BIODEGRADABLE CONTINUOUS FIBRE REINFORCED COMPOSITES BASED ON HYBRID YARNS

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1 Introduction

During the last four decades the biodegradable polymers have found their place in special applications in biomedical and technical fields. [1-4] However, their worldwide production volumes are still marginal compared with non-biodegradable polymers. One of the major restricting factors for the wider use of biodegradable polymers in the field of load bearing medical devices, packaging, and consumer goods is the lack of mechanical properties and cost of goods. For instance, one of the most widely used biodegradable polymers, polylactide (PLA), for non-load bearing medical devices, fibres, nonwovens, films, and disposable articles is a comparably hard and brittle material. Regarding to mechanical properties of PLA no significant improvements have been achieved since the development of self-reinforced PLA [5]. Natural way of improving mechanical properties of PLA products is to use PLA as a matrix for biodegradable composites.

Glass fibres (GF) have traditionally been used as reinforcing phase in composites. However, the non-existence of biodegradable GF in the market is restricting the development of biodegradable GF reinforced polymer composites. Recently, the work with biodegradable glass has mainly been focused on porous scaffolds [6], glass particles and self reinforced PLA [7]. Current biodegradable glass formulations are not suitable for continuous fibre drawing due to their thermal properties. However, the existence of high strength biodegradable continuous fibre reinforcements due to improved mechanical properties of biodegradable polymers would open up totally new application fields for biodegradable polymers such as manufacturing of load-bearing screws, plates, pins and cages in medical device sector as well as manufacture of “green” composites for car and commodity plastic industries.

The hybrid yarn technology is one method to manufacture continuous fibre reinforced thermoplastics [8]. Its main advantages are related to the high degree of flexibility regarding the final shape of the composites as well as to the high fibre volume contents and the correspondingly high mechanical properties of the composites.

In this work latest results of processing continuous GF/PLA hybrid yarns, composites thereof and mechanical as well as interface properties will be presented.

2 Experimental

As base materials for the hybrid yarn spinning, silica based biodegradable glass from *Vivoxid Ltd*. [9] as well as different PLA grades (Purasorb PLDL 7028, *Purac Biomaterials* and Ingeo 2002D, *NatureWorks LLC*) were used. In-situ commingled hybrid yarns (yarn fineness 140 tex) consisting of 204 glass and 102 PLA filaments, respectively, were spun at the *Leibniz-Institut für Polymerforschung Dresden*. Filament winding of the hybrid yarns followed by compression moulding was used to manufacture unidirectional composites with a GF weight fraction of 50 %. Specimens for the mechanical testing were cut out of the unidirectional plates using a rotating diamond saw. Compression shear tests (CST) [10], tensile tests (ISO 527-5), transverse tensile tests (ISO 527-4, gauge length 80 mm), Charpy impact tests (ISO 179/1eU, specimens were tested transverse to the fibre direction, because no break could be achieved for specimens prepared with

longitudinal fibre direction) as well as 3 point bending tests (ASTM D790) were performed.

The single fibre tensile tests of the GF were performed using the Favigraph semi-automatic fibre tensile tester (Textechno, Germany) equipped with a 1 N load cell, according to DIN EN ISO 5079 and DIN 53835-2, respectively. The fibres have gauge lengths of 50 mm and the cross head velocity was 25 mm/min.

Moreover, single fibre pull-out tests have been used to investigate the fibre/matrix interaction for differently sized GF. A series of developed model sizings (Tab. 1) were investigated in comparison with a reference bioresorbable finish (S0) consisting of compatibilizer and emulsifier. This finish is biocompatible and intended to be used for implants. The film formers of the tailored sizings S1, S2 and S3 are based on epoxy, polyurethane and chitosan (polyaminosaccharide) dispersions, respectively. The silane coupling agents of the sizings used were adapted by using 3-Ureido-propyl-trimethoxysilane or N-Aminoethyl-3-Amino-propyl-trimethoxysilane. The sizing content of the hybrid yarns and the fibre volume fraction of the composites, respectively, was determined from parallely spun pure glass filament yarns and consolidated plates, respectively, using pyrolysis at 650°C for 30 min.

Using a self-made embedding apparatus enabling PC-controlled temperature and time cycles, the model microcomposites for the single fibre pull-out test were prepared by accurately embedding the single fibres in PLA-matrix at 250°C with embedded lengths of 50 through 800 µm. The pull-out test was carried out on an institute-made pull-out apparatus with force accuracy of 1 mN and displacement accuracy of 0.07 µm with identical pull-out velocities (0.01 µm s^{-1}) at ambient temperature. From each force-displacement curve, the force at debonding, the maximum force F_{max}, and the embedded length l_e were determined. The fibre diameter $d=2r_f$ of each pulled-out fibre was measured microscopically and the pulled-out fibres were collected for AFM investigation. Each GF/PLA combination was evaluated by about 15 to 20 single tests.

The fracture surfaces of single pulled-out fibres were investigated using AFM Tapping Mode. An AFM (a Digital Instruments D3100, USA) was used as a surface imaging tool to evaluate the fibre fracture surface topography. The cantilever (ULTRASHARP NSC16/50, MikroMasch, Estonia) has a normal spring constant of 35 N/m, a tip cone angle of 20°, radius of 5 to 10 nm and modulus of 160 GPa to assure good imaging resolution.

Tab. 1: Characterization of E-Glass/PLA model composites based on different sizings on GF/PLA hybrid yarns

Design.	Organic content sizing [wt%]	GF-Fibre volume fraction [%]	Fineness Hybrid yarns Tt [g/1000 m]
S0	0.57	37.5	194
S1	0.40	38.5	195
S2	0.59	37.6	194
S3	0.19	37.9	193

The dynamic mechanical properties were investigated using a dynamic mechanical analyzer (Q800, TA Instruments). Rectangular specimens with dimensions 40 x 10 x 2 mm^3 were tested in 0° and 90° fibre direction in a single cantilever bending mode from -50°C to 150°C and a frequency of 1.0 Hz within nitrogen atmosphere.

3 Results and Discussion

3.1 Single Fibre Tensile Strength of Biodegradable GF

The tensile strength of the spun GF (average diameter 14 µm) was 1750 MPa ± 250 MPa. There is only limited data available on the mechanical properties of biodegradable GF. The commonly used phosphate based GFs are reported to have tensile strengths of about 300 MPa [11]. Therefore, the significantly increased tensile strength of the silica based GFs used in this study highlights the potential of this GF type for mechanically demanding biocomposite applications.

3.2 Mechanical Properties of Unidirectional GF/PLA (Purac Purasorb) Composites

In order to demonstrate the potential of the hybrid yarns, the unidirectional GF/PLA composites were characterized mechanically. Figure 1 shows selected properties of the biocomposites. The CST yields information on the fibre/matrix interaction. The

determined value of 13 MPa is relatively low compared with E-GF reinforced systems for industrial applications [12], indicating the possibility to improve the composites properties by a suitable sizing system. However, the tensile and 3 point bending strength, respectively, show a high level of mechanical performance as shown in Fig. 1. The tensile strength ranges close to 400 MPa, whereas the bending strength was found to be around 700 MPa. The Young's modulus for both, tensile and bending test is approximately 30 GPa.

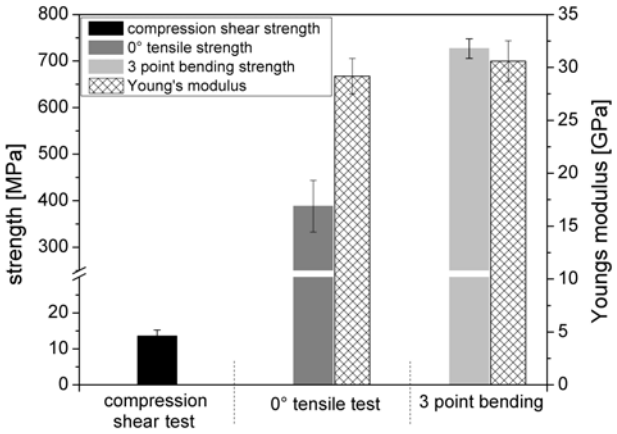

Fig. 1. Selected mechanical properties of biodegradable unidirectional GF/PLA (Purac Purasorb) composites.

Compared to differently manufactured GF/PLA composites, e.g. long fibre reinforced PLA and self reinforced PLA, the mechanical properties of continuous GF fibre reinforced PLA composites are considerably higher. Long fibre reinforced composites based on the same materials as used in this study were determined to have a bending strength of 270 MPa and a Young's modulus of 16 GPa (Tab. 2). The data on self reinforced PLA available from literature [13] reports on bending strengths of 300 MPa and a Young's modulus of 10 GPa.

Tab. 2: Comparison of mechanical properties of GF/PLA composites

Processing method	Fibre content	Bending Strength [MPa]	Young's Modulus [GPa]
Hybrid yarn	Continuous 50 wt%	730	26
Melt impregnation	Continuous 50 wt%	630	25
Injection moulding	LFRP 50 wt%	270	16
Injection moulding	PLA reference	110	3.5

3.3 E-Glass/PLA Model Composites with Tailored Interphase

Within this study, additional E-glass/PLA hybrid yarns were spun using different sizings in order to tailor the interphase. To date, little knowledge on the GF/PLA interphase has been published. Thus, the intention of this study is to vary the interfacial properties of the system using biocompatible sizings as well as sizing systems which have potential for industrial applications.

In a first step, single fibre model composites were prepared for pull-out testing. Due to the different wetting behaviour of the sizings, the pre-selected embedded length strongly varied. Furthermore, the maximum forces at debonding changed in dependence of the adhesion strength level. Fig. 2 displays the debonding forces as a function of the embedded lengths for the sized glass fibres S0 and S3 in comparison. The model composite of S3 sized glass fibres in PLA achieved maximum debonding forces around 500 mN as maximum forces before fibre breaks at embedded lengths of about 200 µm, whereas S0 sized GF could be pulled out up to an embedded length of 800 µm. The different load-displacement behaviour is indicative of a significantly improved fibre-matrix bonding of the S3 system. The AFM fracture surfaces of pulled-out fibres reveal very different fracture behaviour in dependence of the sizings used. The S0 sized GF showed a very smooth surface having an average roughness of 0.7 nm (Fig. 3). On the contrary, the S3 sized GF changed from adhesive to cohesive failure of very high average roughness (Fig. 4) demonstrating an improved adhesion strength at the interphase. A more comprehensive micromechanical testing is in progress and will be published soon [14]

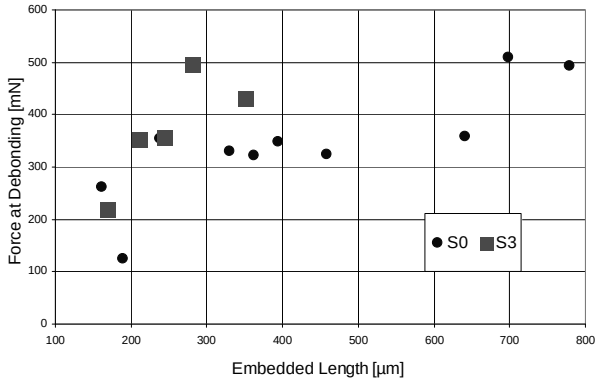

Fig.2. Comparison of maximum forces as a function of embedded length of single fibre pull-out tests for S0 and S3 sized GF in PLA-matrix

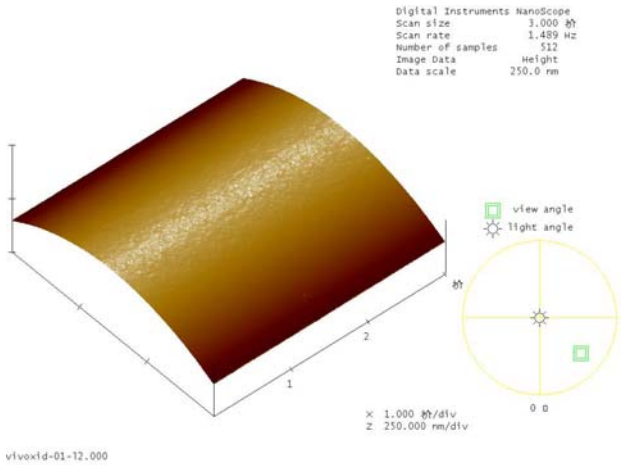

Fig. 3. AFM height image of a fracture surface of S0 sized GF (x, y: 1000 nm / div, z: 250 nm / div)

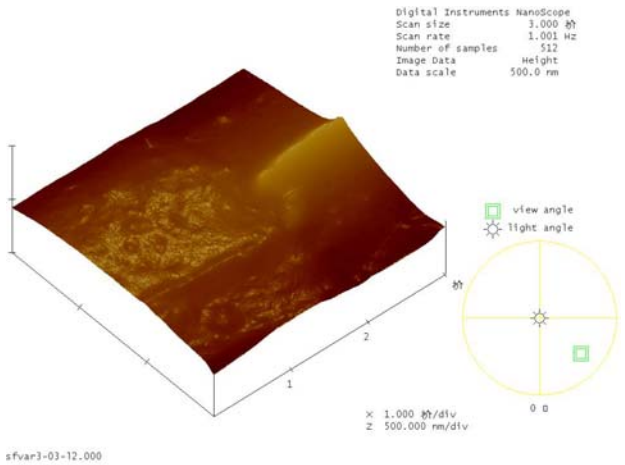

Fig. 4. AFM height image of a fracture surface of S3 sized GF (x, y: 1000 nm/div, z: 250 nm / div)

3.4 Mechanical Properties of Unidirectional E-Glass/PLA Composites with Tailored Interphase

Firstly, transverse tensile tests and interlaminar compression shear tests were performed in order to evaluate the fibre/matrix bonding. Fig. 5 displays average stress-strain curves of GF/PLA transverse tensile test specimens for different sizings S0 to S3 in comparison. The early drop of the maximum stress at very low strain for S0 and S2 indicates a very weak interfacial adhesion strength, as was revealed for S0 after pull-out testing before. In contrast of this behaviour, S1 and S3 sized GF behave differently and indicate a much more improved stress transfer leading to both increased maximum stresses and strains compared with S0 and S2 sizings. The data in Fig. 6 confirm an about threefold increase of average stresses and strains at force maximum by changing the sizing from S0 to S3. This is a potential route because S3 sizing is also biocompatible. The results of the compression shear test (Fig. 7) confirm the ranking of the transverse tensile stresses regarding the sizings, although the absolute values are different.

In longitudinal fibre direction, the tensile tests of unidirectional specimens did not fail correctly within the gauge lengths. The high stress values of three point bending tests (Fig. 8) reflect the high fibre volume fraction and improved interfacial stress transfer of especially S1 and S3 sized GFs compared with S0 sized ones. A similar behaviour was also found for storage moduli as a function of temperature. The storage moduli in longitudinal direction achieved average values of 22 GPa at a temperature of 23°C for all differently sized GF/PLA composites tested.

However, the storage moduli in transverse fibre direction revealed significant differences due to different fibre/matrix bond strengths of the composite specimens. Highest storage moduli (Fig. 9) were determined for S1 and S3 sized GFs. These results are in a good agreement with results of other mechanical tests transverse to the fibre direction.

Finally, the toughness of different GF/PLA composites was determined by Charpy impact tests (Fig. 10). Specimens with longitudinal fibre direction did not break. The data for the specimens with differently sized GFs in transverse fibre direction showed same ranking as discussed for

transverse tensile tests, compression shear tests and DMA tests before.

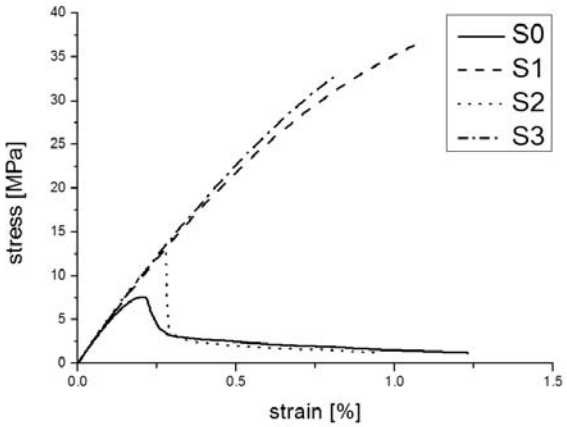

Fig.5. Average stress-strain curves of GF/PLA transverse tensile test specimens for different sizings S0 to S3 in comparison

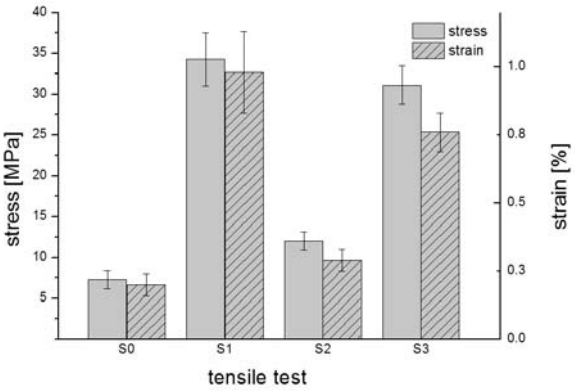

Fig. 6. Results of transverse tensile tests in terms of average stresses and strains at force maximum for specimens with differently sized GFs

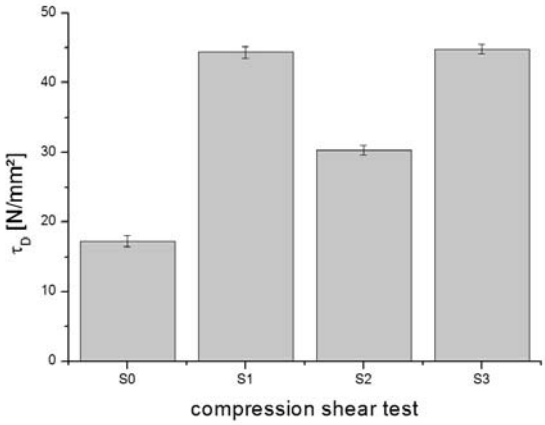

Fig. 7. Compression shear stresses τ_D of intralaminar tested specimens with differently sized GFs

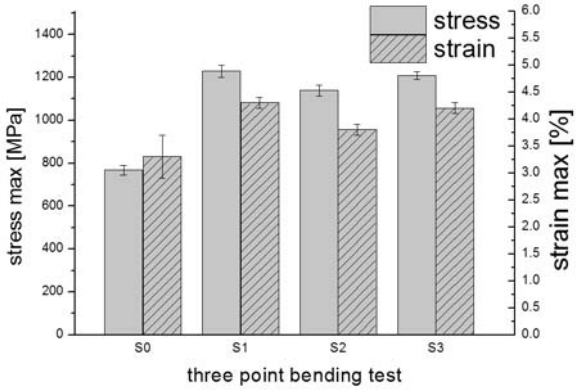

Fig. 8. Results of three point bending test in terms of average stresses and strains at force maximum for specimens with differently sized GFs

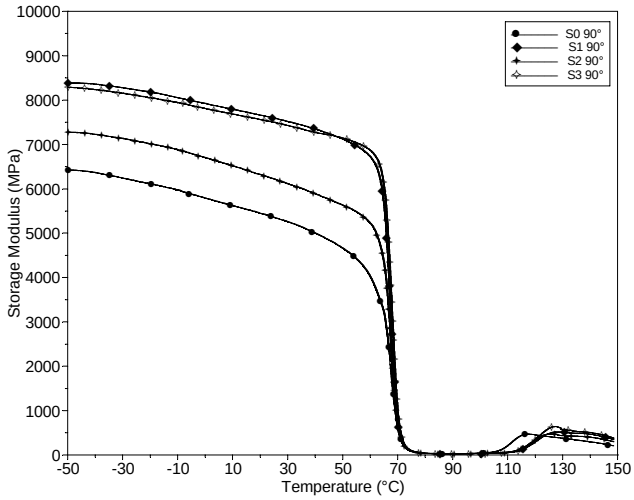

Fig. 9. Storage moduli of DMA tests in transverse fibre direction for specimens with differently sized GFs

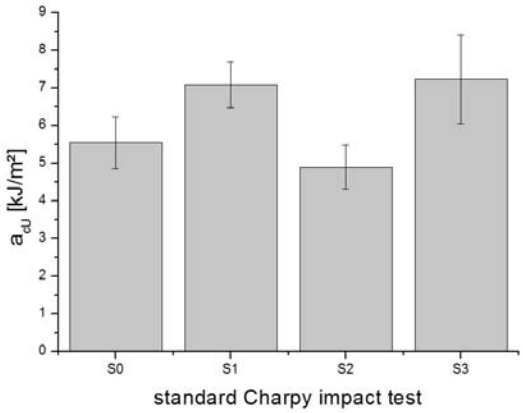

Fig.10. Charpy impact toughness a_{cU} in transverse fibre direction for specimens with differently sized GFs

4 Conclusions

The successful spinning of GF/PLA hybrid yarns and the high mechanical properties of the thereof prepared unidirectional composites demonstrate the potential of this technology for the manufacturing of medical devices. Especially when it comes to biodegradable composites meant for mechanically demanding applications, the hybrid yarn technology allows realizing a superior level of mechanical properties compared to long fibre reinforced and self reinforced PLA, respectively.

The use of different sizing systems shows that compared to the reference sizing which was used as a benchmark-system for biocompatible sizing, one can significantly improve the interphase adhesion strength of the GF/PLA-systems. The epoxy film former based sizing as well as the chitosan-based sizing showed a significant increase in interphase strength being reflected in improved mechanical properties of the composites. Being evidenced by enhanced transverse tensile strength, interlaminar compression shear strength and bending strength, respectively, as well as improved Young's moduli as determined by DMA analysis and increased Charpy impact toughness.

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References

[1] J.C. Middleton, A.J. Tipton, Biomaterials 21 (2000) 2335-2346.
[2] L.S. Nair, C.T. Laurencin, Prog. Polym. Sci. 32 (2007) 762-798.
[3] D.W., Farrington et al "Poly(lactic acid) fibers." Biodegradable and sustainable fibres. Woodhead Publishing Limited, 2005.
[4] S. Fakirov, D. Bhattacharyya, Handbook of Engineering Biopolymers, Carl Hanser Verlag, 2007.
[5] P. Törmälä et. al., US 4743257
[6] L.C. Gerhardt, A.R. Boccaccini, Materials 3 (2010) 3867-3910.
[7] T. Niemelä et al., Acta Biomat. 1 (2005) 235-242.
[8] N. Svensson et al. J of Thermopl Comp Mat 11(1998), pp 22-56.
[9] patent pending, WO 2010122019 (A1)
[10] K. Schneider et al., Appl Comp Mat, 8, pp. 43-62, 2001.
[11] S. Coszien-Cazuc et al. proceedings ICCM15, Durban, South Africa, 2005.
[12] Rausch et al., Exp Poly Lett, 4, pp. 576-588, 2010.
[13] P. Törmälä, Clinical Materials 10 (1992) 29-34.
[14] E. Mäder et al., in preparation.