

Plasma Modification of Man-made Cellulose Fibers (Lyocell) for Improved Fiber/Matrix Adhesion in Poly(lactic acid) Composites

Nina Graupner,¹ Katharina Albrecht,¹ Dirk Hegemann,² Jörg Müssig¹

¹University of Applied Sciences Bremen, Dept. Biomimetics, Working Group Biological Materials, D-28199 Bremen, Germany

²Empa, Swiss Federal Laboratories for Materials Science and Technology, CH-9014 St. Gallen, Switzerland

Correspondence to: N. Graupner (E-mail: nina.graupner@hs-bremen.de)

ABSTRACT: The present study investigates the influence of different plasma treatments on the tensile characteristics of lyocell fibers and the interfacial interactions of lyocell fibers in a poly(lactic acid) matrix. For the investigations, the fibers were coated by an amine-functional, nanoporous layer (a-C:H:N) using a gaseous mixture of NH₃:C₂H₄ of 1:1 and 5:3, respectively, an oxygen-functional layer (a-C:H:O) with CO₂:C₂H₄ and CO₂ posttreatment, or an oxygen-functional layer (a-C:H:O) comprising hydroxyl groups with H₂O:C₂H₄ and H₂O posttreatment. As reference, uncoated fibers and fibers coated with a crosslinked, amorphous hydrocarbon layer (a-C:H) without functional group incorporation were investigated. While the different treatments maintained the tensile strength of the lyocell fibers, which were all in the range between 295 and 338 N/mm², the interfacial shear strength, measured by the pull-out test, was clearly influenced. The best improvement of the fiber/matrix adhesion was obtained by a plasma treatment with a mixture of water vapor and ethylene resulting in an interfacial shear strength of 17.8 N/mm² in comparison to the untreated lyocell fiber with 10.3 N/mm². Amine-functional plasma polymers (a-C:H:N) were also found to be suitable for adhesion-promoting interlayers on lyocell fibers in poly(lactic acid). © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 4378–4386, 2013

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INTRODUCTION

Surface properties such as chemistry, roughness, wettability, morphology, cleanliness, etc., are known to influence the adhesion of polymer composite.¹ All these properties can effectively be adjusted using plasma surface treatments. Low temperature plasmas, which are excited by electric fields, interact with material surfaces by radicals, energetic particles, and radiation yielding ablation, crosslinking, and deposition reactions. Polymer surfaces modified with nonpolymerizable gases (plasma activation), however, show restructuring effects with time, also called aging. Therefore, ultrathin films of crosslinked plasma polymers became interesting as adhesion-promoting interlayers in fiber-reinforced composites.^{2,3}

Plasma polymerization of ethylene was found to increase the adhesion strength between polyethylene terephthalate fibers and a polyethylene matrix,⁴ while pyrrole (azole) or acetylene (ethyne) as monomer gases increased the pull-out force of aramid cords embedded in rubber by up to 90% with negligible decrease in single-fiber tensile strength.^{2,5} Ooij et al. used a semicontinuous DC plasma reactor to treat the aramid cords.² Ultrathin (<50 nm) plasma-polymerized acetylene layers (mixed

with air) were also found to increase the tensile strength of carbon fibers due to its crosslinked network of molecular chain structure.⁶ A mixture of acetylene and oxygen (2:1) was used by Feih and Schwartz⁷ to deposit plasma polymers on PAN-based carbon fibers to increase the fiber–epoxy resin adhesion in composites. A 90% improvement in interfacial shear strength (IFSS) was accompanied by no significant change in the tensile strength of the carbon fibers, which was attributed to carbonyl and hydroxyl groups on the surface as well as long-living free radicals entrapped within the plasma polymer. Allylamine plasma polymerization was investigated for the improvement of fiber–matrix adhesion in polyethylene fiber-reinforced epoxy resins⁸ or aramid fiber-reinforced composites.⁹

It could also be demonstrated that the plasma deposition of amine-functional a-C:H:N films is applicable for fiber-reinforced composites using ammonia/hydrocarbon radio frequency (RF) discharges.¹⁰ The interfacial adhesion of plasma-treated flax fibers in a poly(lactic acid) (PLA) matrix was found to be noticeably enhanced.¹¹ Similarly, the adhesion of aramid fibers in a HNBR rubber matrix could be increased, resulting in pull-out forces comparable to the conventional RFL dip coating.

A clear increase of the IFSS of sisal fiber-reinforced polypropylene (PP) by plasma treatment was reported by Yuan et al.¹² They determined an IFSS of 3.1 N/mm² by an air-plasma treatment and 2.6 N/mm² by an Ar-plasma treatment with a power of 60 W and a pressure of 266.64 Pa for a time of 30 s. The untreated sisal-PP composites showed an IFSS value of 2.5 N/mm². A longer treatment time (60 and 120 s) resulted in clearly lower IFSS values. The decrease was clearly higher for Ar-plasma treated samples while the tensile strength of the fibers was reduced more significant by the air-plasma treatment.

Previous works have shown nonoptimal fiber/matrix adhesion resulting in big gaps between fiber and matrix.^{13,14} Therefore, the surface of cellulose fibers should be modified for an improved fiber/matrix adhesion. One possibility for an improved interface is the plasma treatment. This work investigates the effect of plasma polymers as adhesion-promoting interlayers for lyocell fiber (regenerated cellulose fiber)-reinforced PLA composites using different hydrocarbon/reactive gas mixtures. Lyocell fibers were chosen due to their reproducible quality. In comparison to natural fibers like bast or leaf fibers, they are more expensive but a comparison of different plasma treatments is easier with fibers, which have a low variability in their fiber surface. Natural fibers display a high variability in their surface constitution and roughness. Therefore, regenerated cellulose fibers were used to reach the main objective of the study, which deals with the investigation of the effects of different plasma treatments for the improvement of the fiber/matrix adhesion of cellulose fiber-reinforced PLA composites. During this study, the following hypotheses were tested:

- Plasma treatment is applicable for surface modification of lyocell fibers.
- Plasma treatment can lead to poor tensile characteristics of the fibers.
- Plasma treatment improves the fiber/matrix adhesion due to nanoporous and functional interlayers.
- Different plasma treatments and gaseous mixtures lead to variable IFSS values.

EXPERIMENTAL

Fiber and Matrix

Lyocell staple fibers produced by Lenzing (Lenzing AG, Lenzing, Austria) with a fiber fineness of 15.0 dtex, a length of 60 mm, and a density of 1.5 g/cm³ were used for the plasma treatment.

As matrix, thermoplastic PLA Ingeo fibers type SLN 2660 D (Eastern Textile, Taipei, Taiwan) were used with a fiber fineness of 6.7 dtex and a length of 64 mm. The fibers were produced from a NatureWorksTM PLA with a density of 1.24 g/cm³, a melting temperature of 160–170°C and a glass transition temperature of 60–65°C.

The PLA is processed at a press temperature of 180°C due to the thermal characteristics, which were determined in a previous study by differential scanning calorimetry measurements. Melting temperature was determined as double peak with two maxima at 161°C and 175°C, presumably caused by the presence of two different crystalline structures.¹⁵ A study of Kobayashi et al.¹⁶ has shown an improved tensile strength of jute/PLA

composites with an increasing processing temperature from 170 to 180°C. With higher temperatures, the values decreased due to the beginning degradation of the materials. Lower values for composites produced at 170°C can be explained by the high viscosity of the matrix on a bad wetting of the fibers with the matrix. Hence, the press temperature was set to 180°C.

Plasma Treatment

A home-built pilot-scale plasma reactor was used for the plasma treatments.¹⁷ The reel-to-reel web coater with 2 m in height contained an internal cylindrical electrode (drum with 59 cm in diameter and 65 cm in width) driven by 13.56 MHz RF. A power up to 1200 W can be applied by the RF generator (Cesar 1312, Dressler). The gas inlet was placed at four different positions around the drum controlled by mass flow controllers. Paralyzed staple fibers of lyocell were spread and fixed around the drum. During the plasma treatment, the drum was rotating in order to attain a homogeneous deposition. Prior to the plasma polymerization, plasma cleaning with Ar/O₂ was performed for all experiments (1 min at a power input of 400 W and a pressure of 10 Pa). Ethylene (C₂H₄) was used as hydrocarbon monomer (for a-C:H films), while ammonia (NH₃), carbon dioxide (CO₂), and water vapour (H₂O) were selected as additional reactive gases yielding different functional a-C:H:N and a-C:H:O films. In order to enhance the incorporation of oxygen functional groups at the crosslinked a-C:H:O surface, a post-treatment with either CO₂ or H₂O (by shutting down the monomer flow) was performed for 5 min. The pressure was maintained at 10 Pa (0.1 mbar) in all experiments. The deposition conditions are summarized in Table I.

Fiber Types Produced by Plasma Treatment

Six different kinds of fibers were investigated for their fiber/matrix interactions:

- Reference 1 (Ref 1): Untreated lyocell fibers;
- Reference 2 (Ref 2): Lyocell fibers B0924a (C₂H₄ plasma), coated with a crosslinked, amorphous hydrocarbon layer (a-C:H) without functional group incorporation;
- Plasma-treated lyocell fibers B0721a (NH₃:C₂H₄ 1:1), coated by an amine-functional, nanoporous layer (a-C:H:N);
- Plasma-treated lyocell fibers B0819a (NH₃:C₂H₄ 5:3), coated by an amine-functional, more dense layer (a-C:H:N);
- Plasma-treated lyocell fibers B0728a (CO₂:C₂H₄ + CO₂ post-treatment), coated by an oxygen-functional layer (a-C:H:O); and
- Plasma-treated lyocell fibers B0924b (H₂O:C₂H₄ + H₂O post-treatment), coated by an oxygen-functional layer (a-C:H:O) comprising hydroxyl groups.

Tensile Characteristics of the Fibers

The tensile characteristics of the fibers were determined by a tensile tester type Fafegraph M manufactured by Textechno (Mönchengladbach, Germany) working with a load cell of 100 cN and pneumatic clamps covered with hard PVC. The testing speed was set to 2 mm/min at a gauge length of 10 mm. A clamp with a mass of 200 mg was used for pretensioning the fibers to remove crimp. Tensile strength, Young's modulus, and elongation at break values were used for the evaluation of the test results. The Young's modulus was determined for each

Table I. Plasma Conditions Used for the Plasma Polymerization of a-C:H (N,O) Coatings

| Process gas | Gas ratio | Power input in W | Duration in min | Posttreatment | Approx. thickness in nm |
|--|-----------|------------------|-----------------|------------------|-------------------------|
| C ₂ H ₄ | - | 400 | 15 | - | 75 |
| NH ₃ :C ₂ H ₄ | 1:1 | 800 | 30 | - | 75 |
| NH ₃ :C ₂ H ₄ | 5:3 | 550 | 40 | - | 50 |
| CO ₂ :C ₂ H ₄ | 4:3 | 1000 | 5 + 5 | CO ₂ | 20 |
| H ₂ O:C ₂ H ₄ | 3:2 | 600 | 5 + 5 | H ₂ O | 20 |

individual fiber as secant modulus in the linear-elastic region of the stress-strain curves.

Interfacial Investigations

Fiber Pull-out Length Measurements. Single fibers were placed unidirectionally on a glass slide coated with a Teflon foil type 0903 AS (Böhme Kunststofftechnik GmbH KG, Schwarzenbek, Germany) and were fixed by adhesive tape (Tesa SE, Hamburg, Germany) as shown in Figure 1. The fibers were covered with 0.3 g of the PLA fibers and were sheeted with a second glass slide coated with Teflon foil. Prepared samples were preheated in an annealing furnace (Jürgens Laborbau GmbH, Bremen, Germany) at 180°C for 5 min and were melted for another 5 min under a pressure of 1.3 kPa at 180°C. Following this, the samples were cooled down to room temperature (approximately 20–25°C). Resulting specimens with a thickness of 150–300 μm were cut into stripes with a width of 5 mm and a length of 30 mm. These specimens were fractured in axial direction to the fiber orientation in a universal testing machine Zwick Z020 (Zwick/Roell GmbH, Ulm, Germany) operating with manual clamps and a load cell of 500 N with a testing speed of 2 mm/min and a gauge length of 10 mm.

For the fiber pull-out length measurement (FPLM), the fractured specimens were positioned in a slide frame (type antinewton super-slide; Gepe, Zug, Switzerland) and were scanned with a scanner CanoScan FS 4000 (Canon, New York, USA) with a resolution of 4000 dpi. The evaluation of the fiber pull-outs was done with the image analyzing software ImageJ 1.3.7v (Wayne Rastand, National Institute of Health) following a calibration with scale paper. The pull-outs of the obverse parts of the tensile fractured specimens were measured. If no pull-out could be observed, the value 0 μm was adopted.

Single Fiber Pull-out Test—SFPT. For determining IFSS (interfacial shear strength), PLA films with a thickness of 100–150

μm were produced. The PLA films were manufactured in an annealing furnace (Jürgens Laborbau GmbH) at 180°C between two steel plates covered with teflon foil for 5 min. Following this, the foil was cooled down at room temperature for approximately 15 min. The foil was cut into specimens of approximately 8 × 8 mm², which were equipped with a little hole by a sewing needle. A Teflon foil type 0903 AS (Böhme Kunststofftechnik GmbH KG, Schwarzenbek, Germany) with the dimensions 15 × 15 mm² was additionally equipped with a little hole. The fiber was first pushed through the hole of the Teflon foil and was fixed on the one side with adhesive tape (Tesa SE, Hamburg, Germany). The other end of the fiber was pushed through the PLA film and was fixed in a metal frame to adjust the fiber in vertical direction as shown in Figure 2 (left). After this, the sample was stored in the annealing furnace for 5 min at 180°C whereby the PLA was molten and surrounded the fiber. Afterwards, the samples were cooled at room temperature for approximately 15 min.

The pull-out force was measured by pulling out the fiber of the matrix. As testing device, the Fafegraph M (Textechno) was used. For fixing the specimen in the testing machine, a rectangular metal frame was fabricated. The frame has a slot with a width of approximately 700 μm. The upper clamps of the testing machine were closed, and the frame was laid on them. The specimen (PLA foil with the fiber) was laid in the metal frame, and the fiber was pushed through the slot (see Figure 2, right) and was fixed with the lower clamps under a pressure of 3 bar. The testing machine operated with a load cell of 100 cN, the gauge length was set to 5 mm, and the testing speed was 2 mm/min. The calculation of the IFSS was carried out according to Ref. 18:

$$\text{IFSS} = F_{\text{max}} / (d\pi/l_{\text{ef}}) \quad (1)$$

F_{max} is the maximal load in N, d is the diameter of the fiber in mm, and l_{ef} is the embedded length of the fiber in the matrix in mm.

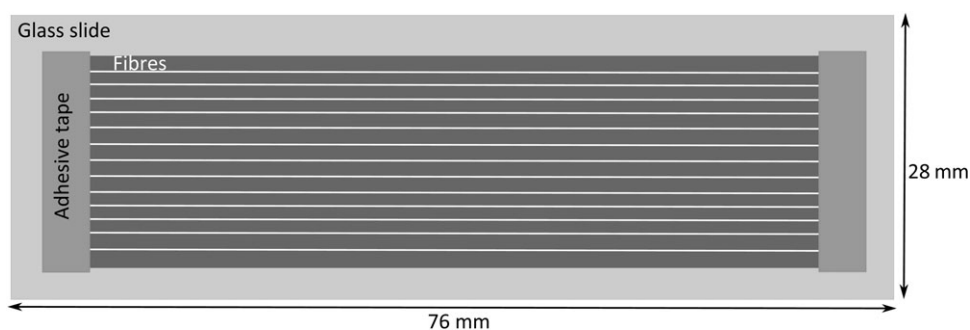


Figure 1. Preparation of lyocell fibers for the measuring of the pull-out length.

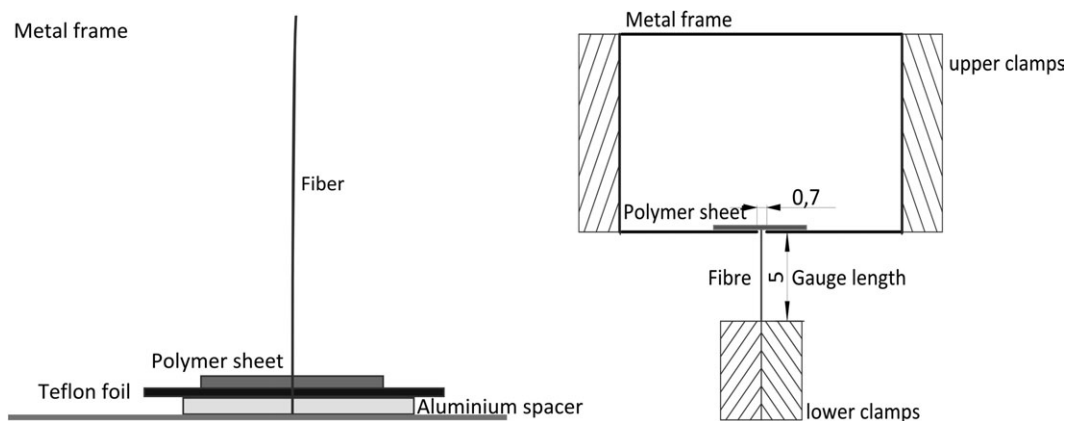


Figure 2. Sample preparation for the pull-out test (left) and testing device for the pull-out test (right).

Atomic Force Microscopy

Atomic force microscopy (AFM) investigations were carried out with a NanoWizard[®] AFM of the company JPK (Berlin, Germany). Sample surfaces were scanned via the contact mode. The cantilevers of the type Arrow (NanoWorld, Neuchâtel, Switzerland) have a spring constant of 0.2 N/m and a resonance frequency of 14 kHz. The scanning speed was set to 1.5 Hz and the set point was configured <1 V.

Statistical Analysis

Results were investigated with regard to a normal distribution by a Shapiro–Wilk test ($\alpha = 0.05$). If the results are distributed normally, a Tukey–Kramer HSD Test ($\alpha = 0.05$) was used for the determination of significant differences between the samples. For results that were not distributed normally, the Wilcoxon test ($\alpha = 0.05$) was used. Statistical investigations were carried out with the software JMP[®] 8.0 (SAS Institute Inc., Cary, NC, USA).

RESULTS AND DISCUSSION

Because many results are not distributed normally, the median values are used for the interpretation of the test results instead of the mean value. All results are presented as box-whisker plots.

Tensile Characteristics of the Fibers

As shown in Figure 3, from the statistical point of view, lyocell B0924a (Ref 2) (a-C:H plasma coating) shows a significant higher tensile strength in comparison to the water vapor/ethylene-treated fibers (B0924b). However, in an overall consideration, the values of all samples are in the range of the boxes from each fiber, which means that the plasma treatment did not affect the tensile strength of the fibers negatively. The tensile strength was measured in the range between 298 and 339 N/mm².

The highest Young's modulus was measured by trend for lyocell B0924a (Ref 2) (C₂H₄) with a value of 9826 N/mm² as well as for lyocell B0728a (CO₂ + C₂H₄) with a mean value of 9899 N/mm². In comparison to the untreated fibers, which display a value of 6531 N/mm² the Young's modulus could be increased in trend by the plasma treatment (Figure 4).

Due to the higher Young's modulus, the elongation at break was slightly reduced by the plasma treatment in comparison to the untreated fibers (Ref 1) with a mean elongation of 8.3% and Reference 2 with an elongation of 9.1%. Plasma-treated fibers

reached mean elongations ranging between 7.3% and 8.2% (see Figure 5).

Generally, changes in mechanical (bulk) properties induced by plasma treatments are considered to be small, since the interaction is limited to the outermost surface. However, radicals, energetic particles, and VUV-radiation yield crosslinking and/or chain scission reactions depending on the used gas mixture.^{19,20} Thus, also the mechanical properties of polymers and fibers can be affected by plasma cleaning/activation or plasma polymerization processes.^{1,21} In addition, plasma polymer coatings were found to influence the crack initiation depending on the coatings thickness (with an optimum around 50 nm) due to the brittleness and the number of surface flaws, and they are bearing a part of the applied load.⁶ Therefore, we assume that the best tensile characteristics as obtained for B0924a (Ref 2) (C₂H₄ plasma) are related to the most crosslinked yet still elastic (polymer-like) hydrocarbon coatings.²² Regarding the incorporation of functional groups (required for adhesion improvement), the

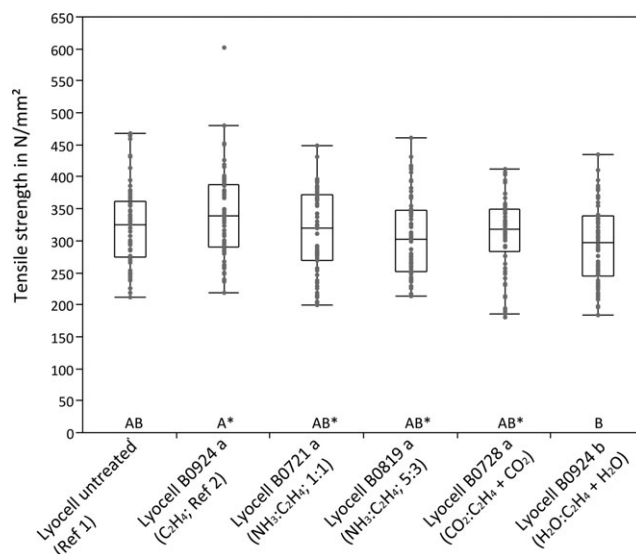


Figure 3. Tensile strength of the reference samples and the plasma-treated lyocell fibers shown as box-whisker diagram (different letters mean significant differences, *results of samples that are not normally distributed).

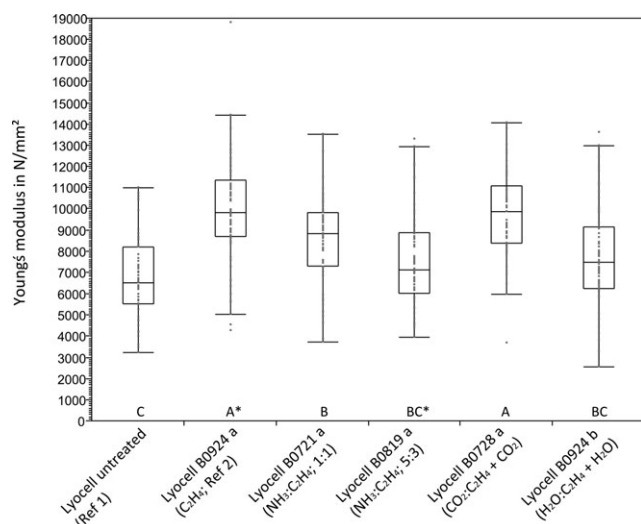


Figure 4. Young's moduli of the reference samples and the plasma-treated lyocell fibers shown as box-whisker diagram (different letters mean significant differences, *results of samples that are not normally distributed).

$\text{CO}_2:\text{C}_2\text{H}_4$ plasma polymers can be considered to perform best with respect to mechanical properties. Here, the crosslinked hydrocarbon structure contains oxygen-functional groups enhanced by the posttreatment.

AFM Investigations

Figure 6 shows lyocell surfaces coated with $\text{NH}_3:\text{C}_2\text{H}_4$, 1:1 (sample B0721a) and $\text{CO}_2 + \text{C}_2\text{H}_4$ (sample B0728a) measured by an atomic force microscope. A structuring (porosity) of nanometer scale could be revealed, which might enhance the adhesion to the matrix due to accessible functional groups within the surface layer and the corresponding higher specific surface area.²³ It can be seen that the investigation of the surface of sample B0721a [Figure 6(A''')] resulted in a more complex surface structure resulting in higher roughness in comparison to the surface of sample B0728a [Figure 6(B''')], which appears flat. Figure 6(A'',B'') show the measured height of the plasma-treated lyocell surfaces. Also, in the height profiles in Figure 6(A',B'), it is visible that the specific surface area of sample B0721a [Figure 6(A')] is enhanced in comparison to sample B0728a [Figure 6(B')]. Determined average roughness values (mean values of surface height) were 5.4 nm for sample B0721a and 1.4 nm for sample B0728a. Peak to valley roughness (maximum observed range in a sample area – distance between the highest peak and the lowest valley) yielded a value of 42.2 nm for sample B0721a and 12.4 nm for sample B0728a.

These observations agree with the finding that $\text{CO}_2/\text{C}_2\text{H}_4$ plasma polymers exhibit higher film densities when deposited at comparable plasma conditions than $\text{NH}_3/\text{C}_2\text{H}_4$ (1:1) films. An increasing $\text{NH}_3/\text{C}_2\text{H}_4$ ratio, on the other hand, was found to result in more dense, smooth a-C:H:N coatings.^{24,25}

Fiber/Matrix Interactions

Determination of FPLM. All results were found to be not normally distributed and show from the statistical point of view no

significant differences (compare Figure 7). Considering the median values, the determination of the fiber pull-out length values has shown an improved fiber–matrix bonding resulting in shorter fiber pull-out lengths of the plasma-treated samples in comparison to both reference samples.

The untreated lyocell fibers (Ref 1) have a pull-out-length value of 77 μm , Ref 2 (B0924a) has a pull-out length value of 59 μm and the shortest pull-out length values were measured for the ammonia/ethylene plasma-treated fibers.

Fiber type B0721a ($\text{NH}_3:\text{C}_2\text{H}_4$ 1:1) reached values of 60 μm , while a pull-out length value of 13 μm was determined for the fiber type B0819a ($\text{NH}_3:\text{C}_2\text{H}_4$ 5:3). The coating with $\text{H}_2\text{O}:\text{C}_2\text{H}_4$ (B0924b) lead to fiber pull-outs length values with a length of 51 μm , whereas pull-outs with a length value of 45 μm were measured for the fibers treated with carbon dioxide/ethylene (B0728a). The quantile 75 showed the longest fiber pull-outs for the reference samples and clearly lower values for the plasma-treated fibers with one exception: the fibers treated with CO_2 /ethylene (B0728a) gave length values in the same range as the reference samples.

From these results, it can be concluded by trend that better adhesion was observed for the plasma-treated fibers in comparison to the reference samples. Due to the low sensitivity of the testing procedure, no significant differences between the plasma-treated samples could be proved. Due to the low sensitivity, further investigations were carried out by the SFPT.

IFSS Measured with a SFPT. The IFSS was measured for the reference and the plasma-treated fibers embedded in the PLA-matrix as described in the Materials and Methods section. A typical fiber pull-out curve is shown in Figure 8. The fiber was tensile loaded in the linear elastic region up to the maximal load where the fiber began to slip. After the overload, only stress caused by friction was detected.

As shown in Figure 9, the plasma treatment lead to an improved IFSS (mean value) compared to the reference

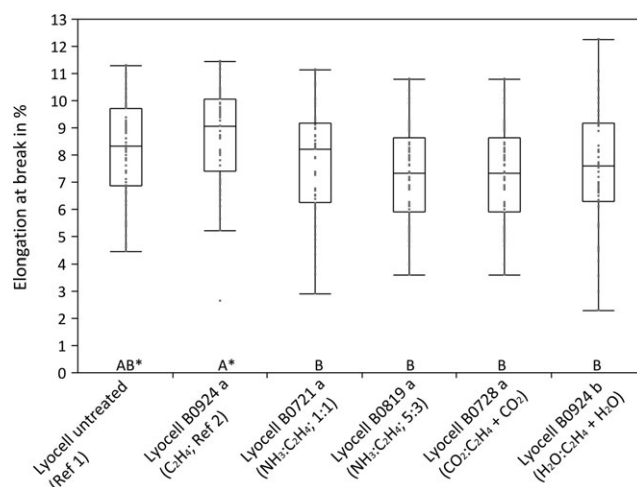


Figure 5. Elongation at break of the reference samples and the plasma-treated lyocell fibers shown as box-whisker diagram (different letters mean significant differences, *results of samples that are not normally distributed).

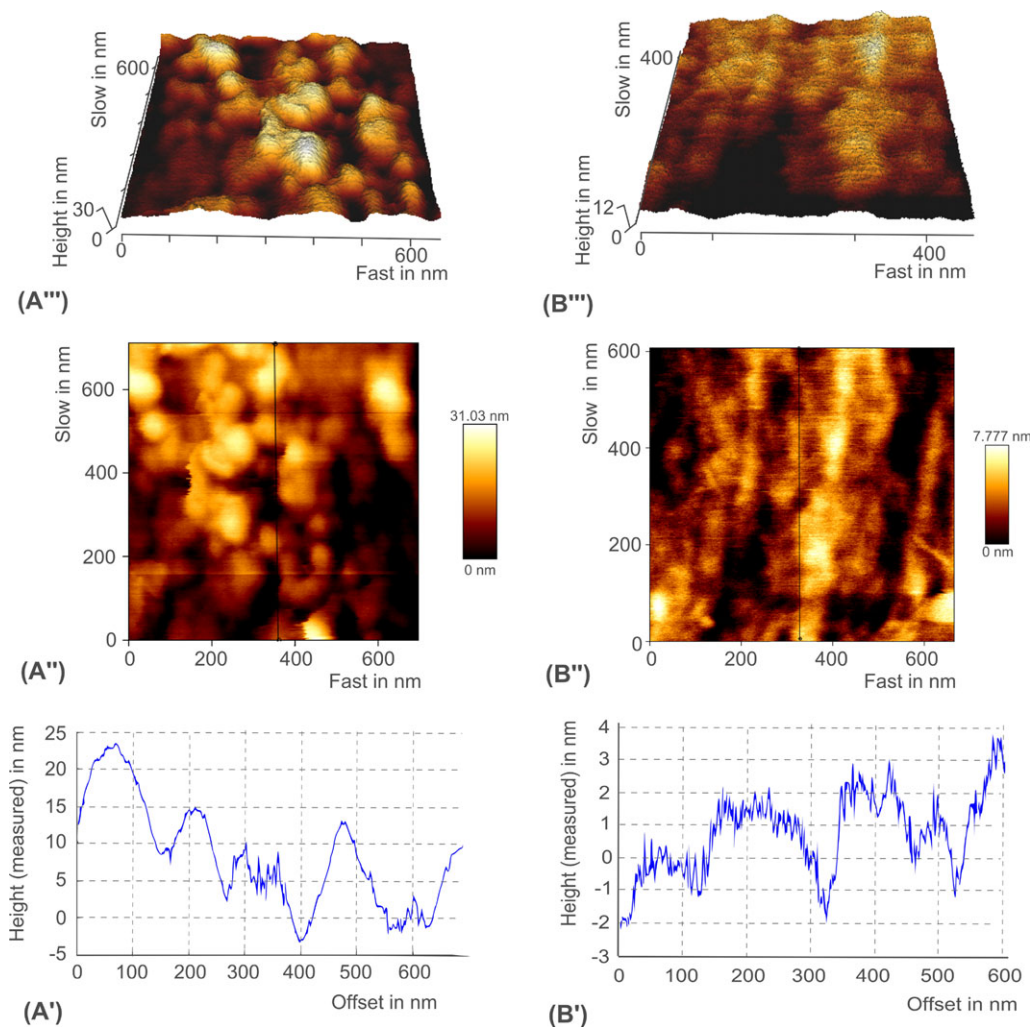


Figure 6. AFM-height image and a measured cross section of a lyocell surface coated with $\text{NH}_3:\text{C}_2\text{H}_4$, (1:1; sample B0721a, left) and $\text{CO}_2 + \text{C}_2\text{H}_4$ (sample B0728a, right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

samples. These trends were also proved by Baltazar-Y-Jimenez et al.²⁶ who determined improved IFSS of flax, hemp, and sisal by atmospheric air plasma treatment for 1 min due to the introduction of functional groups, cleaning of contaminant substances that hinder the adhesive process, and enhanced surface roughness.

The highest shear strength values were measured for the fiber type B0924b treated with H_2O /ethylene with 17.8 N/mm^2 . The untreated fibers (Ref 1) and Ref 2 (B0924a) resulted in a shear strength of 10.3 N/mm^2 and 9.1 N/mm^2 , respectively. The treatment with pure ethylene of Ref 2 (B0924a) did not influence the IFSS between lyocell and the PLA matrix. The values measured for the samples treated with NH_3 /ethylene were 16.8 N/mm^2 for fiber type B0721a ($\text{NH}_3:\text{C}_2\text{H}_4$, 1:1) and 13.6 N/mm^2 for the fiber type B0819a ($\text{NH}_3:\text{C}_2\text{H}_4$ 5:3). The IFSS of the fiber type B0728a (treated with CO_2 /ethylene) was in the same range as the sample B0819a ($\text{NH}_3:\text{C}_2\text{H}_4$, 5:3) with a measured shear strength of 13.6 N/mm^2 .

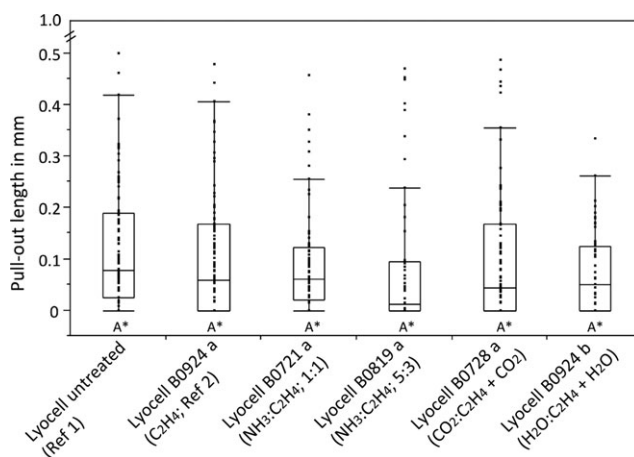


Figure 7. Box-whisker plots of the pull-out length measurements (different letters mean significant differences, *results of samples that are not normally distributed).

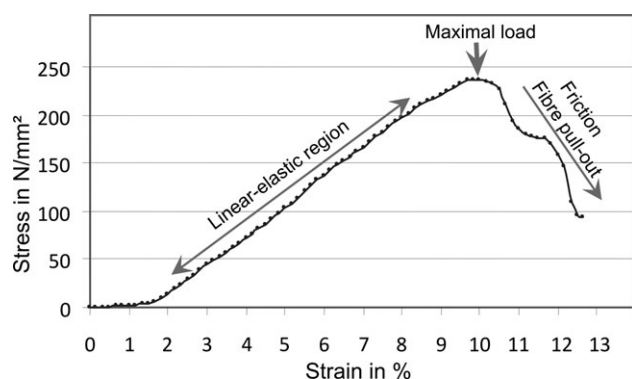


Figure 8. Typical pull-out stress-strain curve of a lyocell fiber from a PLA matrix.

The quantile 25 and quantile 75 values as well as the detected maximal values were clearly higher for the fiber type B0924b in comparison to all other fiber types. This result is in accordance with the FPLM where the smallest pull-out lengths were measured for the ammonium/ethylene as well as for the water vapor/ethylene-treated fibers.

Since nonsignificant differences among the ammonium/ethylene-treated fibers [B0721a ($\text{NH}_3:\text{C}_2\text{H}_4$, 1:1) and B0819a ($\text{NH}_3:\text{C}_2\text{H}_4$, 5:3)] were observed, we suppose that the improved

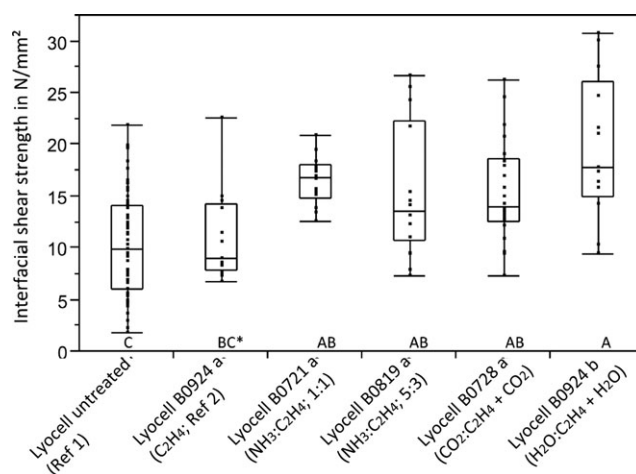


Figure 9. Box-whisker plots for the IFSS measured by the pull-out test (different letters mean significant differences, *results of samples that are not normally distributed).

fiber/matrix adhesion is rather based on the availability of functional $-\text{NH}$ groups and less caused by the porous surface structure, i.e., a possible mechanical interlocking cannot be inferred. Functional $-\text{OH}$ groups, on the other hand, might explain the

Table II. Shear Strength of Cellulose Fiber-Reinforced Polymeric Matrices Measured With Different Testing Procedures

| Testing method | Fiber type | Matrix, additives, and fiber treatment | Shear strength in N/mm^2 | Improvement factor | Reference |
|--------------------|------------|---|--|--------------------|------------|
| Pull-out test | Lyocell | PLA | 10.3 | 1.6 | This study |
| | | PLA/plasma treated ^a | 17.8 | | |
| Fragmentation test | Lyocell | LDPE | 4.8 | 1.7 | 27 |
| | | LDPE/fibrillated ^a | 8.2 | | |
| Microbond test | Jute | PP | 4.6 | 1.4 | 28 |
| | | PP/5% MAPP ^b | 6.4 | | |
| Microbond test | Jute | PLA | 4.6 | 1.2 | 29 |
| | | PLA/radiation (10 kg) ^c | 5.6 | | |
| Pull-out test | Flax | PP | 11.4 | 1.1 | 30 |
| | | PP/5% MAPP ^b | 10.6 | | |
| Pull-out test | Flax | PLA | 12.5 | 1.1 | 31 |
| | | PLA/glycerol triacetate ^b | 14.0 | | |
| Pull-out test | Hemp | PLA | 1.6 | 1.7 | 32 |
| | | PLA/alkali treated ^a | 2.7 | | |
| Pull-out test | Hemp | PLA | 5.6 | 2.0 | 33 |
| | | PLA/alkali treated ^a | 11.4 | | |
| Pull-out test | Hemp | PLA | 5.6 | 1.5 | 33 |
| | | PLA/alkali treated ^a | 8.2 | | |
| Microbond test | Kenaf | PLA | 10.7 | 1.1 | 34 |
| | | PLA/static tap water treated ^a | 11.5 | | |
| Fragmentation test | Henequen | HDPE | 4.2 | 1.4 | 35 |
| | | HDPE/alkali treated ^a | 6.0 | | |

Improvement factors are related to the used additives and fiber treatments.

^aFiber treatment, ^bAdditive, ^cTreatment of composite.

superior adhesion properties for the water vapor/ethylene-treated fibers (B0924b).

Regarding the effectiveness of the plasma treatment for the improvement of the fiber/matrix adhesion of lyocell/PLA composites, the shear strength could be increased up to a factor of 1.6 in comparison to the untreated fibers (compare Table II). Plasma treatment lead to a higher improvement in comparison to some conventional adhesion promoters like maleic anhydride grafted polypropylene (MAPP) used for PP matrices as presented in Table II. The shear strength increased up to factors in the range between 1.1 and 1.4. Similar improvements of the shear strength of cellulose fibers in different matrices could be achieved by a fibrillation of lyocell fibers or an alkali treatment. The comparison in Table II shows in the whole consideration that the plasma treatment process is well suitable for the improvement of fiber/matrix adhesion in cellulose fiber-reinforced PLA composites.

SUMMARY AND CONCLUSIONS

In the overall consideration, plasma treatment of lyocell fibers is well suitable and the different methods for determining the interfacial fiber/matrix interactions revealed similar trends, while IFSS (SFPT) showed more stable and less scattering values compared to the FPLM. Plasma treatment leads to an increase of the fiber/matrix interactions and it was shown that different gaseous mixtures lead to differences regarding the IFSS. The best improvement of the fiber/matrix adhesion was obtained by plasma treatment with a mixture of water vapor and ethylene. With this type of a-C:H:O plasma coating comprising –OH groups, the tensile properties of the fibers were found to be mainly unaffected by the plasma treatment, while plasma polymer layers from pure ethylene discharges yielded an increase mainly in Young's modulus. The hypothesis that plasma treatment lead to poor tensile characteristics of the fiber can be corroborated for the investigated treatment methods. The enhancement of the mechanical properties might be related to the deposition of a 75 nm thick crosslinked hydrocarbon layer (a-C:H), which is bearing a part of the applied load. Since similar results for the mechanical properties were obtained for the a-C:H:O coatings from CO₂/C₂H₄ plasmas, it can be concluded that these coatings are also highly crosslinked showing a low degree of functionality despite of the CO₂ posttreatment (compared to H₂O/C₂H₄ plasmas). Amine-functional plasma polymers (a-C:H:N) were also found to be suitable for adhesion-promoting interlayers on lyocell fibers within a PLA matrix independent on the surface nanostructure. Therefore, a specific functionality (hydroxyl or amino groups) of the plasma polymers is the key factor in supporting fiber/matrix adhesion. In general, it can be concluded that selected plasma treatments lead to a clear improvement of the fiber/matrix interactions of lyocell fibers in a PLA matrix. Although the improvements appear to be low, they can clearly improve the tensile properties of composites because of a large amount of individual fibers, which are present in a composite.

REFERENCES

1. Benard, Q.; Fois, M.; Grisel, M.; Laurens, P.; Joubert, F. J. *Thermoplast. Compos. Mater.* **2009**, *22*, 51.
2. Ooij, W. J.; Luo, S.; Datta, S. *Plasma Polym.* **1999**, *4*, 33.
3. Hegemann, D. *Indian J. Fibre Text Res.* **2006**, *31*, 99.
4. Höcker, H. *Pure Appl. Chem.* **2002**, *74*, 423.
5. Luo, S.; van Ooij, W. J.; Mäder, E.; Mai, K. *Rubber Chem. Technol.* **2000**, *73*, 121.
6. Weisweiler, W.; Schlitter, K. *Thin Solid Films* **1992**, *207*, 158.
7. Feih, S.; Schwartz, P. J. *Adhes. Sci. Technol.* **1998**, *12*, 523.
8. Li, Z.-F.; Netravali, A. N. *J. Appl. Polym. Sci.* **1992**, *44*, 333.
9. Shaker, M.; Kamel, I.; Ko, E.; Song, J. W. *J. Compos. Technol. Res.* **1996**, *18*, 249.
10. Hossain, M. M.; Hegemann, D.; Amberg, M.; Müssig, J. Proc. AUTEK, July 25–28, **2007**, Tampere, Finland
11. Hossain, M. M. Plasma Technology for Deposition and Surface Modification; Dissertation, University Bremen: Logos Verlag, Berlin, **2008**.
12. Yuan, X. W.; Jayaraman, K.; Bhattacharyya, D. In Handbook of Engineering Biopolymers—Homopolymers, Blends, and Composites; Fakirov, S.; Bhattacharyya, D., Eds., Carl Hanser Verlag: Munich, Germany, **2007**.
13. Huber, T.; Müssig, J. *Compos. Interfaces* **2008**, *15*, 335.
14. Graupner, N.; Müssig, J. *Compos. Appl. Sci. Manuf.*, **2011**, *42*, 2010.
15. Fischer, H.; Werwein, E.; Graupner, N. *J. Compos. Mater.*, to appear.
16. Kobayashi, S.; Yamamoto, T.; Nakai, A. *J. Solid. Mech. Mater. Eng.* **2009**, *3*, 1063.
17. Hossain, M. M.; Müssig, J.; Herrmann, A. S.; Hegemann, D. *J. Appl. Polym. Sci.* **2009**, *111*, 2545.
18. Kelly, A.; Tyson, W. R. *J. Mech. Phys. Solids* **1965**, *13*, 329.
19. Liston, E. M.; Martinu, L.; Wertheimer, M. R. *J. Adhes. Sci. Technol.* **1993**, *7*, 1091.
20. Wertheimer, M. R.; Fozza, A. C.; Holländer, A. *Nucl. Instrum. Methods Phys. Res. B* **1999**, *151*, 65.
21. Keller, M. A.; Fortunato, G.; Körner, E.; Hegemann, D. *Plasma Process Polym.* **2007**, *4*, 1063.
22. Hegemann, D.; Körner, E.; Albrecht, K.; Schütz, U.; Guimond, S. *Plasma Process Polym.* **2010**, *7*, 889.
23. Hegemann, D.; Hossain, M. M.; Balazs, D. J. *Prog. Org. Coat* **2007**, *58*, 237.
24. Guimond, S.; Hanselmann, B.; Amberg, M.; Hegemann, D. *Pure Appl. Chem.* **2010**, *82*, 1239.
25. Guimond, S.; Schütz, U.; Hanselmann, B.; Körner, E.; Hegemann, D. *Surf. Coat Technol.* **2011**, *205*, S447.
26. Baltazar-Y-Jimenez, A.; Bistriz, M.; Schulz, E.; Bismarck, A. *Compos. Sci. Technol.* **2008**, *68*, 215.
27. Karlsson, J.; Blachot, J.-F.; Peguy, A.; Gatenholm, P. *Polym. Compos.* **1996**, *17*, 300.
28. Park, J.-M.; Quang, S. T.; Hwang, B.-S.; DeVries, K. L. *Compos. Sci. Technol.* **2006**, *66*, 2686.

29. Ji, S.; Cho, D.; Park, W.; Lee, B. *Macromol. Res.* **2010**, *18*, 919.
30. Stamboulis, A.; Baillie, C.; Schulz, E. *Angew Makromol. Chem.* **1999**, *272*, 117.
31. Wong, S.; Shanks, R.; Hodzic, A. *Compos. Sci. Technol.* **2007**, *67*, 2478.
32. Islam, M.; Pickering, K.; Foreman, N. *Compos. Appl. Sci. Manuf.* **2010**, *41*, 596.
33. Sawpan, M. A. Mechanical Performance of Industrial Hemp Fibre Reinforced Poly lactide and Unsaturated Polyester Composites. Doctoral Thesis. The University of Waikato, Hamilton, New Zealand, **2010**.
34. Cho, D.; Seo, J. M.; Lee, H. S.; Cho, C. W.; Han, S. O.; Park, W. H. *Adv. Compos. Mater.* **2007**, *16*, 299.
35. Valadez-Gonzalez, A.; Cervantes-Uc, J.; Olayo, R.; Herrera-Franco, P. *Compos. B Eng.* **1999**, *30*, 309.