NATURAL FIBER COMPOSITES WITH ENCYMATICALLY ENHANCED FIBRE MATRIX ADHESION

Hanna M. Brodowsky[1]
[1]Leibniz-Institut für Polymerforschung Dresden, Hohe Str. 6, D-01069 Dresden, Germany
Email: Brodowsky@ipfdd.de, Web Page: http://www.ipfdd.de

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Abstract
The interphase between fibre and matrix plays an essential role for the composites' properties. This interphase may be modified by using a fibre coating or sizing. We present the effect of sizing based fibre surface modifications that improve the adhesion between flax fibre and PLA. Besides, an enzymatic fibre treatment is presented: Flax fibres are treated with Laccase from a variety of fungal sources for a sustainable modification of the fibres. The aim of this study is to use the laccase induced ring opening reaction of lignin in order to covalently bind reactive species to the fibre which can then improve the fiber matrix interaction.

1. Introduction

The interphase between fibre and matrix is essential for the composites' mechanical properties. Conventional reinforcing fibers such as glass, aramid or carbon fibres are usually treated with a sizing or coating in order to improve the adhesion to the polymer matrix. These sizings are made up of coupling agents, which can ideally covalently bind to both fibre and matrix, and film formers, which ensure the processability of the fibre and may also aid in adhesion. In natural fiber composites, surface treatments are seldom used, even though they would increase the composites mechanical properties (1,2,3). Such sizings need to be optimized with the specific fibre matrix combination in mind. We present the effect of sizing based fibre surface modifications that improve the adhesion between natural fibre and PLA.

One major focus is an enzymatic fibre treatment: Flax fibres are treated with Laccase from a Cerrena unicolor polypore fungus for a sustainable modification of the fibres. Laccase is e fungal enzyme abundant in nature and used e.g. in the food industry, which catalyzes a ring opening reaction of lignin, inducing bonds to either amino or hydroxyl moieties. This may be used to covalently bind reactive species to the fibre which can then improve the fiber matrix interaction. Surface structure and mechanical studies of laccase treated fibres as well as mechanical studies of flax PLA composites made of sized fibres are presented.

2. Materials and Methods

Flax fibres (250 tex) were obtained from composites evolution (France). Fibres were exposed to laccase in pH 5.0 Malonate buffer.

Longitudinal tensile strength of the single fibres was determined in a Favigraph (Textechno, Germany). The fineness is determined vibrationally for each individual fibre. Consecutively, the single fibre modulus and strength are determined. The measurement is performed 50 fold.

3. Results and Discussion

Fibres are exposed to 25 U/ml Laccase from Cerrena Unicolor in malonate buffer at 25°C and 50 °C for 2h, control fibre were exposed to neat buffer without enzymes. In order to determine whether the laccase will not only modify the fibres' lignin but also harm the cellulose, the tensile strength of the treated fibres was measured in a 50 fold measurement. The single fibre tensile strength and Young's modulus as well as the Weibull distribution are shown in fig. 1

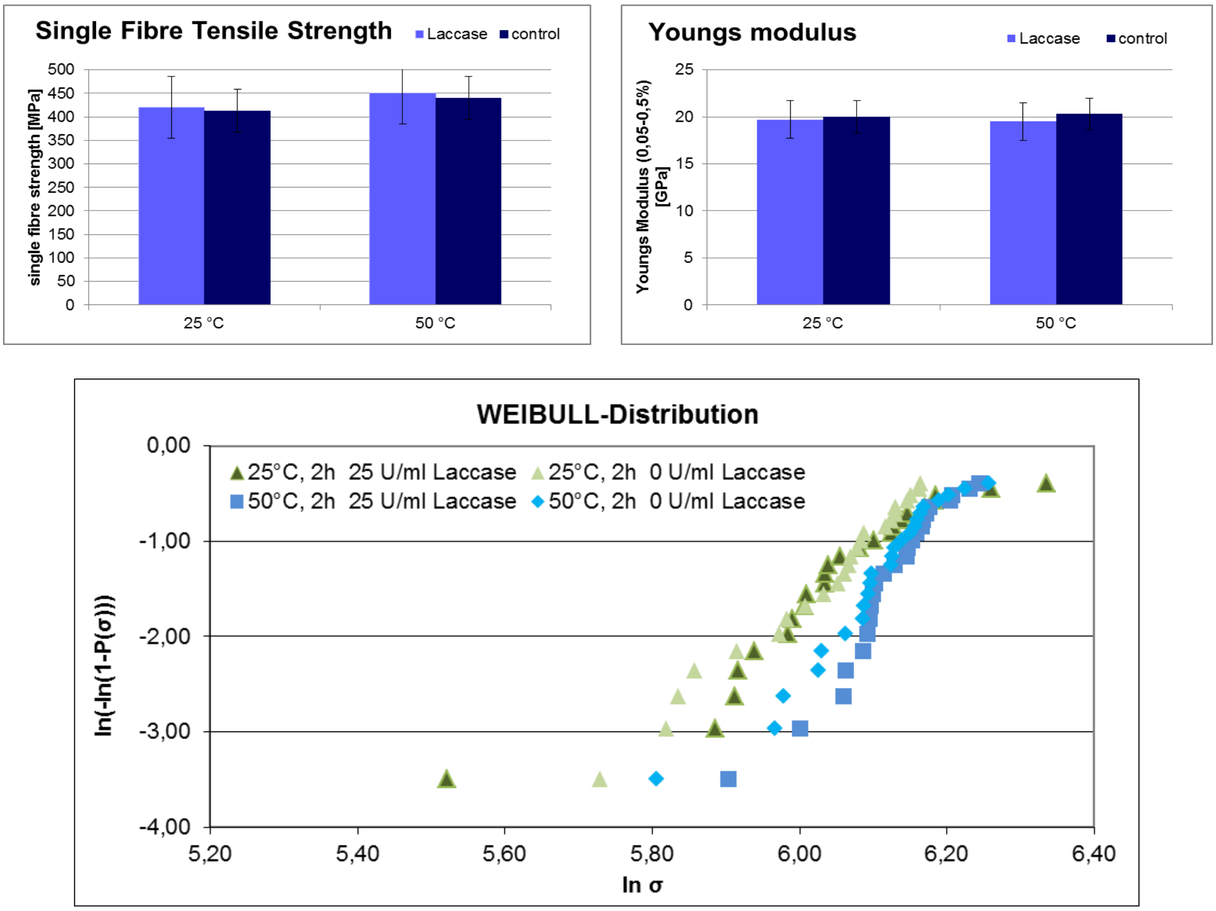
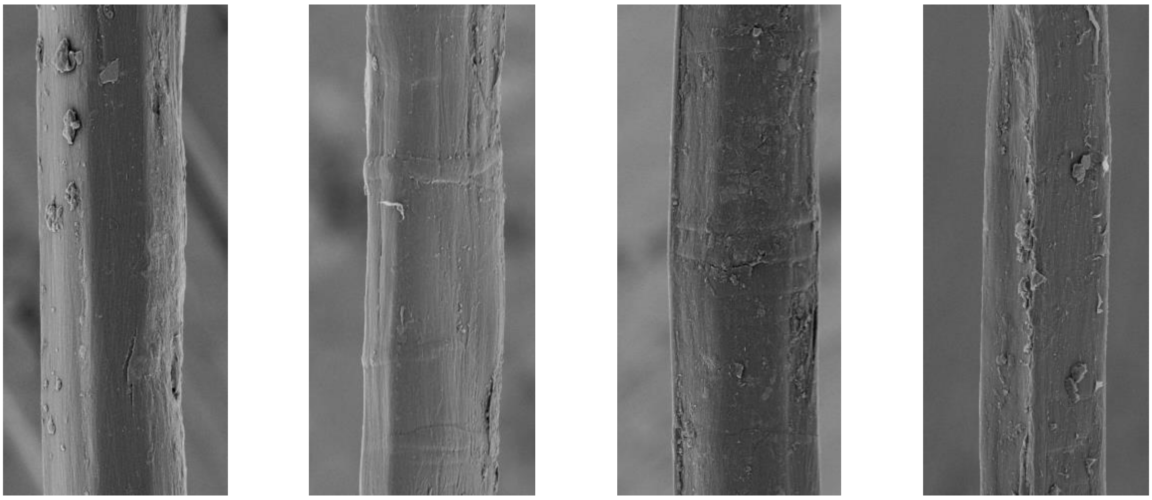


Figure 1. Results of single fibre single fibre tensile tests of Laccase treated fibres and control fibres for 25 °C and 50 °C: top left: tensile strength, top richt: modulus and bottom Weibull Distribution

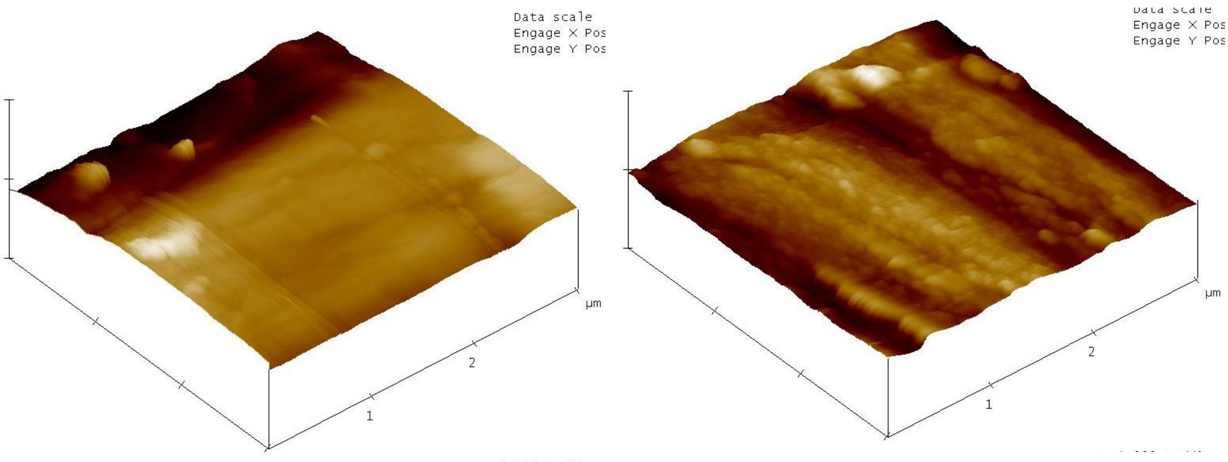
The tensile strength is not reduced by the laccase treatment. Laccases mainly catalyze the ring opening reaction in Lignin, but may also damage the cellulose as a side effect. In current study, we can see this is not the case, not even at a higher reaction temperature. The Laccase induced lignin catalysis even seems to have a tendency to improve fibre strength. The treatment at higher temperature also improves the strength, while no difference between laccase treated fibre and control fibre are seen. The fibre modulus is not affected by the Laccase treatment. In the Weibull representation ot the data, the higher temperature strength probability data are shifted to higher strengths but there is no shift due to laccase activity.

The fibres were then exposed to laccase at 3,3 U/ml in malonate buffer with two substrates containing an amino and a hydroxyl moiety, namely dopamine and amino-hexanol. Both have been described to be substrates for Laccase [4]. Dopamine is a typical representative of Laccase substrates, which almost always have a ring structure. Amino-Hexanol is one of the few linear molecules that have been seen to act as Laccase substrates. The fibres are imaged by scanning electron microscopy (SEM) and atomic force microscopy (AFM) after treatment with buffer only, buffer and laccase, buffer + laccase + substrate, buffer+ substrate only. The micrographs with are shown in Figs. 2 and 3. The dopamine binding effect of laccase is evident inREM (Fig. 2 c) and AFM (Fig. 3b) which is more pronounced than the polydopamin layer formed without Laccase. With amino-hexanol as a substrate, no fibre surface modifications are seen in REM or AFM.



A B C d

Figure 2. REM images of flax fibres: a: buffer only, b: buffer + laccase, c: buffer + laccase + dopamine, d: buffer - dopamine

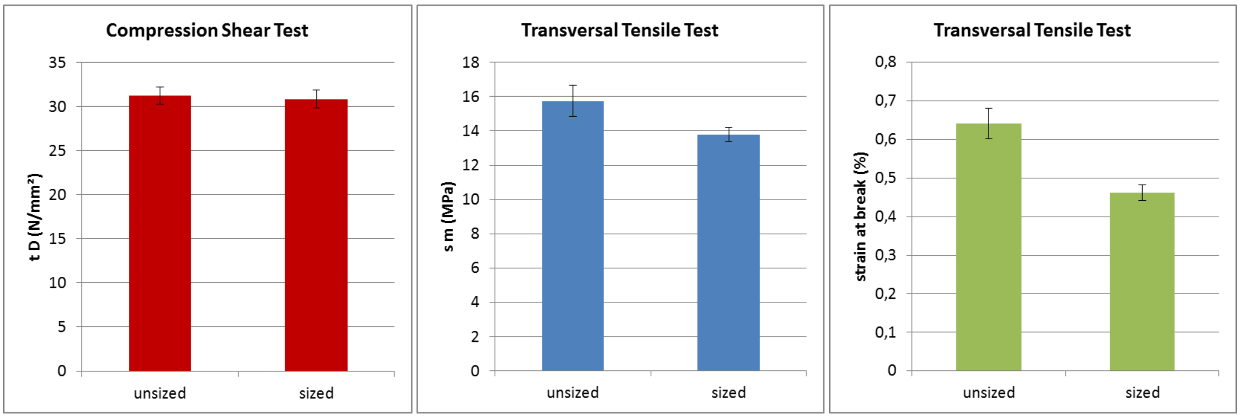


A b

Figure 3. AFM images of flax fibres: a: buffer only, b: buffer + laccase + dopamine

Natural fibre composites with a matrix made from a biopolymer have an especially low ecological footprint A next step will be to study the interfacial bonding of laccase-dopamine treated natural fibres with PLA.

In order to improve the interfacial bonding of the flax yarn and PLA, a sizing made of an aqueous suspension of silane (GPS) and film former (chitosan) was used to modify the yarn. PLA was spun into fibres. The PLA was then combined with the flax yarn into a hybrid twisted yarn (40 % Flax, 60% PLA), wound onto a mandrel, or alternatively deposited side by side onto the mandrel (again 40 % Flax, 60% PLA). The hybrid yarn was hot pressed into unidirectional composite plates of 15 x 20 cm². The side by side deposition led to better composites with fewer voids and better fibre orientation. The resulting unidirectional flax PLA composites were studied in transversal tensile test and compression shear test, as these test are especially interphase sensitive. The results are shown in Fig. 4. The used sizing did not lead to an improvement of the interphase.



a b C

Figure 3. Interphase sensitive tests of unidirectional flax-PLA composites:
(a) compression shear test, (b) transversal tensile test: σ_m and (c) transversal tensile test: strain at break.

4. Conclusion

Laccase is a fungal enzyme that can infer a ring opening reaction in lignin and thereby bond substrates to natural fibre. If these substrates are bifunctional, they have the potential of also binding to a corresponding matrix.

Acknowledgments

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