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The fibre-matrix interface in loncell® cellulose fibre composites and its implications for the mechanical performance

Mindaugas Bulota^{1,2}, Simona Sriubaite², Anne Michud¹, Kaarlo Nieminen¹, Mark Hughes¹, Herbert Sixta¹, Michael Hummel¹

¹ Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, P.O. Box 16300, FI-00076 Aalto, Finland

² Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu pl. 19, LT-50254 Kaunas, Lithuania

Correspondence to: Mindaugas Bulota (E-mail: *mindaugas.bulota@ktu.lt*), Michael Hummel (E-mail: *michael.hummel@aalto.fi*)

ABSTRACT

Fiber-reinforced composites based on natural fibres are promising alternatives for materials made of metal or synthetic polymers. However, the inherent inhomogeneity of natural fibres limits the quality of the respective composites. Man-made cellulose fibres (MMCFs) prepared from cellulose solutions via wet or dry-jet wet spinning processes can overcome these limitations. Herein, MMCFs are used to prepare single fibre epoxy composites and unidirectional composites with 20, 30, 40 and 60 wt % fibre loads. The mechanical properties increase gradually with fibre loading. Young's modulus is improved three times while tensile strength doubles at a loading of 60 wt%. Raman spectroscopy is employed to follow conformational changes of the cellulose chains within the fibres upon mechanical deformation of the composites. The shift of the characteristic Raman band under strain indicates the deformation mechanisms in the fibre. Provided stress transfer occurs through the interface, it is a direct measure of the fibre-matrix interaction, which is investigated herein. The shift rate of the 1095 cm⁻¹ band decreases in single-fibre composites compared to the neat fibres and continues to decrease as the fibre loading increased.

1. INTRODUCTION

Fibre composites are used in a wide range of products varying from small-scale medical devices to large-scale applications in aerospace and aeronautics. This broad range of applications requires a large spectrum of properties. Although the majority of composites are made using synthetic fibres, natural cellulose fibres are increasingly important, as they are renewable, lightweight and abundant.^[1] The heterogeneity of natural fibres coupled with intrinsic flaws and mechanical damage caused during isolation, however, effectively decreases their performance and, thus, limits their broader use.^[2] For this reason, there is growing interest in the use of man-made cellulose fibres. They offer the advantages of renewability and lightweight, but are produced under industrially controlled conditions resulting in uniform and homogeneous structures.

The introduction of natural fibers into an epoxy matrix results in an increase in specific mechanical properties and cost reduction, whilst improving renewability, biodegradability and ensuring minimum shrinkage during curing. Epoxy is widely used in industry thus even the replacement of a small amount of polymer with natural fibre would result in a significant reduction in the environmental impact.

To overcome the inherent flaws in natural fibres, cellulose dissolution and regeneration into a continuous filament was industrialized more than one hundred years ago. In fact, a speciality rayon fibre (a viscose-based process) has been successfully used as reinforcement in automobile tyres for decades and is known as tirecord or Cordenka™ fibre in the market. However, the yielding of these fibres at small strain and limited mechanical properties have prevented their broader use. Another class of man-made cellulosic fibres, known nowadays as Lyocell fibres, emerged in the 1960s and became commercially available in the early 1990s.^[3] In this process, cellulose is directly dissolved without derivatization and the fibre formation is the result of simple coagulation in an anti-solvent. The dry-jet wet spinning technique allows considerable filament stretch in the air gap, which results in fibres with pronounced orientation of the cellulose molecules parallel to the fibre axis. This ordered structure is reflected in the good mechanical properties of these fibres.^[3] In addition, the endless filaments are extremely uniform, which makes them attractive as reinforcements for composites.

Recent research on regenerated cellulose fibre composites has focused on textile grade *N*-methylmorpholine *N*-oxide (NMMO)-Lyocell fibres. Epoxy-Lyocell composites have been studied and stiffness values of 15 GPa for unidirectional composites at 67 wt% fibre load ^[4] and 9 GPa at 33 % have been reported.^[5] Around 20 GPa has been reported for the stiffness of composites reinforced with Lyocell yarns at 55 % volume fraction ^[6] with a strain at break of 4 %. Nevertheless, fibre and matrix debonding in composites has been noted to occur at

low strains and thus surface modification has been suggested. Raman spectroscopy has been identified as powerful tool for investigating fibre-matrix interactions in various systems, where characteristic Raman bands are followed with respect to deformation of the fibre. It has been successfully used to study the stress transfer in single fibre hemp-epoxy,^[7] Bocell-epoxy^[8,9] and Lyocell-polystyrene^[10] systems.

The study at hand aims to improve the understanding of the fibre-composite interaction under deformation. The stress-transfer in composites is affected by the internal structure of the fibres, surface interface and fibre network build-up within the polymer matrix. Thus, a controlled balance of these factors is the key to high performance composites with tuneable properties. Raman spectroscopy is a readily available tool to understand the interplay of these effects. Herein, the mechanical properties and stress transfer in unidirectional (UD) regenerated cellulose fibre composites were investigated. A novel Lyocell-type fibre, Ioncell®, was used for this study. Ioncell® fibres are dry-jet wet spun using a superbase-based ionic liquid (IL) as non-derivatizing solvent. Various ILs have been proposed meanwhile.^[11] 1,5-Diazabicyclo[4.3.0]non-5-ene-1-ium acetate ([DBNH]OAc) used herein proved to be an exceptionally powerful solvent and can dissolve a wide spectrum of cellulosic material such as dissolving pulp,^[12] paper-grade pulp,^[13] waste paper and cardboard,^[14, 15] and cotton textile waste.^[16, 17] The fibre properties can be tailored through adjustment of the spinning parameters.^[18] The mechanical behaviour of the respective composites was correlated with the weight fractions of fibres, whilst the fibre-matrix interface was investigated using Raman spectroscopy. It has been reported previously that the Raman band at 1095 cm⁻¹ correlates with the C-O-C bond in a cellulose chain and thus is a direct measure of stress transfer as well as indication of matrix interface adhesion.^[19] Raman shifts in composites with different weight loadings of fibres were compared against the shifts observed in single fibre systems. The insights gained thereby and implications for the micromechanics of the composites are discussed.

2. EXPERIMENTAL

2.1. Fibres preparation

1,5-Diazabicyclo[4.3.0]non-5-ene-1-ium acetate ([DBNH]OAc) was prepared by adding an equimolar amount of acetic acid (glacial, 100%, Merck, Germany) to 1,5-diazabicyclo[4.3.0]non-5-ene, DBN, (99%, Fluorochem, UK). The reaction is exothermic and should be conducted with appropriate caution. Birch (*Betula pendula*) prehydrolysis kraft pulp ([η] = 476 ml/g, DP = 1133, M_n = 65.9 kDa, M_w = 269.3 kDa, polydispersity index 4.1, Enocell Speciality Cellulose, Finland) was dissolved in pre-molten [DBNH]OAc using a

vertical kneader system as described previously^[20]. Air dried pulps were mixed with [DBNH]OAc and kneaded for 1.5 hours at 80 °C and 10 rpm under reduced pressure (50-200 mbar). The resulting solutions were filtered using a hydraulic press filter device (metal filter mesh with 5 µm absolute fineness, Gebr. Kufferath AG, Germany) at 80 °C to remove undissolved substrate impurities. Filaments were spun on a customized laboratory piston spinning system (Fourné Polymertechnik, Germany) as described previously.^[12] The spin solution was then extruded through a 36-hole spinneret with a capillary diameter of 100 µm and a length to diameter ratio (L/D) of 0.2. After passing through a 1 cm air gap, the filaments were coagulated in a water bath (15 °C) in which the filaments were guided by Teflon rollers to the godet couple. The extrusion velocity (v_e) was set to 1.60 ml/min (5.66 m/min) while the take-up velocity (v_{tu}) of the godet was set to produce filaments with a DR of 8.3. The draw ratio is defined as $DR = v_{tu} / v_e$. The fibres were washed in hot water (60°C) and dried in air. The mechanical properties of the fibres were determined elsewhere,^[21] in short, the average diameter of a fibre was 14 microns, tensile strength 684 MPa and modulus 19.1 GPa.

2.2. Composites preparation

A bespoke glass mould with recesses 5 mm in width and 75 mm in length was used to produce unidirectional composites of uniform size. Ioncell® fibres were brushed with a metal brush in order to separate and align the fibres in each sample. Epoxy resin (Araldite LY5052; Huntsman, US) was mixed with hardener (Aradur 5052) in the ratio 100:38 by weight as recommended by the manufacturer. The mixture was stirred for approximately 30 min under vacuum to remove entrapped air. The degassed resin was poured onto the fibres, which were fixed to a glass mould and another glass plate was placed on top in order to spread the resin evenly and achieve a constant specimen thickness. A weight of 10 kg was placed on top to ensure uniform thickness and full penetration of the fibres by the resin. After 24 h of curing at ambient room conditions, the composites were placed in a conventional oven for 4 h at a temperature of 120 °C to post cure them. Finally, the composites were removed from the moulds and cut into strips of 1.5 x 35 mm for tensile testing using a single edged razor blade. Each sample has been visually inspected by means of an optical microscope and samples showing microcracks were discarded. Composites with weight fractions of 20, 30, 40 and 60 % were prepared which corresponds to the following volume fractions 16.7, 25.5, 35 and 55 respectively. The theoretical densities of the resulting composites, in accordance with the fibre loadings, were as follows 1.25, 1.28, 1.3 and 1.36 g/cm⁻³

Single fibres were embedded into the resin following the same process as described above, the only exception being that the single fibres were taped to the surface of a glass plate and

then a second glass plate was placed on top. Cover slips were used as spacers to achieve a uniform thickness of composites.

2.3. Mechanical testing

Tensile testing was carried out on a MTS 400 universal tester at a speed of 1 mm/min under conditions of constant humidity and temperature (50 % RH and 23 °C). Prior to the tests, all samples were left in the aforementioned conditions for at least 72 hours. Deformation was calculated from the movement of the cross-head. The thickness and width of the samples were measured using a micrometer in three locations and then the arithmetic average was used for calculations. A minimum of 5 samples were tested in each group. ANOVA was performed to compare the means (Tukey's test) at a confidence level of 95 %.

2.4. Raman spectroscopy

Samples were mounted in a tensile testing apparatus (Deben UK Ltd., Woolpit, UK) equipped with a 200 N load cell for composites and 20 N for single fibres. The same sample size as used in the tensile testing was employed although the gauge length was 15 mm. The specimens were deformed stepwise (0.015mm, i.e. 0.1% strain) with a Raman spectrum being collected at each point. A Witec Alpha300 (WITec GmbH, Ulm, Germany) Raman microscope equipped with a laser of 532 nm was used to collect the spectra. An integration time of 10 s and 600 g/mm grating were used. The laser light was polarized along the axis of the samples in order to enhance the signal of the cellulose chains parallel to the sample axis. Prior to each test, the Raman scattering detector was calibrated using mica plate (silica) as the reference material. In the data analysis, curve fitting was applied. A Lorentzian function was fitted to the spectra between 1050 and 1150 cm^{-1} in order to define the position of the peak maximum of the 1095 cm^{-1} band and to calculate the strain induced shifts. Second order polynomial curves were fitted to the Raman band shift data with respect to strain and the gradients were calculated from the first derivatives solved at 0.5 % strain, i.e. prior to the macroscopic yielding point of the fibres.^[21] A linear trend was fitted (up to 0.06 GPa) to the band shifts with respect to stress in order to determine the gradient. This method allows to evaluate the effect of fibre bundling in composites and to determine the effective fibre loading in composites in terms of stress-transfer efficiency knowing that bundling can change the fibre-fibre interactions.

2.5. Scanning electron microscopy

Cross-sections of the samples after tensile testing were imaged using a Supra 40 (Carl Zeiss AG, Germany) scanning electron microscope. The specimens were fixed to a sample holder and sputter coated with platinum in a sputter coater to obtain a coating thickness of around 5 nm. The samples were imaged at an operating voltage of 3 kV.

3. RESULTS AND DISCUSSION

Mechanical properties analysis

In order to evaluate the reinforcing effect of the Ioncell® fibres, composites consisting of an epoxy matrix and gradually increasing fibre weight fractions of 20, 30, 40 and 60 % were prepared. The fibre loading was chosen to resemble weight fractions that are commercially relevant and to provide sufficient amounts fibres to be traced by Raman spectroscopy. The stress-strain curves (Fig. 1) depict the mechanical behaviour of neat matrix and composites under tensile deformation. The increasing slope of the curves upon the addition of fibres indicates the improvement in the stiffness of composites. The strain at break slightly decreases when fibres are introduced to around 2 % which indicates that fibres act as stress concentrators due to an uneven distribution at lower fibre loadings. Similar strains have been reported by Hajjar et al. at 19 and 33 wt% fibre loads.^[5]

A detailed summary of the mechanical properties is shown in Table 1.

FIGURE 1. Representative stress-strain curves of neat epoxy and fibre composites.

The yielding point, which is measured as the deviation from a linear curve fit, is not effectively altered upon the addition of fibres up to a weight fraction of 40 %. The yielding point shifts to the left (i.e. decreases) when 60 wt% of fibres are added, which is accompanied by a slight increase in the strain at break, attributed to a local crazing effect.

This also indicates fibre bundling due to the increased fibre loading. It has been shown by Shen et al.^[22] using modelling and empirical investigations that local crazing failure does take place in carbon nanotubes polymer composites. Single fibres have a yield point at around 0.5 % and their strain at break is around 9.2 %^[3, 23] implying that as the fibre content increases, the properties of the composites approach those of the single fibres. Young's modulus and tensile strength both increased with weight fraction, reaching maximum values at 60 wt%. Although the differences between the tensile moduli at 0 and 20 wt% as well 30 and 40 wt% loads are statistically insignificant, a distinct trend is visible. The tensile strength increases further at 60 wt% load, showing a 2-fold improvement, meanwhile the Young's modulus exhibits a more than 3-fold increase over neat resin. The stiffness reported herein, however, is slightly lower than mentioned in the literature for Lyocell-type fibres, namely, 9 GPa at 33 v% which translates to around 40 wt%^[5] and around 15 GPa (measured in bending) for 67 wt% loading.^[4] The discrepancies may be due to different types of epoxy resin being used, slight misalignment and different mechanical behaviour of the fibres. Furthermore, the deformation herein has been followed indirectly, i.e. by cross-head movement. A possible error is also implied by the fact that the mechanical properties of the resin measured herein, are below the values of approx. 3 GPa for Young's modulus and around 80 MPa for tensile strength, provided by the manufacturer.

TABLE 1. Summary of the mechanical properties ($\pm$ standard deviations)

Fibre loading (wt%)	Young's modulus (GPa)	Tensile strength (MPa)	Yielding strength (MPa)	Yielding strain (%)	Strain at break (%)
0	2.2 $\pm$ 0.4	50.2 $\pm$ 6.5	13.3 $\pm$ 4.9	0.66 $\pm$ 0.4	4.1 $\pm$ 0.5
20	3.0 $\pm$ 0.5	58.3 $\pm$ 12	22.4 $\pm$ 3.4	0.86 $\pm$ 0.25	2.8 $\pm$ 1.2
30	4.5 $\pm$ 0.5	72.5 $\pm$ 7.7	36.7 $\pm$ 16.1	0.88 $\pm$ 0.36	2.1 $\pm$ 0.2
40	4.9 $\pm$ 1.2	62.7 $\pm$ 16.5	39.5 $\pm$ 1.6	0.7 $\pm$ 0.17	1.6 $\pm$ 0.4
60	7.2 $\pm$ 0.8	102.8 $\pm$ 28	30.3 $\pm$ 11	0.49 $\pm$ 0.14	4.0 $\pm$ 1.8

Yield strength increased slightly upon the addition of fibres, although the yield strain does not show a statistically significant difference. The experimental data and theoretical calculations were compared. The Young's modulus of the single fibre is 19.1 $\pm$ 1.9 GPa as has been reported elsewhere.^[24] For the calculations, a matrix modulus of 2.2 GPa was used as determined from the mechanical tests. The result shows that the experimental values

reach approximately 55 % of the theoretical maximum values based on the rule of mixtures, Fig. 2. The deviation occurs partially due to the indirect observation of the deformation, which leads to an underestimation of stiffness as described earlier, though for the comparative purposes used here, this approach is deemed valid.

FIGURE 2. Comparison of the experimental data with theoretical models

In addition, discrepancies between experimental results and theory may occur due to a number of reasons such as imperfections in the fibre-matrix interface, fibre misalignment and defects in both matrix and fibres. The porosity of the composites was not measured since SEM micrographs of the composite cross-sections did not reveal any voids, hence it was assumed that the density is close to the theoretical one which was quoted earlier.

Raman spectra analysis

Raman spectroscopy was employed to investigate the interfacial properties. Typical Raman spectra are shown in Fig. 3. The Raman band at 1095 cm^{-1} is associated with the C-O-C bond^[25] and the shifts of the band under strain are directly linked to the deformation of cellulose chains. Raman shifts of pure Ioncell® fibres under deformation were reported already earlier.^[27] A distinct band associated to the epoxy resin is seen at 1610 cm^{-1} but there is no interference with the cellulose C-O-C band at 1095 cm^{-1} . Consequently, the bands in the spectrum of a composite could be clearly assigned to its constituents (Fig. 3).

FIGURE 3. Typical Raman spectra of regenerated cellulose fibre (bottom), epoxy (middle) and composites (top).

The shift of the characteristic Raman band under tensile straining indicates the deformation mechanisms in the fibre. Provided stress transfer occurs through the interface, it is a direct measure of the fibre-matrix interaction. The shift of the Raman band at 1095 cm^{-1} with respect to stress/strain is shown in Fig. 4.

FIGURE 4. Raman band 1095 cm^{-1} shifts with respect to strain and stress for a single fibre (circles), fibre embedded in epoxy (diamonds) and fibre composites with 20 (squares) and 60 wt% (triangles) loadings. The R^2 values of all fits were above 0.8.

Raman band shift rates were previously determined via linear^[7,9] or quadratic polynomial^[27] fits. In accordance to previous studies on loncell fibers a quadratic polynomial fit was chosen herein.^[27] The Raman band shift rate in a single fibre-epoxy composite is $-0.72\text{ cm}^{-1}/\%$ with respect to strain, which is slightly lower than the $-1.19\text{ cm}^{-1}/\%$ reported for single hemp^[7] or Bocell^[9] but corresponds well to the shift rate of neat loncell® fibres investigated by Wanasekara et al. where the lower shift rate has been attributed to the draw ratio during

the spinning process, i.e. diameter and orientation of cellulose chains within the fibre are different.^[27] For better clarity, only the shifts in composites with 20 and 60 wt% loadings are shown in Fig. 4. A summary of all results is given in Table 2. Above the percolation threshold, in composites with 20 wt% loading and more, properties are governed by the network of fibres thus the importance of fibre-matrix interactions diminishes. Rahatekar et al.^[26] found the percolation threshold for high-aspect ratio aligned fibres at higher fibre loads compared to short fibres with a lower aspect ratio. This is supported by the observed mechanical properties (Table 1), i.e. the addition of fibres beyond the percolation threshold results in a moderate increase of mechanical performance. Only a high loading of fibres (60 wt%) lead to significant changes. There is a clear difference in the shift rate between the fibre and composites indicating that fibres are deformed less once embedded in the matrix. The shift rate with respect to strain is around 65% of the neat fibre shift rate. Model calculations (Fig. 2) showed that the stiffness only reached 55% of the theoretical value implying that the fibre-matrix interface plays the major role in the mechanical performance of these composites. Moreover, the plateau of the shift rate at around 2 % strain corresponds well with the stress transfer curve of 60 wt% composites in Fig. 1, where a kink between 2 and 3 % strain appears. This is indicative of the onset of fibre/matrix breakage, which is also evident in a SEM micrograph of 60 wt% composite fracture surface in Fig. 5. Increase in the shift rate at higher strain implies that the stress is taken over by the remaining intact fibres, thus higher tensile strength and strain at break is observed (Table 1).

The microstructure of fibres and their mechanical properties can be correlated assuming an aggregate structure for the deformation of high performance rigid-rod polymers as suggested by Northolt.^[28, 29] This was also shown for Ioncell® fibres earlier.^[3] Based on such an aggregate structure, the Raman band shift rate is proportional to the elastic modulus.^[27] These shift rates indicate clear differences between composites, single fibre embedded in epoxy and neat single fibre. The later has a universal shift rate of $-3.9 \text{ cm}^{-1}/\text{GPa}$ previously reported for natural fibres,^[7] Ioncell®,^[27] and other cellulose II fibres.^[30]

The stress induced shift rate increases to $-7.6 \text{ cm}^{-1}/\text{GPa}$ for the single fibre composite to around $17.6 \text{ cm}^{-1}/\text{GPa}$ in case of composites, irrespectively of the fibre loading. Earlier studies have shown that fibres with high draw ratio exhibit a uniform stress behaviour,^[31] which indicates that the strain induced shift rate is proportional to the modulus of fibre and independent of stress. Herein, we observe that the Raman shift rate in composites is neither proportional to strain nor stress. However, shift rates observed for the single fibre embedded in epoxy clearly suggest that as the fibre loading increases the behaviour of the composites is governed by uniform strain. Thus, it seemed expedient to calculate the theoretical properties using the mixing rule. On the other hand, significant deviation from the theoretical values indicate poor stress-transfer. It has been elsewhere reported that

silane-treated Lyocell fibres exhibit poor adhesion to the composite matrix. This correlates with the results presented herein and implies that mechanical interlocking is needed to capitalize on the fibres' mechanical properties.^[32]

TABLE 2. Raman band at 1095 cm⁻¹ shifts with respect to strain and stress

	Strain cm ⁻¹ /%	Stress cm ⁻¹ /GPa
Fibre	-0.84 ± 0.19	3.7 ± 0.07
Single fibre	-0.72 ± 0.19	7.2 ± 0.6
20	-0.56 ± 0.11	17.6 ± 3.5
30	-0.58 ± 0.05	14.3 ± 2.9
40	-0.65 ± 0.17	14.1 ± 4.9
60	-0.52 ± 0.03	17.3 ± 1.25

Single fibre composites exhibit a slight plateau at around 0.5 % strain, which corresponds to the macro yielding point of the fibres.^[21] The absence of a distinct plateau in the shift rate with respect to strain indicates that there is no full fibre-matrix debonding during the deformation of the composites. The Raman shift increases again at 60 wt% load, meaning that stress-transfer is supported by the tight network of fibres even in unidirectional composites.

Micro fracture analysis

Micrographs of the cross-section of a fractured composites with 20 wt%, 30 wt% and 60 wt% of fibres are shown in Fig. 5.

FIGURE 5. Scanning electron micrograph of a fracture surface after tensile testing of a composite with 20, 30 wt% and 60 wt% loadings of fibres. The inset shows a magnified view of a single fibre after fracture.

The number of pull-outs is very small and the majority of the fibres broke at the fracture surface, supporting the Raman results which implied no full fibre-matrix debonding prior the ultimate failure. It is known that epoxy matrix and cellulose form hydrogen bonds, but often to a limited extent due to the cellulose's strong intramolecular H-bonds. Thus, the interface could be improved by surface modification in order to achieve greater mechanical performance. However, one has to consider increased brittleness since crack-blunting would be prevented.

4. CONCLUSIONS

Composites with different weight fractions were prepared using regenerated cellulose fibres spun from a cellulose solution in ionic liquid. The Young's modulus and tensile strength of the 60% weight fraction composites showed 3-fold and 2-fold improvements

over the neat epoxy, respectively. The comparison with theoretical models revealed that values corresponding to around 55 % of the maximum have been reached. The interfacial fibre-matrix properties have been assessed using Raman spectroscopy, in particular, the 1095 cm⁻¹ band shift with respect to strain and stress. The shift rate in composites with respect to strain decreased by around 40 % as compared to the neat fibre which is in accordance with the theoretical Young's modulus values. Hence, we conclude, that the interface is the governing factor in the performance of these composites. Nevertheless, the mechanical performance and Raman shifts have indicated that fibre-fibre network interactions become prevailing at 60 wt% loading and to some extent compensated the lack of fibre-matrix interaction. This was supported by the transition from a uniform stress mechanical model to uniform strain as observed by Raman spectroscopy.

5. ACKNOWLEDGMENTS

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