

Ductile unidirectional continuous rayon fibre-reinforced hierarchical composites

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Abstract

Endless rayon fibres (Cordenka[®]) were used to reinforce polyhydroxybutyrate (PHB) nanocomposites containing 2.5 wt.% nanofibrillated cellulose (NFC) to create truly green hierarchical composites. Unidirectional (UD) composites with 50-55% fibre volume fraction were produced using a solvent-free continuous wet powder impregnation method. The composites exhibit ductile failure behaviour with a strain-to-failure of more than 10% albeit using a very brittle matrix. Improvements at a model composite level were translated into higher mechanical properties of UD hierarchical composites. The Young's moduli of rayon fibre-reinforced (NFC-reinforced) PHB composites were about 15 GPa. The tensile and flexural strength of hierarchical PHB composites increased by 15% and 33% as compared to the rayon fibre-reinforced neat PHB composites. This suggests that incorporation of NFC into the PHB matrix binds the rayon fibres, which does affect the load transfer between the constituents resulting in composites with better mechanical properties.

1.0 Introduction

Numerous research efforts have been directed towards the synthesis of commodity or engineering polymers derived from renewable resources. However, the commercial applications of renewable thermoplastics are still somewhat limited compared to standard commodity polymers. Polylactide (PLA), for instance, is a commercially available biodegradable thermoplastic derived fully from renewable resources with high tensile stiffness and strength of up to 3.5 GPa and 52 ± 4 MPa, respectively [1]. PLA possesses low

melt strength and heat deflection temperature, which limits its service temperature to below 58 °C [2]. Poly(hydroxybutyrate) (PHB) is another biodegradable polyester that has been extensively studied. PHB possesses relatively low melting temperature (~180 °C) but high degree of crystallinity [3]. Due to PHB's high crystallinity [4], PHB is very brittle and not well suited for processing using conventional polymer processing techniques.

For renewable polymers to compete with commodity polymers, a composite approach, *i.e.* combining renewable reinforcements with renewable polymers, can be taken. In this context, natural fibres are the prime candidate renewable reinforcements due to their cost and wide availability [5]. In fact, natural fibre-reinforced polymer composites are extensively being used in the automotive industry [6, 7]. Nevertheless, there are still drawbacks associated with the use of natural fibres. The mechanical properties of natural fibres vary along the fibre length and depend on the harvesting time and method used to extract the fibres [8, 9]. They are susceptible to seasonal changes resulting in batch-to-batch variability [5, 10]. Natural fibres also possess defects, such as dislocations, micro-compressions, curls, crimps and kinks, which affect fibre properties [10]. It is not clear as to where these fibre defects originate from but defects have been observed in cautiously extracted hemp fibres grown under wind-free conditions. The number and severity of the defects increase when the fibres were grown in windy condition [11].

Synthetic or regenerated cellulose fibres are another class of renewable reinforcements for polymers. Regenerated cellulose fibres offer similar advantages to natural fibres, *i.e.* wide availability and biodegradability, with the additional advantages of a uniform fibre quality and high strain-to-failure. Adusumali et al. [9] characterised and compared tensile properties of regenerated cellulose fibres with those of natural fibres (flax fibres). The authors concluded that both types of fibres performed in a similar manner with regards to the tensile strength and elastic modulus, because of the significant variability of the tensile results of flax fibres. However, it was highlighted that the elastic modulus and work of fracture of regenerated cellulose fibres are superior to that of natural fibres. The high strain-to-failure of regenerated cellulose fibres offers a method to absorb large amounts of energy and provide toughening qualities when incorporated into polymers [12-14]. Furthermore, regenerated cellulose fibres are also available as continuous filaments or cords, which should allow to utilise the full tensile stiffness and strength of regenerated cellulose fibres when used in unidirectional (UD) continuous cellulose fibre-reinforced polymers. UD continuous

regenerated cellulose fibre (Lyocell)^{*}-reinforced poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) was manufactured by Bourbon et al. [15]. The composites were manufactured by first impregnating regenerated cellulose fibres in-line with PHBV powders in a fluidisation chamber (based on electrostatic interaction), followed by a blower to remove excess powders. The impregnated fibres were then heat consolidated to produce UD continuous PHBV thermoplastic prepregs. The prepregs were then stacked and hot-pressed to produce the final UD composites. The authors reported tensile moduli, strengths and strain-to-failures of up to 11.4 GPa, 278 MPa and 4%, respectively, for composites with a fibre volume fraction (v_f) of 26.5 vol.%. This study clearly shows the potential of continuous regenerated cellulose fibres to be used as reinforcement to produce high performance UD fibre-reinforced polymers. Seavey et al. [16, 17] manufactured UD Lyocell fibre-reinforced cellulose acetate butyrate (CAB) composites. Instead of dry powder impregnation, the authors used a solution impregnation route; Lyocell fibres were impregnated with CAB powders by pulling them through a solvent bath (acetone or methyl ethyl ketone) containing CAB powders and surfactants. The CAB powder impregnated fibres, were dried in an oven followed by consolidation into UD Lyocell fibre-reinforced CAB composites. The authors reported tensile moduli, strength and strain-to-failure for their UD Lyocell fibre-composites of up to 22 GPa, 250 MPa and 2%, respectively for composites with a fibre volume fraction (v_f) of 60%.

Even though high performance composites can be produced using Lyocell fibres as reinforcement, these composites possess a rather low strain-to-failure of 2 - 4%. Whilst the reason behind the low strain-to-failure of the UD composites reinforced by Lyocell fibres is not known, it was shown that UD rayon fibre-reinforced CAB possess higher strain-to-failure of up to 6% compared to the same UD composite reinforced with Lyocell fibres. Rozite et al. [18] produced UD rayon fibre-reinforced thermosets with $v_f = 40 - 50\%$ and tensile modulus, strength and strain-to-failure of up to 17 GPa, 250 MPa and 7%, respectively. Inspired by these studies, we discuss the use of rayon fibres as reinforcement for a brittle PHB matrix to produce high performance UD continuous rayon fibre-reinforced PHB composites with enhanced ductility. Hierarchical composite structures are not new to the composite community. The combination of micro- and nanometre sized reinforcements, which form a hierarchical structure have been shown to improve mechanical properties of composites. Recent studies of us [20-23] have shown that nanocellulose improves the mechanical

^{*} An independent publication by Seavey et al. [16] disclosed that the regenerated cellulose fibres used in the study of Bourbon et al. [14] were Lyocell fibres.

performance of conventional natural fibre-reinforced polymer composites. Furthermore, Hajlane et al. [19] showed that cellulose nanowhiskers (CNW) grafted rayon fibre reinforced epoxy enhanced the transverse tensile strength and modulus by 5% and 44%, respectively as compared to neat rayon reinforced epoxy composites. However, these improvements seen for hierarchical composites are still far below the tensile strength of the epoxy matrix used. Furthermore, the authors used a rather tedious fibre modification method to graft the CNW. Therefore in this work, we further investigate the possibility of using nanocellulose by means of an easier production route for manufacturing continuous UD rayon fibre-reinforced PHB hierarchical composites with enhanced properties.

2.0 Materials and Methods

2.1 Materials

Two types of regenerated cellulose fibres, kindly supplied as continuous fibres by Cordenka GmbH (Obernburg, Germany), were used in this study; sized and unsized Cordenka[®] rayon fibres with a linear mass density of 2440 dtex and density of 1.6 g cm⁻³. PHB (P226, M_w = 460 kDa, density = 1.25 g cm⁻³, Biomer, Krailling, Germany) was used as matrix in powder form with a measured particle diameter d_{50} of 33 ± 2 µm. Never-dried, (2, 2, 6, 6-tetramethyl-piperidin-1-yl)oxy (TEMPO) oxidised nanofibrillated cellulose (NFC) in an aqueous dispersion with a consistency of 2.5 wt.% was kindly supplied by UPM-Kymmene Corporation (Helsinki, Finland). Cremophor A25 (BASF, Ludswighafen, GmbH) was used as surfactant to aid the dispersion and prevent irreversible aggregation of PHB powder in water for the UD composite manufacturing process. Ethanol (99% purity) was purchased from VWR International Ltd., West Sussex, UK and n-dodecane, 99% purity) was purchased from Fisher Scientific (Leicestershire, UK).

2.2 Manufacturing UD rayon fibre-reinforced (NFC-reinforced) PHB composites

UD rayon fibre-reinforced PHB composites were manufactured by wet powder impregnation using our laboratory scale composite production line [24]. Four spools of continuous rayon fibres were fixed on a tension let-off unit (Izumi International, Greenville, SC, USA) and drawn through the impregnation bath containing 5 wt.% PHB dispersed in an aqueous solution containing 2 wt.% (with respect to PHB powder) surfactant. The impregnation bath was equipped with a series of pins at various positions to increase the fibre pre-tension to enhance fibre spreading. The bath was continuously stirred and constantly topped-up (at

15 min intervals) with fresh concentrated PHB slurry (20 wt.%) to maintain the bath concentration throughout the manufacturing process. To produce continuous UD rayon fibre-reinforced (NFC-reinforced) PHB hierarchical composites, 2.5 wt.% of NFC relative to PHB was added to the powder impregnation bath.

The powder-impregnated fibres exiting the bath were passed through an infrared heated oven operated at 110 °C to dry the fibres and then a second infrared heated oven at 175 °C to melt the PHB powder on the fibres. The melt impregnated fibres then passed through three heated shear pins to provide a smooth surface finish of the composite tape. The manufacturing speed was set to 1 m min⁻¹. The manufactured composite tapes were endless with a width of 12 mm and thickness of 0.15 mm. The fibre volume fraction, v_f , of the produced composites was controlled by adjusting the concentration of PHB powder in the impregnation bath. v_f was determined gravimetrically and calculated as follows:

$$v_f = \frac{\rho_m w_f}{\rho_f w_m + \rho_m w_f} \quad (1)$$

$$w_m = w_{\text{composite tape}} - w_f \quad (2)$$

where ρ is the density of the constituents, w the linear weight of the constituents (g/m), subscripts m and f denote matrix and fibre, respectively. v_f of the produced composite tapes was controlled to be 50 - 55%.

2.3 Preparation of mechanical test specimens

The resulting UD rayon fibre-reinforced (NFC-reinforced) PHB composite tapes were cut into 200 mm long strips. Individual cut tapes were cleaned with ethanol and left to dry. For tensile specimens, 11 tapes were laid on top each other into a steel mould with a cavity of 200 mm × 12 mm × 10 mm. A steel bar was placed on top of the tapes and the mould was placed into a hydraulic press (Carver Inc, Indiana, USA) operated at 165 °C and pre-heated for 8 min. The pressure was increased slowly to 0.5 t and kept constant for 3 min. The mould was then transferred to a cooler hydraulic press operated at 70 °C (crystallisation temperature of PHB) and pressed again at 0.5 t weight for 10 min to anneal the PHB. After this stage, the mould was removed from the press and left to cool at ambient temperature for 15 min before the specimen was demoulded. For the preparation of flexural and short beam specimens, a total of 21 tapes was used in the same process described. The test specimens were then cut into the required dimensions (1 mm for tensile and 2 mm thick for flexural and short beam specimens) for mechanical testing using a diamond blade cutter (Diadisc 4200, Mutronic GmbH, Rieden am Forggensee, Germany).

2.4 Characterisation of the rayon fibres

2.4.1 Morphology of the fibres

The morphology of both sized and unsized fibres was analysed using scanning electron microscopy (JEOL JSM 5610 LV (0.5-35 kV) JEOL, Hertfordshire, UK). The accelerating voltage was set to 5 kV. Loose fibres were glued onto aluminium SEM stubs using carbon tabs. Prior to the SEM, the specimens were coated with Cr (K550 sputter coater, Emitech Ltd., Ashford, Kent, UK) for 1 min at a coating current of 75 mA.

2.4.2 Determination of equivalent fibre diameters

The equivalent fibre diameter of single rayon fibres was determined using two techniques; by microscope image analysis and using the modified Wilhelmy method. For the microscopic analysis, a few strands of dry fibres were placed between two microscope slides (VWR International Ltd., West Sussex, UK). The microscope slides were then embedded in a polishing epoxy/hardener solution with ratio of 100:20 (EpoKwick® Resin 20-80136-128 and EpoKwick® 20-8138-032 Hardener, from Buehler GmbH, Düsseldorf, Germany) and cured for 3 h. The cured epoxy containing the embedded fibres was polished using a polishing machine (Metaserv Motopol 12, Buehler GmbH, Düsseldorf, Germany). The machine was operated at a speed of 150 rpm. The specimens were polished using a series of progressively finer sandpapers (P120, P320, P800, P1200) and finally with diamond suspensions to produce flat surface. The polished specimens were then inspected using an optical microscope (Olympus BX41M, Essex, UK) equipped with an XY stage (Prior Scientific, Cambridge, UK) and CCD camera (AVT Marlin, Burnaby, Canada), which was used to capture images. The diameter of the fibres was analysed using Image-J.

Modified Wilhelmy method is a gravimetric method used to determine fibre diameters. Individual fibres were immersed and withdrawn from n-dodecane, which completely wets the fibres (as indicated by the absence of any contact angle hysteresis). The equivalent fibre diameter d_f can be determined (based on the assumption that the fibres are spherical):

$$d_f = \frac{m \cdot g}{\pi \cdot \gamma_{lv}} \quad (3)$$

where m is the mass change recorded during the immersion or emersion of the fibres, g the acceleration due to gravity (9.81 m s^{-2}) and γ_{lv} the surface tension of the test liquid (n-dodecane, 25.4 mN m^{-1}). The equivalent fibre diameter was determined from at least 25

individual fibres. The results presented are the average values. The errors are standard deviations. A detailed explanation of the experimental setup and procedures can be found in [25].

2.4.3 Tensile properties of single rayon fibres

Single fibre tensile tests were carried out according to BS ISO 11566:1996. Individual fibres were mounted onto a paper frame of 3 cm × 2 cm with various gauge lengths. The gauge lengths were set to be 15, 25 and 30 mm. Cyanoacrylate (CN) adhesive (Tokyo Sokki Kenkyujo Co. Ltd, Japan) was used to fix the fibres in position on a paper frame. The single-fibre test specimens were then placed into the testing frame (Deben Microtest, DEBEN, Suffolk, UK) equipped with 200 N load cell. The test speed was set to 1 mm min⁻¹ and the specimen loaded until failure. A minimum of 15 specimens were prepared and tested. The Young's modulus of the fibres was corrected by subtracting the machine's compliance C from the overall stiffness given by the load vs. displacement plot according to BS ISO 11566:1996 Method B:

$$E = \frac{E^*}{1 - \left(C \cdot \frac{E^* \cdot A}{L} \right)} \quad (4)$$

where E^* is the apparent stiffness calculated from the stress-strain curve, A the equivalent fibre area (i.e. $\frac{\pi}{4} d_f^2$) and L the gauge length. 10 specimens were tested for every gauge lengths. The results presented are the average values and errors are from standard deviation from the average.

2.5 ζ -potential measurements of rayon fibres and unreinforced PHB

The surface properties of as-received sized and unsized rayon fibres and unreinforced PHB were characterised by streaming potential measurements in 1 mM KCl electrolyte solution using the electrokinetic analyser (EKA, Anton Paar KG, Graz, Austria). ζ -potential of the fibres was measured as a function of pH starting from pH 5.7 to pH 2 by adding 0.1 M HCl and from pH 5.7 to pH 10 by adding 0.1 M KOH using an auto-titrating unit (RTU, Anton Paar KG, Graz, Austria). Prior to the measurement the fibres were equilibrated in the electrolyte solution. The pH was measured using a pH probe and the results were logged. A similar approach was made to determine the ζ -potential of unreinforced PHB powders to understand the surface characters of all constituents used in this study.

2.6 Characterisation of rayon fibre-reinforced (NFC-reinforced) PHB composites

2.6.1 Fibre-matrix interface between rayon fibres and PHB

The interfacial adhesion between rayon fibres and PHB was characterised using single fibre pull out tests. Single fibre model composites were prepared by embedding a single rayon fibre into a PHB melt droplet at 175 °C using an embedding apparatus [26]. The PHB melt droplet was left to cool to room temperature. The single fibre model composite was then placed into a testing frame equipped with 50 N load cell and piezo drive. The fibre was pulled out of PHB at a speed of 0.2 $\mu\text{m s}^{-1}$. During the test, the load and displacement were recorded. The apparent interfacial shear strength τ_{IFSS} was calculated using:

$$\tau_{IFSS} = \frac{F_{max}}{\pi d_f L} \quad (5)$$

where F_{max} is the maximum force required to debond the fibre from PHB, d_f the fibre diameter, and L the embedded length. The test was repeated using (NFC-reinforced) PHB as matrix for single rayon fibre model composite. A powder slurry containing 10 g of PHB was prepared the same way as the PHB slurry used in the impregnation bath of the composite line (section 2.2). 2.5 wt.% of NFC was weighed and added to the polymer slurry. The solution was dried overnight in a vacuum oven to obtain a NFC coated PHB powder. This powder was then used and melted at 175 °C in an embedding apparatus as mentioned previously. The results presented are average values of the 6 measurements.

2.6.2 Thermal behaviour of rayon fibre-reinforced (NFC-reinforced) PHB composites

The thermal behaviour of rayon fibre-reinforced (NFC-reinforced) PHB composites was characterised using differential scanning calorimetry (Discovery DSC, TA Instruments, Eschborn, Germany). Approximately 10 mg of samples were placed and sealed in a Tzero-aluminium pan. N_2 was used as the carrier gas in the chamber. A heat-cool-heat regime was employed; samples were heated from -70 to 200 °C at a heating rate of 10 °C min^{-1} , followed by cooling and re-heating. Heat of melting ΔH_m and melting temperature T_m were obtained from the heat flow curves. The degree of crystallinity X_c of PHB was calculated using the equation (4):

$$X_c = \frac{\Delta H_m}{(1-w_f)H_f^\circ} \times 100\% \quad (6)$$

where w_f is the weight fraction of fibres in the composites and H_f° the heat of fusion of 100% crystalline PHB (146 J g^{-1}) [27].

2.6.3 Density of rayon fibre-reinforced (NFC-reinforced) PHB

The true density of sized and unsized rayon fibre-reinforced neat and (NFC-reinforced) PHB was measured using a pycnometry (Accupyc 1330, Micromeritics Ltd., Dunstable, UK). Approximately 0.8 g of composite specimen were cut and placed into a measuring cell and placed into the equipment. The measurement was conducted at room temperature. A total of up to ten runs were conducted for each specimen to obtain a statistically significant average. The void content χ_v of the manufactured composites were determined using:

$$x_v = \frac{\rho - \rho_T}{\rho_T} \times 100\% \quad (7)$$

where ρ is the true composite density and ρ_T is the apparent theoretical composite density based on equation (1).

2.6.4 Mechanical properties of rayon fibre-reinforced (NFC-reinforced) PHB composites

The (hierarchical) UD rayon-reinforced (NFC-reinforced) PHB composite laminates were tested in tension and 3-point bending along the fibre length in accordance to ASTM D3039, ASTM D7264 and ASTM 2344, respectively, using an Instron universal tester (Model 4505, High Wycombe, Buckinghamshire, UK) equipped with 100 kN load cell. The tensile test specimens possessed dimensions of 200 mm $\times$ 12 mm $\times$ 1.0 mm. Prior to the test, glass fibre-reinforced polyester end tabs of 50 mm $\times$ 12 mm were glued to the specimens using CN adhesives (Tokyo Sokki Kenkyoujo Co. Ltd, Japan). The distance between the end tabs was 100 mm. Strain gauges (FLA 2-11, Tokyo Sokki Kenkyoujo Co. Ltd., Japan) were glued onto the centre of the test specimens using CN adhesives. The tensile tests were conducted at a crosshead speed of 1 mm min⁻¹. Flexural test was conducted on the same Instron but equipped with 1 kN load cell. The flexural specimens possessed dimensions of 100 mm $\times$ 10 mm $\times$ 2 mm. A span-to-thickness of ratio and crosshead speed of 32 and a 1 mm min⁻¹, respectively, were used for this test. Short beam tests are similar to flexural tests except that the span-to-thickness ratio is much smaller to generate shear failure within the specimens. The specimens with dimensions of 20 mm $\times$ 10 mm $\times$ 2 mm were mounted onto a 3-point bending rig having a span to thickness ratio of 6. The test was carried out with a crosshead speed of 1 mm min⁻¹. A total of 8 specimens were tested for each mechanical test to attain statistically significant values. The results presented are the average values and the errors quoted are standard deviations.

3. Results and Discussion

3.1 Morphology and tensile properties of rayon fibres

The SEM images of sized and unsized rayon fibres are shown in Figure 1 (a) and (b). Both types of fibres possess a smooth fibre surface. The cross-sections of the fibres were not spherical instead they had a ‘kidney bean’ shape (Figure 1 (c)). The equivalent fibre diameters are tabulated in Table 1. It can be seen that the fibre diameters measured by both techniques are very similar. For the purpose of this study, the equivalent fibre diameter calculated from the wetted length of the fibre determined using the modified Wilhelmy method was used for subsequent analysis.

Single fibre tensile tests revealed that the fibres exhibited a rather non-linear, ductile tensile behaviour having a strain to failure of $12 \pm 0.7\%$. These results agree with those reported previously in the literature [18, 28-30]. The strain-to-failure was much higher as compared to stiffer fibres, such as AS4 carbon and S2 glass fibres having strain to failure of $1.7\%^{\dagger}$ and $5.7\%^{\ddagger}$, respectively. This fibre characteristic renders them favourable for use as reinforcement for rubbers used for manufacturing high performance tyres and hoses[§]. The tensile strength of sized and unsized rayon fibres was similar (943 ± 0.6 MPa) and the Young’s moduli were 27 ± 4 GPa and 29 ± 3 GPa, respectively (Table 1). These results are expected as both sized and unsized fibres are essentially the same, except for the sizing.

3.2 ζ -potential of rayon fibres and PHB

According to Jacobasch [31] the adhesion between composite constituents can be predicted by the difference between the ζ -potential plateau values of the function $\zeta = f(\text{pH})$. He proposed that the dispersion, acid-base and electrical double-layer forces are the main causes to promote adhesion between polymers and other materials. Therefore, streaming ζ -potential measurements were conducted to study the surface character of sized and unsized rayon fibres as well as PHB. The pH dependent ζ -potential ($\zeta = f(\text{pH})$) showed that both fibres have an acidic surface character; their isoelectric point (IEP) was 4.1 and 5.0 for sized and unsized rayon fibres, respectively (Figure 2). This shows that the presence of -COOH groups was the dominant mechanism for the formation of the electrochemical double layer [32-34]. The ζ -

[†] Hexcel Product data of AS4 carbon fibres. Link in: <http://www.hexcel.com/resources/datasheets/carbon-fiber-data-sheets/as4.pdf>. Last accessed on 06.08.2015.

[‡] AGY Product data of S2 glass fibres. Link in: http://www.agy.com/wp-content/uploads/2014/03/High_Strength_Glass_Fibers-Technical.pdf. Last accessed on 06.08.2015.

[§] Cordenka GmbH Products and Applications. Link in: http://www.cordenka.com/products_applications.php. Last accessed on 06.08.2015.

potential plateau values of the sized and unsized rayon fibres were negative and very similar at -14.8 mV and -15.4 mV, respectively. This behaviour is comparable to that reported by Stana-Kleinscheck et al. [33], who measured the $\zeta=f(\text{pH})$ of three types of regenerated cellulose fibres, namely Viscose, Modal and Lyocell. They reported that all fibres exhibited a ζ -plateau at pH 7 with ζ -potential plateau values of approximately -7.5 mV. Unfortunately, the authors did not report the IEP values.

The $\zeta=f(\text{pH})$ curve of pure PHB also indicated that it has an acidic surface character with an IEP of pH 2.4 (Figure 2), which is expected as one of the end groups of PHB is a carboxylic acid. ζ_{plateau} was determined to be -55 mV. Asran et al. [35] reported a much higher IEP for PHB at pH 6.9 with ζ_{plateau} of -42.0 mV. The ζ -potential plateau of the same NFC was measured by electrophoresis and reported previously to be -41 mV (Figure 4) [36]. This shows that all the constituents used in this study have an acidic surface character. All of them possess negatively charged surface possibly from abundant carboxylic acid groups on the surface.

3.3 Adhesion between rayon fibres and PHB

In order to use rayon fibres in composite applications, it is important to understand the compatibility of these fibres to potential matrices. The apparent interfacial shear strength τ_{IFSS} between sized and unsized fibres, and neat PHB was only 6.8 ± 0.3 MPa and 7.0 ± 0.3 MPa, respectively. This shows that both fibres adhere poorly to PHB. The low interfacial adhesion could be due to both constituents having similar surface character according to the ζ -potential measurements. The differences in the ζ_{plateau} between both constituents are also very small, which led to poor adhesion. τ_{IFSS} depends on the embedded fibre length; it decreases with increasing embedded length (Figure 3) indicating a brittle fracture behaviour of the model composites during single fibre pull-out [26]. This is expected since PHB is a very brittle matrix having a strain to failure of only 1.0% [37]. Therefore, to improve the interface between rayon fibres and PHB, we introduced NFC into the PHB matrix. The τ_{IFSS} between sized and unsized rayon fibres and (NFC-reinforced) PHB improved by 24% and 41.4% to 8.4 ± 0.8 MPa and 9.9 ± 0.5 MPa, respectively. Nevertheless, τ_{IFSS} still depends on the embedded fibre length as shown in Figure 3. The improvement at a single fibre model composite level shows that addition of NFC enhances the interface properties between rayon fibres and NFC-reinforced PHB. We hypothesise that NFC adsorbs to the fibres and stiffens the surrounding matrix resulting in the increased τ_{IFSS} .

3.4 Thermal properties of rayon fibre-reinforced (NFC-reinforced) PHB composites

The DSC curves of both rayon fibre-reinforced (NFC-reinforced) PHB composites are shown in Figure 4. Two melting peaks were observed in the second heating curve for all the composites, one at about 150 °C and one at 162 °C (Figure 4A). The two melting peaks with different intensities observed in PHB could be due to (i) the first melting and further re-crystallisation of PHB crystals, which may influence the reorganisation of these crystals during the second heating or (ii) the existence of two lamella structures within PHB crystals [38, 39]. During cooling however only one re-crystallisation peak at about 79 °C was observed for unreinforced PHB and both rayon fibre-reinforced (NFC-reinforced) PHB composites (Figure 4B). It is also evident that the upper melting peaks were more dominant which suggest that the PHB contains stable crystals and a small portion of unstable crystals [39]. Therefore, the two melting peaks could be associated with the reorganisation of these crystals during second heating. The melting temperature of all composites manufactured also shifted by upwards about 8 °C compared to the unreinforced PHB.

The DSC results of the composites normalised to the weight fraction of PHB in the composites of the second heating curves are tabulated in Table 2. The crystallinity of neat PHB was found to be 55%. The crystallinity of the composites studied decreased by about 10% as compared to the unreinforced PHB with an exception of the unsized rayon fibre-reinforced (NFC-reinforced) PHB which exhibited the lowest crystallinity (44%). The heat of melting ΔH_m for rayon fibre-reinforced (NFC-reinforced) PHB did also decrease as compared to the neat composites. This could imply that incorporation of NFC into the composite reduced the number of nucleation sites for crystallization, thus reducing the overall the crystallinity of the composites.

3.5 Mechanical properties of rayon fibre-reinforced (NFC-reinforced) PHB composites

Unidirectional rayon reinforced neat PHB and rayon reinforced (NFC-reinforced) PHB composites with $v_f = 50 - 55\%$ were successfully manufactured. The composite densities were characterised and tabulated in Table 2. The increased density of the hierarchical composites suggests that NFC was picked-up by the rayon fibres during the fibre impregnation step. To illustrate this, rayon fibres were dipped into a water bath containing 2.5 wt.% NFC and dried prior to taking SEM images. We observed a thin membrane-like nanocellulose paper sheet surrounding the fibres (Figure 5). Similarly, we also dipped rayon

fibres into a water bath without NFC and dried and SEM images were taken. The SEM images of the latter fibres are very similar to those shown in Figures 1 (a) and (b). Therefore, it is evident from Figure 5 that NFC does act as a binder holding the rayon fibres together, which could enhance the load transfer between the fibres in the composites.

Typical stress-strain curves of rayon fibre-reinforced (NFC-reinforced) PHB composites are presented in Figure 6. The strength of sized rayon fibre-reinforced neat PHB was determined to be 221.7 ± 12.1 MPa (Table 3). With the addition of 2.5 wt.% NFC into the composite, the tensile strength of the composite improved by 14.5% to 253.9 ± 8.5 MPa. Similarly, the tensile strength of unsized rayon fibre-reinforced neat PHB was found to be 235.5 ± 11.1 MPa and the addition of 2.5 wt.% of NFC leads to an improvement in the tensile strength of up to 15.7% to 273.2 ± 5.8 MPa. These values are comparable to the ones reported by Rozite et al. [18] for Cordenka reinforced acrylated epoxidised soy oil resin (Tribest) (Table 4) and Cordenka reinforced epoxidised pine oil resin (EpoBioX) having $v_f = 40 - 50\%$. The Young's modulus of both neat and (NFC-reinforced) PHB composites remained the same $\sim 14 - 15$ GPa. A Young's modulus of 15.4 GPa was predicted using the rule of mixture.

Comparison with various literature reports on tensile properties of UD regenerated cellulose fibre-composites are tabulated in Table 4. The tensile strength of Lyocell reinforced PHBV as reported by Bourban et al. [15] was extraordinary but no other researchers were able to achieve this performance despite using the same reinforcing fibres [16, 40]. When comparing the literature results with ours; the most significant result is the enhanced strain to failure of our composites. Despite using a very brittle matrix, the composites failed at $\sim 12\%$, which corresponds to the strain-to-failure of rayon fibres. Previous attempts have focused on improving the strain-to-failure of PHB by blending it with other polymers and/or plasticisers; Parra et al. [41] studied the mechanical properties of PHB polyethylene glycol (PEG) blends. They reported an improvement in the strain-to-failure of the blend by about five times upon the addition of 40 wt.% of PEG however, the tensile strength of the polymer was reduced by half. Wang et al. [42] reported a strain-to-failure of 7% for 50:50 PHB cellulose acetate butyrate (CAB) blends, but yet again the tensile strength of the polymer blend decrease by almost half. El Taweel et al. [43] reported blending of PHB with polyvinylacetate (PVAC). Two plasticisers, atactic synthetic PHB [P(*R,S*-3BH)] and atactic *R,S*-PHB-OH, were used in the blend. The authors reported strain-to-failures of up to 5% for blends of PHB, PVAC and the atactic *R,S*-PHB-OH with 40:30:30 ratio, but the tensile strength and modulus was

significantly reduced by 74% and 98%, respectively. All of these attempts to improve the ductility of PHB were successful but at the expense of the polymer's tensile strength and modulus. In this work, we demonstrated that ductile composites can be produced even when the composite contained 45 - 50 vol.% brittle polymer matrix (e.g. PHB).

The flexural strength and modulus of sized rayon fibre-reinforced neat PHB was measured to be 132 ± 5 MPa and 9.9 ± 0.4 GPa, respectively (Table 3). With the addition of 2.5 wt.% of NFC into the composites, the flexural strength and modulus improved 32% and 30% to 175 ± 6 MPa and 12.9 ± 0.3 GPa, respectively. On the other hand, the flexural strength and modulus of unsized rayon fibre-reinforced neat PHB were found to be 156 ± 5 MPa and 11.7 ± 0.3 GPa. The flexural strength and modulus improved 14.8% and 5% to 179 ± 7 MPa and 12.3 ± 0.3 GPa, respectively, when 2.5 wt.% of NFC were introduced into the unsized rayon fibre-reinforced PHB composites. All of these composites failed via buckling under the loading point, regardless of its void content (Table 2), which again showed the ductility of the material. Conventional stiffer and low strain to failure composites such as carbon fibre-reinforced polymers usually exhibit a tensile behaviour when the composite is strained excessively in the test configuration. Similar results were obtained for short beam shear. The interlaminar shear strength (ILSS) of sized rayon fibre reinforced PHB composites was measured to be 4.4 ± 0.1 MPa. With the addition of 2.5 wt.% of NFC, the ILSS improved by 55% to 6.8 ± 0.2 MPa. As for the unsized rayon fibre-reinforced PHB composites, the ILSS was measured to be 7.0 ± 0.1 MPa while the incorporation of 2.5 wt.% NFC into the composites improved the ILSS by 11%. These measured improvements in ILSS confirm the IFSS of the model composites. All the results presented demonstrate improvements in the mechanical properties of the hierarchical composites containing 2.5 wt.% NFC, which may be attributed to the better stress transfer between the fibres due to the presence of a 3D NFC network in the composites.

4.0 Conclusions

We demonstrated that the wet impregnation method, which is commonly used to manufacture high performance thermoplastic composites, can also be used to produce rayon fibre reinforced PHB with control over the fibre volume fraction of the composites. We successfully produced hierarchical rayon fibre reinforced PHB by incorporating 2.5 wt.% with respect to PHB of NFC into the composites. The presence of NFC in the hierarchical composites is evident from the increased density of the composites. From the measured ζ -

potentials, it was concluded that both reinforcements (rayon fibres and NFC) and PHB have acidic surface characters with PHB having the most negative ζ -potential. Furthermore, single fibre pull out tests indicated that rayon fibre reinforced NFC/PHB nanocomposites had higher apparent interfacial shear strength as compared to model composites with neat PHB, which showed that the presence of NFC improves the fibre-matrix interface properties, which was also confirmed by ILSS measured by short beam shear tests. The increased adhesion leads to better stress transfer between the fibres and, therefore, better composite properties of rayon fibre-reinforced (NFC-reinforced) PHB with a high strain to failure and up to 16%, 33% and 55% higher tensile, flexural and interlaminar shear strengths, respectively, as compared to rayon fibre-reinforced neat PHB.

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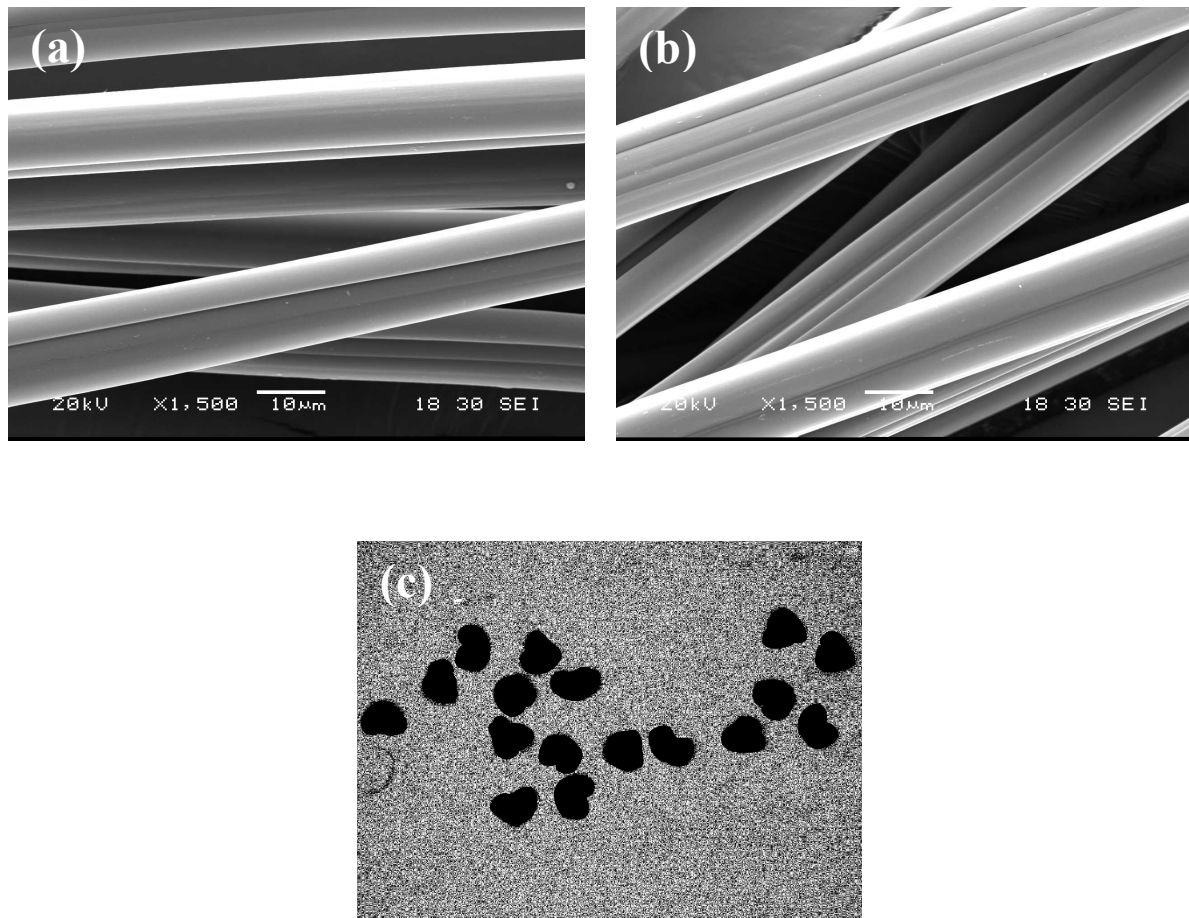


Figure 1. Scanning electron micrographs of (a) sized, (b) unsized rayon fibres and (c) microscope image of rayon fibre (Image taken at 100x magnification).

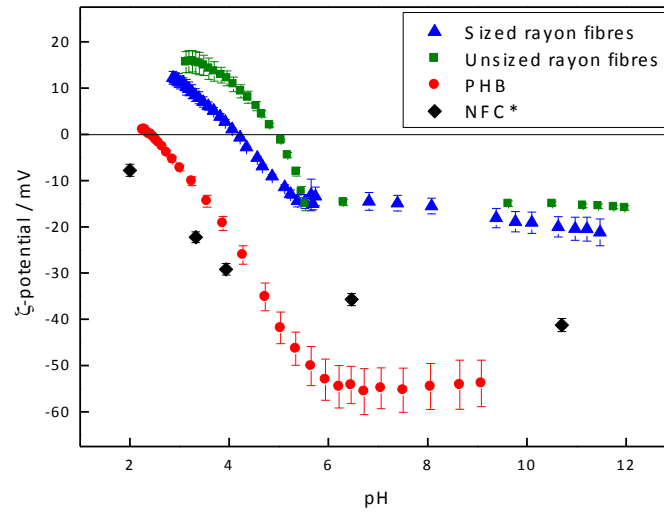


Figure 2. ζ -potential as a function of pH for sized and unsized rayon fibres, neat PHB and NFC¹.

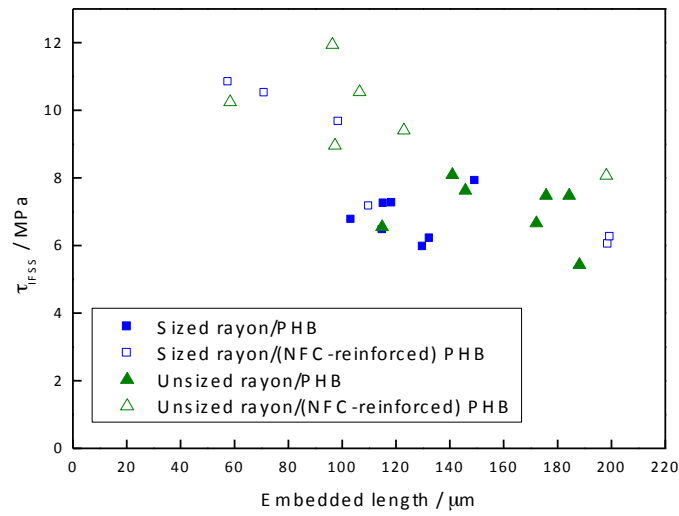


Figure 3. Apparent interfacial shear stress τ_{IFSS} as a function of embedded length for sized and unsized rayon fibre-reinforced neat and (NFC-reinforced) PHB single fibre model composites

¹ Values of zeta potential = f[pH] of NFC was taken with permission from reference [33]

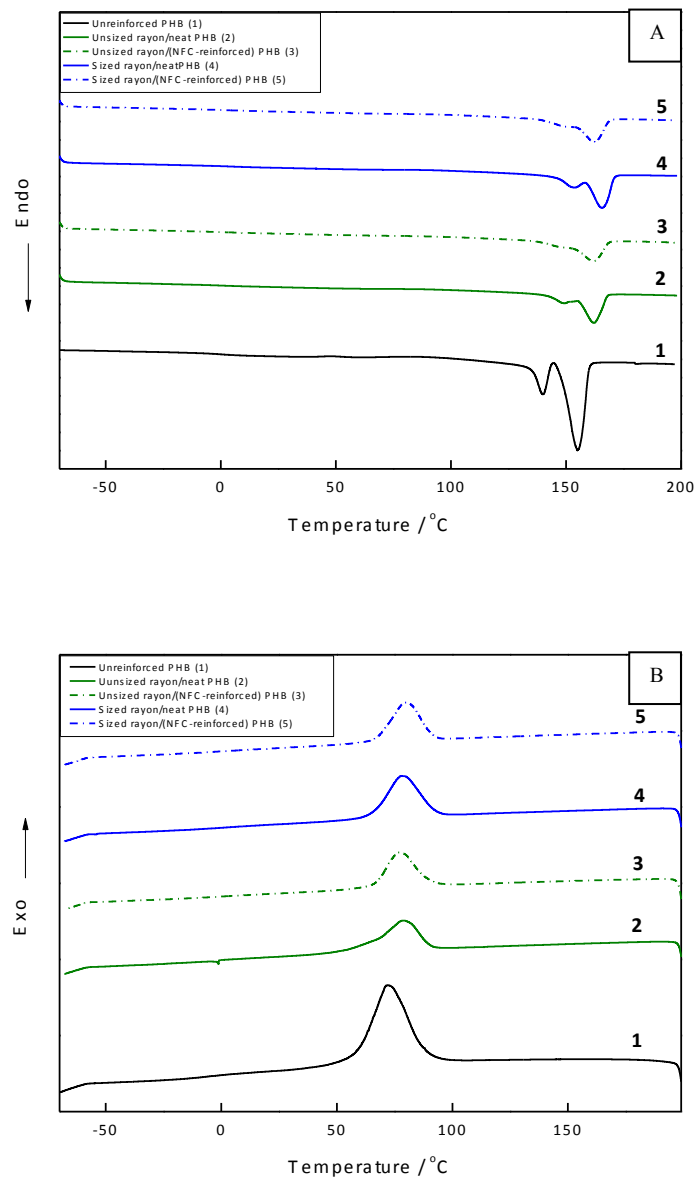


Figure 4. 2nd Heating (A) and Cooling (B) curves of rayon fibre-reinforced neat and (NFC-reinforced) PHB composites observed during DSC scan.

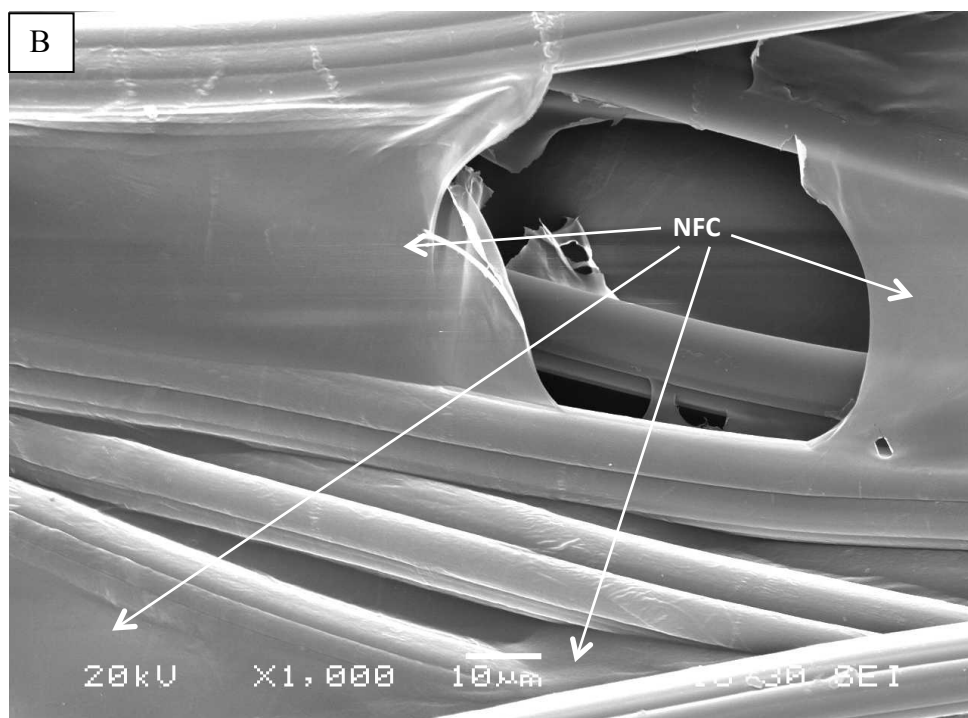
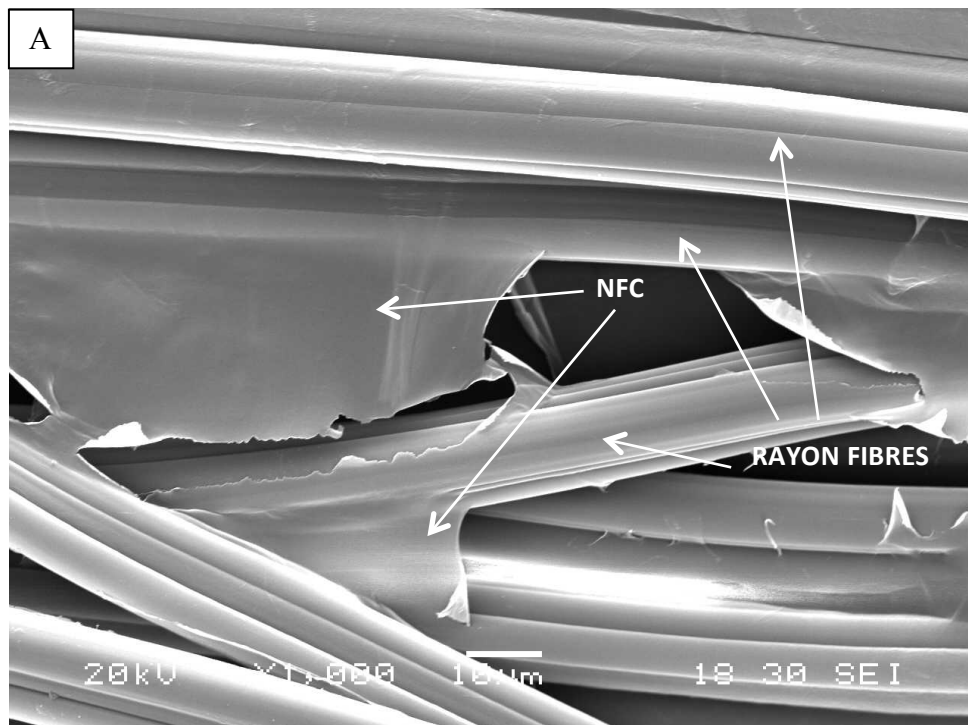


Figure 5 Scanning electron micrographs of (A) sized and (B) unsized rayon fibres when dipped in in a bath of water containing 2.5 wt.-% of NFC. The NFC binds the fibres creating a bridge from fibre-to-fibre.

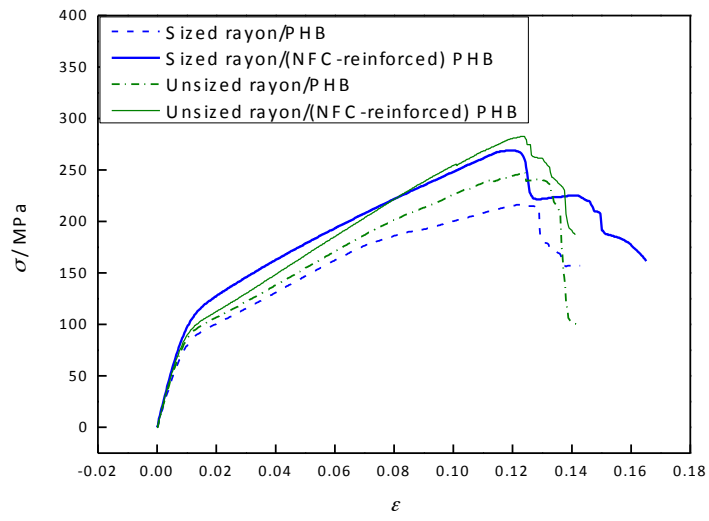


Figure 6. Typical stress (σ) – strain (ϵ) curves for sized rayon fibre-reinforced neat and (NFC-reinforced) PHB composites and unsized rayon fibre-reinforced neat and (NFC-reinforced) PHB composites

List of tables:

Table 1: Rayon fibre diameter and tensile properties

Sample	Fibre diameter		Tensile Properties		
	$d_{f, \text{Wilhelmy}}$ (μm)	$d_{f, \text{optical}}$ (μm)	σ_f (MPa)	E_f (GPa)	ε (%)
Sized rayon	14.0 ± 0.4	14.4 ± 0.5	943.8 ± 22	27.4 ± 4	10.2
Unsize rayon	12.6 ± 1.5	13.5 ± 0.2	943.0 ± 94	28.8 ± 3	10.4

Table 2: Density (ρ_{comp}), void content (χ_v), melting temperature (T_m), crystallisation temperature (T_c), enthalpy of melting (ΔH_m) and crystallinity (X_c) of unreinforced PHB, sized and unsized rayon fibre-reinforced (NFC-reinforced) PHB composite (normalised to the weight fraction of PHB in the composites) based on 2nd heating.

Sample	ρ_{comp} (g cm^{-3})	Void, χ_v (%)	$T_{m, 1}$ ($^{\circ}\text{C}$)	$T_{m, 2}$ ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	ΔH_m (J g^{-1})	X_c (%)
Unreinforced PHB	-	-	140	155	72	79.7	54.6
Sized rayon/neat PHB	1.42 ± 0.02	0.6	153	166	78	30.2	52.5
Sized rayon/(NFC-reinforced) PHB	1.56 ± 0.01	6.1	139	163	79	27.4	47.9
Unsize rayon/neat PHB	1.52 ± 0.00	6.0	149	162	78	28.6	48.5
Unsize rayon/(NFC reinforced) PHB	1.54 ± 0.01	4.7	138	165	76	25.8	44.4

Table 3: Tensile strength (σ_T), Young's modulus (E_T), strain-to-failure (ε), flexural strength (σ_F), flexural modulus (E_F) and Interlaminar shear stress ($ILSS$) of unreinforced PHB, UD rayon fibre-reinforced (NFC-reinforced) PHB composites. τ_{IFSS} denote the apparent interfacial shear strength between rayon fibres and PHB (nanocellulose composites) measured using single fibre pull-out and $ILSS$ denotes the interlaminar shear strength of rayon from short beam test.

Sample	σ_T (MPa)	E_T (GPa)	ε (%)	σ_F (MPa)	E_F (GPa)	$ILSS$ (MPa)	τ_{IFSS} (MPa)
Unreinforced PHB	$21.0 \pm 2^*$	$0.9 \pm 0.08^*$	$1.01^\#$	-	-	-	-
Sized rayon/neat PHB	222 ± 12	15.6 ± 0.9	11.7	132 ± 5	9.9 ± 0.4	4.4 ± 0.1	$6.8 \pm 0.$
Sized rayon/(NFC-reinforced) PHB	254 ± 8	15.5 ± 0.1	12.2	175 ± 6	12.9 ± 0.3	6.8 ± 0.2	$8.4 \pm 0.$
Unsize rayon/neat PHB	236 ± 11	15.1 ± 0.3	11.6	156 ± 5	11.7 ± 0.3	7.0 ± 0.1	$7.0 \pm 0.$
Unsize rayon/(NFC-reinforced) PHB	273 ± 6	14.6 ± 0.3	12.7	179 ± 7	12.3 ± 0.3	7.8 ± 0.2	$9.9 \pm 0.$

*[#]Values from Ref [25] and Ref [34], respectively

Table 4: Tensile strength (σ_T), Young's modulus (E_T), strain-to-failure (ϵ), fibre volume fraction (v_f) of various UD regenerated cellulose fibre-composites reported in literature.

Composite type	v_f	σ_T (MPa)	E_T (GPa)	ϵ (%)	References
Lyocell/PHB-V	27	278	11.4	4	[14]
Lyocell/CAB	60	250	22.0	2	[15]
Rayon/Tribest	40-50	250	15.0	7	[17]
Rayon/PHB	50-55	222-236	15.1-15.6	11.6	This study