Deformation micromechanics of natural cellulose fibre networks and composites

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Abstract

The deformation micromechanics of cotton and flax single natural cellulose fibres in relation to their use in cellulose-based networks and composite materials is reported. The deformation of such fibres induces a shift in the 1095 cm\(^{-1}\) Raman band, corresponding to the ring structure of the particular polymorph, which can be calibrated against strain. It is shown that this band shift can be used to monitor the deformation micromechanics of fibrous networks (cotton paper) and the composite micromechanics of single natural cellulose fibre unidirectional composites. The shear lag approach of Cox [Br. J. Appl. Phys. 3 (1952) 72] is investigated for the fibrous network and composite materials. For the network it is demonstrated that this theory does not apply since bonding across the end modifies the stress transfer by 'shear-lag'. For the natural fibre composites it is thought that bonding occurs across the ends, also modifying this effect, but other possibilities are discussed in detail.

Keywords: A. Fibres; A. Short-fibre composites; B. Fibre/matrix bond; C. Deformation; D. Raman spectroscopy

1. Introduction

The polymeric family of cellulosics includes several crystallographic forms; native (cellulose I), regenerated (cellulose II) and the higher forms of types III, IV and V. There are also chemical derivatives of these forms such as cellulose acetate and cellulose nitrate. In native cellulose the chains are thought to be in a parallel packed conformation and for regenerated cellulose this conformation is thought to be antiparallel [2,3]. Cellulose I is also known to be a composite form of two suballomorphs; \(I_a\) and \(I_b\) [4] which have been shown to have a “parallel-up” packing conformation in the unit cell [5]. Regeneration of cellulose is achieved by dissolving native cellulose in a polar solvent, followed by recrystallisation [6]. This produces continuous filament fibres with a variety of properties that are mainly utilised industrially in the textiles and clothing industries.

Raman spectroscopy of cellulose was first undertaken by Blackwell, Vasko, and Koenig [7]. This involved partially deuterating their samples and recording spectra over several hours, however a later study by Atalla and Nagel [8] used pure plant material with reduced exposure times. The assignment of cellulose Raman bands has been carried out by Atalla and co-workers [9]. They have assigned most bands, in particular the 1095 cm\(^{-1}\) peak to C–O ring stretching modes and possible glycosidic linkage stretching and the 895 cm\(^{-1}\) to mixed modes including angle bending.

This Raman technique has also been used quite extensively to measure the micro-strains and stresses in a variety of fibrous materials. The technique relies on calibrating the shift of a Raman peak with respect to strain and/or stress. The effect was first discovered and analysed theoretically at the end of the 1970s [10,11] in terms of the anharmonicity of the force constant of the vibrating bond. Subsequently, a large amount of work has been done on single fibre deformation micromechanics using this technique [12], in particular for both natural and regenerated cellulose fibres [13,14]. Some initial work on regenerated cellulose fibres [15] showed that for low-modulus fibres there was little precision or accuracy in the data, however later studies [13,14] have shown that high precision calibrations against strain and stress can be achieved.

The investigation of composite micromechanics, especially at the interface of the fibre and the matrix material, has benefited greatly from the use of Raman
spectroscopy [16]. This work has mainly focussed on determining the interfacial shear stress using standard techniques such as fragmentation [17], pull-out testing [18] and microbond testing [19]. More specifically, using single-fibre unidirectional composites as model systems, it has been shown that by scanning along an embedded end of a fibre, the shear-lag theory developed by Cox [1] generally applies [16]. It has also been shown that it is possible to determine the onset of debonding close to fibre breaks and ends [16]. Some micromechanical analysis has been conducted using Raman spectroscopy on natural composites such as wood and fibrous networks [13], but as far as the authors are aware nothing has been reported on natural fibre reinforced resin composites. This is what this paper seeks to address.

2. Experimental

2.1. Materials

The natural fibres used in this study were flax, and cotton (also formed into paper sheets). The flax was grown in France as hackling tow, decorticated and hackled and then steam exploded to release the technical fibres. The cotton was provided by the Department of Paper Science, UMIST and paper was manufactured from this base material on a pilot-plant Foudrinier paper machine.

2.2. Equipment

A Renishaw 1000 Raman imaging microscope was used in this work to record the spectra of fibre monofilaments at a low power of 25 mW. Two types of laser were used for the single fibre deformation experiments and the fibrous network and composite deformation, namely Helium-Neon (633 nm) and Near-Infra Red (785 nm) respectively. When focussed onto the fibre surfaces the spot size was roughly 2 μm in diameter and had a power of about 1 mW. Back scattered light was collected using a ×50 lens and an Olympus microscope. The excited Raman radiation was then filtered using a holographic notch filter and the resultant radiation converted to a spectrum by a diffraction grating. A highly-sensitive Peltier-cooled charge-couple device (CCD) detector recorded all spectra and these were collected on a computer.

2.3. Single fibre deformation

The methods used to determine single-fibre mechanical properties of natural cellulose have previously been reported in depth [13,14]. Single fibres were extracted from the natural plant material by soaking fibres in hydrogen peroxide for 48 h and pulling out single ultimate fibres (8 mm) with tweezers under a dissection microscope. These fibres were then transferred and secured to a cardboard window using Ciba-Geigy HY/LY1927 two part cold-curing epoxy resin. The regenerated cellulose fibre samples were prepared in a similar way to this, without the need for chemical extraction. These samples were allowed to cure for 48 h at constant temperature and humidity. The cardboard windows were then secured to a customised stress-rig housing a 0–2 N load cell, which was attached to a transducer that recorded the load. By burning the edges of the window the fibres were then able to be deformed freely. Deformation took place at varying increments (0–0.5%) as has been reported elsewhere in greater detail [13,14]. After each strain level increment the fibres were exposed to laser radiation for a period of 120 s and the process was then repeated. All data were fitted with a mixed Lorentzian/Gaussian function, using an algorithm developed by Marquardt [20] to determine the peak positions at each strain/stress level.

2.4. Fibrous network deformation

The fibrous networks in the form of cotton paper were cut using a razor blade to a size of 15×5 mm and then secured to a straining rig. At successive strain levels (0.05–0.1%) spectra were taken with the near-IR laser using a 120 s exposure time. Spectra were also recorded whilst tracking along a single fibre within the network between each strain level. Only fibres that were orientated in the tensile direction were chosen for this study.

2.5. Composite micromechanics

For the composite micromechanics it was necessary to produce thin films of matrix epoxy with a single fibre embedded within because the resin often impairs the signal from the fibre. This was achieved by using two polished plates of glass pre-coated with Freekote™ release agent, and by placing a small amount of LY5052/HY5052 cold-curing epoxy onto one sheet of glass. Then a fibre was placed with tweezers into this drop of epoxy and the process repeated many times. The other sheet of glass was then placed carefully over the top of the epoxy and fibres and lowered slowly onto the plane of the other sheet of glass. This was restrained at the sides, so that the glass would not slip, and left for 7 days to cure. After this period of time, the sheets of glass were parted and the thin film (~500 μm) was cut into narrow strips (20×5 mm) around the location of the fibres. Care was taken to choose fibres whose axes were straight. These thin sections were then polished along their sides using fine sandpaper and secured to a straining rig with cyanoacrylate adhesive. The gauge length of the samples was determined using a micrometer and the macro-strain of the samples was deter-
mined from the displacement of the cross-head. The Raman laser beam was initially located at the end of a fibre and by tracking using 10 μm steps, the local strain profile was monitored at different levels of matrix strain. Using polarised light, defects within fibres were also located (appearing as regions with different contrast) and then these were mapped across using the Raman laser beam at incremental strain levels.

3. Results

3.1. Fibre deformation

A typical peak shift for the 1095 cm⁻¹ Raman band is shown in Fig. 1 and the shifts in the 1095 cm⁻¹ peaks for the two fibres with respect to strain are reported in Fig. 2. It can be seen that there is a discernable shift in the peak with strain (Fig. 1) and that the shift rates with respect to strain are different for each fibre type (Fig. 2). This shift rate has been found to be proportional to the modulus of cellulose fibres [13]; the factor 3 difference in the shift rates in Fig. 2 for the cotton and flax is consistent with the Young’s modulus of flax being about three times that of cotton [21]. Moreover it is found that the shift rate with stress is invariant at a value of ~4.5 cm⁻¹/GPa [13] consistent the structure of cellulose fibres being modelled as a linear series aggregate uniform stress construction [22–24].

3.2. Fibrous network deformation

The deformation of fibrous networks has also been investigated and a typical result of the strain monitored in a fibre within the sheet is reported in Fig. 3. Fig. 3(a) shows the initial shift in the 1095 cm⁻¹ Raman band indicating axial fibre deformation and then at about 0.4% the fibre debonds from the network. During the post-debonding phase there is a relaxation of the fibre, until at about 1.0% strain the sheet fractures. The result of scanning along a fibre from a bonded end is shown in Fig. 3(b) and it can be seen that there is a decrease in wavenumber at increasing levels of overall strain, indicating local tensile deformation of the fibre in the network. The Cox model [1] predicts that there ought to be zero strain at the end of a fibre, which then increases rapidly into the fibre-centre where this value reaches a plateau. However, this is found to be untrue for the particular system investigated, wherein the fibres chosen were flat and clearly well bonded to the network at their
ends. The results of this experimental investigation are in agreement with the findings of Raisanen et al. [25] who proved theoretically that the Cox shear lag model does not apply in general to random fibre networks. This model was originally developed for such fibrous structures [1], but is now generally used for composite materials where it has been found to be widely applicable [16].

3.3. Single fibre composite deformation

A typical result of scanning along the ends of a natural fibre embedded in an epoxy matrix at different levels of strain is shown in Fig. 4(a). The geometry of the ends is also shown in Fig. 4(b) indicating the “splayed” end of a fibre induced after cutting. This geometry is identical to aromatic fibres studied [26] which give well-defined stress transfer profiles predicted accurately by the Cox model [16]. It is clear, however, that there is little stress transfer of this type in the natural fibre/epoxy system, which suggests that the fibres are bonded across their ends. This may be possible since natural fibres such as flax and hemp have lumens (holes) running down their centres [27], and recent SEM micrographs of jute fibres (which also have lumens) show epoxy resin impregnating this volume [28]. However, another possible explanation is that there is only a factor of 15–20\(^{\text{x}}\) difference between fibre and matrix modulus. This is not large compared to high modulus fibre composite systems analysed in the same way [16] where steeper stress-transfer profiles are observed and as such the effect may not be as apparent with natural fibre/epoxy systems.

To model bonding across the ends, various authors have attempted to modify the Cox model to fit this situation where stress transfer does not take place over the ends [29–31]. One suggestion [31,32] is that the stress at the end of a fibre is simply the average of the matrix stress and the stress within the centre of the fibre. The standard Cox equation is found to be [32]

\[
\varepsilon_f = \varepsilon_c \left[ 1 - \cosh(nz/r) \cosh^{-1}(ns) \right]
\]

where \(\varepsilon_f\) is the fibre strain and \(\varepsilon_c\) is the applied composite strain, \(z\) is the distance from a fibre end, \(r\) is the fibre radius, \(s\) the fibre aspect ratio and \(n\) is a constant defined by [32]

\[
n = \left[ \frac{2E_m}{E_f(1 + \nu_M) \ln(1/f)} \right]^{1/2}
\]

where \(E_m\) is the matrix modulus, \(E_f\) is the fibre modulus, \(\nu_M\) is the Poission’s ratio of the matrix and \(f\) is the volume fraction of fibres.

If one assumes that the strain at the fibre end is not zero, but the average of the strain in the middle of the fibre and the far field strain given by shear lag theory [1] then one can readily obtain the expression [32]

\[
\varepsilon_f = \frac{E_M}{E_f} \left[ \frac{E_f - E_M}{E_f} \right] \cosh \left( \frac{12}{15} \right) \cosh^{-1}(ns)
\]

This expression has been used to model the present situation with natural fibre composites, the results of which are plotted in Fig. 4(a) where a comparison is made with stress transfer profiles derived from the standard Cox model using similar parameters. It is clear that there is somewhat better agreement with the modified model than the original Cox model, and the strain at the fibre ends is not zero, indicating that this is an adequate model of the behaviour. However, a more geometrically specific model such as that described by Nairn [33], who considered a transversely isotropic fibre with a hollow centre, may be more appropriate. No fit is shown for the 1.0% level of strain because at this level the data showed rather different behaviour, possibly due to debonding along the fibre length. However, it can clearly be seen that the fibre strain does not fall to zero at the fibre end as predicted by the Cox model [1].

3.4. Fibre defects in composites

When one scans across a defect in a fibre embedded in a composite under strain, large stress concentrations in the vicinity of the defect are observed as highlighted by Fig. 5(a). It is worth noting at this point that defects in natural fibres are quite common [a typical one is repor-
ated in Fig. 5(b) due to the processing of the plant to yield such material. The occurrence of stress concentrations may be due to the fact that damage within the defect gives rise to a smaller amount of material bearing the load. It has been shown by other workers [34] that these stress concentrations can give rise to the propagation of cracks into the matrix. If there is a good interface between the fibre and the matrix, as has already been proven from the previous section, then the propagation of cracks into the matrix material is likely to occur. Improvements made to the interface between fibres and the matrix material will further increase the ability of cracks to propagate through the material, and thus reduce its fracture toughness.

4. Conclusions

Raman spectroscopy is a powerful technique that can be applied to the deformation of a number of polymeric materials, and this paper has further emphasised this with natural cellulose fibres. The shifts in the Raman bands give information on the molecular stressing in the cellulose. The technique has been applied to the deformation of a fibrous network, where it has been shown to be vital for measuring local strain profiles in fibres, which until now could only be assumed for most models of the deformation of such structures. It was also shown experimentally that the shear-lag model of Cox [1] does not apply to fibrous networks, confirming recent theoretical predictions [25]. The Raman technique has been applied many times to conventional fibre composite systems [16], but this work has shown that it can be applied also to natural fibre composites. Furthermore, the results suggest that bonding occurs across fibre ends and that stress is not transferred in this region. This fact highlights that natural fibres offer a good potential for reinforcement since as there is good stress transfer across their ends, there is no need for continuous reinforcement. The effect of local defects on the micromechanics of the interfacial deformation also shows that large stress concentrations occur within these regions. Combining this with the previous result leads to the implication that there may be no need to improve the adhesion of natural fibres to the resin since this might only reduce the toughness of the composite without improving its strength.

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References

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