Impregnation studies and mechanical characterization of cellular, natural, fiber-reinforced, composite structures

Sirko Geller[1)], Oliver Weissenborn[1), *)], Maik Gude[1)], Andrzej Czulak[1)]

DOI: dx.doi.org/10.14314/polimery.2016.125

Abstract: With the use of natural fibers as a substitute for synthetic reinforcements, a significant contribution towards advanced ecological and efficient lightweight structures can be made. Within this article, the polyurethane (PUR) spray coat method is used for the manufacture of natural fiber-reinforced composites based on the fiber materials linen and hemp. Both the investigation of the mechanical properties and the yarn impregnation, as a reference for the composite quality, are of major interest and help to evaluate the potential of these bio-based materials as a contribution towards advanced lightweight components.

Keywords: natural fibers, fiber-reinforced plastics, polyurethane spray coat method, cellular matrix.

Impregnacja włókien naturalnych i właściwości mechaniczne kompozytów z ich udziałem

Streszczenie: Kompozyty wzmocnione włóknami naturalnymi na bazie lnu i konopi wytwarzano metodą warstwowego natrysku poliuretanu (PUR). Zbadano proces impregnacji przędzy i właściwości mechaniczne otrzymanych kompozytów oraz oceniono możliwości zastosowania takich materiałów pochodzenia naturalnego w zaawansowanych lekkich elementach konstrukcyjnych.

Słowa kluczowe: włókna naturalne, tworzywa polimerowe wzmocnione włóknami, metoda warstwowego natrysku poliuretanu, matryca komórkowa.

In recent years, the use of fiber-reinforced composites in industrial applications has significantly intensified. With mechanical properties comparable to glass fibers, in combination with a low density and modest production costs, natural fibers have a high potential to substitute conventional fiber materials [1—3]. In contrast to synthetic fibers, the material properties are subject to certain variability due to the individual growth processes. In combination with inappropriate matrix systems, this often results in a unsatisfactory composite quality [4—6]. Therefore, appropriate solutions have been developed for the processing of natural fibers, which are traditionally integrated in composite structures as mats or other non-wovens [7]. One possibility for producing natural-fiber-reinforced composites is to spray a thermoset matrix system based on foamable polyurethanes (PUR) onto the reinforcement, followed by compression molding [8]. Foamable matrix systems and polyurethane in particular, gain an increasing relevance with natural fillers for composites materials [9, 10] using linen and hemp-fibers [1, 11], banana-fiber [12], hardwood-pulp [13] and other reinforcements [2, 3, 14]. Comprehensive studies on the mechanical, thermal and, in some cases, dielectrical properties were performed and offer a high potential for use in lightweight composite structures. The development of components made from natural fiber-reinforced composites requires a deep understanding about the material behavior and the effects of the manufacturing process on the resulting properties. For the purpose of lightweight construction, and in the context of the conservation of resources, the use of natural fibers is of particular interest. Within this article, natural fiber-reinforced composite structures manufactured using the polyurethane spray coat method are analyzed with respect to the resulting mechanical properties. Furthermore, the composite structure, in particular yarn impregnation as a main criterion for high quality composites is evaluated to assess the potential of the selected natural fiber products for the use in lightweight applications.

EXPERIMENTAL PART

Materials

In preparation for manufacturing studies, attention was paid to select a representative range of native natural fiber fabrics based on linen and hemp. It was ensured that each textile structure differs only in terms of a single parameter, such as fiber type, weave and grammage in

[1)] Dresden University of Technology, Institute of Lightweight Engineering and Polymer Technology (ILK), Holbeinstraße 3, 01307 Dresden, Germany.

[*)] Author for correspondence; e-mail: oliver.weissenborn@tu-dresden.de

T a b l e 1. Overview of selected semi-finished products with structural properties (*own measurement)

Designation of specimen	UD190LI	UD300LI	TW315LI	TW330HP
Weave	UD	UD	Twill 2/2	Twill 2/2
Titer weft direction, tex	28.0	28.0	139.0	74.1*
Titer warp direction, tex	42.0	135.0	139.0	76.9*
Thread density (weft), 1/cm	3.0	3.0	12.0	5.0*
Thread density (warp), 1/cm	42.5	21.0	10.0	15.0*
Grammage, g/m^2	190.0	300.0	315.0	330.0
Yarn twist (weft), U/m	670	520	250	-
Yarn twist (warp), U/m	550	208	250	-
Fiber type	linen	linen	linen	hemp
Manufacturer	Sicomin Epoxy Systems[1)]			A. Pavani OHG[2)]

[1)] Sicomin Epoxy Systems, 13220 Chateauneuf les Martigues, France.

[2)] Anita Pavani OHG, 35452 Heuchelheim, Germany.

order to directly assess their influence on the composite's characteristics. Table 1 shows the selected fabrics and their structural properties; all selected textiles are commercially available. Only the structural properties for titer, thread density and yarn twist for the hemp fiber fabric could not be provided by the manufacturer. Therefore, the titer and the yarn density were determined by our own measurements.

T a b l e 2. Properties of the polyurethane resin Elastoflex E3851/102

Property	Polyol	Isocyanate
Density (25 °C), g/cm^3	1.07	1.23
Viscosity (25 °C), mPa·s	1600	220
Mixing ratio, g	100	215
Polyurethane mixture		
Free rise density, kg/m^3	125	
Starting time, s	85	
Rising time, s	135	

All the mentioned natural fibers were treated in alkaline solutions and washed with water prior to the weaving process. This conditioning step helps to remove any remaining pectins and other pollutants, which could have a negative impact on the impregnation of natural fibers. The foamable polyurethane system Elastoflex E3851/102 from BASF Polyurethanes GmbH serves as the reactive thermosetting resin for the impregnation of the natural fiber fabrics. The component properties are taken from the material data sheet provided by the mentioned manufacturer (Table 2) [15].

Preparation of test specimens

The manufacture of test specimens was performed using the polyurethane spray coat method with an SCS (Structural Component Spraying) — mixing and spraying unit provided by KraussMaffei Technologies GmbH. With the use of the high pressure counter flow injection method, the reaction components polyol and polyisocyanate were mixed together and discharged into an open mold whose bottom cavity was covered with the inserted fabric structures (Fig. 1).

In contrast to conventional manufacture methods, the impregnation was performed solely using the expansion pressure of the polyurethane in the thickness direction of the fabric rather than in the plane inside the closed mold. After a defined reaction time of 300 s, the cross-linking was complete and the fiber-reinforced cellular component was ready for extraction. The manufacture of the test specimen was based on the

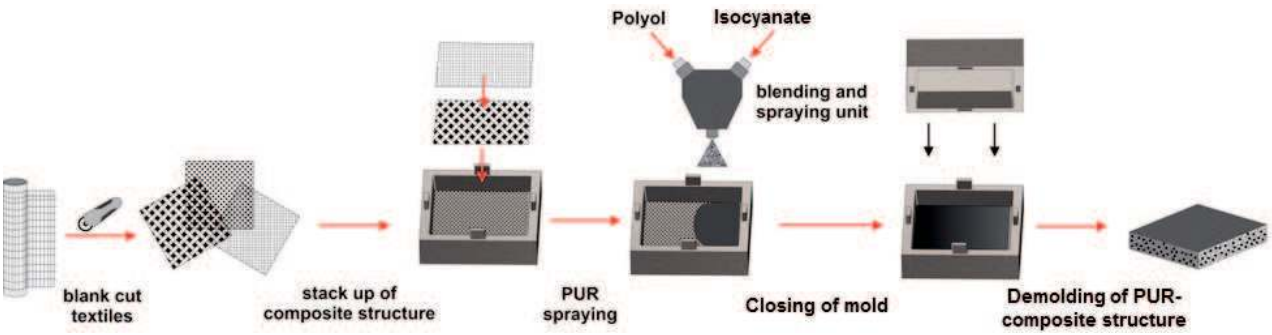

Fig. 1. Manufacturing of test specimen using the polyurethane spray coat method

process parameters listed in Table 3 and kept constant throughout the investigations.

T a b l e 3. Process parameters for the manufacture of specimen

Property	Value
Mold temperature, °C	80
Processing temperature PUR, °C	23
Reaction time, s	300
Size of plates, mm	650.0 × 650.0 × 2.0
Matrix mass, g	500

Prior to the manufacturing process, the textile structures were stored at room temperature in a dry and light protected place to avoid degradation of the textile structures. However, with the insertion of the textiles into the heated mold, drying of the textiles was observed. Out of the injected plates, specimens with geometries according to standards for tensile- and bending tests were manufactured using water jet cutting methods. The cut surface is characterized by a high quality (surface roughness $R_z \geq 16$ μm) and low tolerances (± 0.1—0.2 mm).

Methods of testing

Mechanical properties

The mechanical properties of the natural, fiber-reinforced, polyurethane composites were evaluated using a tensile test and 3-point-bending test. The testing conditions, including the size and preparation of specimens, complied to DIN EN ISO 527 for the tensile test and DIN EN ISO 14125 for the 3-point-bending test. Both tests were executed using a ZWICK 1465 machine with a load cell of 50 kN. The deformation of the specimen was measured with a macro extensometer for the tensile test and with a bending sensor for the bending test. The test speed was adapted according to the standard with 2.0 mm/min for the tensile and 1.33 mm/min for the bending test.

Yarn impregnation

The mechanical properties of fiber-reinforced plastic components are highly dependent on both the type of reinforcement and the matrix material, as well as on the adhesion between fiber and matrix. With the manufacture of composite structures using a polyurethane spray coat method, the formation of a cellular matrix during cross-linking is intended, as the expansion pressure of the matrix is the driving force for impregnation. Due to the expansion and formation of the polyurethane foam, the composite has a cellular structure with voids inside the yarn, between textile layers and matrix dominated areas. Since voids are considered as weak spots inside composite structures, leading to a reduced fiber-matrix-adhesion and therefore favoring the emergence of stress peaks, the composite quality needs to be evaluated using an appropriate method.

One way to evaluate the composite quality is to analyze the yarn impregnation by measuring the size of air inclusions inside the yarn structure. With the help of micrographs, taken with a light microscope and the image software AxioVision — both developed by ZEISS, the total pore size in relation to the total yarn size was determined. Since the micrographs are black and white, the image analysis is based on the processing of grey value distributions (Fig. 2).

The histogram of the micrograph, which shows a distribution of grey value over the number of pixels, helps to identify the associated grey value of the pores, which are significant for analyzing the composite structure. For the evaluation of the impregnation quality, the value of the total pore area inside the yarn cross section is calculated in order to determine the ratio between the total yarn size and the size of the impregnated region. This ratio represents the yarn impregnation and helps to assess the influence of changes in the process and varying textile parameters. To receive a statistically secure result for the yarn impregnation of one composite structure, at least ten different yarn cross sections evenly distributed across the composite width were measured and analyzed.

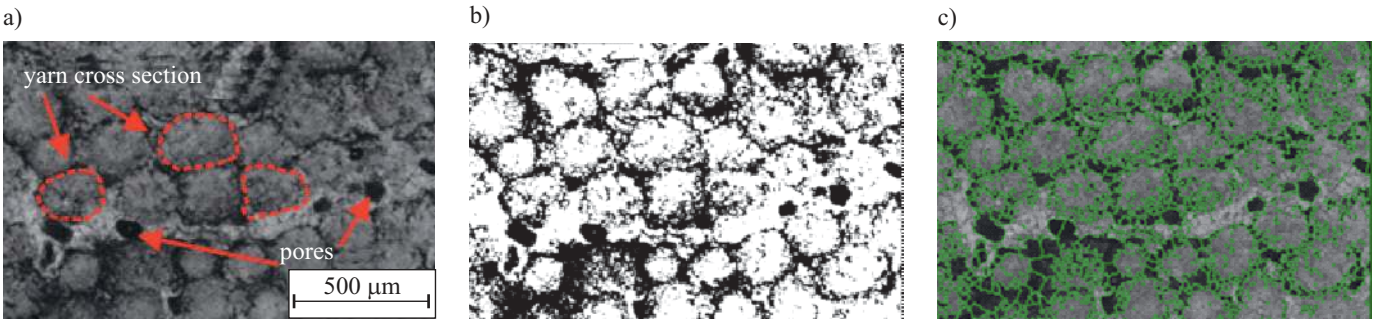

Fig. 2. Micrograph of: a) the cross sections of a natural fiber-reinforced polyurethane composite, b) converted into a binary representation where black areas represent pores and white areas fiber and matrix components, c) evaluated pore areas inside the composite structure

RESULTS AND DISCUSSION

Mechanical properties

The material behavior under defined loads can be determined by analyzing the characteristics of the stress--strain-curve. The presentation of the results is divided into the directions of the acting loads, whereas the fiber-direction of the unidirectional and the warp-direction of the twill fabrics coincide with the acting 0° - load. The material behavior is strongly dependent on the reinforcement structure. Composite structures with unidirectional fiber orientation show a rather brittle behavior, whereas twill-weave composites are characterized by a distinctive, large strain-curve (Fig. 3a).

This phenomenon is based on the fiber crimp due to characteristic weave structures, like twill- and plain--weave. Within these weave structures, warp and weft yarns form ondulation-points resulting in fibers with a deflected, rather than a straight, orientation. In the course of acting loads, the fibers increasingly move towards a stretched position leading to a larger strain compared to the already straight oriented unidirectional weaves [16]. With the alteration of the load direction, the stress-strain curves for unidirectional fiber-reinforced structures show a significantly different course due to the matrix dominated load path (Fig. 3b). Furthermore, both twill-weave structures also have a different material behavior whilst changing the load direction due to a varied structure in the weft and warp directions of the fabric.

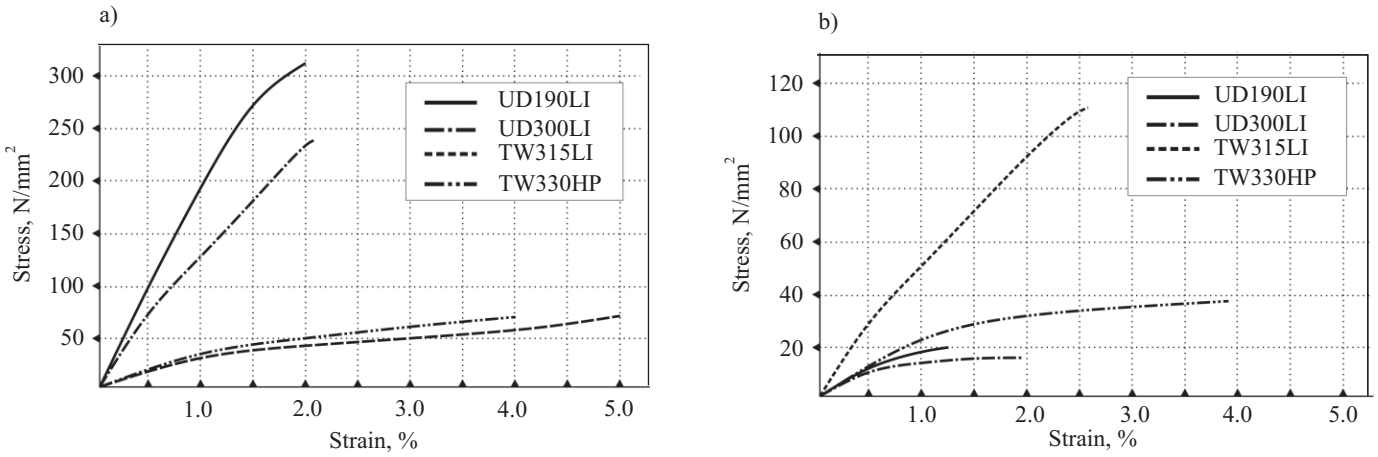

Fig. 3. Stress-strain curve of the natural fiber composites in the tensile test: a) 0° - direction, b) 90° - direction

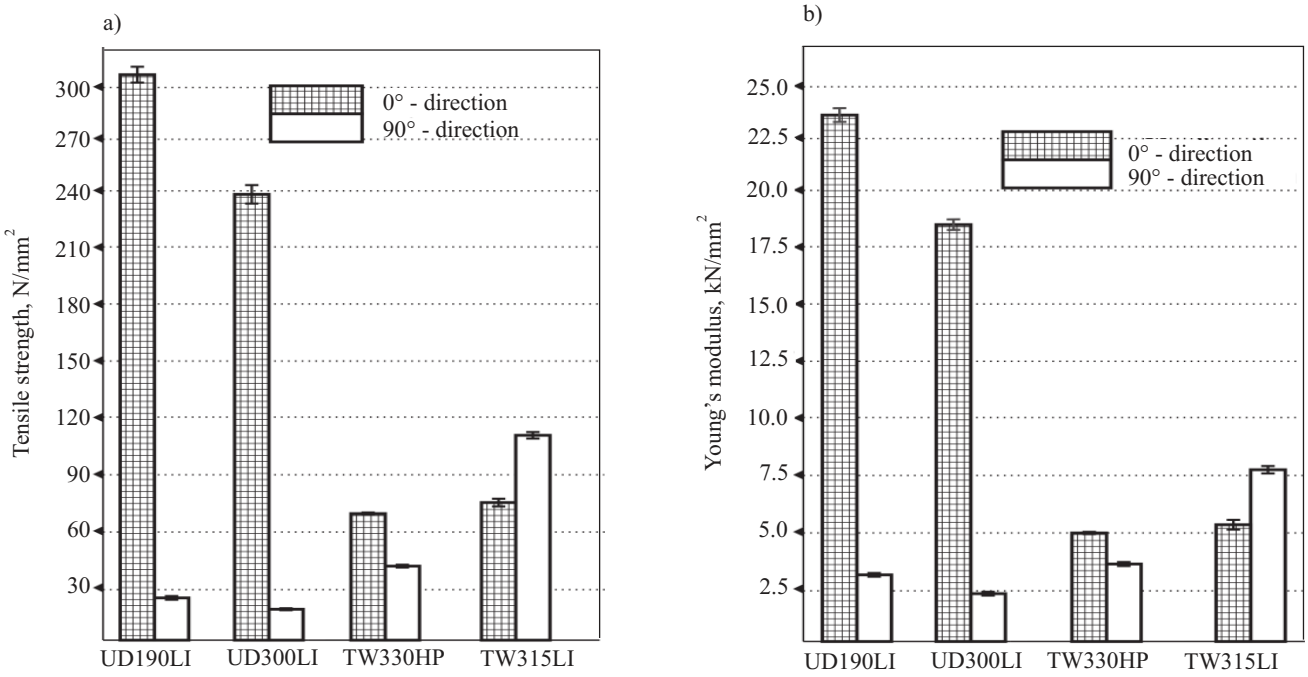

Fig. 4. Mechanical properties: a) tensile strength, b) Young's modulus; the 0° - and 90° - directions are reported in both panels for the examined specimens

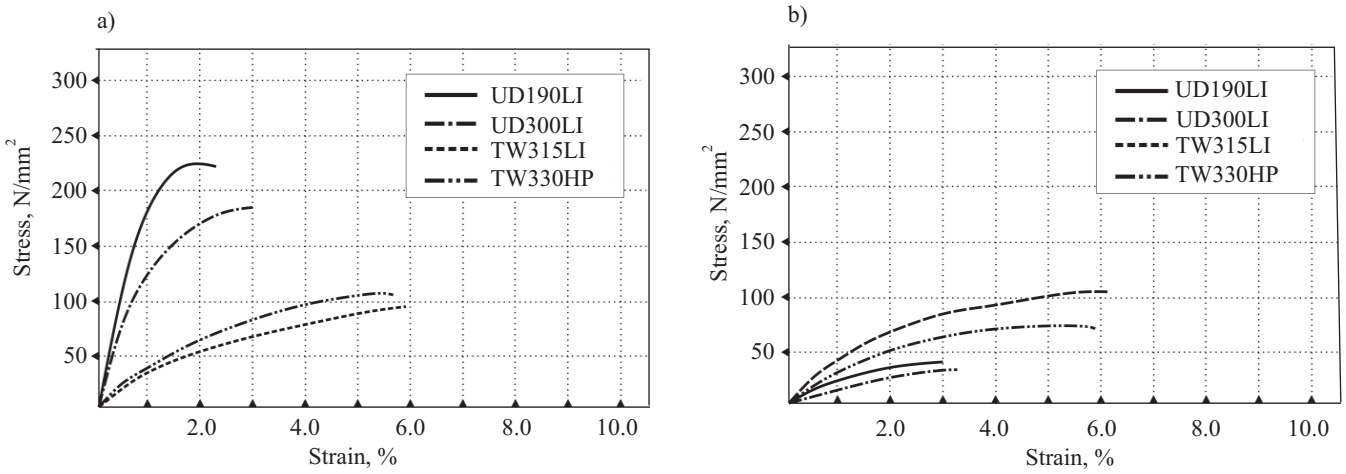

Fig. 5. Stress-strain curve of natural fiber composites in bending test: a) 0° - direction, b) 90° - direction

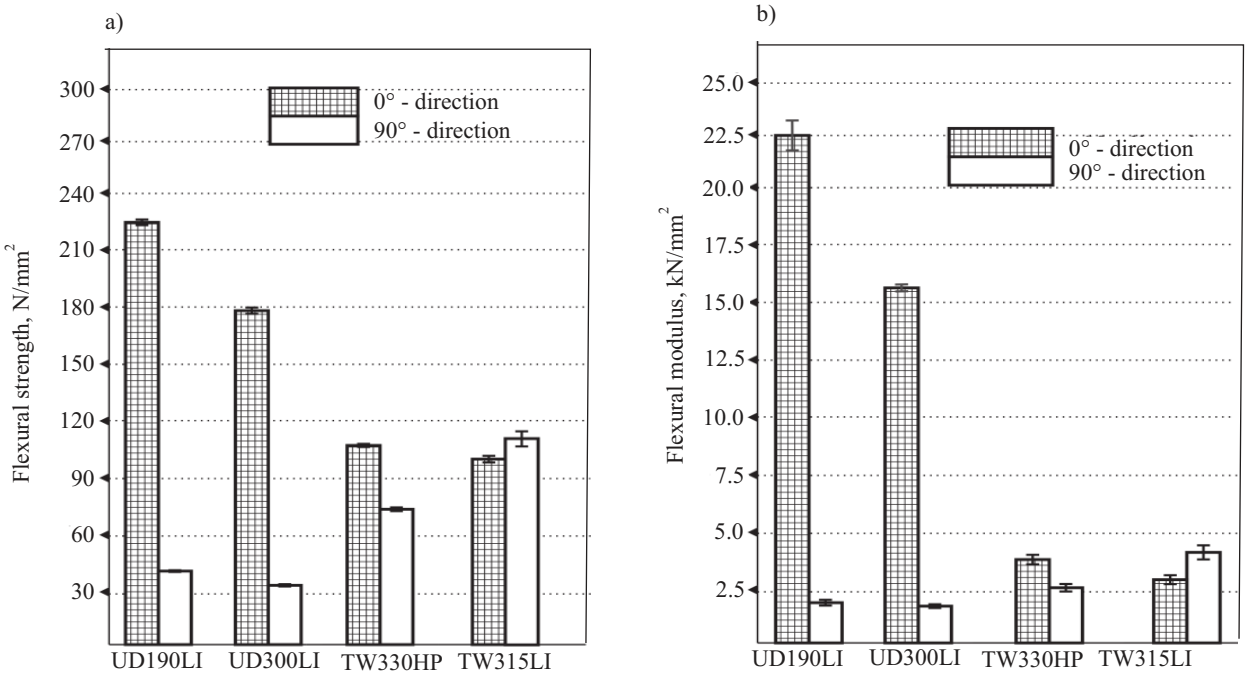

Fig. 6. Mechanical properties: a) flexural strength, b) flexural modulus in 0° - and 90° - direction for the examined specimen

In addition to the stress-strain curve, two mechanical properties (tensile strength and Young's modulus) were evaluated (Fig. 4). The linen fabrics with the unidirectional fiber orientation were characterized by the highest strength and modulus compared to the twill weave structures. It is evident that the mechanical properties are significantly reduced when the test load acts transverse to the fiber orientation for unidirectional reinforced composites.

The mechanical properties also show the influence of weave between UD300LI and TW315LI with otherwise comparable properties regarding the textile structure. Further, the results indicate a difference in the resulting properties between warp and weft direction for the twill weave structures, mainly caused by the varying properties of the warp and weft structure. It is also evident from the gained results that the determined standard deviation is low compared to the absolute mechanical properties, which shows a high reproducibility of the manufacturing process.

In theory, the bending test results represent a close approximation of the Young's modulus gained with the uniaxial tensile test due to an additional acting shear stress. As a result of this additional acting load, the determined values for the bending tests are generally lower than those of tensile tests. Furthermore, the alternative specimen size and bearing could also lead to significant differences in the resulting material properties. In accordance to the tensile tests, a stress-strain curve was determined to evaluate the material behavior under bending loading. With the fiber reinforcement oriented in the direction of the acting bending stresses, the unidirectional reinforced specimens show a rather brittle behavior compared to the twill-weave structures. In contrast to the ten-

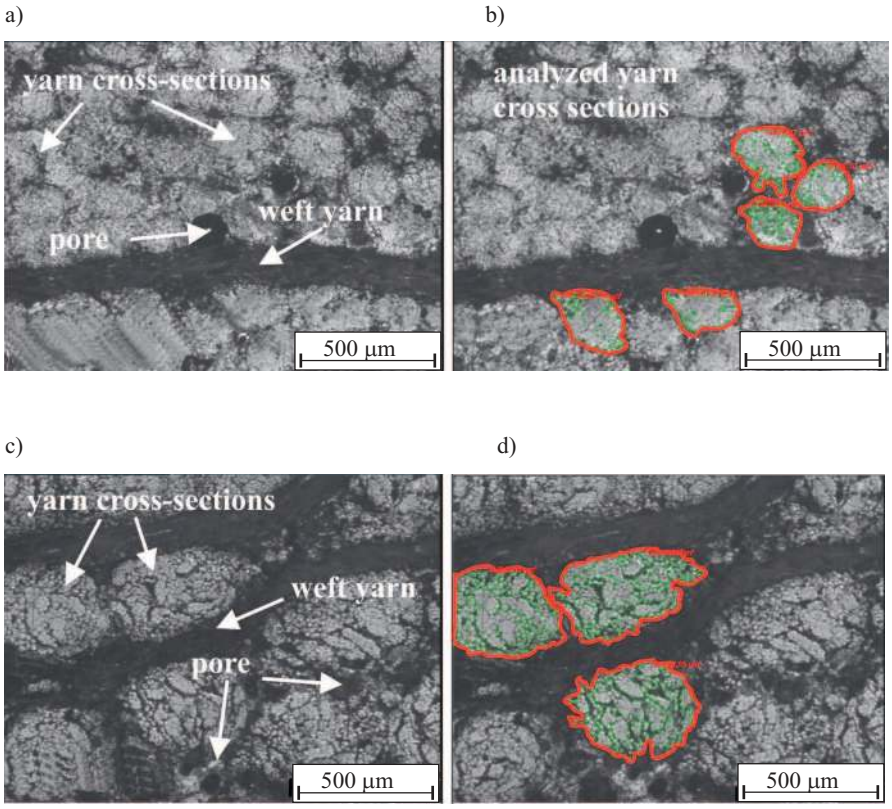

Fig. 7. Structure and analyzed yarn impregnation of the unidirectional fiber-reinforced polyurethane composites: a, b) UD190LI, c, d) UD300LI

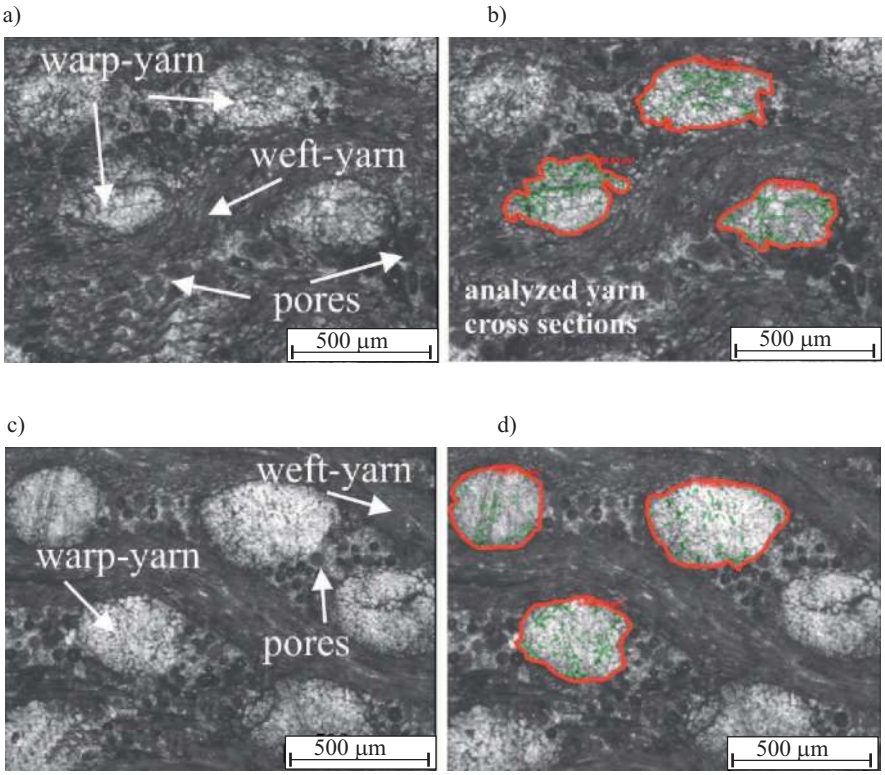

Fig. 8. Structure and analyzed yarn impregnation of the twill weave fiber-reinforced polyurethane composites: a, b) TW330HP, c, d) TW315LI

sile tests, the failure of the unidirectional reinforced specimens is not characterized by a sudden collapse but a short, ductile behavior (Fig. 5a).

With the alteration of the acting load, the stress-strain curves change drastically for the unidirectional reinforced specimens due to the matrix dominated structure

in the direction of the acting load (Fig. 5b). A slight difference between the twill structures with the acting load in the warp or weft direction could be determined. With consideration to the specimen size, the mechanical properties flexural modulus and flexural strength mainly correlate with the results gained in the tensile tests. Solely regarding the absolute values, a difference could be determined. In addition, the flexural strength of the twill weave composites exceeds the resulting tensile strength (Fig. 6).

Yarn impregnation

The yarn impregnation of the natural fiber-reinforced composites was determined by analyzing the ratio of the impregnated area to the total yarn size using micrographs. The images in Fig. 7 give an impression about the inner structure of the composite and the distribution of the cellular matrix. It is evident that the composites with unidirectional reinforcement show a homogeneous microstructure consisting mainly of fiber and compact matrix due to a rather high fiber volume content. Only in individual cases can regions with single pores emerge although the employed polyurethane system has generally a cellular structure.

In contrast to the unidirectional reinforced laminates, the composites with twill-weave show a different structure and distribution of fibers, compact matrix and cellular matrix. Whereas the yarn structure itself still keeps a compact shape with only small pores (<10 μm) that tend to merge into medium-size cellular areas (<50 μm) with undefined shape, the regions within the crossover area of the twill weave have a distinctive cellular structure with mainly large size pores (>50 μm) and a rather homogeneous pore distribution (Fig. 8).

T a b l e 4. Yarn impregnation of natural fiber-reinforced composites in relation to their fiber mass content, fiber volume content, foam density and foaming degree

Specimen	Yarn impregnation, %	Fiber volume content, %	Fiber mass content, %	Foam density g/cm^3	Foaming degree 1
UD190LI	60.9	43.9	65.8	1.05	8.40
UD300LI	53.9	34.7	58.4	0.91	7.28
TW330HP	53.4	28.9	50.9	0.83	6.64
TW315LI	55.6	36.5	60.4	0.93	7.44

The pores inside the yarn structures vary strongly within their size mainly because the surrounding pores merge to form complex cellular areas with a characteristic shape, which are strongly influenced by the textile structure. The distribution of pores in the matrix areas and micropores inside the yarn are homogeneous throughout the thickness of the specimen. During the manufacture of the specimens, the number of textile layers for each composite structure was kept constant in order to attain comparable fiber mass contents between different specifications. However, preliminary manufacturing studies revealed an unsatisfactory impregnation and surface quality for the TW330HP specimens. Due to the textile structure, the number of layers was adapted from the original 6 layers to 4 in order to attain an improved quality throughout the composite width. Therefore, the fiber mass content differs within a certain range and influences the resulting yarn impregnation, which in turn also has an influence on the mechanical properties (Table 4).

The results in Table 4 indicate that natural fiber-reinforced composites with a cellular polyurethane matrix reach a high yarn impregnation. In contrast to PUR-composites with synthetic fibers, the impregnated yarn structure has larger, connected cellular areas and only a few single micropores [17]. The yarn impregnation itself is influenced by the textile structure, for instance the yarn titer and the weave, which in turn contribute to the fiber mass content and the resulting foaming degree of the matrix system. In general, an increase in foaming degree contributes to the impregnation quality due to the higher expansion pressure.

CONCLUSIONS

The use of natural fibers in composite structures offers a high potential in terms of weight reduction and a significant reduction of the carbon footprint due to the bio-based feedstock of the reinforcement structure. The evaluation of tensile and bending tests reveals mechanical properties similar to glass fiber composites in addition to a very low standard deviation, which implies reproducible processing methods for the fiber material itself and the composite structure. Here, the polyurethane spray coat method represents a high potential production process for the manufacture of fiber-reinforced polyurethane composites with a cellular and, therefore, weight reduced matrix but also a high yarn impregnation. The results indicate that the textile structure and the foaming degree directly influence the resulting yarn impregnation.

ACKNOWLEDGMENTS

Within the framework of the project MATLEV, the Warsaw University of Technology and the Technische Universität Dresden (Institute of Lightweight Engineering and Polymer Technology, ILK) work in cooperation with TAPS Company S.Z.T.K. on lightweight generic components based on natural fibers for the use in electric low-emission vehicles. The authors are grateful to the Bundesministerium für Wirtschaft und Energie (BMWi) and the executing organisation Deutsches Zentrum für Luft- und Raumfahrt (DLR) for funding and support of the research activities within the project MATLEV.

REFERENCE

[1] Yan L., Chouw N., Jayaraman K.: *Composites Part B* **2014**, *56*, 296. http://dx.doi.org/10.1016/j.compositesb.2013.08.014

[2] Zakikhani P., Zahari R., Sultan M.T.H., Majid D.L.: *Materials and Design* **2014**, *63*, 820. http://dx.doi.org/10.1016/j.matdes.2014.06.058

[3] Shah D.U., Porter D., Vollrath F.: *Composites Science and Technology* **2014**, *101*, 173. http://dx.doi.org/10.1016/j.compscitech.2014.07.015

[4] Bismarck A., Mishra S., Lampke T.: "Natural Fibers as Reinforcements for Green Composites" (Eds. Mohanty A.K., Misra M., Drzal L.T.), Taylor & Francis Group 2005. http://dx.doi.org/10.1201/9780203508206.ch2

[5] Bledzki A., Sperber V., Faruk O.: "Natural and Wood Fiber Reinforcement in Polymers", Rapra Review Report, Sally Humphreys, Shropshire 2002, ISSN: 0889-3144.

[6] Stamboulis A., Baille C., Garkhail S. *et al*.: *Applied Composite Materials* **2000**, *7*, 273.

[7] Medina L., Schledjewski R., Lahm M., Jungmann H.: *Kunststoffe International* **2004**, *3*, 92.

[8] Hufenbach W., Gude M., Geller S., Czulak A.: *Polimery* **2013**, *58*, 473.

[9] Fan H., Tekeei A., Suppes G., Hsieh F.: *International Journal of Polymer Science* **2012**. http://dx.doi.org/10.1155/2012/474803

[10] Bledski A., Zhang W., Chate A.: *Composites Science and Technology* **2001**, *61*, 2405.

[11] Kuranska M., Prociak A.: *Composites Science and Technology* **2012**, *72*, 299.

[12] El-Meligy M.G., Mohamed A.H., Mahani R.M.: *Carbohydrate Polymers* **2010**, *80*, 366.

[13] Gu R., Sain M., Konar S.: *Industrial Crops and Products* **2013**, *42*, 273.

[14] Bakare I., Okieimen F., Pavithran C., Abdul Khalil H., Brahmakumar M.: *Materials and Design* **2010**, 31, 4274. http://dx.doi.org/10.1016/j.matdes.2010.04.013

[15] BASF Polyurethanes GmbH, "Elastoflex E 3851/102 Material Data Sheet", Version 01, 15.02.2007.

[16] Schürmann H.: "Konstruieren mit Faser-Kunststoff-Verbunden", Springer-Publishing, Berlin, Heidelberg 2007, vol. 2, p. 59.

[17] Gude M., Geller S., Weissenborn O.: *International Journal of Plastics Technology* **2015**, *11*, 1.

Received 8 I 2015.

W kolejnym zeszycie ukażą się m.in. następujące artykuły:

— *J. Čulin* — Kompozyty poliuretanowe z wzajemnie przenikającą się siecią polimerową stosowane do tłumienia drgań (*j. ang*.)

— *M. Wenda, R. Jeziórska, M. Zielecka, M. Panasiuk* — Zastosowanie nanocząstek srebra do modyfikacji polimerów

— *S. Paszkiewicz, I. Pawelec, A. Szymczyk, Z. Rosłaniec* — Właściwości mechaniczne i termiczne hybrydowych nanokompozytów polimerowych otrzymanych metodą polimeryzacji *in situ* (*j. ang*.)

— *H. Mąka, T. Spychaj, R. Pilawka, P. Dziedzic* — Wpływ hybrydowych nanonapełniaczy węglowych na proces sieciowania i właściwości materiałów epoksydowych (*j. ang*.)

— *P. Dmowska-Jasek, W.M. Rzymski, A. Smejda-Krzewicka* — Proces sieciowania i właściwości niekonwencjonalnych mieszanin kauczuku chloroprenowego z częściowo uwodornionym kauczukiem butadienowo-akrylonitrylowym

— *K. Wilczyński, K. Buziak, M. Bartnik* — Badanie przepływu kompozytów polimerowo-drzewnych w procesie wytłaczania jednoślimakowego

— *I. Michalska-Pożoga, T. Rydzkowski* — Wpływ warunków wytłaczania w ślimakowo-tarczowym układzie uplastyczniającym na właściwości mechaniczne kompozytów polimerowo-drzewnych (WPC) (*j. ang*.)