissolution. This activated cellulose was then dehydrated in acetone and then in N,N-dimethylacetamide (DMAc) for 5 h and 4 h, respectively. Following this, the DMAc was decanted from the dehydrated cellulose. An 8% solution (by total weight) of LiCl was then added to the DMAc; 8 g of LiCl in 100 g of DMAc. This solution was stirred at 120 °C for 30 min until the LiCl had completely dissolved. This solution was then added to

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