

Bio-Composites for Structural Applications: Poly-L-Lactide Reinforced with Long Sisal Fiber Bundles

Marek Prajer,^{*} Martin P. Ansell[†]

Department of Mechanical Engineering, BRE Centre for Innovative Construction Materials, University of Bath, Bath, BA2 7AY, United Kingdom

^{*}Present address: Central European Institute of Technology (CEITEC), Brno University of Technology, Technicka 3058/10, 616 00 Brno, Czech Republic

[†]Present address: Martin P. Ansell, Department of Mechanical Engineering, University of Bath, Claverton Down, Bath, BA2 7AY, United Kingdom

Correspondence to: M. Prajer (E-mail: marek.prajer@gmail.com)

ABSTRACT: Fully bio-based and biodegradable composites were compression molded from unidirectionally aligned sisal fiber bundles and a polylactide polymer matrix (PLLA). Caustic soda treatment was employed to modify the strength of sisal fibers and to improve fiber to matrix adhesion. Mechanical properties of PLLA/sisal fiber composites improved with caustic soda treatment: the mean flexural strength and modulus increased from 279 MPa and 19.4 GPa respectively to 286 MPa and 22 GPa at a fiber volume fraction of $V_f = 0.6$. The glass transition temperature decreased with increasing fiber content in composites reinforced with untreated sisal fibers due to interfacial friction. The damping at the caustic soda-treated fibers-PLLA interface was reduced due to the presence of trans-crystalline morphology at the fiber to matrix interface. It was demonstrated that high strength, high modulus sisal-PLLA composites can be produced with effective stress transfer at well-bonded fiber to matrix interfaces. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40999.

KEYWORDS: biopolymers and renewable polymers; cellulose and other wood products; composites; mechanical properties; morphology

Received 11 November 2013; accepted 13 May 2014

DOI: 10.1002/app.40999

INTRODUCTION

Biocomposites for structural applications are load bearing materials where both the matrix and the fiber reinforcement are derived from renewable resources. Such materials are intrinsically biodegradable because both the matrix and the reinforcement are plant derived. Cultivation, extraction, and processing require limited energy compared to the production of synthetic fibers and resins.^{1–3} No harmful and carcinogenic petrochemicals are used as a polymer matrix to bind the reinforcing fibers together.

Poly(lactic acid)/polylactide is a commercially available biopolymer of considerable interest for structural composites. It is a semicrystalline thermoplastic polyester formulated from renewable resources with a glass transition temperature (T_g) of between 50 and 60°C and a melting temperature (T_m) of 168–172°C.

Poly(lactic acid) can be prepared by direct polycondensation of lactic acid or through ring opening polymerization of its inter-

mediate cyclic dimer-lactide.⁴ Direct polymerization leads to poly(lactic acid) \approx PLA.⁵ Indirect polymerization via lactide leads to poly(lactide) \approx PLLA.⁶ In literature such a strict distinction is not common and both products are referred to as PLA.

Thermoplastic matrices are increasingly used for industrially fabricated fiber reinforced polymer composites to make more sustainable transportation.⁷ They offer several advantages in comparison with thermosets. Their processing is faster, requiring no curing times, they are less expensive, they have no toxic by-products and finally they are easy to recycle. Properties of fiber reinforced composites are improved when compression molding is used instead of injection molding. It is because long fibers can be used and their orientation can be controlled.⁸

Density and thermal properties are limiting criteria for selecting a suitable polymer matrix. Low polymer density is important for making a lightweight product. The glass transition temperature (T_g) is important for predicting the polymer behaviour at ambient conditions. Melting temperature (T_m) of semicrystalline

Table I. Thermo-Mechanical Properties of Thermoplastic Competitors of PLLA

| | PCL | PHB | PP |
|------------------------|------------|---------|------------|
| Tensile strength (MPa) | 21-42 | 40 | 26-41 |
| Tensile modulus (GPa) | 0.21-0.44 | 3.5-4 | 0.95-1.8 |
| T_g (°C) | -60 to -65 | 5-15 | -10 to -23 |
| T_m (°C) | 58-65 | 168-182 | 160-176 |

polymers is related to energy consumption in production. High melting temperatures increase the processing temperature, cost of processing and create further environmental stress. PLA/PLLA is probably the best choice as a matrix for all bio-based composites due to its low density, acceptable mechanical properties, high T_g , and relatively low energy consumption in processing ($T_m - T_g$ for PLLA is only $\sim 100^\circ\text{C}$). Apart from its low density and good thermo-mechanical properties, the recyclability and low cost of PLA/PLLA as well as its wide use as a substitute for polypropylene should be also considered in its favour (Table I).^{9,10}

Natural fibers as reinforcement are attractive because of their favorable specific mechanical properties, low price, health advantages, and recyclability.¹¹

In this paper the term “natural fiber” refers to plant fibers which exist as stem (or bast) fibers (e.g., jute), leaf fibers (e.g., sisal), seed fibers (e.g., cotton), and fruit fibers (e.g., palm).¹² Plant fibers usually consist of multicellular arrays of elongated cells with high length to diameter ratio and a hollow central cavity. Each cell is called an ultimate fiber in engineering terminology or tracheid in botanical terminology. Tracheids are the cells whose primary task is the distribution of water and nutrients from plant roots into the whole plant.¹³ They are long, strong, and stiff and thus of technical interest and can be used as reinforcement in polymer composites. The cellular arrays which are used as fibers for polymer reinforcement or spun into yarns in textile applications are called fiber bundles.¹⁴ Plant cells are surrounded by a rigid cell wall. During the plant growth, when the fiber is fully developed, intracellular organelles die and a hollow cavity called the lumen is formed. The cell wall consists of four layers; each layer is micro-structured and composed of cellulose, hemicelluloses and lignin at molecular level. Cellulose polymer chains are organized in parallel arrays which are called microfibrils. Cellulose organized into microfibrils can be viewed as the “fiber” component of the cell wall whereas hemicelluloses and lignin can be viewed as the “matrix”. Cellulose, which has a high theoretical strength (15 GPa) and modulus (138 GPa), is the main constituent responsible for the mechanical properties of natural fibers.¹⁵

Sisal is a clean natural fiber extracted from the leaves of the *Agave sisalana* plant with high cellulose content of 43–78% and a low microfibril angle ($10-22^\circ$), high tensile strength of ≈ 840 MPa, Young's modulus of ≈ 22 GPa, specific tensile strength of

≈ 580 MPa and specific Young's modulus of ≈ 15 GPa (the reported specific properties were ratio of the strength (modulus) and their specific gravity $\approx \rho_{\text{fiber}}/\rho_{\text{water}}$).¹² The main disadvantage of natural fibers compared to artificial fibers like glass fibers is their variability in mechanical properties due to the fact that they are biological structures.

The low density and highly crystalline cellulose content of natural fibers lead to their excellent specific properties, which enable them to compete with traditional glass fibers in structural applications.

The great advantage of natural fiber composites is their after use disposal: the material can be converted into heat energy by controlled burning, disposed of in a controlled landfill or composted.

Fiber length, yarn twist (if applicable), distribution, and orientation of the fiber in the matrix and fiber volume fraction are some of the key parameters which determine the ultimate mechanical properties of natural fiber reinforced polymers as well as the processing method: for example Madsen and Lilholt prepared unidirectional composites made of polypropylene and hemp fibers with a fiber weight fraction of 0.5 which resulted in an axial tensile strength of 251 MPa and axial tensile modulus of 27 GPa.¹⁶ The Young's modulus value is much greater compared with the 1.6 GPa modulus of compression molded polypropylene reinforced with kenaf nonwovens prepared by Hao et al.¹⁷

A review of the literature shows that natural fiber composites with bio-based thermoplastic matrices have the best axial mechanical properties if they use unidirectional aligned fiber systems, the polymer matrix is evenly distributed among the fibers and the whole assembly is compression molded (Table II).

Improvement in fiber to matrix adhesion is usually achieved through covalent linkages between fiber and matrix or through hydrophobization of the cellulose surface. Maleic anhydride grafted low molecular weight polymers dispersed at the fiber to matrix interface are often used to covalently bind the cellulosic fibers to the polymer matrix. Polylactide grafted maleic anhydride (PLLA-g-MA) was examined as a compatibilizer between jute fibers and PLLA.^{24,25} Contrary to expectations, the application of PLLA-g-MA considerably diminished mechanical properties of the compression molded composites.

Alkali treatment is a simple yet effective method to modify mechanical properties of natural fibers and their adhesion to polymer matrices. Because of its simplicity, low cost, and low environmental impact it is very well suited to the fabrication of natural fiber composites. Application of aqueous sodium hydroxide solution on cellulose results in cellulose swelling and the conversion of its crystalline structure from Cellulose I to Cellulose II.²⁶⁻³⁰ The action of an alkali solution interrupts the inter- and intra-molecular hydrogen bonds which hold cellulose micro-fibrils together. On the molecular level the incorporation of alkali hydrate ions into the structure of cellulose I results in the dislocation of glucopyranose rings which lay in the 101 planes from their previous positions. Thus the hydroxyl groups

Table II. Natural Fiber Composites with Bio-Based Thermoplastic Matrices

| Fiber/matrix | Processing method | d_{η_0} | $^a w_f$ | $^f V_f$ | Tensile strength | Flexural strength | Tensile modulus | Flexural modulus | Reference |
|---|-------------------|--------------|----------|----------|------------------|-------------------|-----------------|------------------|-----------|
| | (-) | (-) | (-) | (-) | (MPa) | (MPa) | (GPa) | (GPa) | |
| Flax/PLA | ^b IM | 0.12 | 0.3 | - | 53 | - | 8.3 | - | 18 |
| Flax/PLLA | ^c CM | 0.3 | 0.3 | - | 100 | - | 9.5 | - | 19 |
| Hemp/starch based thermoplastic | CM | 1 | - | 0.7 | 365 | 223 | - | - | 20 |
| Curaua/starch based thermoplastic | CM | 1 | - | 0.7 | 327 | - | 36 | - | 21 |
| Curaua ^a /starch based thermoplastic | CM | 1 | - | 0.7 | 334 | - | 32 | - | 21 |
| Kenaf/PLA | CM | 1 | - | 0.7 | 223 | 254 | 23 | 23 | 22 |
| Ramie/cellulose thermoplastic polyester | CM | 1 | - | 0.84 | 460 | - | 28 | - | 23 |

^a Caustic soda-treated fiber.

^b Injection molding.

^c Compression molding.

^d Orientation efficiency factor [8].

^e Fiber weight fraction.

^f Fiber volume fraction.

pendant on carbon atoms C(6) and C(2) project out of the plane into the wider space between the 101 planes.³¹

Cellulose II is reported to have lower mechanical properties compared to Cellulose I. The elastic modulus of crystalline Cellulose I in the direction parallel to the polymer chain axis was measured by X-ray diffraction and determined to be 138 GPa.¹⁵ The low crystal modulus of Cellulose II (88 GPa) can be explained by the polymer chain contraction in the crystal lattice and the decreased f -value (a force necessary to stretch the molecule by 1%) and their synergistic effect on intra-molecular hydrogen bonds. The chain contraction after caustic soda treatment can be explained by the molecule rotation around the main chain ether linkage between the glucopyranose rings.³²

The positive effect of alkali treatment on mechanical properties of natural fibers is usually explained by the removal of waxes and pectins from the fiber surface. The surface of the treated sisal fibers remains clean and smooth compared with the surface of the untreated sisal fiber and contains less surface imperfections and cracks introduced into the fiber when separated from the leaves of the agave plant.^{26–30}

This article focuses on mechanical properties and morphology of biocomposites where both the matrix and the reinforcement are bio-sourced and biodegradable. Such composites were compression molded from unidirectionally aligned sisal fiber bundles and a poly-L-lactide polymer matrix. Untreated and caustic soda-treated sisal fibers were chosen as a reinforcement because of their low microfibril angle which is closely parallel to the cell axis and their availability as long, straight fiber bundles.¹² The choice of poly-L-lactide as a matrix was obvious.

EXPERIMENTAL

Fibers and the Polymeric Matrix

Poly(lactide) polymer (PLLA, Biomer 9000) was purchased from Biomer GmbH, Krailing, Germany. Sisal fiber bundles (*Agave*

sisalana) were sourced in Tanzania. Sisal fiber bundles were washed for 2 h in a hot water bath at 90°C to remove all dust particles and impurities. Wet fibers were placed in between paper tissues at room temperature for 12 h and after that dried in a circulating air oven at 80°C overnight. Dried fibers were stored in sealed polyethylene bags at room temperature with a calcium chloride dehumidifier.

Caustic Soda Treatment

Some of the cleaned sisal fiber bundles was treated with caustic soda (Sigma Aldrich, UK). Fibers were immersed in 6 wt % NaOH solution (i.e., in the ratio of 6 g of NaOH to 94 g of distilled water) for 48 h, then rinsed with an excess of distilled water and neutralised with dilute acetic acid (1 wt % solution) before drying.

Single Fiber Tensile Test

Untreated and caustic soda-treated sisal fibers were tested in tension. Selected fibers were glued to supporting paper cards with a gauge length of 20 mm using a cyanoacrylate adhesive. To keep the fiber aligned during the adhesive curing the fiber was attached to the supporting paper card with a paper tape. The adhesive was allowed to cure at room temperature for 24 h. Paper cards with fibers were gripped in the jaws of an Instron 3369 tensile testing machine equipped with a 100 g load cell. The sides of the supporting paper cards were cut with a pair of scissors after clamping and the fibers were preloaded to 50 mN, then loaded in tension at a cross-head speed of 1 mm/min until failure. At least 20 fibers of each experimental group were successfully tested. The strain was measured from the machine displacement taking into account the system compliance. Young's modulus was taken from the slope of the initial linear portion of the stress-strain curve. The strength and strain distribution of the fibers was modeled with a two parameter Weibull distribution function.^{33–36}



Figure 1. (a) Fiber preforms - aligned untreated sisal fibers glued onto a supporting paper card; (b) Opened compression mold showing the upper clamping part of the mold; (c) Arranging fiber preforms into a mold slot; (d) Combining fiber preforms with polymer foils; (e) Closed mold after consolidation prepared for hot pressing; (f) Mold transferred into a hot press. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Fiber Cross-Sectional Area Determination

The shape of the sisal fiber cross-section is irregular and varies along the fiber length. The effective cross-sectional area of untreated and caustic soda-treated sisal fibers was determined with the gravimetric method (Archimedes principle, buoyancy

method). The Archimedes principle states that a body immersed in a fluid apparently loses weight by an amount equal to the weight of the fluid it displaces. This method allows determination of the density of solids of irregular shapes. Sisal fibers of known weight which was recorded as W_{fa} were immersed in a



Figure 2. PLLA/sisal fiber unidirectional composite (100 x 15 x 1 mm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solvent of lower density (benzene) than the expected density of the fiber. The weight of fibers submerged in the solvent was recorded as W_{fs} . All the measurements were taken at 21°C. The bulk (apparent) density was calculated using the following equation:

$$\rho_{fb} = \frac{\rho_s W_{fa}}{W_{fa} - W_{fs}} \quad (1)$$

where ρ_{fb} is the bulk density of the fiber in kg/m^3 , ρ_s is the solvent density in kg/m^3 , W_{fa} is the weight of the fiber in air in kg and W_{fs} is the weight of the fiber in the solvent in kg.

Knowing the fiber density (ρ_{fb}), its weight (m_f) per length (l_f), the effective cross sectional area A of a sisal fiber was calculated as:

$$A = \frac{m_f}{\rho_{fb} l_f} \quad (2)$$

Composites Processing

For the manufacture of fiber composites it was necessary to convert the polymer granules into polymer sheets. PLLA granules were oven dried overnight at 50°C and compression molded in foils of 0.3–0.4 mm thickness placing 5 g of PLLA between two steel plates (200 × 200 × 2 mm). Composite molding was carried out in three stages: 5 min at 190°C with no pressure, 2 min at 190°C, and 100 kPa compression, then 24 h cooling to ambient temperature with no pressure. Molded sheets were stored at room temperature in polyethylene sealed bags with a calcium chloride dehumidifier.

Unidirectional composites of PLLA reinforced with long sisal fiber bundles were manufactured via compression molding. Figure 1 describes in detail the manufacturing process. During the compression molding of sisal fiber reinforced PLLA it was necessary to overcome a few limiting factors such as high matrix viscosity, matrix degradation at temperatures above 230°C and the fact that at temperatures in excess of 150°C, most natural fibers are unable to withstand prolonged periods at such temperatures without significant deformation or degradation. To reduce the adverse effect of high temperatures and to maximize the reinforcing potential of the fibers the following measures were taken: (a) Sisal fiber bundles were aligned prior to compression molding to ease the polymer melt to flow among the fibers and wet them properly. Aligned fibers were attached to supporting paper cards with a tape [Figure 1(a)]. Before the mold filling the supporting paper card was cut off—only ends were left to hold the fibers together, (b) The mold was made of aluminium, so it was possible to heat it up and

cool it down quickly. Thus both the polymer and the fibers could stay in the mold for a shorter period of time and the possibility of their degradation was reduced [Figure 1(b)], (c) Pre-forms of aligned fibers were uniformly combined with polymer sheets [Figure 1(d)].

Once the aligned fibers with both ends secured with the tape were stretched and combined with PLLA foils in an open mold (the front and back walls were temporarily removed), the whole assembly was heated up to above the PLLA glass transition temperature (T_g) and clamped at 0.05 MPa and 80°C for 10 min. The supporting paper tabs with fiber ends were cut off and the mold was closed tightly. The closed mold with aligned fibers and polymer foils was transferred into the hot press. It was kept at a temperature of 190°C under 50 kPa pressure for 5 min. After this preheating stage the mold was compressed at 200°C at 100 kPa for 3.5 min. At the end of this stage the hot mold was immediately transferred to a cold press and a pressure of 3000 kPa was applied to squeeze out the excess of polymer resin. The mold was left in the cold press to cool down at room temperature for 2 h at a pressure of 3000 kPa. Figure 2 shows the final composite laminate.

Fiber Volume Fraction

Transformation of fiber weight fraction to fiber volume fraction was calculated by the following expression assuming no voids in the matrix (i.e., $V_m + V_f = V_c$):

$$V_f = \frac{\left(V_c - \frac{w_c - w_f}{\rho_m} \right)}{V_c} \cdot 100 \quad (3)$$

where V_c is the volume of the composite in m^3 , w_c is the weight of the composite in kg, ρ_m is the matrix density in kg m^{-3} , V_f is the fiber volume fraction and w_f is the fiber weight fraction.

Mechanical Testing of Composites

The Instron 3369 universal testing machine was used to carry out mechanical tests of composites reinforced with untreated and caustic soda-treated sisal fibers. Composites were tested in tension, in three-point bending and in a short beam shear test promoting interlaminar failure in flexure. Composites with 0.5 fiber volume fraction were tested in tension, composites with 0.4 fiber volume fraction were tested for interlaminar shear strength and composites with 0.4 and 0.6 fiber volume fraction

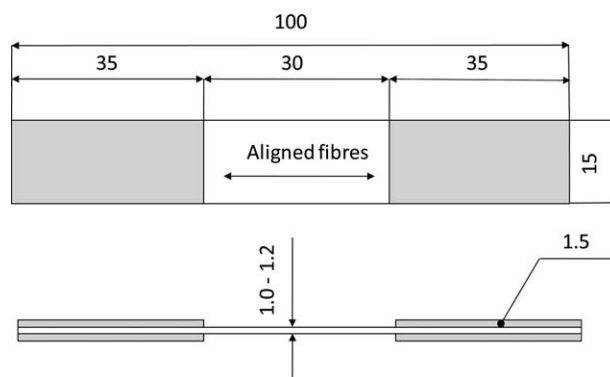


Figure 3. Dimensions of the end-tabbed tensile test specimen (in mm).

Table III. Measured Physico-Mechanical Properties of PLLA Matrix

| | | |
|---|------------------------------|------------------|
| Tensile strength | (MPa) | 62.8 ± 4.9 |
| Tensile modulus | (GPa) | 2.7 ± 0.4 |
| Strain at break | (%) | 2.9 ± 0.5 |
| Flexural strength | (MPa) | 114 ± 16 |
| Flexural modulus | (GPa) | 3.6 ± 0.5 |
| T_g (DSC-midpoint) | (°C) | 56 ^a |
| T_m (DSC-peak) | (°C) | 169 ^a |
| Melt flow index (2.16 kg/190°C) | (g/10 min) | 5 |
| Molecular weight (M_w) (SEC) Density | (g/mol) (kg/m ³) | 178,846 1.24 |

SEC, size exclusion chromatography: Sample was dissolved in chloroform at a concentration of 0.10 mg/mL and the SEC analysis was performed on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 μ m MIXED-D 300 × 7.5 mm column. Separation according to molecular size was performed at 35°C using THF solvent as an eluent at flow rate of 1 mL/min. The polymer was referenced to 10 narrow molecular weight polystyrene standard with a range of M_w 615–568 kDa; DSC, differential scanning calorimetry: Samples of 5 mg in weight were sealed in an aluminum pan and heated from 20°C to 250°C at a scanning rate of 10°C/min. A nitrogen flow of 25 mL/min was maintained throughout the test.

^aAs received pellet.

were tested in three-point bending. Flexural specimens of pure PLLA resin were machined from the central part of the compression molded dog-bones.

Tensile Test

Composites were tested in tension at a cross head speed of 2 mm/min. The dimensions of test specimens were 100 × 15 × 1 mm. Tensile test specimens were end tabbed with aluminum plates of 35 × 15 × 1.5 mm to avoid the test machine grips damaging the specimen (Figure 3).

The inner face of the end tab was abraded with a Silicon Carbide paper (400 #), washed with acetone and etched with acidic ferric sulphate to promote better adhesion between the end tab and the composite specimen. End tabs were attached with epoxy

adhesive (Hysol 9461) on both sides of the composite ends. Cold cure adhesive was chosen because of the low glass transition temperature of the PLLA polymer. The gauge length of the composite specimens was set to 30 mm. Tensile strength was calculated according to the eq. 4 and the Young's modulus was calculated from the slope of the initial part of the stress-strain curve.

$$\sigma_T = \frac{F}{A} \quad (4)$$

where σ_T is the tensile strength in MPa, F is the load at failure in N and A is the cross section in mm². The tensile test samples of pure PLLA resin were molded dog bones 4 mm thick and 150 mm long with nominal length of 115 mm and gauge length of 50 mm. The width of the samples was 8 mm. At least six specimens of each experimental group (composites and pure resin) were tested.

Three-Point Bending Test

The flexural test was performed at a cross head speed of 2 mm/min. The span of supporting members was adjusted to provide a span to thickness ratio of $L/h = 16$. Average width and thickness of the specimens were measured using a Vernier calliper and recorded. Six specimens of composites reinforced with untreated and caustic soda-treated sisal fibers were tested at fiber volume fractions of 0.4 and 0.6. Flexural strength was calculated as the flexural stress sustained by the specimen at maximum load according to eq. 5

$$\sigma_{fm} = \frac{3F_m L}{2bh^2} \quad (5)$$

where σ_{fm} is the flexural stress at maximum load in MPa, F_m is the maximum load in N , L is the span in mm, and b is the width of the specimen in mm. Flexural modulus was calculated as the tangent slope of the initial linear portion of the load-deflection curve following the eq. 6:

$$E_f = \frac{L^3 m}{4bh^3} \quad (6)$$

where E_f is the flexural modulus in MPa, L is the support span in mm, b is the sample width in mm, h is the sample thickness

Table IV. Mechanical Properties of Sisal Fibers Together with the Parameters of Weibull Distribution

| Fiber treatment | ^a Weibull modulus | ^b Scale parameter | Mean | Median | Max. | Min. | Standard deviation | ^c CoV |
|-------------------------------|------------------------------|------------------------------|-------|--------|-------|-------|--------------------|------------------|
| Tensile strength (MPa) | | | | | | | | |
| Untreated | 6.35 | 518 | 482 | 489 | 663 | 312 | 89 | 0.18 |
| Treated | 3.4 | 627 | 563 | 563 | 821 | 214 | 183 | 0.33 |
| Strain at break (%) | | | | | | | | |
| Untreated | 5.31 | 4.3 | 3.96 | 4.01 | 5.61 | 2.65 | 0.86 | 0.22 |
| Treated | 5.92 | 3.12 | 2.89 | 2.93 | 3.8 | 2.01 | 0.57 | 0.2 |
| Tensile Modulus (GPa) | | | | | | | | |
| Untreated | - | - | 17.58 | 18.9 | 22.8 | 10.08 | 3.19 | 0.18 |
| Treated | - | - | 27.45 | 28.08 | 35.22 | 15.61 | 6.15 | 0.22 |

^aDimensionless.

^bScale parameter of the Weibull distribution—characteristic strength or strain.

^cCoefficient of variation.

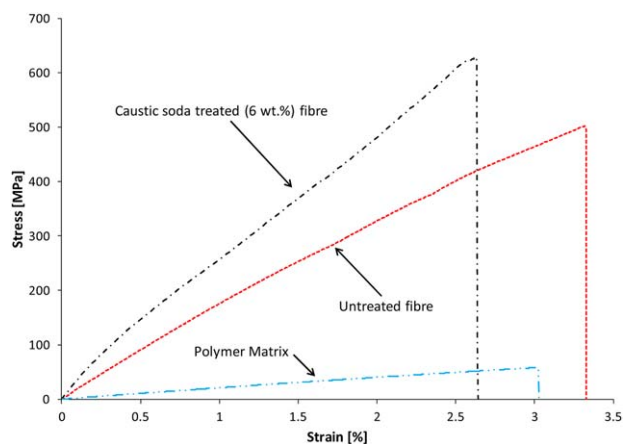


Figure 4. Stress–strain curves of untreated sisal fiber, caustic soda-treated sisal fiber and polylactide matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in mm and m is the slope of the tangent to the initial linear section of the load–deflection curve [N/mm].

Short Beam Shear Test

The test was performed at a cross head speed of 1 mm/min. The width b , thickness h , and the length l of the specimen satisfied the following relations: $b/h = 5$ and $l/h = 10$. The span L to thickness ratio was $L/h = 5$. The interlaminar shear strength was calculated according to the following equation:

$$\tau_{\max} = \frac{3F_{\max}}{4bh} \quad (7)$$

where τ_{\max} was the interlaminar shear strength, F_{\max} was the maximum load in N, b was the width of the specimen, and h was the thickness of the specimen. Eight specimens for each case of composites reinforced with untreated and caustic soda-treated sisal fibers with a fiber volume fraction of 0.4 were tested.

Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis was performed on a Triton Tritec 2000 DMA in single cantilever bending mode with a span of 16 mm. The deformation frequency of 1 Hz, heating rate of 2°C/min and a temperature range of 20–100°C were selected and the storage modulus (E'), loss modulus (E'') and loss factor ($\tan \delta$) were measured as a function of temperature. Glass transition temperature (T_g) was taken as a midpoint of the inflectional tangents to the storage modulus curve. Composite samples for DMTA were cut from compression molded laminates. Samples of pure polymer matrix were cut from the central part of compression molded dog bones.

Scanning Electron Microscopy (SEM)

Cross sections of compression molded composites were embedded into an epoxy resin (Struers Specifix 40) and polished. A series of wet abrasive SiC papers was used (600-, 1200-, 2400-, and 4000) for the polishing operation. Final polishing was done with 0.04 μm silica suspension on Struers MD Chem cloth. Samples were gold coated (Edwards Sputter coater model S 150 B) and inspected under the SEM microscope (JEOL 6310, Micro Analysis Suite at University of Bath). A low accelerating voltage of 10 kV was used to limit the loss of surface detail in

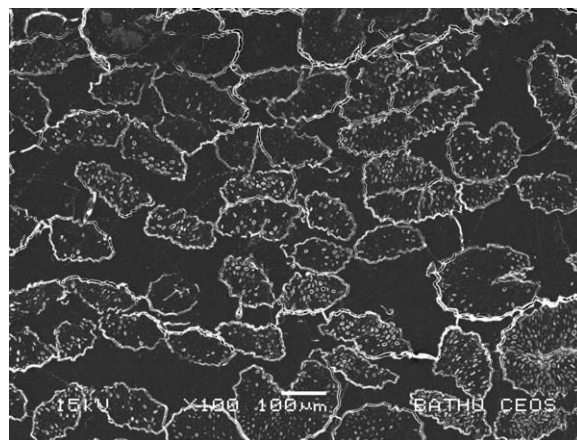


Figure 5. SEM micrograph of a section through a specimen of PLLA reinforced with untreated sisal fibers ($V_f = 0.6$).

the micrographs resulting from excessive depth of penetration of the electron beam within the polymeric samples. Microphotographs were used for qualitative analysis of interfacial bonding between sisal fibers and the polymer matrix. Fractured surfaces of composites failed in tension were gold sputtered and inspected under the JEOL 7200 SEM microscope at TU Delft, Faculty of Aerospace Engineering.

RESULTS AND DISCUSSION

Polymer Matrix and Sisal Fiber Characterization

Polylactide/polylactic acid is perhaps the best choice of a matrix for composites of all bio-based polymers available on the market due to its low density, reasonably good mechanical properties, high glass transition temperature, and relatively low melting temperature (Table III shows measured physico-mechanical properties of PLLA Biomer). Other bio-based thermoplastic polymers which could be potentially used in the manufacture of all-biobased polymer composites reinforced with natural fibers are polycaprolactone and polyhydroxybutyrate.

Tensile strength, strain at break, and Young's modulus of tested untreated and caustic soda-treated sisal fibers are summarized in Table IV. Tensile strength and strain at break of sisal fibers



Figure 6. Failed tensile test specimen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Mechanical Properties of Composites Reinforced with Untreated Sisal Fibers

| Matrix/fiber system | PLLA/UN | | | |
|-----------------------------------|---------|------------|------------|-------------|
| | V_f | 0.4 | 0.5 | 0.6 |
| Flexural strength (MPa) | | 236 ± 36 | - | 279 ± 43 |
| Flexural modulus (GPa) | | 9.8 ± 0.95 | - | 19.4 ± 1.36 |
| Tensile strength (MPa) | | - | 164 ± 22 | - |
| Tensile modulus (GPa) | | - | 9.5 ± 1.47 | - |
| Interlaminar shear strength (MPa) | | 8.4 ± 1.2 | - | - |

UN, untreated sisal fibers.

were modeled with a two parameter Weibull distribution. The parameters of the Weibull distribution were deduced using Weibull plots and least squares method. The tensile modulus was determined to follow a normal distribution. The cross-sectional area of sisal fibers was determined from the gravimetric method and apparent density of the fibers.

The apparent density of untreated sisal fibers was determined to be 1.115 g/cm³. The density of caustic soda-treated sisal fibers was determined to be 1.4382 g/cm³. The strength and modulus of caustic soda-treated sisal fibers tested at the gauge length of 20 mm was found to be higher compared to untreated sisal fibers. Caustic soda-treated sisal fibers strained less at break compared to untreated sisal fibers. Untreated sisal fibers possessed a mean tensile strength of 482 MPa and Young's modulus of 17.6 GPa. Caustic soda-treated sisal fibers were found to be stronger and stiffer. They had a tensile strength of 563 MPa and Young's modulus of 27.5 GPa. Typical stress-strain curves for untreated and caustic soda-treated sisal fibers together with a stress-strain curve of PLLA are shown in Figure 4. Untreated and caustic soda-treated sisal fibers showed linear-elastic behavior. Caustic soda treatment increased the strength and stiffness of sisal fibers and reduced the strain at break as can be deduced from Figure 4.

Caustic soda treatment of natural fibers is widely used as an inexpensive method to improve the mechanical properties of natural fibers.

Composites Processing

Combining sisal fibers with a PLLA matrix to manufacture composites with good mechanical properties was a challenging process. The melting temperature (T_m) of PLLA is about 170°C and processing temperatures for semicrystalline thermoplastics are usually about $T_m + 30-40$ °C. Riedel and Nickel stated that the viscosity of thermoplastics should be reduced to 100 mPa s, which is a viscosity value equivalent to an infusion or RTM molding resin, in order to wet natural fibers as easily as thermosetting matrices do.³⁷ Such a low viscosity is not achievable by simply increasing the melt temperature because damage to the molecular structure of the polymer will result in the loss of

mechanical properties. Furthermore the manufacturer does not recommend processing PLLA at temperatures above 230°C.

Sisal fiber bundles were unidirectionally aligned to maximize their properties in a resulting composite system as recommended by Bader.⁸ PLLA/sisal fiber composites were manufactured by compression molding. The influence of water and alkali on cellulose and polylactic acid at high temperatures was analyzed due to the fact that alkali treated fibers are combined with PLLA and due to the fact that water can develop as a thermal degradation product and both the water and the alkaline environment can catalyze further polymer degradation.³⁸⁻⁴² The degradation processes are chemical reactions driven not only by thermodynamics laws but also by means of kinetics. Measures were taken to reduce the molding times in order to avoid the possible matrix and fiber degradation during the processing and void development in the composites. Aligned fiber preforms were combined with polymer sheets in order to facilitate the polymer melt flow in between the fibers and promote a good fiber to matrix adhesion. A thin-walled aluminum mold was designed to be heated up/cooled down quickly. Thus both the polymer and the fibers remained in the mold for a shorter period of time and the possibility of degradation was reduced.

Mechanical Properties of Composites

Composites laminates for mechanical testing were manufactured by compression molding and tested in tension, flexure, and flexure with a short span to thickness ratio to promote the interlaminar shear failure in a short beam shear test. Tensile and flexural strength and modulus as well as interlaminar shear strength of composites reinforced with untreated and caustic soda-treated sisal fibers were determined. Figure 5 shows an SEM micrograph of a cross section of a PLLA matrix with 0.6 fiber volume fraction. The SEM revealed good fiber to matrix adhesion between sisal fibers and PLLA.

Figure 6 shows the failure of a composite specimen tested in tension. Mechanical properties of composites tested in three point bending, tension, and short beam shear test are summarized in Tables V and VI. A statistical Student's *t*-test, conducted

Table VI. Mechanical Properties of Composites Reinforced with Caustic Soda-Treated Sisal Fibers

| Matrix/fiber system | PLLA/CS | | | |
|-----------------------------------|---------|-------------|-----------|-----------|
| | V_f | 0.4 | 0.5 | 0.6 |
| Flexural strength (MPa) | | 240 ± 10 | - | 286 ± 18 |
| Flexural modulus (GPa) | | 11.1 ± 0.69 | - | 22 ± 1.18 |
| Tensile strength (MPa) | | - | 205 ± 17 | - |
| Tensile modulus (GPa) | | - | 12 ± 1.39 | - |
| Interlaminar shear strength (MPa) | | 14.8 ± 2.6 | - | - |

CS, caustic soda-treated (6 wt % solution for 48 hours) sisal fibers.

Table VII. Experimentally Determined and Theoretically Calculated Elastic Moduli of PLLA/Sisal Fiber Composites

| Matrix/Fiber | V_f (-) | ${}^b E_f$ (GPa) | V_m (-) | ${}^c E_m$ (GPa) | E_c (calculated ^d) (GPa) | E_c (experimental) (GPa) |
|---------------------------------|--------------|---------------------|--------------|---------------------|--|----------------------------------|
| Flexure | | | | | | |
| PLLA/untreated sisal | 0.4 | 17.6 | 0.6 | 2.7 | 8.7 | 9.8 |
| PLLA/treated sisal ^a | 0.4 | 27.5 | 0.6 | 2.7 | 12.6 | 11.1 |
| PLLA/untreated sisal | 0.6 | 17.6 | 0.4 | 2.7 | 11.6 | 19.4 |
| PLLA/treated sisal ^a | 0.6 | 27.5 | 0.4 | 2.7 | 17.6 | 22 |
| Tension | | | | | | |
| PLLA/untreated sisal | 0.5 | 17.6 | 0.5 | 2.7 | 10.2 | 9.5 |
| PLLA/treated sisal ^a | 0.5 | 27.5 | 0.5 | 2.7 | 15.1 | 12 |

^aFibers treated with aqueous caustic soda solution (6 wt %) for 48 h.

^bData taken from Table IV.

^cData taken from Table III.

^dValues calculated from the rule of mixtures assuming that the correction factors default to unity. $E_c = V_f E_f + V_m E_m$ (eq. 10); subscripts m , f , and c have the meaning of matrix, fiber, and composite.

on the strength means showed that caustic soda treatment had significant effect on the mechanical properties of the composites at a significance level greater than 95%.

As expected, mechanical properties improve as fiber volume fraction increases for composites with both fiber types. Flexural strength of composites reinforced with untreated sisal fibers increased by 18% as the fiber volume fraction increased from 0.4 to 0.6. Flexural strength of composites reinforced with caustic soda-treated sisal fibers with 0.4 and 0.6 fiber volume fraction increased by 19% from 240 MPa to 286 MPa. Flexural moduli as a function of fiber volume fraction increased by 13% for composites of both fiber types.

The interlaminar shear strength of laminar composites reinforced with a fiber volume fraction 0.4 improved by 76% after the application of caustic soda treatment to sisal fibers. Tensile strength of composites reinforced with untreated and caustic soda-treated sisal fibers with a fiber volume fraction of 0.5 was 164 and 205 MPa, respectively. The tensile modulus increased by 26% for composites reinforced with treated sisal fibers. The interlaminar shear strength (ILSS) of reported PLLA/sisal fiber composites obtained from the short beam shear test are in good relation to the interfacial shear strength (IFSS) results obtained from the microbond shear test in a previous paper.⁴³

Mechanical properties of composites can be theoretically estimated from the properties of their constituents. Assuming that both the fiber and the matrix deform elastically and provided that

$$\sigma_f > \sigma_m; E_f > E_m \quad (8)$$

$$\varepsilon_m > \varepsilon_f \quad (9)$$

i.e., the fiber is stronger, stiffer and strains less to break compared to the matrix, then the modified "rule of mixtures" proposed by Virk et al., which takes into account the irregular

cross-section of natural fibers, can be applied to predict the properties of natural fiber reinforced composites⁴⁴:

$$E_c = \kappa \eta_d \eta_l \eta_o E_f V_f + E_m (1 - V_f) \quad (10)$$

$$\sigma_c = \kappa \sigma_f V_f + (\sigma_m)_{ef} (1 - V_f) \quad (11)$$

where κ is the fiber area correction factor, η_d is the fiber diameter distribution factor, η_l is the length correction factor, η_o is the orientation efficiency factor. E , σ , ε , and V are the modulus, strength, elongation and volume fraction. The subscripts c , f , and m denote composite, fiber and matrix and $(\sigma_m)_{ef}$ is the matrix stress at strain that is equal to the fiber failure strain. It should be pointed out that eq. 11 applies only to unidirectional composites aligned with the stress.

Because well-characterized fibers with gravimetric determination of fiber cross-sectional area were used, both the fiber area correction factor and fiber diameter distribution factor will default to unity. Experimentally determined and theoretically calculated (eq. 10) elastic moduli of PLLA/sisal fiber composites showing good correlation between the theory and the experiment are summarized in Table VII.

Manufactured composites of PLLA reinforced with long sisal fiber bundles possessed mechanical properties which were superior to the mechanical properties of some wood species, for example superior to Douglas fir which has a flexural strength of 85 MPa and flexural modulus of 13.4 GPa.⁴⁵

Figure 7 shows SEM micrographs of composite specimens which failed in tension and three-point bending. A transcrystalline layer of PLLA was observed on the surface of caustic soda-treated sisal fiber bundles embedded in a polymer matrix [Figure 7(a,b) in detail]. Tensile failed specimens of PLLA reinforced with untreated sisal fibers contained broken fiber bundles and good fiber to matrix adhesion [Figure 7(d,e)]. Figure 7(f) shows a longitudinal

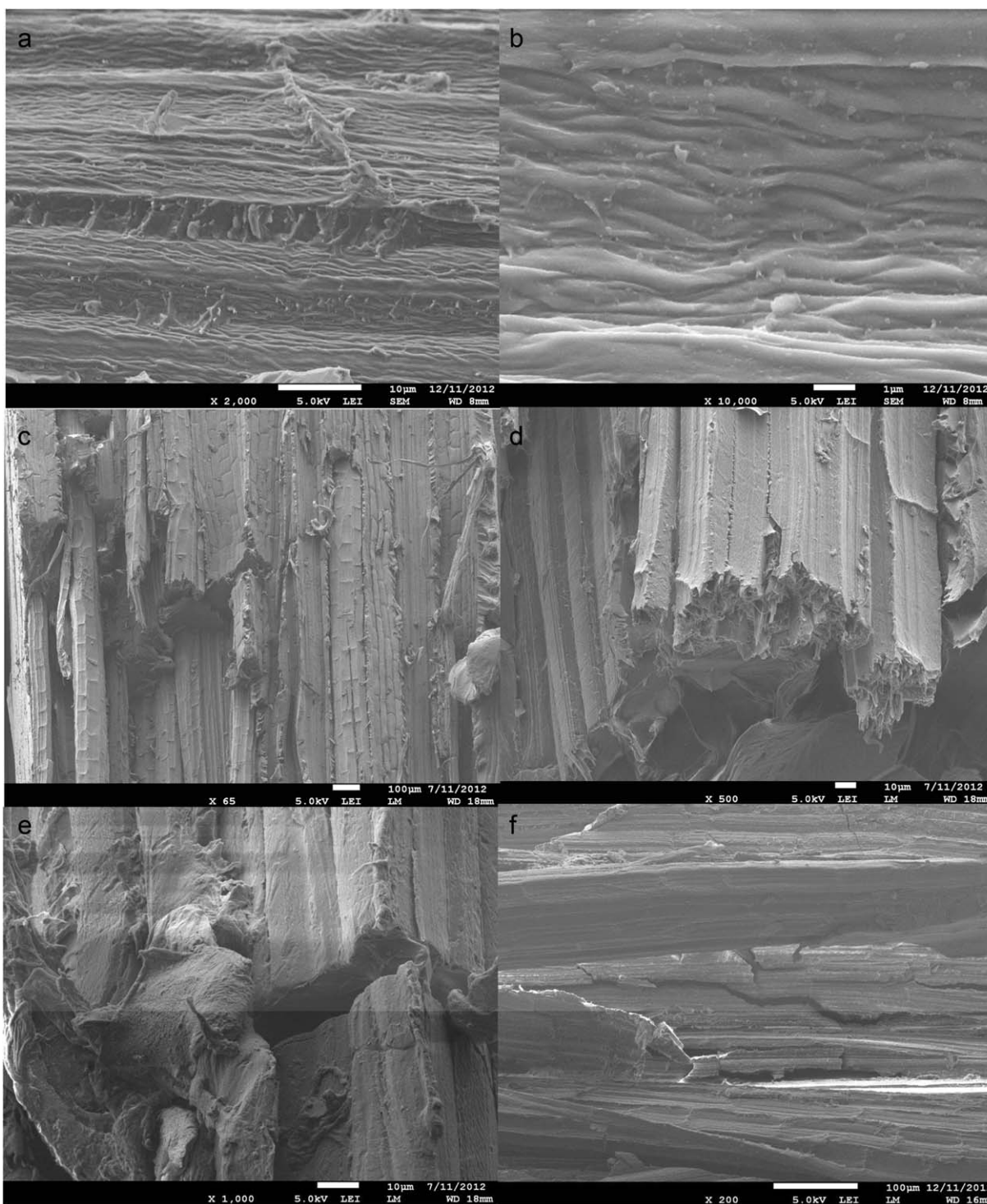


Figure 7. SEM micrographs of sisal fiber/PLLA composites failed in tension (a-e) and in flexure (f); (a) transcrystalline layer of PLLA on the surface of caustic soda-treated sisal fibers; (b) a detail of the transcrystalline layer; (c) composite failed in tension with a detail of a broken untreated sisal fiber bundle cross-section (d) and a detail of fiber to matrix adhesion with separated tracheids in a fiber bundle (e); Longitudinal section of a PLLA reinforced with untreated sisal fibers after the flexural test with a crack detail (f).

section of three-point bend specimen of PLLA/untreated sisal fiber composite broken in liquid nitrogen after the flexural test. The micrograph is a detail of an inter-ply crack going through the sisal fiber bundle indicating reasonably good fiber to matrix adhesion.

Dynamic Mechanical Thermal Analysis

Untreated and caustic soda-treated sisal fiber/PLLA composites were tested in a single cantilever fixture at a frequency of 1 Hz and a constant rate of heating of 2°C/min. to determine the effect of the reinforcement on the glass transition temperature

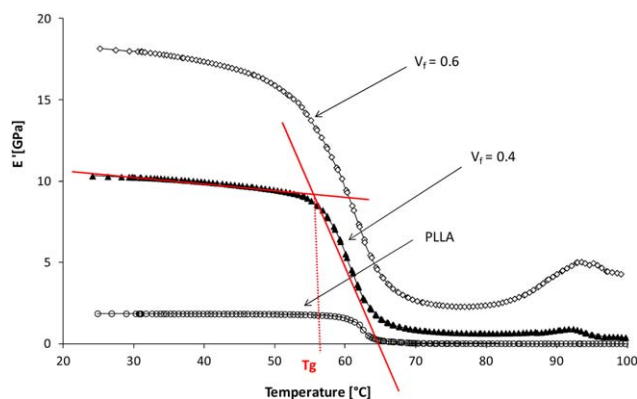


Figure 8. Storage modulus of untreated sisal fiber-poly lactide composites as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of PLLA. A heating rate of $2^{\circ}\text{C}/\text{min}$ was employed to avoid artificial damping peaks.⁴⁶ A single cantilever fixture was used because flexure modes are more sensitive to changes at the fiber to matrix interface.⁴⁷ The choice of a flexural fixture also influences the measured glass transition temperature: in a single cantilever fixture the area of specimen under the clamps is lower compared to, for example, a dual cantilever fixture which results in less difference between the sample temperature and that determined by the instrument.⁴⁸

Figure 8 shows the storage modulus of untreated sisal fiber-poly lactide composites as a function of temperature and fiber volume fraction. The storage modulus (E') at room temperature increases with the fiber volume fraction. Cold crystallization is responsible for the E' modulus increase above the T_g in the temperature range of $90\text{--}100^{\circ}\text{C}$.⁴⁹ Figure 8 also shows the tangent construction for the determination of the onset glass transition temperature (T_{eig}). Murayama and Lawton characterized fiber to matrix adhesion using dynamic mechanical measurements and related the energy dissipation ($\tan \delta$) to poor fiber to matrix adhesion.⁵⁰ Composites with good fiber to matrix adhesion tend to dissipate less energy compared to the ones with poor interfacial adhesion.⁵¹ The damping peak of the composites reinforced with untreated sisal fibers was lower com-

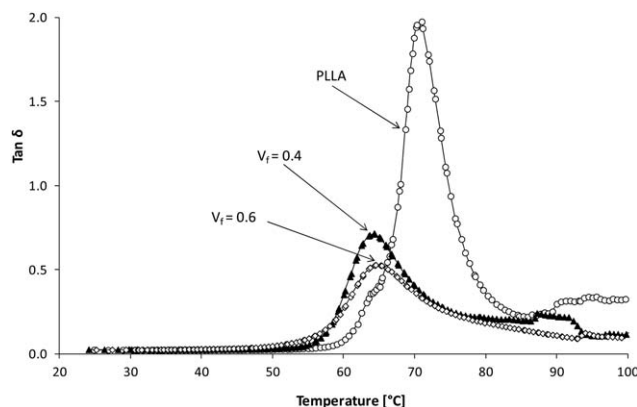


Figure 9. Damping ($\tan \delta$) of untreated sisal fiber-poly lactide composites as a function of temperature.

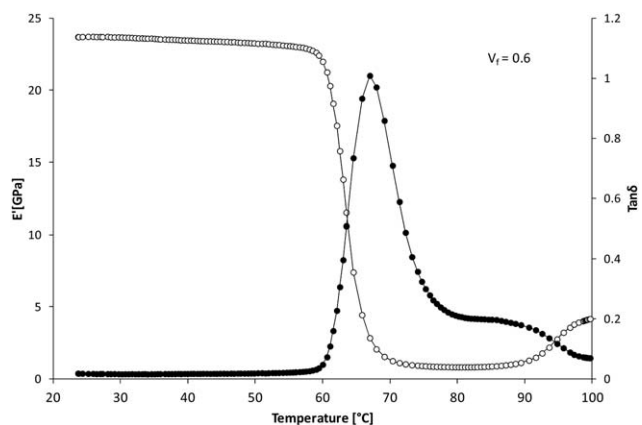


Figure 10. Storage modulus (E') and $\tan \delta$ of caustic soda-treated sisal fiber-poly lactide composites as a function of temperature.

pared to the neat poly lactide and its maximum was shifted to lower temperatures (Figure 9). Composites with higher fiber volume fractions have larger interfacial area and thus more energy is dissipated at the interface. Figure 10 shows the storage modulus and $\tan \delta$ of caustic soda-treated sisal fiber-poly lactide composites of $V_f = 0.6$ as a function of temperature. The stiffness of the sample at room temperature considerably increases compared with the samples reinforced with untreated sisal fibers. The untreated as well as the caustic soda-treated sisal fibers reinforcement significantly improved the storage modulus relative to unreinforced PLLA below and above the glass transition temperature as suggested by Table VIII showing the E' moduli at selected temperatures. Table IX summarizes the glass transition temperatures of untreated and caustic soda-treated sisal fiber-poly lactide composites which were determined by different methods. The extrapolated onset initial glass transition temperature (T_{eig}) is highlighted because it is often reported as “the T_g ”. The tangent construction for T_{eig} determination is illustrated in Figure 8. Comparing the T_g of composites with untreated sisal fibers with the one of pure PLLA it can be concluded that the addition of fibers to the matrix leads to the depression of the glass transition temperature. In the case of composites with caustic soda-treated sisal fibers the glass transition temperature is slightly higher than that of neat poly lactide polymer matrix. The reason could be the improved adhesion between caustic soda-treated fibers and the polymer matrix or

Table VIII. Storage Modulus as a Function of Temperature PLLA Reinforced with Sisal Fibers

| Matrix | Fiber | Fiber treatment | V_f | E' (25°C) (GPa) | E' (40°C) (GPa) | E' (60°C) (GPa) |
|--------|-------|---------------------------|-------|-------------------|-------------------|-------------------|
| PLLA | - | - | - | 1.9 | 1.8 | 1.5 |
| PLLA | Sisal | - | 0.4 | 10.3 | 10 | 5.5 |
| PLLA | Sisal | - | 0.6 | 18.2 | 17.4 | 9.5 |
| PLLA | Sisal | Caustic soda ^a | 0.6 | 23.7 | 23.5 | 22 |

^a Fibers treated with aqueous caustic soda solution of 6 wt % concentration for 48 h.

Table IX. Glass Transition Temperature Determined from DMTA Scans of PLLA Reinforced with Sisal Fibers

| Glass transition temperature ^{a,b} (°C) | PLLA | PLLA/sisal (V _f = 0.4) | PLLA-sisal (V _f = 0.6) | PLLA/treated sisal ^c (V _f = 0.6) |
|---|------|-----------------------------------|-----------------------------------|--|
| T _g (E'') _{max} | 60.7 | 60.9 | 62 | 63.7 |
| T _g (tan δ) _{max} | 69.4 | 64.3 | 64.5 | 67.0 |
| T _{mg} | 60 | 60.4 | 60 | 63.9 |
| T _{eig} | 58.4 | 56.1 | 53.5 | 60.0 |
| T _{efg} | 63.9 | 64.8 | 66.3 | 65.8 |
| (T _{ef} - T _{ei}) _g | 5.5 | 8.7 | 12.8 | 5.8 |

^aProcedures of T_g determination are explained in Ref. 52.

^bSubscripts: g = glass, m = midpoint, e = extrapolated onset, i = initial, f = final.

^cFibers treated with aqueous caustic soda solution of 6 wt % concentration for 48 h.

the development of crystalline morphology at the fiber to matrix interface during compression molding [Figure 7(a,b)]. The transcrystalline layer has a specifically organized morphological structure which restrains the motion of polymer chains at the interface.

CONCLUSIONS

Fully bio-based and biodegradable composites were manufactured from unidirectionally aligned long sisal fiber bundles and a polylactide polymer matrix. Mechanical properties of sisal fibers were investigated in the untreated state and following caustic soda treatment. Caustic soda treatment was employed to modify the strength of fibers and to improve fiber to matrix adhesion. The mean strength of untreated and caustic soda-treated sisal fibers at a gauge length of 20 mm was 482 and 563 MPa, respectively. Composites with fiber volume fraction from 0.4 to 0.6 were compression molded. Mechanical properties were measured as a function of fiber volume fraction and properties improved with increasing fiber content. Scanning electron micrographs of the polished cross sections of composites revealed good fiber to matrix adhesion. Caustic soda treatment of fibers improved mechanical properties of the composites and flexural strength and modulus increased from 279 MPa and 19.4 GPa, respectively, to 286 MPa and 22 GPa at a fiber volume fraction of 0.6. Overall it has been demonstrated that high strength, high modulus sisal-PLLA composites can be produced with effective stress transfer at well-bonded fiber to matrix interfaces.

ACKNOWLEDGMENTS

The first author would like to acknowledge the BRE Trust for funding his PhD.

REFERENCES

- Dissanayake, N. P. J.; Summerscales, J.; Grove, S. M.; Singh, M. M. *J. Biobased. Mater. Bio.* **2009**, *3*, 245.
- Dissanayake, N. P. J.; Summerscales, J.; Grove, S. M.; Singh, M. M. *J. Nat. Fibers.* **2009**, *6*, 331.

- Vink, E. T. H.; Rábago, K. R.; Glassner, D. A.; Gruber, P. R. *Polym. Degrad. Stabil.* **2003**, *80*, 403.
- Södergård, A.; Stolt, M. *Prog. Polym. Sci.* **2002**, *27*, 1123.
- Ajioka, M.; Enomoto, K.; Suzuki, K.; Yamaguchi, A. *J. Polym. Environ.* **1995**, *3*, 225.
- Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841.
- Reyes, G.; Cantwell, W. J. *Compos. Sci. Technol.* **2000**, *60*, 1085.
- Bader, M. G. *J. Microsc.* **2001**, *201*, 110.
- Van de Velde, K.; Kiekens, P. *Polym. Test.* **2002**, *21*, 433.
- Van de Velde, K.; Kiekens, P. *Polym. Test.* **2001**, *20*, 885.
- Ansell M. P.; Mwaikambo, L. Y. In *Handbook of Textile Fibre Structure: Natural, Regenerated, Inorganic And Specialist Fibres*; Eichhorn, S.; Hearle, J. W. S.; Jaffe, M.; Kikutani, T., Eds.; Woodhead Publishing: Cambridge, **2009**, Vol. 2, Chapter 2, p 62.
- Aziz, S. H.; Ansell, M. P. In *Green Composites: Polymer Composites and the Environment*; Baillie, C. Ed.; Woodhead Publishing: Cambridge, **2004**; p 154.
- Toonen, M.; Ebskamp, M.; Kohler, R. In *Improvement of Crop Plants For Industrial End Uses*; Ranalli, P., Ed.; Springer: Dordrecht, **2007**, p 155.
- Vincent, J. F. V. *J. Mater. Sci.* **1982**, *17*, 856.
- Nishino, T.; Takano, K.; Nakamae, K. *J. Polym. Sci. Part B Polym. Phys.* **1995**, *33*, 1647.
- Madsen, B.; Lilholt, H. *Compos. Sci. Technol.* **2003**, *63*, 1265.
- Hao, A.; Zhao, H.; Jiang, W.; Yuan, L.; Chen, J. Y. *J. Polym. Environ.* **2012**, *20*, 959.
- Oksman, K.; Skrifvars, M.; Selin, J. F. *Compos. Sci. Technol.* **2003**, *63*, 1317.
- Bodros, E.; Pillin, I.; Montrelay, N.; Baley, C. *Compos. Sci. Technol.* **2007**, *67*, 462.
- Ochi, S., *Compos. Part A-Appl. S.* **2006**, *37*, 1879.
- Gomes, A.; Matsuo, T.; Goda, K.; Ohgi, J. *Compos. Part A-Appl. S.* **2007**, *38*, 1811.
- Ochi, S. *Mech. Mater.* **2008**, *40*, 446.
- Soykeabkaew, N.; Arimoto, N.; Nishino, T.; Peijs, T. *Compos. Sci. Technol.* **2008**, *68*, 2201.
- Plackett, D. *J. Polym. Environ.* **2004**, *12*, 131.
- Plackett, D.; Andersen, T. L.; Pedersen, W. B.; Nielsen, L. *Compos. Sci. Technol.* **2003**, *63*, 1287.
- Mwaikambo, L. Y.; Ansell, M. P. *Angew. Makromol. Chem.* **1999**, *272*, 108.
- Mwaikambo, L. Y.; Ansell, M. P. *J. Appl. Polym. Sci.* **2002**, *84*, 2222.
- Mwaikambo, L. Y.; Ansell, M. P. *J. Mater. Sci.* **2006**, *41*, 2497.
- Mwaikambo, L. Y.; Ansell, M. P. *J. Mater. Sci.* **2006**, *41*, 2483.
- Bismarck, A.; Mohanty, A. K.; Aranberri-Askargorta, I.; Czaplá, S.; Misra, M.; Hinrichsen, G.; Springera, J. *Green Chem.* **2001**, *3*, 100.

31. Krässig, H. A. Cellulose: Structure, Accessibility, and Reactivity; Gordon and Breach Science Publishers: Yverdon, **1993**, p 258, 306.
32. Nishino, T. In Green Composites: Polymer Composites and the Environment; Baillie C., Ed.; Woodhead Publishing: Cambridge, **2004**, p 54.
33. Virk, A. S.; Hall, W.; Summerscales, J. *Compos. Sci. Technol.* **2010**, *70*, 995.
34. Zafeiropoulos, N. E.; Baillie, C. A. *Compos. Part A-Appl. S.* **2007**, *38*, 629.
35. Naito, K. *J. Appl. Polym. Sci.* **2013**, *128*, 1185.
36. Nordström, Y.; Joffe, R.; Sjöholm, E. *J. Appl. Polym. Sci.* **2013**, *130*, 3697.
37. Riedel, U.; Nickel, J. *Angew. Makromol. Chem.* **1999**, *272*, 34.
38. McNeill, I. C.; Leiper, H. A. *Polym. Degrad. Stabil.* **1985**, *11*, 267.
39. McNeill, I. C.; Leiper, H. A. *Polym. Degrad. Stabil.* **1985**, *11*, 309.
40. Tang, M. M.; Bacon, R. *Carbon* **1964**, *2*, 211.
41. Jamshidi, K.; Hyon, S.-H.; Ikada, Y. *Polymer* **1988**, *29*, 2229.
42. Scheirs, J.; Camino, G.; Tumiatti, W. *Eur. Polym. J.* **2001**, *37*, 933.
43. Prajer, M.; Ansell, M. P. *Compos. Interface* **2012**, *19*, 39.
44. Virk, A. S.; Hall, W.; Summerscales, J. *Mater. Sci. Technol.* **2012**, *28*, 864.
45. Forest Product Laboratory, Wood handbook-wood as an engineering material; General Technical Report FPL-GTR-113, U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, 1999.
46. Thomason, J. L. *Polym. Compos.* **1993**, *11*, 105.
47. Dong, S.; Gauvin, R. *Polym. Compos.* **1993**, *14*, 414.
48. Atkinson, K. E.; Jones, C. J. *Adhesion* **1996**, *56*, 247.
49. Menard, K. P. *Dynamic Mechanical Analysis: A Practical Introduction*; CRC Press: London **1999**, p 75, 100.
50. Murayama, T.; Lawton, E. L. *J. Appl. Polym. Sci.* **1973**, *17*, 669.
51. Edie, D. D.; Kennedy, J. M.; Cano, R. J.; Ross, R. A. In *Composite Materials: Fatigue and Fracture*; Stinchcomb, W. W.; Ashbaugh, N. E., Eds.; ASTM: Philadelphia, **1993**, ASTM STP 156, Vol. 4, p 419.
52. Ehrenstein, G. W.; Riedel, G.; Trawiel, P. *Thermal Analysis of Plastics: Theory and Practice*; Hanser Gardner Publications: New York, **2004**, p 236.