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Modeling and characterization of the moisture-dependent bilinear behavior of regenerated cellulose composites

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Abstract In this study, we investigate the tensile mechanical properties of unidirectional Lyocell/epoxy composites under wet and dry conditions using a multi-scale analysis approach. Characterization of the samples shows a bilinear stress–strain behavior of the fibers and composites under tension loading. The bilinear elastic–plastic stress–strain response of the Lyocell fibers is incorporated into a *p*-version finite element model for presenting a methodology for structural analysis of this composite system. The proposed finite element models were successfully able to relate the micro to macro-mechanical behavior enabling an approach for determining the 3D orthotropic elastic–plastic constants of regenerated cellulose/epoxy composites.

Keywords Finite element method · Composites · Regenerated fibers · Multi-scale modeling

Introduction

Bio-based composites have been manufactured from natural fibers and bio-based polymers such as poly(lactic acid), natural oils and various epoxies with large bio-based sources. Natural fibers reinforcements for composites are becoming increasingly attractive for many product applications [1–4]. One class of natural fibers consists of regenerated cellulose fibers which are produced by dissolving cellulose, then regenerating it by extrusion and precipitation. Regenerated cellulose fibers have generally less variable properties compared to other natural fibers and result in more uniform shape, tensile strength, diameter, and failure stress [5]. Adusumali et al. [6] compared single fibers of several types of regenerated cellulose fibers to glass and flax fibers for modulus of elasticity, tensile strength and interfacial shear strength with polypropylene. They found that regenerated cellulose fibers could exceed both flax and glass fibers in their strain to failure; making them particularly useful for composites applications in which a higher fracture toughness is required. Cheng et al. [4, 7] investigated the effects of process and source of cellulose fibrils by measuring its elastic modulus using atomic force microscopy on the fibrils. The research estimated the elastic modulus of Lyocell to be approximately 98 ± 6 GPa for fibrils with diameters ranging from 150 to 180 nm. The modulus, however, drops dramatically for fibrils with diameters exceeding 180 nm. Gindl and Keckes [5] studied the strain hardening of Lyocell and viscose forms of regenerated cellulose fibers by straining fibers under cyclic tensile tests and observing the increase in tensile modulus. The strain hardening was larger for Lyocell that showed more crystallinity and fiber orientation of cellulose chains in addition to a 47 % increase in its modulus compared with only 28 % for viscose. Research into regenerated cellulose-based composites has also been reported in the literature as well as using recycled cellulose for its generation [8]. A surface selective dissolution method to prepare high modulus all-cellulose composites from Lyocell and Bocelli fibers was investigated by electron microscopy, tensile testing and X-ray diffraction [2]. The fibers were found to have excellent mechanical properties that can be tuned depending on preparation parameters. The use of regenerated fibers for composites was also addressed by several studies. Graupner and Mussig [1] used

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compression molding to prepare cellulose composites with Kenaf and Lyocell in poly(lactic acid) (PLA) and poly (3-hydroxybutyrate) matrices. Lyocell–PLA composites showed the highest Young's modulus (9.3 GPa) with 30 % Lyocell by mass. They also found that Lyocell–poly (3-hydroxybutyrate) had the highest impact strength at 70 kJ/m^2. Other testing has showed that Lyocell–PLA composites have high tensile and impact strength as well as a high Young's modulus, although achieving a good bonding between the fibers and the matrix was problematic [9]. The tensile and flexural properties of chopped Lyocell–polypropylene composites prepared by wet layup and compression molding were also investigated [10]. The Lyocell produced with steam exploded wood fibers showed a retention of 90 % of the flexural strength and 98 % of the tensile modulus at 41.2 % of the cost of the reference-based Lyocell composite. Raman spectroscopy analysis of the molecular deformation of regenerated cellulose fibers in epoxy and polyester has shown the presence of large interfacial shear stress between the fibers and the resin [11]. Use of biocompatible resins has been found to result in higher properties when incorporating regenerated cellulose fibers [12]. The incorporation of cellulose in thermosetting resins with large amounts of bio-content has also been an area of the research of the first author [13]. The viscosity of the epoxy was considered a main obstacle in processing of the cellulose-based composite. In this study, we present the results of a computational and experimental investigation on the tensile behavior of Lyocell/bio-based epoxy composites. The mechanical properties of Lyocell tows are investigated for tensile properties under dry and wet conditions to characterize the constitutive behavior. The composite is then prepared using wet layup and resin infusion to investigate the effects on the mechanical behavior. The *p*-version finite element analysis (*p*-FEA) is used to generate a unit cell model incorporating the elastic–plastic bilinear constitutive response for the regenerated fibers and is proposed within a possible framework for possible modeling of composite products made from these materials. Experimental data are used to calibrate and verify the FE model for this composite system and its predictive capability is assessed.

Modeling framework

The bilinear behavior of the Lyocell fibers and their dependency on the moisture conditions suggest the need for a suitable analysis framework for these composites. The constitutive response of the regenerated fibers is very dependent on the moisture condition. The results presented in the subsequent section show how the regenerated fibers possess a bilinear material behavior with elastic–plastic tendencies. Under moisture exposure, the elastic response gradually dissipates and results in a largely plastic unrecoverable behavior. In this study, we used a type of multi-scale analysis approach for simulation of Lyocell/bio-based epoxy composites that use a representative unit cell where the behavior of the constituents is independently recognized. The result is then a homogenized behavior of the composites that can be used for a structural level analysis (Fig. 1). In Fig. 1, $E1$ and $E2$ correspond to the elastic and 'plastic' stiffness. ε_y and σ_y are the limit strain and stress at the knee point whereas ε_f and σ_f are the failure strain and stress of the composite. This modeling approach is implemented in a *p*-FEA approach. In *p*-FEA, the refinement is achieved by increasing the polynomial degree of the elements, which is directly related to degrees of freedom in the model. The primary advantage of this approach is the ability to check the convergence of the solutions with increasing element order reducing the dependency on the mesh size. Increasing the polynomial degree of the elements is related to the error of approximation. These errors are reduced exponentially as the number of degrees of freedom is increased. The global energy norm is calculated for each polynomial order as an indicator of the convergence of the solution. In addition to the global energy norm, the quantity being investigated is also checked for convergence with each polynomial order solution. Commercially available *p*-FEA software is used for the simulations of the micromechanical models (Stress Check V9.0; ESRD, St. Louis, Missouri, USA). The typical unit cell model used for the hexagonal packing contained 178 elements consisting of 72 hexahedral and 106 pentahedral elements. A hexagonal packing geometry was considered the most representative for the models performed, although other packing geometries can also be considered. The nonlinear material properties of the Lyocell fibers are accounted for using a bilinear elastic–plastic stress–strain relationship to the experimental data. The polymeric epoxy matrix is assumed to be linear. The model was calibrated for one set of fiber volume fraction (FVF) for validation purposes. The model was then run with different FVF for validation purposes of the modeling capability. The loading was applied to the model in the form of a constant displacement on one face in the fibers direction. Boundary conditions were applied to restrict in- and out-of-plane displacement on the opposing face. No restrictions to the out-of-plane boundary conditions on the other four faces were applied to account for Poisson ratio effects as a tension load is applied in fibers' direction. The results of *p*-FEA modeling were compared to those obtained by experiments in the fiber direction by calculating the average stress resulting on the loaded surfaces.

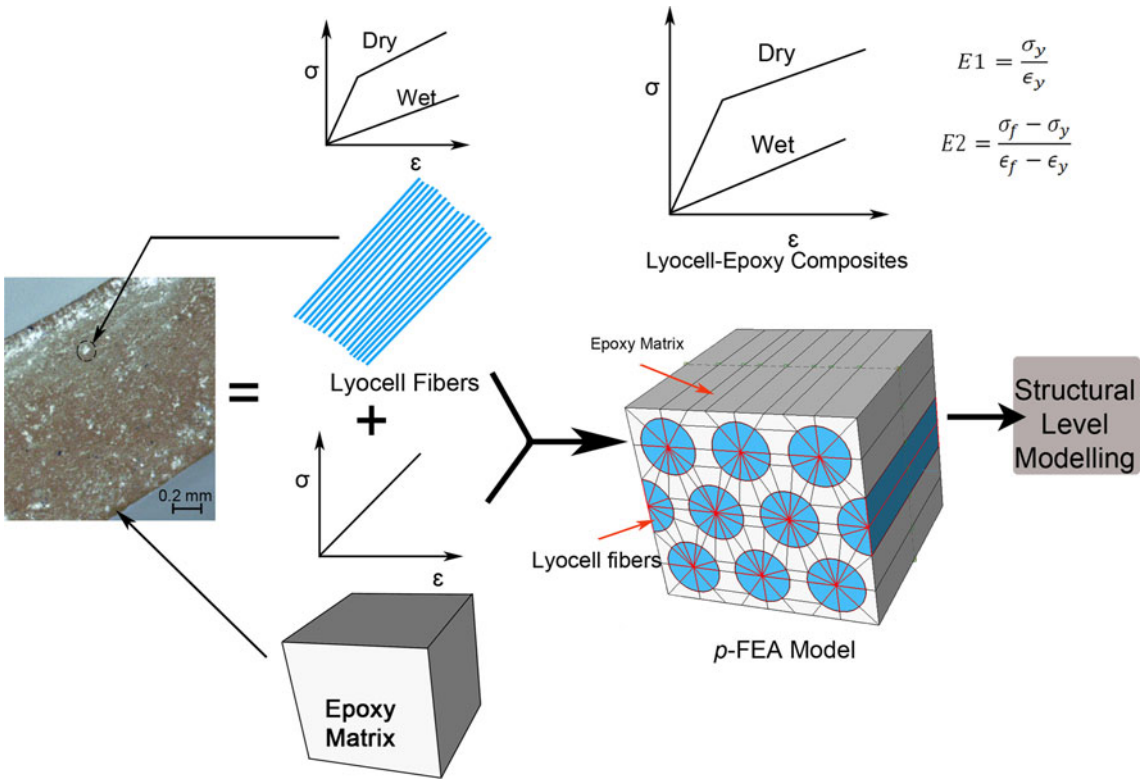

Fig. 1 Schematic of analysis approach for Lyocell/epoxy composites with bilinear elastic–plastic fiber response

Experimental method

In this section, the tension behavior of the dry and wet Lyocell fibers (Tencel; Lenzing Fibers Inc., Axis, AL, USA) and composites made with different fiber volume concentrations are studied. The fiber tows obtained were in an uncrimped and unbleached state with staple fibers form. Lyocell density is 1.5 g/cm^3 (0.054 lb/in^3) at 20 °C (68 °F). The fibers are approximately 10 microns in diameter (with fibrils smaller in diameter), nonvolatile, insoluble in water, and have a decomposition temperature above 175 °C (347 °F). All experiments were carried out at room temperature of 21 ± 1 °C (70 °F). The humidity level at which the experiments were carried ranged between 30 and 35 %. The ASTM 3822 [14] standard was used for determining the fiber properties. Tow strands of the same weight and gauge lengths of 25.4 mm (1.0 in.) were tested in a uniaxial testing machine. For each specimen, a cardboard square piece of 25.4 mm (1.0 in.) was used to attach the fiber tow using a small amount of epoxy. A total of nine samples were prepared. Three samples were tested under dry conditions and three under wet conditions by soaking in a water bath for a 120 ± 5 min period. The other three were tested under wet conditions by extending the soaking period to 240 ± 5 min. Samples were soaked at a temperature of 20 ± 1 °C (68 °F) and the change in weight was recorded. Samples were tested under direct tension by applying load from an electro-mechanical loading machine using a load cell of maximum capacity of 2220 N (500 lb). To account for the compliance of the loading machine, samples of different gauge lengths were prepared for Lyocell yarns. Two samples of each gauge length 127, 50.8 and 14.0 mm (5, 2 and 0.55 in.) were prepared and tested in the same manner described above and under the same conditions. The data were processed to plot the graph of compliance in mm/N (in./lb) versus nominal gauge length in mm (in.). The best-fit straight line was plotted for the data points, and compliance of the loading machine was calculated as the *y*-intercept for the equation of the linear graph. The load versus crosshead displacements for these tests is shown in Fig. 2 for both dry and wet conditions.

The composite specimens were prepared using a wet layup and resin infusion methodology. The Lyocell fibers were weighted to the nearest 0.0005 g to back-calculate the FVF. The epoxy chosen for this study is a high bio-content-based epoxy resin (Super Sap 100 Epoxy; Entropy Resins Inc., Gardena, CA, USA). The resin has a high amount of bio-content. As opposed to traditional epoxies that are primarily made of petroleum-based materials, this resin formulation contains bio-renewable materials sourced as co-products or from waste streams of other industrial

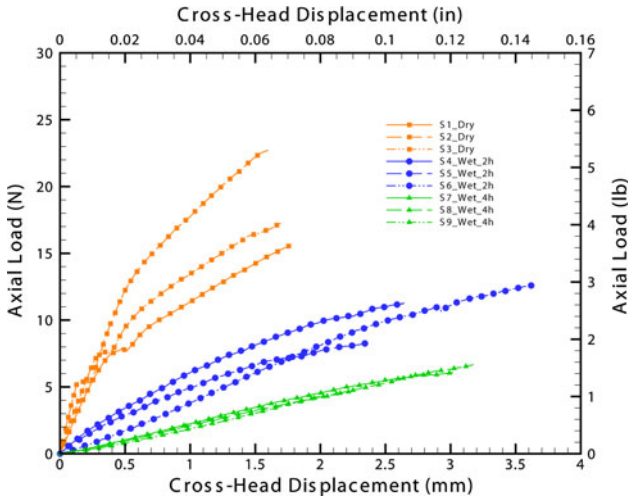

Fig. 2 Load versus cross-head displacement response of Lyocell tows

processes, such as wood pulp and bio-fuels production. Several methods were investigated for producing the composite materials. Samples with low FVF (5–10 %) were prepared in a dogbone shape according to the standards of the ASTM ID: D638 [15]. Samples of pure epoxy resin were prepared according to the same standard and were also tested for modulus measurement. To produce higher FVFs for the Lyocell–epoxy composite, the manufacturing of panels using a resin infusion process was introduced. Resin infused samples were prepared by uniformly spreading a known mass of unidirectional fibers between two Teflon sheets in a vacuum bag and applying vacuum pressure up to 635.0 mmHg (25 in Hg) from a vacuum pump. Manual layup panels on the other hand were prepared by wet layup, folding the cloth over the panel and using squeegees to uniformly distribute the resin over the fibers and removing the excess resin. The panels produced using wet layup resulted in a maximum FVF of 0.33, whereas the ones with resin infusion resulted with a volume fraction of 0.35. Specimens of lower fiber content were also manufactured for use in analysis and predictive purposes. Testing of composite coupons was performed under direct tension according to the ASTM ID: D3039 [16]. Strain properties were measured across a 25.4-mm (1.0 in.) guage length in the middle of coupons by the use of an extensometer for a subset of the specimens.

Results and discussion

The load versus crosshead displacement results for the tow testing is shown in Fig. 2. All the specimens tested had approximately the same length and similar weights. The results show a bilinear elastic–plastic response in the behavior. This knee in the stress–strain response can be attributed to a more preferable molecular orientation of the fibers which is produced by stretching the fibers and stabilized by interconnections between crystalline regions and by hydrogen bonding [17]. The behavior of the wet specimens shows a change in the constitutive response. The soaking of fibers represents a severe case in which the fibers are not protected by any polymer and are totally submerged. For surface-dried fibers, an increase in weight by 1.8 times the original weight was tracked for the 2 h soaking period and a 1.9 times the original weight for 4 h of soaking. The loss of modulus as the fibers are wetted is clearly shown by the loading curves. Some variability is shown for 2 h soaking in the behavior of the fibers during loading. The results are more consistent, however, for 4 h soaking and show a drastic loss in modulus and a nonlinear behavior of the fibers. The specimens have a lower failure stress, yet the typical specimens tend to show a higher strain to failure. Additionally, the knee seen in the loading curves for the dry fibers is shifted toward the (0, 0) point of the curves as the level of moisture increases in the fibers due to the removal of the hydrogen bonds [17]. Thus, the behavior of the wet fibers is primarily a plastic one. Out of all experimented fabrication procedures examined for composites manufacturing for Lyocell–epoxy composites, panel preparation by wet layup followed by degassing produced better samples than other procedures. Pilling and fibrillation are inherent in the structure of this fiber and add additional difficulties to the manufacturing process. Using resin infusion, thinner samples with higher FVF could be produced, especially when several resin entry points are used perpendicular to fibers direction. However, good infusion of the resin with the fibers could not be achieved for the whole panel and some areas were left unwetted. The equal distribution of fibers among the panel and waviness prevention were the major challenges of the wet layup method. These challenges were overcome by using tape to stretch and fix the fibers in position. The panels produced showed good wetting with epoxy and only minor waviness. Degassing the samples with a vacuum pump after wet layup also insured minimal porosity.

The bilinear elastic plastic behavior of the regenerated fibers shows the need for a suitable analysis methodology. The *p*-FEA model proposed was calibrated for one set of experimental values using the specimens having a fiber content of 33 % (FVF of 0.33). Error analysis is performed on the results by examining the global energy norm versus the polynomial order and degrees of freedom. Convergence is achieved rapidly in all cases with the error less than 0.01 % achieved after 20,000 degrees of freedom. The predictive properties of the stress strain graphs are shown in Fig. 3 superimposed with the FE calibration curve. The results show some variation in the plastic region;

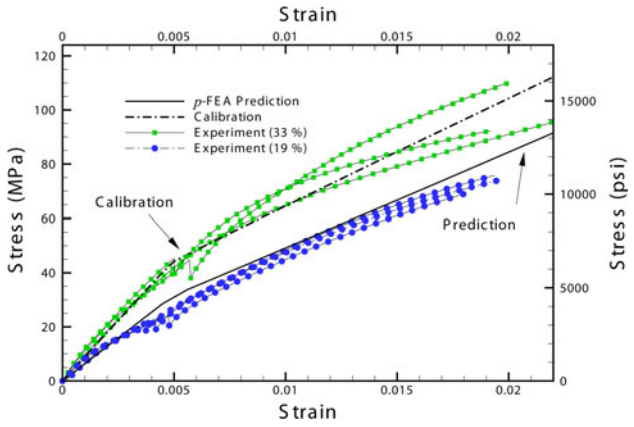

Fig. 3 Calibration & prediction of stress–strain response for dry Lyocell/epoxy composites

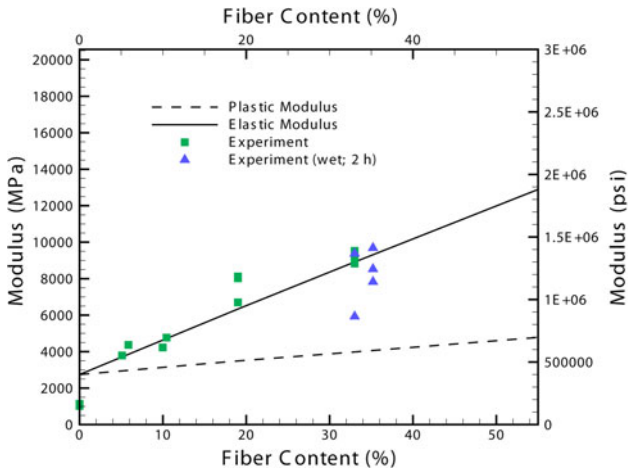

Fig. 4 Effect of fiber volume fraction on the elastic modulus of Lyocell/epoxy composites

nevertheless, an approximate bilinear behavior can still be seen for the composites. The results of *p*-FEA modeling were compared to those obtained by experiments in the fiber direction by calculating the average stress resulting on the loaded surfaces. The *p*-FEA model was successfully used to capture the experimental stress–strain behavior of the composites and the FE model was calibrated to average the differences seen in the plastic region for the samples. The results show that it is possible to reproduce accurate results for different FVFs. The model was run with the same parameters, boundary conditions and material properties used to produce the calibration curve except for the FVF which was reduced from 33 to 19 %. The verification model shows a good match to the experimental values with a little overestimation of strength and elasticity in the plastic region. Changes in the elastic and plastic modulus of Lyocell–epoxy composites with different fiber contents are shown in Fig. 4. A linear change is seen which can be attributed to the use of a bilinear stress–strain curve for Lyocell and a linear one for epoxy. This characteristic is expected to change with the wet composites where the nonlinearity of the Lyocell loading curve is expected to lead to nonlinearity in the stress–strain curve of the composites. Five of the coupons with high FVF were soaked for 2 h to primarily investigate the effect of moisture on Lyocell composites and how they compare to the model of dry Lyocell composites. The result of these is shown in Fig. 4 and marked as "Wet, 2 h". The results indicate that complete saturation does not occur after 2 h of soaking the composite specimens.

Conclusions

In this study, the results are presented of a computational and experimental investigation on the tensile behavior of Lyocell/epoxy composites. The limitations of assumptions of using linear elastic properties in modeling of regenerated cellulose composites are illustrated. The mechanical properties of Lyocell tows are investigated under dry and wet conditions showing bilinear and nonlinear elastic–plastic responses. A multi-scale unit cell model incorporating a bilinear elastic–plastic stress–strain behavior can be approximated for the dry fibers. As the fibers absorb moisture, the knee of the stress–strain response shifts to the early stages of loading. Nonlinear behavior and a drastic loss in modulus are observed for the wet fibers. In composite form, the behavior under wet conditions was less pronounced due to the barrier properties of the epoxy resin. Manufacturing composites from Lyocell fibers possesses unique challenges due to the hydrophilic and pilling nature of these fibers. The use of resin infusion produced higher FVF but some unwetted areas were seen even at high vacuum pressures. The use of wet layup followed by degassing overcomes that problem, but may be an issue when thicker parts or more complex geometries are desired. The speed of preparation is also an issue since the resin takes around 35 min to harden and mold filling of large structures would need to account for this. The FE approach using *p*-FEA incorporating the bilinear constitutive response of Lyocell was proposed for possible modeling of these composites and predicting the composite behavioral response. The results show that the model was successfully used to predict the loading behavior of these composites under different fiber contents in dry conditions. The model can also be easily extended to determine the elastic–plastic orthotropic material constants by varying the boundary conditions. Future structural mechanics tools can use the proposed approach to incorporate the effects of moisture absorption on thermoset/regenerated cellulose composites.

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References

1. Graupner N, Mussig J (2011) A comparison of the mechanical characteristics of kenaf and lyocell fibre reinforced poly(lactic acid) (PLA) and poly(3-hydroxybutyrate) (PHB) composites. Compos A Appl Sci Manuf 42(12):2010–2019
2. Soykeabkaew N, Nishino T, Peijs T (2009) All-cellulose composites of regenerated cellulose fibres by surface selective dissolution. Compos A Appl Sci Manuf 40(4):321–328
3. Wool RP, Susan Sun X (2005) Bio-based polymers and composites, 1 edn. Elsevier Science & Technology Books, Burlington, MA
4. Cheng Q, Wang S, Harper DP (2009) Effects of process and source on elastic modulus of single cellulose fibrils evaluated by atomic force microscopy. Compos A Appl Sci Manuf 40(5): 583–588
5. Gindl W, Keckes J (2006) Strain hardening in regenerated cellulose fibres. Compos Sci Technol 66(13):2049–2053
6. Adusumali R-B, Reifferscheid M, Weber H, Roeder T, Sixta H, Gindl W (2006) Mechanical Properties of Regenerated Cellulose Fibres for Composites. Macromol Symp 244(1):119–125
7. Cheng Q, Wang S (2008) A method for testing the elastic modulus of single cellulose fibrils via atomic force microscopy. Compos A Appl Sci Manuf 39(12):1838–1843
8. Silva MC, Lopes OR, Colodette JL, Porto AO, Rieumont J, Chaussy D, Belgacem MN, Silva GG (2008) Characterization of three non-product materials from a bleached eucalyptus kraft pulp mill, in view of valorising them as a source of cellulose fibres. Ind Crops Prod 27(3):288–295
9. Graupner N, Herrmann AS, Müssig J (2009) Natural and man-made cellulose fibre-reinforced poly(lactic acid) (PLA) composites: an overview about mechanical characteristics and application areas. Compos A Appl Sci Manuf 40(6):810–821
10. Johnson RK, Zink-Sharp A, Renneckar SH, Glasser WG (2008) Mechanical properties of wetlaid lyocell and hybrid fiber-reinforced composites with polypropylene. Compos A Appl Sci Manuf 39(3):470–477
11. Mottershead B, Eichhorn SJ (2007) Deformation micromechanics of model regenerated cellulose fibre–epoxy/polyester composites. Compos Sci Technol 67(10):2150–2159
12. Wollerdorfer M, Bader H (1998) Influence of natural fibres on the mechanical properties of biodegradable polymers. Ind Crops Prod 8(2):105–112
13. Masoodi R, El-Hajjar RF, Pillai KM, Sabo R (2011) Mechanical characterization of cellulose nanofiber and bio-based epoxy composite. Mater Des 36:570–576
14. ASTM D3822 (2007) Standard test method for tensile properties of single textile fibers. ASTM International, West Conshohocken
15. ASTM D638 (2010) Standard test method for tensile properties of plastics. ASTM International, West Conshohocken
16. ASTM D3039 (2008) Standard test method for tensile properties of polymer matrix composite materials. ASTM International, West Conshohocken
17. Morton WE, Hearle JWS (2008) Physical properties of textile fibres, 4th edn. Woodhead Publishing, Cambridge