Monitoring the Stress-Transfer at the Interface of Bacterial Cellulose/Poly-L-lactic acid Laminate Composites using Raman Spectroscopy

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Introduction

Composites are the combination of materials (ceramics, polymers, metals…) resulting in a material having intermediate mechanical properties depending on the volume fraction of each phase. Interfacial properties are crucial in composite materials and need to be optimised in order to produce high strength. They can be characterised by measuring the stress-transfer from the matrix to the reinforcing phase. However such measurement is not obvious and only a few techniques are relevant to evaluate stress-transfer between reinforcements and a resin material. Literature reports the use of X-ray diffraction from a synchrotron source[1,2] as well as Raman spectroscopy. The latter has been extensively used to monitor stress-transfer at the interface of cellulosic composites[3,4,5].

Aims

We aim to produce green composites having enhanced mechanical properties and low cost to increase the use of environmentally friendly materials. These green composites would be potentially fully biodegradable, and entirely obtained from renewable resources. Bacterial cellulose (BC) is a natural polymer having high mechanical properties and has the potential to reinforce green resins[6,7]. Since monitoring the stress-transfer at the interface is crucial, we need to demonstrate that Raman spectroscopy is a relevant tool to characterise the interface between BC and poly-L-lactic acid (PLLA).

Experimental methods

Materials

Gluconacetobacter xylinum (no. 13693; National Institute of Technology and Evaluation, Tokyo, Japan) and Hestrin-Schramm[8] medium were used to produce BC pellicles (Figure 1a).

The cells for the inoculum were cultured in test tubes statically at 27 ºC for 2 weeks. The thick gel produced was then squeezed aseptically to remove the embedded cells. The cell suspension (25 ml) was then transferred as an inoculum for the main culture (500 ml of medium), which was incubated statically at 27 °C for 6 days. Bacterial cellulose pellicles (35 mm in diameter) were purified by boiling with 2% NaOH for 2 h, and then by washing with distilled water, followed by hot pressing at 2 MPa and 120 ºC for 4 min to completely remove the bulk water.

Poly-L-lactic acid (PLLA L9000; molecular weight (M_w) > 150000 g/mol, density 1.25 g/cm^3) was purchased from Biomer® (Krailing Germany).

Sample preparation

BC pellicles were cut into strips of 1 mm width using a razor blade. PLLA pellets were dried overnight at 40 °C and transparent films (Figure 1c), approximately 160 µm in thickness, were prepared by compression moulding at a temperature of 180 °C and 12 MPa pressure. BC/PLLA composites were prepared by further compression moulding (Figure 1b). These samples were prepared by taking BC strips which were then moulded between two PLLA films again at a temperature of 180 °C and 12 MPa pressure.

(a) (b) (c)

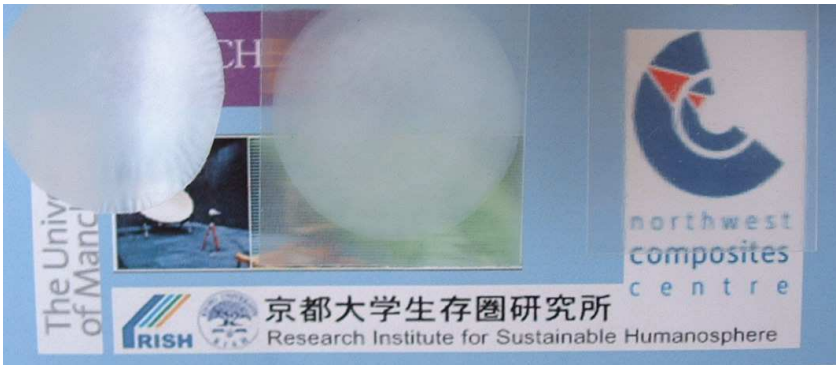

Figure 1: An image of the bacterial cellulose networks and composites:
(a) BC, (b) BC/PLLA and (c) PLLA.

Raman spectroscopy

A Renishaw system-1000 Raman spectrometer coupled to a 785 nm NIR (near infrared) laser was used to follow the molecular deformation of the samples. The laser was focused to a 2 µm spot using a ×50 long working distance lens. The laser power at the sample surface was 1 mW. Samples were deformed in tension using a customized deformation rig (Deben®

MICROTEST^{TM}) incorporating a 2 kN load cell. Strain was incremented in 0.1 % steps and the elongation rate was set at 0.033 mm min^{-1} between these increments. This experimental setting is shown in Figure 2. A Raman spectrum was recorded at each increment using an exposure time of 30 s and 4 accumulations. The peak positions of the 1095 cm^{-1} Raman band was determined by fitting using a mixed Gaussian/Lorentzian function and an algorithm based on the work of Marquardt[9]. The resolution of the spectrometer is < 0.1 cm^{-1} and so shifts greater than this value are observable.

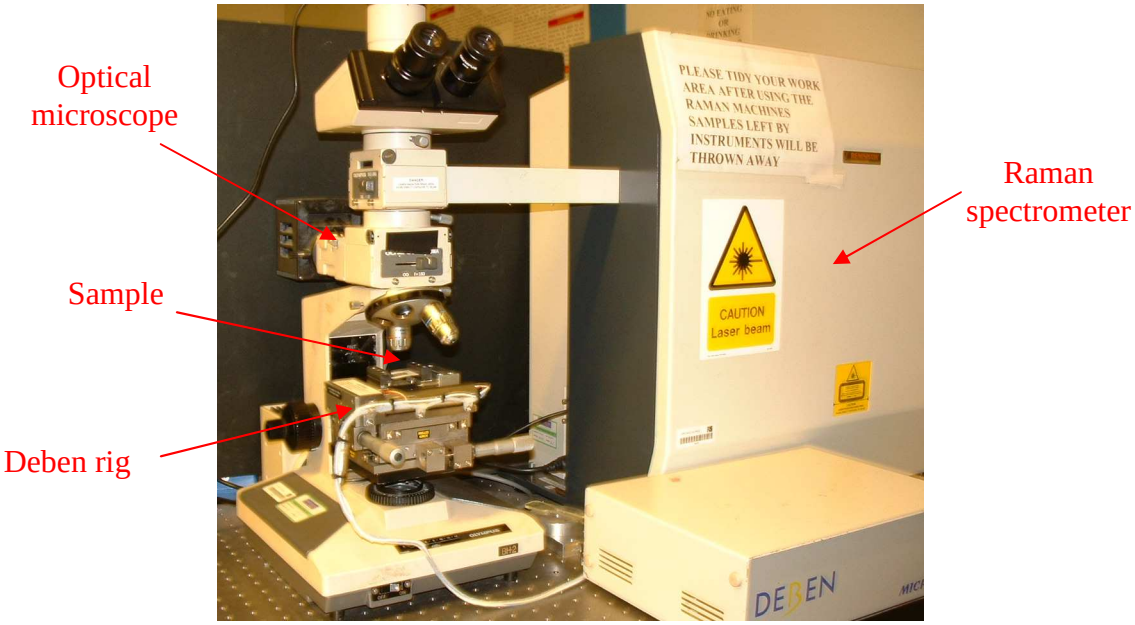

Figure 2: An image showing the experimental set-up in order to perform stress-transfer measurements using Raman spectroscopy.

Results and discussions

Figure 3a reports Raman spectra of BC, PLLA and BC/PLLA composite for a range from 1070 to 1150 cm^{-1}. The first step was to check if the 1095 cm^{-1} Raman band from cellulose is detectable when the BC is embedded in PLLA. It is clear from Figure 3a that the 1095 cm^{-1} Raman band is detectable. It is important to note that a low intensity peak is observed for PLLA, and that peak was found not to interfere with the fitting process of the 1095 cm^{-1} Raman band.

The second step was to deform BC strips as well as BC/PLLA composites in order to check if the 1095 cm^{-1} Raman band shifts towards a lower wavenumber position when bacterial cellulose is embedded in PLLA. Figure 3b reports the shift of the 1095 cm^{-1} Raman band of bacterial cellulose before and after tensile deformation. This shift is directly related

to the microdeformation of bacterial cellulose nanofibrils. A higher shift rate has been observed when BC is embedded in PLLA.

Figure 4a and 4b report the shifts in the peak position of the 1095 cm^{-1} Raman band with respect to strain and stress respectively. One can clearly see the higher band shift rate of the Raman band located at 1095 cm^{-1}, and consequently a better stress-transfer when BC is embedded in PLLA. Indeed Figure 4a reports a value of -1.78 $cm^{-1}\%^{-1}$ when BC is embedded in PLLA, whereas a value of -0.93 $cm^{-1}\%^{-1}$ is found for BC. When the Raman band shift is plotted as a function of the stress the difference is even more pronounced, mainly due to the lower stress level the composite can support compared to a BC sheet. Figure 4b reports values of -5.74 $cm^{-1}GPa^{-1}$ for BC and -44.59 $cm^{-1}GPa^{-1}$ when BC is embedded in PLLA.

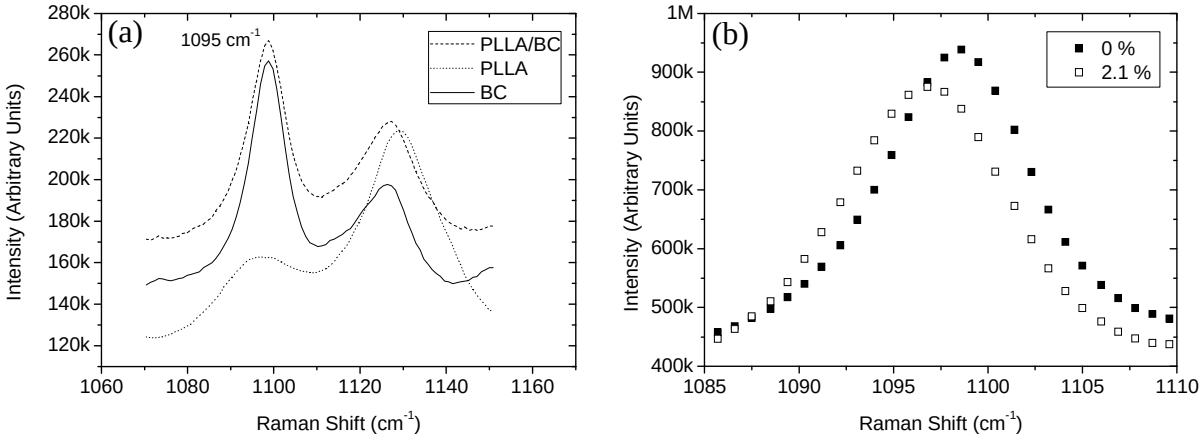

Figure 3: (a) BC/PLLA composite, PLLA and BC in the region close to the 1095 cm^{-1} band. (b) Shift in 1095 cm^{-1} Raman band at 0 % and 2.1 % strain for BC.

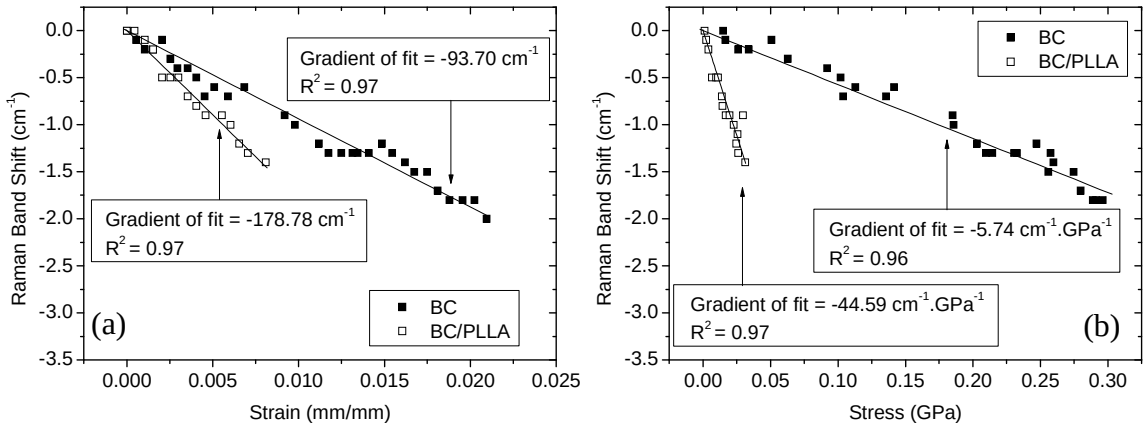

Figure 4: Shifts in the peak position of the 1095 cm^{-1} Raman band with respect to strain (a) and stress (b).

Conclusion

This study has shown that Raman spectroscopy is a powerful tool for following the stress-transfer process in a BC/PLLA laminate composite material. This has been achieved by hot-pressing PLLA resin around bacterial cellulose strips. The 1095 cm^{-1} Raman band from the cellulose has been shown to be spectroscopically distinct from resin material, making it possible to follow the stress-transfer properties of the composite material. This stress-transfer process is clearly revealed by comparing the band shift rates of the 1095 cm^{-1} Raman band with respect to both strain and stress. Better stress transfer is obtained for bacterial cellulose networks when pressed within the resin material, and this is revealed by an enhanced shift rate compared to the pure sheet material.

The usefulness of the Raman spectroscopic technique for following stress-transfer in this form of composite is clear, and further work will develop its use for following the effect of the modification of both the interfaces between fibres within the network and between the resin and the network of fibres.

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References

[1] Eichhorn, S. J., J. A. Bennett, et al. (2006). "Analysis of interfacial micromechanics in microdroplet model composites using synchrotron microfocus X-ray diffraction." Composites Science and Technology 66(13): 2197.

[2] Shyng, Y. T., J. A. Bennett, et al. (2006). "Analysis of interfacial micromechanics of model composites using synchrotron microfocus X-ray diffraction." Journal of Materials Science 41(20): 6813.

[3] Sturcova, A., G. R. Davies, et al. (2005). "Elastic modulus and stress-transfer properties of tunicate cellulose whiskers." Biomacromolecules 6(2): 1055.

[4] Rusli, R. and S. J. Eichhorn (2008). "Determination of the stiffness of cellulose nanowhiskers and the fiber-matrix interface in a nanocomposite using Raman spectroscopy." Applied Physics Letters 93(3).

[5] Mottershead, B. and S. J. Eichhorn (2007). "Deformation micromechanics of model regenerated cellulose fibre-epoxy/polyester composites." Composites Science and Technology 67(10): 2150.

[6] Gindl, W. and J. Keckes (2004). "Tensile properties of cellulose acetate butyrate composites reinforced with bacterial cellulose." Composites Science and Technology 64(15 SPEC. ISS.): 2407.

[7] Kim, Y., R. Jung, et al. (2009). "Transparent nanocomposites prepared by incorporating microbial nanofibrils into poly(l-lactic acid)." Current Applied Physics 9(1 SUPPL.): S69.

[8] Hestrin S, Schramm M. (1954) "Synthesis of cellulose by Acetobacter-xylinum .2. Preparation of freeze-dried cells capable of polymerizing glucose to cellulose." Biochem J 58:345–352.

[9] Marquardt DW(1963) "An algorithm for least-squares estimation of nonlinear parameters." J Soc Ind Appl Math 11:431–441.