

RAMAN SPECTROSCOPIC ANALYSIS OF THE MICRODEFORMATION IN CELLULOSIC FIBRES

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SYNOPSIS

This paper addresses the application of Raman spectroscopic techniques to analyzing the deformation micromechanics of regenerated cellulosic fibres. In addition to information obtained on the macroscopic deformation, Raman spectroscopy enables the study of changes in *internal* strain associated with creep and recovery. The analysis of the mechanics of deformation of the fibres begins by following the response of the Raman-sensitive bands to external tensile loading. It is shown that the peak positions of the 895 cm^{-1} and 1095 cm^{-1} Raman bands shift to lower vibrational frequency under the action of tensile stress or strain due to the macroscopic deformation leading to direct stretching of the polymer molecules. Moreover, this approach makes possible the modelling of single fibre properties using simple viscoelastic dynamics; thereby relating the macromechanical properties of stress and strain to those obtained at the microscopic level via spectroscopy.

INTRODUCTION

Raman scattering is essentially the (small) portion of a beam of light that is inelastically scattered by a material — the majority of radiation which is scattered elastically at the same frequency as the incident light is the Rayleigh scattering. It is this inelastically scattered light that carries information about the molecular vibrations in the material, and hence it is useful in the characterization of non-metallic materials. Raman spectroscopy has successfully been used for the analysis of deformation processes in a variety of high-performance polymer fibres, and there exists overwhelming evidence that when such fibres are subjected to tensile stress or strain significant shifts take place in the wave numbers of the Raman bands. This is due to the fact that stressing causes the deformation of the polymer molecules through a combination of bond stretching and bond angle opening (refer, amongst others, to [1-3]). This behaviour may be explained in terms of the macroscopic deformation being transformed directly into stressing the covalent bonds along the polymer backbone and changes in the bond angles as discussed many years ago by Treloar [4].

Raman, as well as infra-red, spectral studies of cellulose have hitherto concentrated solely on discerning polymorphic changes [5] in, and exploring the structure [6] of, cellulose. Our work, which builds upon the wealth of such excellent studies, is part of a large programme dedicated to characterizing the deformation micromechanics in a litany of native and regenerated cellulose fibres using Raman spectroscopic analysis; and utilizing the results thus obtained to model time-dependence phenomena in such fibres. This paper, however, addresses the application of Raman spectroscopy to analyze the deformation of regenerated cellulosic fibres (principally Tencel[®]) by following the shift of the Raman-sensitive bands. This will enable the fundamental micromechanics of the deformation of the molecules within the fibres to be studied in detail. It shall further be shown that the Raman spectroscopic data can lead to infer quantitative information regarding the viscoelastic response of the highly time-dependent cellulosic fibres.

EXPERIMENTAL

Commercial grade 1.6 dtex tencel fibres, produced by solvent-spinning cellulose from wood-pulp (supplied by Courtaulds Fibres Ltd., U.K.), were employed for this study.

Mechanical testing was performed on fibres that were individually mounted —

using a cyanoacrylate adhesive—into testing cards prior to being placed in the jaws of the series IX Instron mechanical testing machine (model 5564). Several hours were allowed for the adhesive to set completely at room temperature in order to minimize slippage errors. Some fibres were irradiated for 1 hour using the 632.8 nm line of a 7mW helium-neon laser focused to a spot size of about $2\text{ }\mu\text{m}$ in the middle of the gauge length of the fibre. The data for the mechanical tests were collected using a 486 IBM-compatible personal computer and the stress-strain curves were directly plotted on the visual display unit of the PC using the Merlin software. A load range of 1 N was used with a 10 N capacity load cell; and a 5 mm gauge length was used. An initial strain rate of $1.67 \times 10^{-2}\text{ s}^{-1}$ was employed, and all experiments were conducted at $50 \pm 2\%$ and $23 \pm 1^\circ\text{C}$. Thirty specimens were used for ascertaining the mechanical properties for both the irradiated and unirradiated fibres (fifteen each).

Raman spectra were, on the other hand, obtained for the tencel fibres during deformation in a Raman microscope system. The Raman system is based upon a SPEX 1000M single monochromator with a holographic laser line filter. The 632.8 nm red line of a 7 mW He-Ne laser was used to excite the spectra to a $2\text{ }\mu\text{m}$ spot on the fibre using a modified Olympus microscope with a 50x objective. The laser beam was polarized parallel to the fibre axis for all of the measurements and the spectra were recorded using highly sensitive Wright Instruments Charge Coupled Device (CCD) camera.

Spectra were obtained from fibres during deformation in a small straining rig which fitted directly on to the stage of the microscope. Individual fibres were fixed between aluminium foil tabs which were placed on to the aluminium blocks of the straining rig using a cyanoacrylate adhesive, giving a gauge length of about 5 mm which could accurately be measured using a micrometer attachment that could be read to $\pm 0.005\text{ mm}$. This gave a precision of $\pm 0.05\%$ for strain measurement. The fibres were loaded to failure in steps of strain of the order of 0.2% and the exposure time used to obtain a spectrum ranged from 10–30 seconds. Moreover, creep studies were performed over a period of time and the macroscopic deformation brought about by a constant load is reported in terms of the change in Raman frequency with respect to strain. All Raman experiments were conducted at $23 \pm 1^\circ\text{C}$ and a relative humidity of $50 \pm 2\%$.

RAMAN SPECTROSCOPIC ANALYSIS OF MICRODEFORMATION

The stress-strain behaviour for tencel fibres typically exhibits no yielding and the

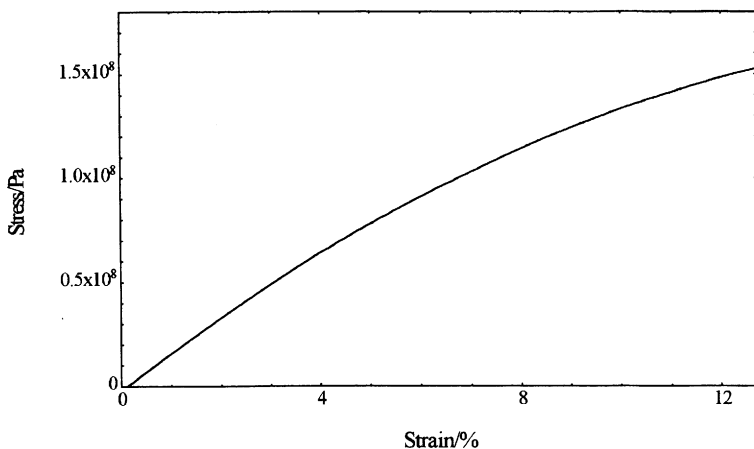


Figure 1: Typical stress-strain curves for (pristine) tencel fibres.

response is principally nonlinear (visco)elastic — refer to Figure 1. Table 1, however, provides average values for fracture strain, ϵ_f , fracture stress, σ_f , and Young's modulus, E , (calculated as the initial slope of Figure 1) for irradiated and pristine fibres. The figures in Table 1 reveal that exposure to 60 minutes of He-Ne laser radiation reduces the fracture strain and stress by less than 7%, and that the Young's modulus is practically unaffected. (The general trend of the curve for irradiated fibres is preserved, and as indicated in Figure 1.) This leads one to confidently discern that exposure of the fibres to the He-Ne laser during deformation (typically no more than 30 minutes) results in no degradation of the fibre (*sic*).

For regenerated cellulose, the classes of internal motions associated with the different spectral features particularly fall in the regions below 1500 cm^{-1} which are the most sensitive to polymorphic change. The two peaks of Figure 2 at 895 cm^{-1} and 1095 cm^{-1} prominently figure in the Raman spectrum for the structure of cellulose

Fibre	ϵ_f^\dagger (%)	σ_f^\dagger (MPa)	E^\dagger (GPa)
Pristine	13.5	150	2.1
Irradiated [‡]	12.7	140	2.1

[†] Values represent the mean of fifteen tested samples in each case.

[‡] Fibres were exposed for 60 minutes to focused 632.8 nm He-Ne laser radiation at a level of 15 mW on the middle of the fibre.

Table 1: Details of the mechanical properties of tencel fibres.

and the molecular deformation is ascertained by following these peaks as the fibres are subjected to external strain. (Figure 2 confirms earlier results by Atalla and Dimick [7] for regenerated celluloses.) The 1095 cm^{-1} peak is indicative of two principal modes: ring stretching together with C-O stretching motions. Whereas the 895 cm^{-1} peak indicates a contribution from angle bending co-ordinates involving heavy atoms only (i.e. CCC, COC, OCC), however, ring and C-O stretches and the external modes of the methylene groups may also be major contributors [8].

The effect of deformation upon the dominant Raman bands due to skeletal modes is clearly shown in Figure 3. The bands shift to lower wave number, decrease in peak intensity and broaden somewhat upon the application of tensile strain (or stress). The shift is an indication of the straining of the fibre causing molecular deformation. The broadening, on the other hand, shows that there is a distribution of the stresses and strains over the molecules within the fibre. Figure 4 depicts the dependence of the peak positions of the 895 cm^{-1} and 1095 cm^{-1} Raman bands, respectively, upon strain. It can be seen that the peaks shift to lower wave number and that the dependence upon strain is approximately linear.

Some of the deformed fibres show some scatter in the Raman measurements. This, by and large, is indicative of intrinsic material behaviour, resulting from the solvent-spinning technique and the chemical/structural changes thus caused, and is not due to any instrument-induced errors. (Laser alignment *et al.* are meticulously checked prior to experimentation.) The average Raman band shift and rate of Raman band

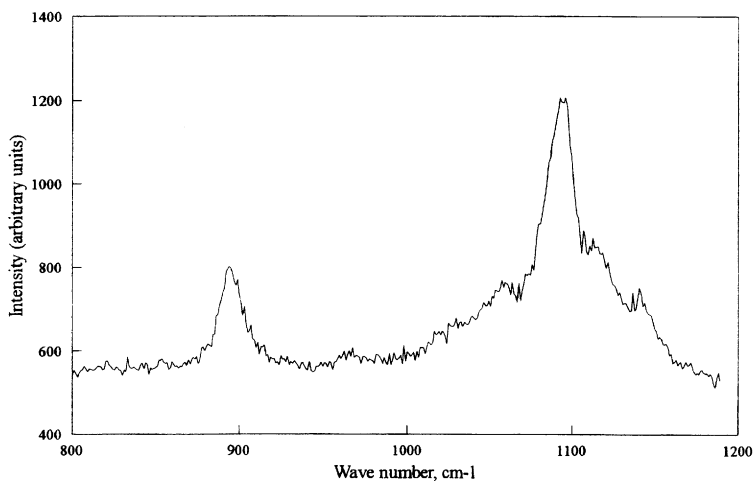


Figure 2: Raman spectrum for a single tencel fibre in the region 850-1150 cm^{-1} obtained using the 632.8 nm radiation from a He-Ne laser (7mW at the fibre).

shift with strain (i.e. strain sensitivity) are calculated for the 1095 cm^{-1} and 895 cm^{-1} , as shown in Table 2. The shifts were reproducible, although there was some drift in the zero-strain peak position due to instrumental factors.

The strain sensitivity, $d\Delta\nu/d\epsilon$, for tencel seemingly falls within the range for conventional polymers: less than $-1 \text{ cm}^{-1}/\%$ for poly(ethylene terephthalate) films [9] and polypropylene fibres [10].

RAMAN-MONITORED CREEP OF FIBRES

The Raman 'Strain Gauge'

The results of the previous section clearly indicate that the macroscopic deformation

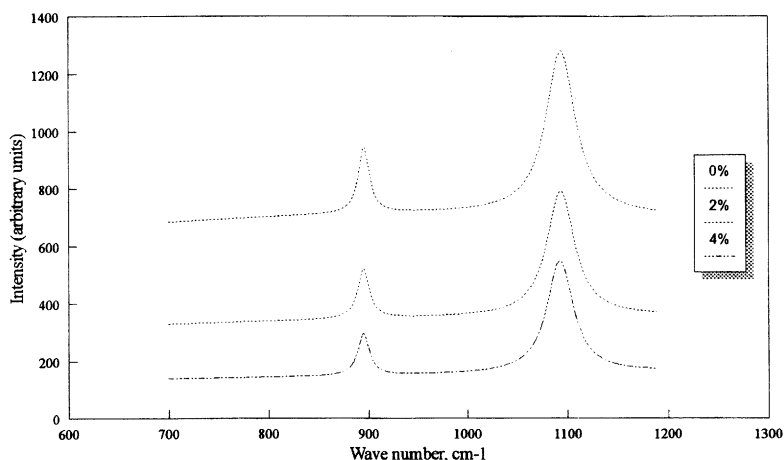


Figure 3: Shift in the position of the 895 cm^{-1} and 1095 cm^{-1} Raman bands for tencel at three levels of strain. (The raw Raman spectra were subjected to a Lorentzian fit so as to eliminate any contribution due to noise and only maintain the two prominent peaks; hence the smooth curves in this figure.)

of tencel is translated directly into molecular deformation; and that the deformation-induced skeletal modes most receptive to the Raman effect are those due to ring stretching together with C-O stretching motions.

The Raman frequency versus strain plots of Figure 4 for each of the Raman-sensitive bands may clearly be approximated by straight lines. To the extent that the Raman effect is calibrated, these straight lines serve to provide a microscopic 'strain gauge' by which internal micro-strains/stresses could be monitored. In the present work, the solvent-spun, regenerated cellulose fibres have been creep tested whilst mounted under the Raman microscope—as per details given in *Experimental*. The results were monitored in terms of the shifts in the 895 cm^{-1} and 1095 cm^{-1} Raman-sensitive peak positions with time. During creep under a positive external tensile

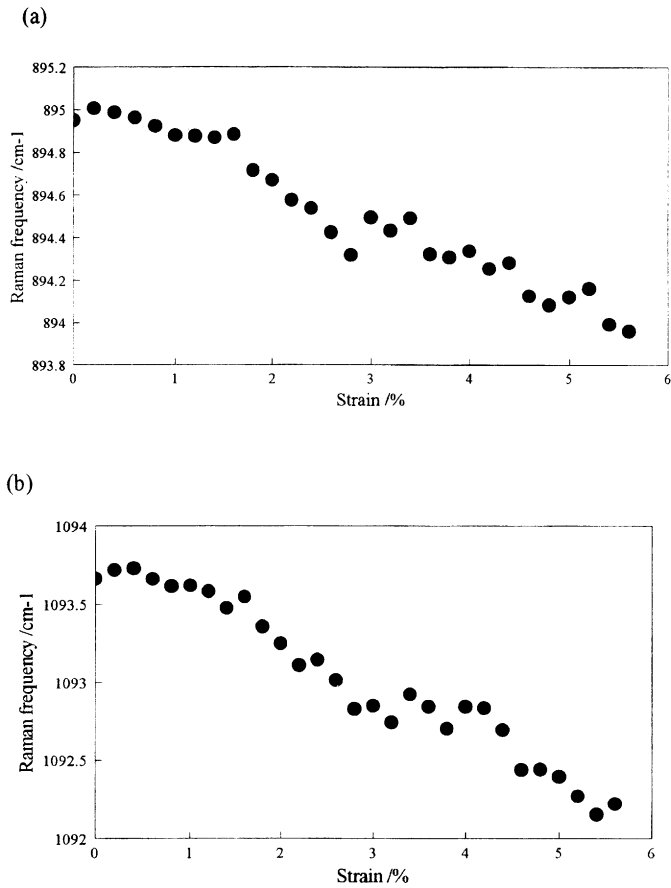


Figure 4: Dependence of the position of the 895 cm^{-1} (a) and 1095 cm^{-1} (b) Raman band peaks for tencel with strain.

1095 cm ⁻¹		895 cm ⁻¹	
$\Delta\nu^\dagger$ (cm ⁻¹)	$d\Delta\nu/d\epsilon^\ddagger$ (cm ⁻¹ /%)	$\Delta\nu$ (cm ⁻¹)	$d\Delta\nu/d\epsilon$ (cm ⁻¹ /%)
-3.26	-0.55	-1.98	-0.39

[†] $\Delta\nu$ = Shift in Raman frequency (or wave number),

[‡] $d\Delta\nu/d\epsilon$ = Strain sensitivity.

Table 2: Details of the Raman band shifts with strain for tencel fibres.

positive external tensile stress, the macroscopic strain and strain rate must both be positive (or possibly zero). During recovery, however, the strain rate will be negative, whereas the macroscopic strain can only be positive or zero as for the loading case.

Figure 5 depicts the variation of Raman frequency with creep time for the two Raman-sensitive bands; and utilizing the linear relationship between Raman frequency and strain for tencel fibres, corresponding plots of (micromechanical) strain versus creep time may be obtained—refer to Figure 6. The response indicated in these figures, as detected by the Raman technique, is somewhat complex. It is evident that during the loading period, the strain components pass through a maximum, followed by a negative strain rate. It shall be demonstrated in the next section that it is possible to account for this observation in a phenomenological way.

Creep Modelling

Based on the foregoing, it is fair to assume that the skeletal (micro)deformation of, primarily, ring stretching together with C-O stretching motions, is linearly related to the corresponding vibrational frequency (Figure 4); and that the Raman band shift, $\Delta\nu$, versus strain sensitivity, $d(\Delta\nu)/d\epsilon$, is the same—and known—for the skeletal ring stretching modes. Thus, the relative strains in each structural region can be inferred from the Raman data; conversely, from a proposed mechanical model of creep, it is possible to simulate curves for strain versus creep time.

The proposed model, which may be referred to as a 3-phase solid model, is a

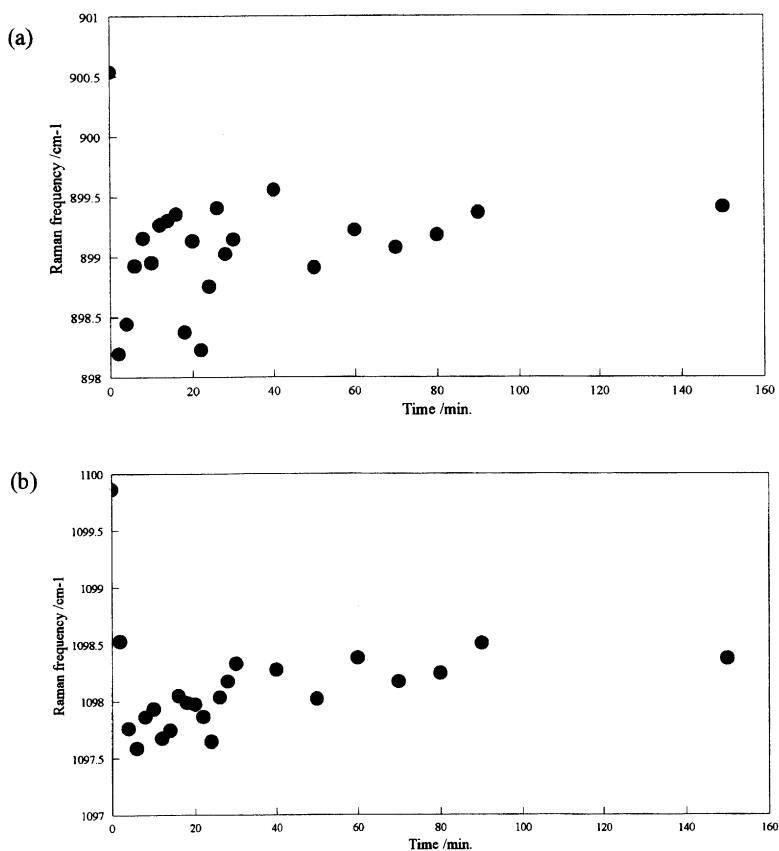


Figure 5: Graphs of Raman shifts versus creep time data for the 895 cm⁻¹ (a) and 1095 cm⁻¹ (b) peak positions for solvent-spun tencel fibres (applied stress, $\sigma = 81.75$ MPa).

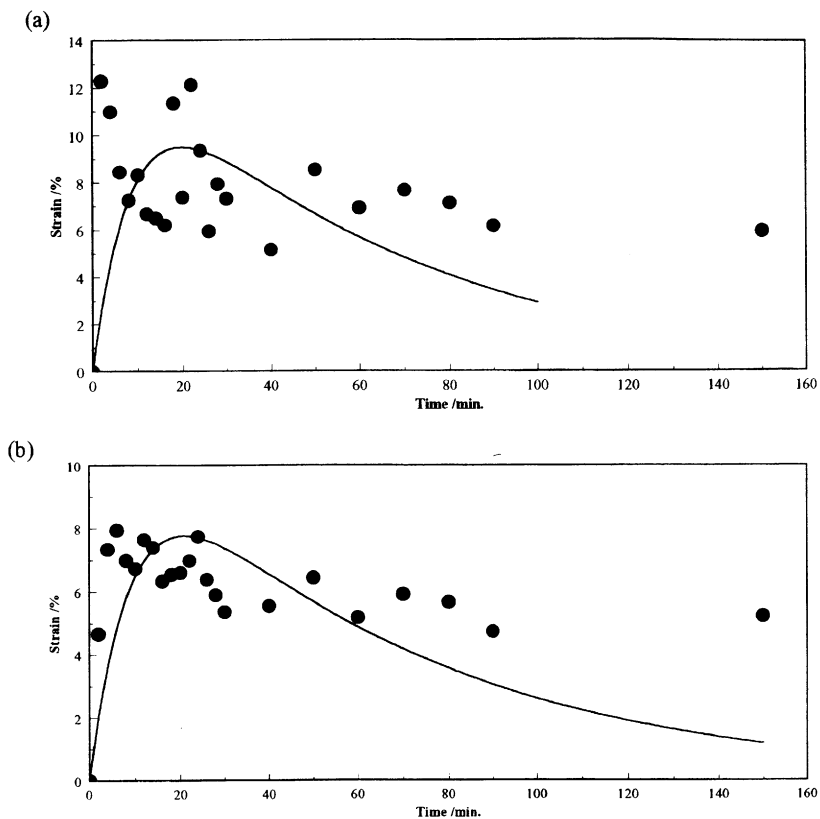


Figure 6: Corresponding graphs of (micromechanical) strain versus creep time data for the 895 cm⁻¹ (a) and 1095 cm⁻¹ (b) peak positions for solvent-spun tencel fibres (symbols) with simulated results (solid lines) based on the 3-phase solid model (applied stress, $\sigma = 81.75$ MPa).

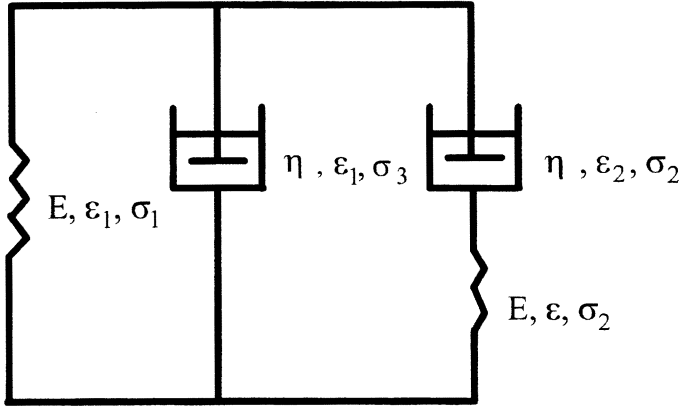


Figure 7: The 3-phase solid model for predicting micromechanical creep in regenerated cellulose fibres.

modified version of the linear (Zener) solid model: with additional damping, represented by the central dashpot, however it is assumed that the two dashpots in the system are identical, as are the two springs—refer to Figure 7. The strain in the right-hand spring predicts the micromechanical strain of the total strain in the system, and the left-hand spring should mirror the macroscopic creep/recovery strains. The model further predicts the development of negative (compressional) strain in the right-hand spring during recovery; and that the strain in the right-hand spring should pass through a maximum at some point during the creep stage.

The general differential equation that must be solved for the micromechanical strain in the system is given by:

$$\epsilon''(t) + \frac{3E}{\eta}\epsilon'(t) + \frac{E^2}{\eta^2}\epsilon(t) - \frac{\sigma'(t)}{\eta} = 0, \quad (1)$$

where ϵ , σ , E and η represent micromechanical strain, applied stress, Young's modulus and damping coefficient, respectively—all symbols correspond to the elements

of Figure 7. Thence, applying the appropriate boundary conditions for creep, the resulting general solution for micromechanical creep in the system is:

$$\epsilon(t) = \frac{\sigma}{\sqrt{5}E} \left(\epsilon^{\frac{E}{2\eta}(\sqrt{5}-3)t} - \epsilon^{\frac{E}{2\eta}(-\sqrt{5}-3)t} \right). \quad (2)$$

Figure 6 illustrates the fit of the latter equation to the Raman data. The agreement between the two is good and the general trend is accurately captured by the model. The corresponding constants for the depicted case of applied stress are given in Table 3.

Raman band (cm ⁻¹)	E (GPa)	η (N.s.m ⁻²)
1095	0.29	7.0 x 10 ¹⁰
895	0.24	5.4 x 10 ⁹

N.B. Values were arrived at by trial and error.

Table 3: Constants for the 3-phase solid model, for an applied stress $\sigma = 81.75$ MPa, fitted to the Raman data of Figure 6.

CONCLUSIONS

It has been demonstrated that Raman spectroscopy is a powerful technique for explicating the deformation micromechanics of (single) regenerated cellulose fibres. The effect of bathing the fibres with He-Ne radiation has been found to have almost no effect on the mechanical properties of the fibres. The high tensile strength of ten-cel, $\sigma_f=150$ MPa, and elongation to failure, $\epsilon_f=13.5\%$, as compared with a Young's modulus value of 2.1 GPa reflect the highly viscoelastic behaviour of these fibres.

The two principal Raman-sensitive bands are the 1095 cm⁻¹ and 895 cm⁻¹ which correspond, in the structure of cellulose, to a combination of ring stretching together with C-O stretching (and a contribution from angle bending co-ordinates involving

heavy atoms in the case of the 895 cm^{-1} band). Significant shifts of 3.26 cm^{-1} and 1.98 cm^{-1} result in the 1095 cm^{-1} and 895 cm^{-1} Raman bands, respectively, upon the application of stress; resulting in both cases in strain sensitivities of $-0.55\text{ cm}^{-1}/\%$ and $-0.39\text{ cm}^{-1}/\%$, respectively. These values are comparable to reported results for other conventional polymers.

Microdeformation has been ascertained by following the shifts of the 1095 cm^{-1} and 895 cm^{-1} Raman-sensitive bands under the application of mechanical stress. The Raman technique was shown to give a direct measure of molecular strain; and that it could be calibrated to provide a microscopic 'strain gauge' by which internal micro-strains/stresses could be monitored. The latter was used to shed light on the creep behaviour of these viscoelastic fibres. A phenomenological model, the 3-phase solid model, capable of predicting micromechanical strains has been proposed which agrees well with the Raman results. The observed creep behaviour is adequately predicted by the model, in spite of the obvious simplicity of the model components: namely, the Newtonian dashpots for a material that is known for some considerable stress non-linearity. An important result is the prediction of a strain maximum in the right-hand spring (corresponding to the micromechanical strain contribution) during the loading period.

ACKNOWLEDGEMENT

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Transcription of Discussion

Raman Spectroscopic Analysis of the Micro-deformation in Cellulosic Fibres

Dr Wadood Hamad, Lecturer, UMIST, UK

Dr Derek Page, IPST, USA

How big is the area which is illuminated in the Raman measurement?

Wadood Hamad

The latest size is 2 micron. Theoretically you can go down to 1 micron but we haven't been able to do that so all the work we have done here is at 2 micron.

John F Waterhouse, Senior Associate Scientist, IPST, USA

A very nice piece of work Dr Hamad. I believe that you can actually examine fibres in going from the wet state to the dry state. Is that correct?

Wadood Hamad

We can, but it hasn't been done yet. We collaborated with a group of people in Sweden whereby we have an environmental chamber and, yes we can; but we haven't done it yet. All the conditioning thus far is at standard 50% relative humidity and at 23°C.

John Waterhouse

So assuming that could you speculate about the possibility of actually measuring the development of residual stresses in fibres?

Wadood Hamad

Well we can with the technique, particularly with the new generation system that we have we can scan various points, a line or a whole area, so we can actually obtain a stress/strain map of the system, an actual stress strain map. We'll be able to give actual results as to the residual stresses and so on.

John Waterhouse

You should be able to see stress reversal and the distribution if you've got 1 micron resolution.

Wadood Hamad

Yes.

Dr Lennart Salmén, Head of Fiber Physics, STFI, Sweden

What scale are we talking about here? If you have a semi-crystalline material of ordered and less ordered regions can you then distinguish between these areas or are you measuring the overall deformation?

Wadood Hamad

It is the overall deformation. The lasers spot size is theoretically close to 1 micron. We have been operating at 2 micron so we are looking at a 2 micron region and basically if you want to go to the atomic level you have to infer.

Derek Page

There must be a theoretical relationship between the strain of a given bond and the frequency change. I didn't find that in your talk. Is there other work on this and is it known?

Wadood Hamad

No. The work was done mostly on polymeric materials. To the best of my knowledge there are some structure-property relationships developed for some polymer fibres.

Derek Page

It seems to me that you would have to find this before you can draw conclusions about the microdeformations in the specimen.

Wadood Hamad

This is not a trivial task; and we will soon develop some understanding of these structure property relations. People in the polymer industry have looked at it for the last 20 years.

Dr Kari Ebeling, Director, UPM Kymmene Group, Finland

Thanks for a very good presentation. Can you comment, if the Raman excitation is a reflective mode or if it is a transparent mode by which you are receiving the signals?

Wadood Hamad

No, it is reflective.

Kari Ebeling

Then you could study surface phenomena; for instance the adsorption of moisture to a strained sheet structure.

Wadood Hamad

Indeed you can. The basic attribute is the scattering principle but you can also operate the technique in confocal mode so you can actually go inside the translucent material to a certain depth which would be useful if one is dealing with wood fibres.

Kari Ebeling

It seems to be a very powerful instrument.

Ian Parker, Australian Pulp & Paper Institute, Australia

With the fibres that you were using the major molecular orientation would be along the axis of the fibres. What would you expect to see if you were looking at wood fibres where the orientation is not parallel to the fibre axis?

Wadood Hamad

I wouldn't hazard a guess.

Derek Page

Are you planning to do it?

Wadood Hamad

Yes, the work is yet to be completed.

Derek Page

Maybe you'll be able to hazard a guess in four years time.