DEFORMATION MICROMECHANICS OF CELLULOSE FIBRE BASED MODEL COMPOSITES

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Abstract

The interfacial shear stress between many different polymers (epoxy, polyester, polypropylene) and high performance cellulose fibres are mapped using a Raman spectroscopy method and X-ray diffraction using a synchrotron source. It is shown that Raman bands shifts are recorded when free fibres are deformed in tension, indicative of molecular deformation. This molecular deformation is shown to be useful in calibrating local stress in a fibre embedded in a composite. However, it is also shown that this method is precluded for opaque resins such as polypropylene. In this case an X-ray diffraction method, using the synchrotron source at the ESRF, Grenoble, is presented. Here, changes in the c-spacings of the crystals, which are aligned along the axis of the fibres, is used to calibrate local fibre stress. A number of models are presented to fit the data, and comparisons made between conventional microbond testing.

1 General Introduction

Natural fibre composites based on cellulose have been a subject of great research interest over a number of decades. Despite many papers being published on the mechanical properties of a wide variety of systems (cellulose-polypropylene [1], cellulose-polyesters [2], cellulose-epoxy [3]) very little information exists on directly measuring the interfacial properties these materials. Single values for the interfacial shear strength of cellulose based composites have been previously reported using techniques such as fragmentation [4] and single fibre pull-out testing [5].

Raman spectroscopy has been shown to useful for mapping the interface between natural fibres and polymeric resins [6]. It has also recently been shown to be useful for following the interface between regenerated cellulose fibres and polymeric resins [7-9]. This technique relies on the fact that the peak position of a particular band can be followed positionally along the fibre, as a function of external deformation, both within the resin and outside. A model composite consisting of a droplet and a single fibre has been used for this purpose for a hemp-epoxy model composite [6]. However, this approach is only appropriate for samples where the resin is optically transparent and where the Raman peaks do not coincide with those required for the stress measurement in the fibre. Recent progress has been made on using X-ray diffraction from synchrotron sources to investigate the interface in model polymer-fibre composites [10,11]. This approach is found to preclude the need for optically transparent resins. Both the use of Raman spectroscopy and X-ray diffraction for the determination of interfacial adhesion of model cellulose-polymer composites will be discussed in this paper. In particular the use of these techniques to follow deformation in regenerated cellulose fibre based systems will be reported.

2 Experimental Methods

2.1 Materials

Bocell™ fibres*, which were a potential commercial cellulose fibre for the tire cord industry were supplied by Acordis, Netherlands. Commercially available polyester and two-part cold curing epoxy resins were also used for this study.

3.2 Sample preparation

To prepare the model composites, single fibres were secured to testing cards using epoxy resin and a small droplet of resin was applied, somewhere along

* Previously called fibre ‘B’ [12,13]

the free length of the fibre, using a pair of tweezers. A range of single fibres were also produced, with no droplets present, for the purposes of mechanical testing. In addition to the droplet model composites, a number of specimens were produced which had glass slides pressed either side of the resin to ensure a flat surface rather than a curved droplet. This was done in order to reduce the optical distortion of the droplets that occurs due to total internal reflection. An image of a typical droplet is shown in Figure 1 where one can see the effect of total internal reflection (dark region surrounding lighter central region where fibre is visible but distorted).

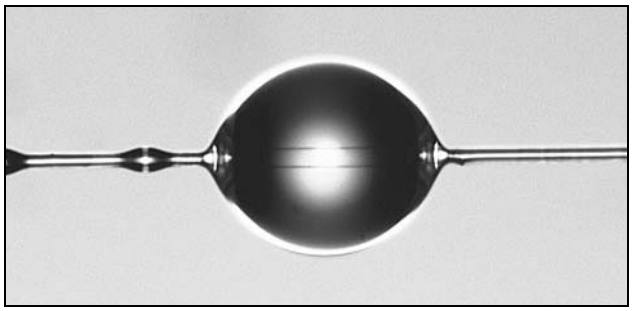


Fig. 1 Image of a polyester droplet model composite (lengthwise dimension of large droplet is 200 μm)

Fibres were deformed in tension on a customized rig.

3.3 Mechanical Properties Methods

Cross-sections of the fibres were determined using Scanning Electron Microscopy of their ends. The load-displacement behaviour of fibres was then recorded using an Instron 1121 tensile testing maching. Single fibres were deformed in tension, using a range of gauge lengths to account for end effects, and the load and cross-head displacement recorded until failure. The load values were converted to stress by dividing by the cross-sectional area, and the displacement to strain by dividing by the original lengths of the filaments.

In order to determine the strength of the interface between resin microdroplets and fibres, the droplets of model composites were gripped on one side using customized adjustable blades fitted to the bottom housing of the Instron tensile tester. The fibres were then deformed in tension, forcing the droplets to be pulled from the resin. The maximum force to do this was recorded and the interfacial shear stress was determined using a standard method [14].

3.4 Interfacial Micromechanics Methods

Raman spectra recorded using a Renishaw system 1000 spectrometer, coupled to a microscope stage onto which the rig was placed. In order to calibrate the local stress state of fibres within droplets, single filaments were deformed in tension and the position of the 1095 cm^{-1} Raman band was recorded as a function of external tensile deformation. Subsequently the model composites were analysed, and by mapping along free fibre and through the resin droplets, it was possible to record the position of the 1095 cm^{-1} Raman band as a function of displacement along the interface. A number of external deformation steps were applied to the fibres in order to analyse the efficacy of the interface, and the process repeated.

A similar method was employed for the opaque resin samples. The experiments were carried out at the beamline ID13, European Synchrotron Radiation Facility (ESRF), France. The beamline was configured with a Kirkpatrick-Baez (KB) type mirror and collimated using a piezo-based block collimation system. This provided an on-sample beam spot-size of approximately 5 μm with a radiation wavelength of 0.095 nm and an energy of 6 GeV. A MARCCD detector with an average pixel size of 257.8 μm^2 was used to collect diffraction patterns. The model composites were deformed in a similar manner to the samples investigated using Raman spectroscopy. At each loading stage diffraction patterns were taken using the X-ray microbeam and exposure times of 1-2 seconds.

3 Results and Discussion

A typical stress-strain curve is shown in Figure 2 for a Bocell fibre [7]. This curve is non-linear, indicating a yield point at about 1 % strain. The mechanical properties of the fibres are summarized in Table 1.

E / GPa	σ_f / GPa	ε_f / %
55.4 ± 1.0	2.6 ± 0.3	5.5 ± 1.4

Table 1 Mechanical Properties of single fibres including the Young's modulus (E), breaking stress (σ) and breaking strain (ε).

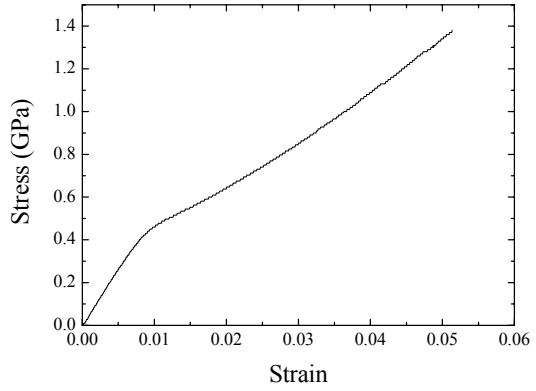


Fig. 2. A typical stress-strain curve for a Bocell™ cellulose fibre [7].

As can be seen the mechanical properties of these fibres are high, and comparable to most high estimates of values reported for natural plant fibres. However, since Bocell fibres are regenerated, they do not suffer from the same problems as natural fibres; namely defects and discontinuous lengths.

A typical result from a microbond test is shown in Figure 3 for an epoxy resin-cellulose fibre interface. As can be seen there is a certain amount of scatter. By applying the standard theory one obtains summarized values as shown in Table 2.

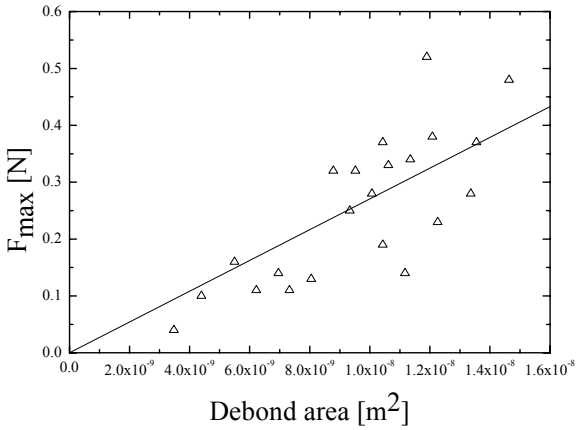


Fig. 3. Typical microbond data for epoxy resin – Bocell model composites. R^2 = 0.6 and gradient suggests an interfacial shear stress of 27 MPa.

A typical band shift in the 1095 cm^{-1} Raman peak for a deformed Bocell fibre is shown in Figure 4. As can be seen a good correlation of band shift with stress is obtained, enabling a calibration of the local stress in a fibre embedded in a composite.

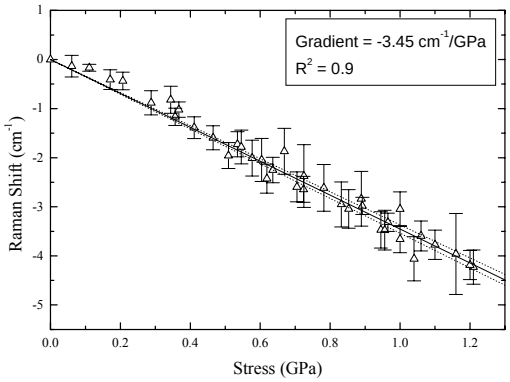


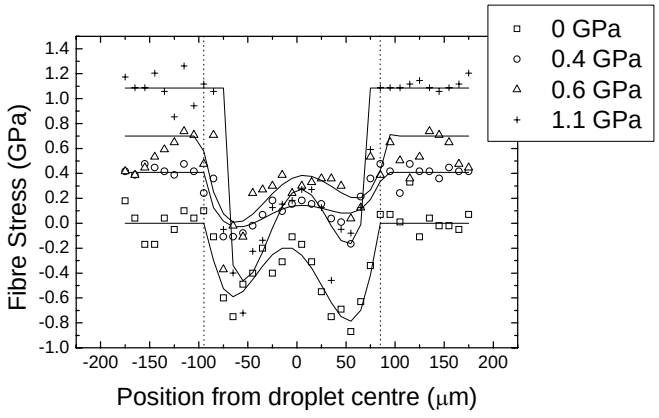
Fig. 4. Raman band shift with respect to stress for a free Bocell fibre in air.

Microbond sample	ISS_{mean} (MPa)
Epoxy	27±2
Polyester	7±1

Table 2 Mean values for interfacial shear stress (ISS_{mean}) calculated from microbond tests on Bocell-epoxy and polyester model composites.

Typical stress profiles for an epoxy and polyester resin microdroplet samples are shown in Figure 5a&b.

(a)



(b)

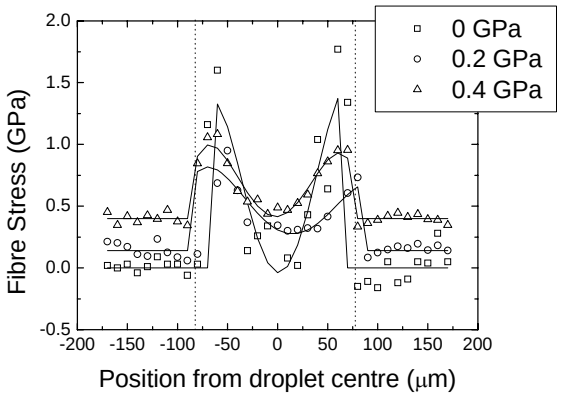


Fig. 5 Stress distributions for model composites of Bocell fibres with (a) epoxy and (b) polyester resin composites.

The interfacial shear stress distributions were also calculated for the samples by taking the derivative of the fits to the data in Fig.5. This can then be converted to ISS by multiplying by half the radius of the fibre [14].

Similar stress distributions can be derived for polypropylene-cellulose based composites and these will be discussed.

4 Conclusions

Raman spectroscopy and X-ray diffraction are useful tools for comparing to conventional microbond testing of composites. The shear stress distributions assumed for the latter are clearly not correct. The modified droplet tests show that the shear stress distribution can be derived in a point-to-point fashion. By using flat specimens the effects of the curvature and the disparity of refractive indices of the resin and air (leading to refraction and optical distortion) can be elminated.

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