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Improving the mechanical performance of PLA composites with natural, man-made cellulose and glass fibers — a comparison to PP counterparts

Summary — In the first part of this study, the improvement of mechanical performance of composites based on polylactide in comparison to petrochemical polypropylene is presented. This approach focuses on understanding the micromechanical aspects of brittle and ductile failure mechanisms of composites with natural fiber abaca, man-made cellulose and glass fiber. The basic principal is hereby the utilization of cellulosic fibers in a biogenic matrix polymer and the comparison to PP-based composites. The findings obtained in the first sections are the main essentials for the second part of this paper: further improvement of crash resistance of PLA composites. The main objective is to improve the mechanical parameters while the primarily targeting is on the impact strength of the brittle polylactide composites. In the course of this thesis, the ultimate proof of the reinforcing effects of cellulosic fibers was provided. Finally, a selective modification of the interphase was accomplished and accordingly, the highest known values of impact strength for PLA composites were achieved.
Keywords: biocomposites, natural fiber, man-made cellulose, glass fiber, polylactide, polypropylene.

WŁAŚCIWOŚCI MECHANICZNE KOMPOZYTÓW PLA WZMACNIANYCH WŁÓKNAMI NATURALNYMI, WŁÓKNAMI REGENEROWANEJ CELULOZY LUB WŁÓKNAMI SZKLANYMI

Streszczenie — W artykule zaprezentowano biokompozyty do zastosowań technicznych, charakteryzujące się właściwościami pozwalającymi na zastąpienie nimi klasycznych kompozytów polipropylen/włókno szklane (PP/GF) i spełniających następujące warunki: zarówno wzmocnienie, jak i osnowa są pochodzenia naturalnego, kompozyt ma mały ciężar właściwy, a jednocześnie zachowuje korzystne właściwości mechaniczne. W charakterze wzmocnienia zastosowano włókna abaki oraz regenerowanej celulozy (Cell). Polilaktyd PLA posłużył jako osnowa kompozytu termoplastycznego, w całości wytworzonego z surowców pozyskiwanych ze źródeł odnawialnych. W celach porównawczych otrzymano kompozyty na bazie surowca petrochemicznego — polipropylenu (PP), a także kompozyty na osnowie PLA wzmocnione włóknem szklanym (GF). Ponadto, za pomocą odpowiednich dodatków modyfikowano warstwę graniczną włókno/osnowa. Szczegółowa ocena właściwości mechanicznych, wykraczająca poza standardowe badania *quasi*-statyczne w kierunku analizy mikromechaniki pękania oraz mikrostruktury, pozwoliła na oszacowanie cech użytkowych opracowanych biokompozytów. Wyniki badań udarnościowych i odkształcalności kompozytu PLA/Cell wskazują, że materiały takie dorównują, a w zakresie właściwości *quasi*-statycznych znacznie przewyższają PP/GF. Modyfikowane powierzchniowo włókna celulozowe wpływają na znaczne zwiększenie odporności PLA na kruche pękanie, umożliwiając tym samym zastosowanie tego biopolimeru do produkcji tworzyw konstrukcyjnych. Udarność z karbem kompozytów PLA/Cell osiąga wyraźnie większe wartości niż w przypadku analogów na osnowie PP. Dodatek włókien abaki wpływa na poprawę sztywności PLA, ale w niewielkim tylko stopniu zmienia właściwości wytrzymałościowe i odporność na kruche pękanie.
Słowa kluczowe: biokompozyty, włókna naturalne, regenerowana celuloza, włókno szklane, polilaktyd, polipropylen.

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INTRODUCTION

In long-established technical areas, the major engineering resin employed is still a PP-based composite, which is mainly reinforced with glass fibers or filled with minerals. Due to the high density and insufficient recyclability of glass fiber reinforced plastics, composites reinforced with natural fibers are beginning to find demand on the market, as well as consumer acceptance for a wide range of technical applications [1—3].

Biobased composites consist of at least two different structural components: reinforcing fibers and a composite matrix. Preferably, both of them are of natural origin. When considering application in technical areas, some basic material properties must be tailored to already existing petrochemical equivalents. For this reason, the entire spectrum of the material performance must be extensively characterized. The processability, and later on, the composite's mechanical feasibility are the essential material data that have to be well defined when considering engineering applications. However, the best possible values can only be achieved by means of optimized processing, and subsequently, with reliable composite properties. The optimization of processing represents a major area of research, and is described in [4]. The second matter, namely composite properties, constitutes the main focus of interest of this research study.

Furthermore, only tailor-made technical cellulosic and glass fibers were used in this study, in order to ensure a reliable analysis of all tested properties. A comparison of a fully and partially biobased composite to a petrochemical equivalent on a PP-basis contributes to establishing fully „green composites" as engineering materials.

EXPERIMENTAL

Materials

Biobased polylactide type PLA 3051D is produced by NatureWorks/USA and is characterized by its low D-Lactide content. A polypropylene from Sabic Europe, type PP 575P (homopolymer), was used as the petrochemical counterpart. Both polymers are predestined for injection molded applications. Detailed information on the polymers used in the study is shown in Table 1.

T a b l e 1. Characterization of polymers used

Parameter	PLA 3051D	PP 575P
Melting temperature (DSC), °C	150—165	150—175
MFR (210/2,16), g/10 min	13	7
Density, g/cm^3	1.250	0.905
D-Lactide content, %	3.7—4.6	—
Residue monomer, %	0.3 (max)	n.s.
Average molecular weight ($\overline{M}_w$)	171 000	509 000
Polydispersity	2.3	5.9

The following fibers were used for the reinforcement of composites:

Abaca: manufactured by Manila Cordage; diameter 150 ± 50 μm, density 1.5 g/cm^3, elementary fiber 10—30 μm in diameter, tensile strength approx. 800 ± 150 MPa [4, 5]. The fiber quality, according to the FIDA (Fibre Industry Development Authority), is S3. The abaca was provided by Rieter Automotive Systems. Advantages of abaca include the possibility to precisely control its growth and preparation (in cooperation with the fiber manufacturer Manila Cordage), as well as an array of improved mechanical properties compared to other natural fibers [6]. Abaca was provided in the form of a *quasi*-endless fiber spooled on 20 kg bobbins.

Man-made cellulose; manufactured by Cordenka GmbH, fiber type Cordenka® 700 Super3, dtex = 2440, number of monofilaments = 1350, tensile strength approx. 900 MPa, elementary fiber diameter 12 μm [4]. Man-made cellulose is a chemical fiber of natural origin. The source of the fiber is cellulose pulp from various wood species [7]. The fibers were delivered on 10 kg spools.

Glass fiber: for both PP and PLA an „electrical" glass fiber type was used. With regard to the matrix, different sizing chemistry was applied. PP based composites were reinforced with E-GF from Owens Corning, type OCV 968-13C with a monofilament diameter of 13 μm and PLA based materials with E-GF from PPG Industries, type HP 3786 with a monofilament diameter of 10 μm. Both glass fiber grades were delivered as chopped fibers with a 4.5 mm nominal length, and processed as described below. Maleic acid anhydride grafted PP (MAH-*g*-PP) from Clariant (TP Licocene PP MA 6452) was applied to PP composites with cellulose and abaca (5 wt. %). The content of MAH-*g*-PP is related to the fiber load. No coupling agent was added to the PLA composites.

A matrix to fiber weight ratio of 70/30 was used for these composites.

Additionally, compositions of PLA with 20 wt. % cellulose modified with maleinated chain extender Joncryl ADR 3229, delivered by BASF, were investigated. The composites containing 0—5 wt. % of Joncryl 3229 were manufactured using the same procedure as described below. The corresponding results are presented in the last section on further improvement of the impact resistance.

Composite processing

PLA was pre-dried in a convection oven with recirculating air (16 h at 110 °C, moisture content <150 ppm), whereas PP was processed without drying. Approximately 12 hours prior to processing, cellulosic fibers were placed in a convection oven and dried at 90 °C. In contrast, glass fibers were used as delivered.

Afterwards, the composites with cellulosic fibers were processed using a special coating technique that was adopted from cable isolation industry. In the first step,

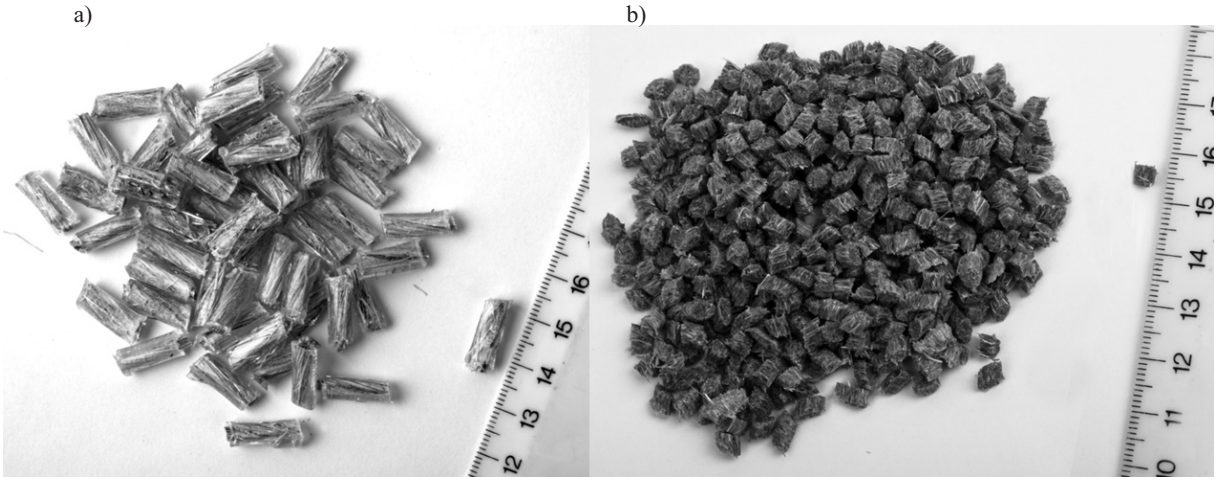

Fig. 1. Exemplary depiction of PLA abaca pellets after first — a and second — b compounding step; fiber content 30 wt. %

the polymers were compounded together with fibers drawn off from an oven. The fiber cord was additionally pre-dried using IR-radiator in a closed chamber (for a couple of seconds at 150 °C). The dried fibers were then immediately introduced into a coating nozzle and covered with melted polymer (using twin-screw extruder from Haake, Rheomex PTW 25/32, $L/D = 32$, $D = 25$ mm). Then the coated cord was cooled in line to the ambient temperature using a fan, and cut to 15 mm long pellets on a granulator. Finally, the pellets were dried for 12 h at 110 °C, compounded on a single-screw extruder (Schwabenthan, Polytest 30P, $L/D = 25$, $D = 30$ mm) and processed to final shape into pellets (cut length approx. 3.0 mm) (Fig. 1). The glass fiber pellets were processed by feeding chopped fibers directly into the single screw extruder, and then proceeding as described for cellulosic fibers.

The second compounding step does not influence the polymer structure significantly [4] and allows trouble--free processing in the following injection molding procedure. Here, the crucial criterion was the improvement of the free flowing property of pellets and their final bulk density. Both parameters are critical regarding to composites with cellulosic fibers, and, if processed incorrectly, stable processing is often disturbed [4]. The exemplary pellets obtained after each processing step are depicted in Fig. 1.

The melt temperature during coating was 200 °C at 100 rpm, and 190 °C at approx. 20—30 rpm during the shaping process. The standard test specimens were produced according to DIN EN ISO 527 type 1A using an injection molding machine, Klöckner Ferromatik FM 85 (clamping force 850 kN, screw diameter 40 mm). Melt temperatures of approximately 190 °C for abaca and 200 °C for cellulose and glass fibers were used. The injection pressure was set between 40 and 60 MPa, depending on the constant injection speed of 200 mm/s, which was calculated for the gauge length for all composites separately. The test specimens according to DIN EN ISO 178 and 179 (flexural and Charpy impact tests) were cut out from the gauge length of injection molded parts.

Methods of testing

Scanning electron microscopy

In order to test the fiber/matrix adhesion and composite morphology, micrographs were taken using scanning electron microscopy (SEM). The SEM fracture surfaces were prepared by using cryo-break fracture. The specimens were at first stored in liquid nitrogen for at least 10 minutes, then removed and immediately broken. A CamScan MV 2300 scanning electron microscope with a wolfram cathode emission gun with 10 kV acceleration voltage was used.

Tensile test

The manufactured test specimens were analyzed in a tensile test according to DIN EN ISO 527. The test was carried out on a Zwick/Roell UPM 1446 universal testing machine. The testing parameters were as follows: 1 mm/min for the estimation of the tensile modulus (E), and 5 mm/min for the estimation of the tensile strength. The test results were summarized using the software testXpert®. The values given below represent the average of 10 separate measurements.

A-notch impact strength

The impact strength was tested in an instrumented A-notch Charpy impact test, in accordance with DIN EN ISO 179/2eA. The force was measured by a piezoelectric sensor, and the displacement was calculated using a double integral formula, as described in the ISO standard. The fracture energy (impact strength) was calculated as the area under the force-displacement curve. Beforehand, the test specimen had been cut out of the parallel gauge length of the test bar. The A-notch was made with the specimen notching machine NOTCHVIS by CEAST. All composites were tested at ambient temperature (23 °C) with a normalized climate of 50 % relative humidity. For each composite at least 10 repetitions were carried out.

RESULTS AND DISCUSSION

Analysis of SEM micrographs

Due to the influence of the fiber/matrix interfacial properties on the mechanical response, the composites were qualitatively characterized using scanning electron microscopy (Fig. 2). It can be observed that PLA composites with man-made cellulose display a higher number of fiber fractures across the surface. This indicates towards relatively good interfacial bonding in contrast to PP Cell composites, and can be explained by the favorable polarity of polyester *vs*. polyolefin, despite the fact that a coupling agent was used for PP. Furthermore, the fracture surface of PP is apparently more ductile than in the case of PLA. This becomes evident, since PLA displays material failure in the form of micro-cracking, which is typical for amorphous and brittle polyesters.

Both effects, noticeable fiber pull-out and weaker interfacial bonding in PP Cell, are also visible in PP GF composites. Despite the fact that the fibers had been sized with adopted finish for each polymer, glass fibers bond obviously better with polylactide than with polypropylene. This once again confirms the improved chemical affinity of polyesters. These elementary fracture mechanisms forecast a significant improvement of the *quasi*-static properties of PLA due to a stronger interphase, and, in addition, favorable shear stress conditions along the fiber. Moreover, the lower shear viscosity of PLA reduces fiber damage during processing. This effect can especially be seen for the ductile cellulose fibers compared to the brittle glass fibers [4]. In contrast, the properties of PP

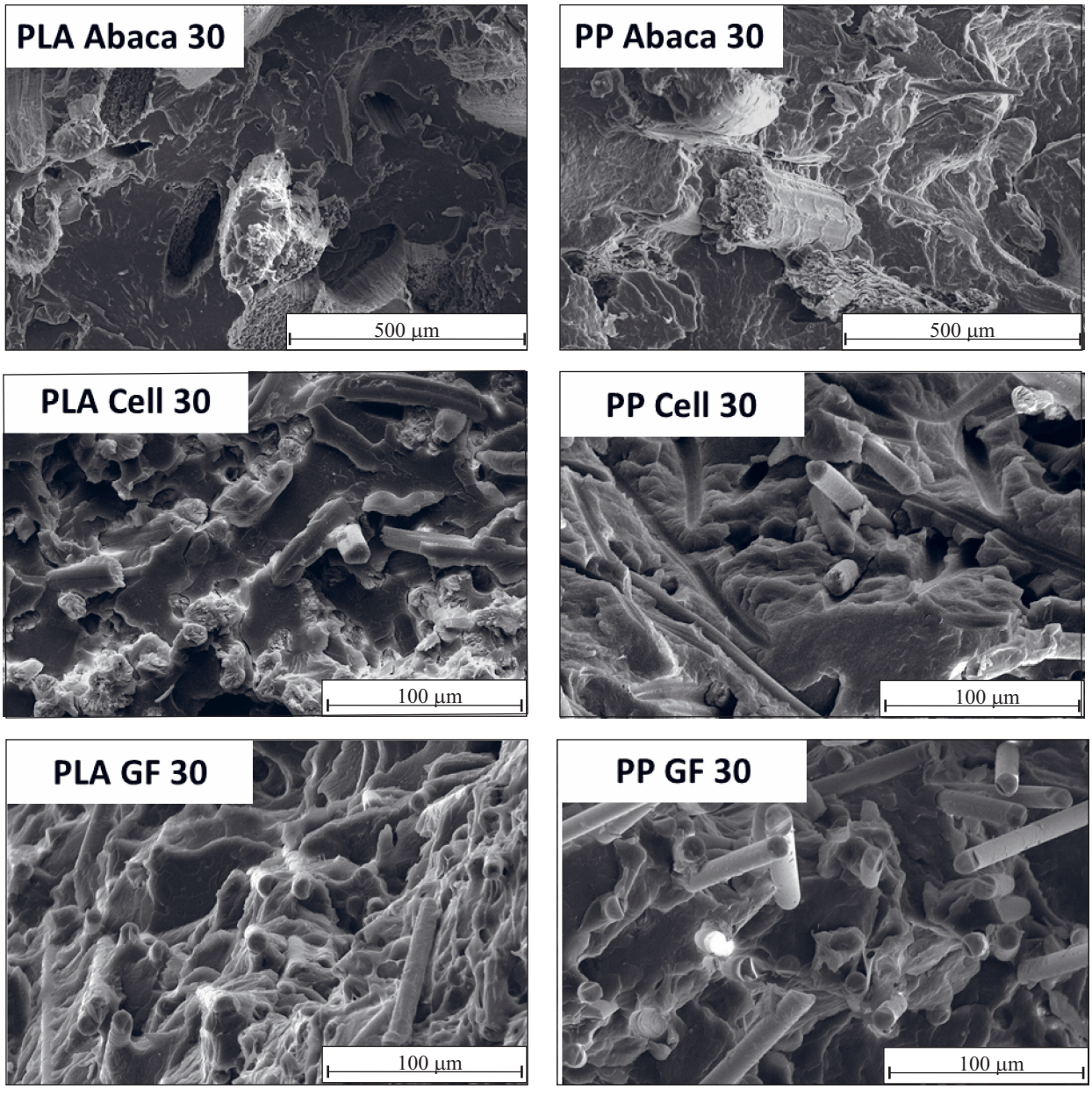

Fig. 2. SEM micrographs of composites with 30 wt. % of fiber content: PLA — left column, PP — right column

composites should result in enhanced impact toughness as the fiber pull-out is the dominating failure mode. Finally, polypropylene shows higher ductility. That is why it can deform considerably more than PLA without cracks, and in the end, absorbs a higher amount of impact energy. In conclusion, the low impact strength of PLA-based composites is one of the main issues which limit the market penetrance of such materials as engineering compounds.

When examining abaca composites, one crucial observation can be made; the fibers are rough-textured and possess a larger fiber diameter. The fibers are subjected to visible damage during processing, so that fracturing occurs both longitudinal and perpendicular to the fiber axis. Hence, a lower strength, which is directly related to the fiber aspect ratio [8—10], and earlier fracturing of these composites can be expected.

Tensile test

Figure 3 illustrates the stress-strain curves measured in the tensile test; the values of the *E* modulus are depicted in the key. Besides a somewhat lower *E* modulus, man-made cellulose composites achieve almost the same tensile strength as their GF equivalents. Furthermore, PLA composites display a noticeably higher performance than their PP counterparts. As a consequence of higher initial values for the *E* modulus of native PLA, all composites based on polylactide possess an improved stiffness in comparison to PP. It is also interesting that reinforcement with man-made cellulose increases not only the stress related properties, like stiffness and strength, but, at the same time, allows larger deformations. Due to the evident longer fiber length of man-made cellulose in the specimen [4], the pulling-out takes longer, and therefore guarantees improved composite's coherence than with GF composites. Especially the extremely high strain-at-break of those materials contributes to the increased toughness, finally ensuring a superior crash performance.

The obvious reinforcing effect of man-made cellulose and glass fibers is caused by their performance and their geometry. Besides the much finer fiber diameter of both cellulose and glass fibers, they are characterized by higher breaking tenacity than abaca [4]. Reinforcing with this natural fiber leads to an improvement in the tensile strength by factors of 1.2 and 1.5, for PLA and PP, respectively. Due to the extraordinary fiber stiffness, all abaca composites show visibly higher *E* modules than polymers with man-made cellulose. Until now, only very few authors published similar studies on abaca reinforced composites. Most of them report an increase only in stiffness, whereas the composite strength remains unchanged or has even deteriorated [11]. Regarding papers published by Müssig [12], Fink and Ganster [13—15], or Einsidel [16], the realized tensile strength enhancement in man-made cellulose composites by factor 1.9 for PLA and 2.5 for PP contribute to further achievements within the course of this study.

Finally, the authors optimized the compounding process by selectively modifying the extrusion line and peripheral devices, as well as adopting relevant processing parameters [4]. As a result, a significant improvement in the mechanical performance was achieved compared to the paper published by Bledzki and Jaszkiewicz in 2008 [17].

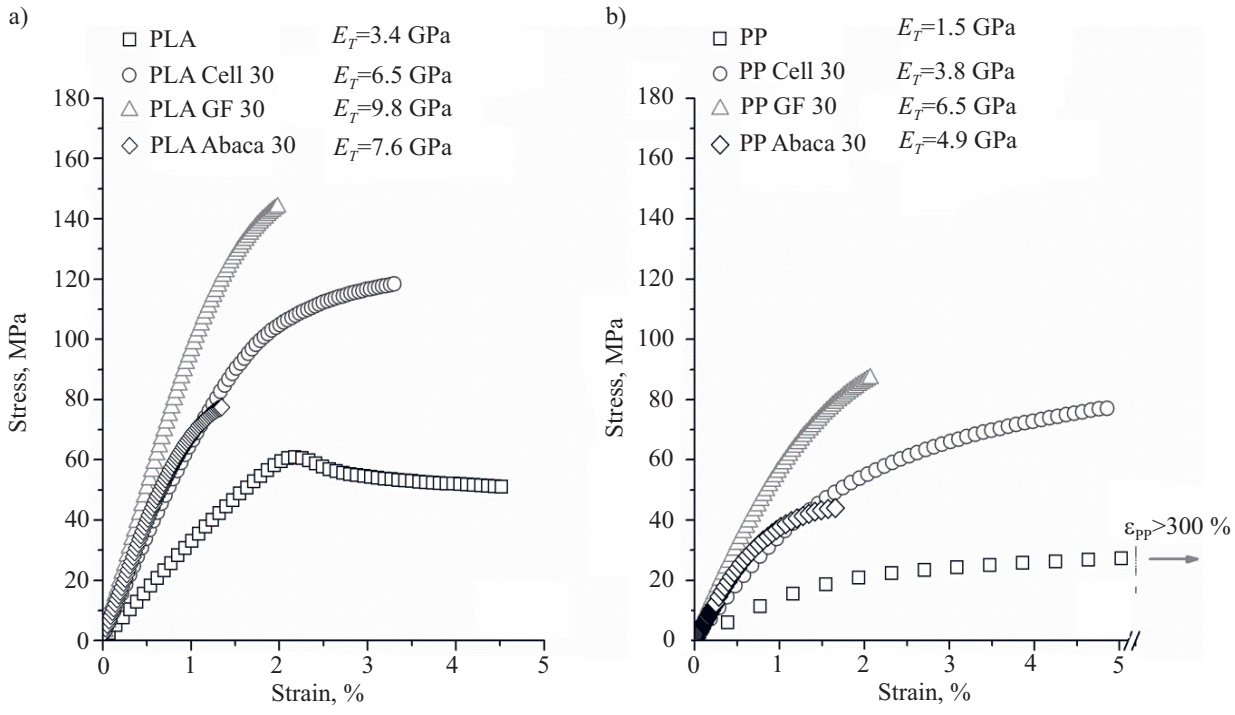

Fig. 3. Stress-strain curves of PLA — a and PP — b composites

In conclusion, when considering the significantly lower density of the composites with cellulosic fibers, most of the presented mechanical properties exceed those of materials reinforced with short glass fibers.

Impact strength

Merely consideration of mean energy values by investigating the fracture behavior of composites under dynamic load is not sufficient for the correct prediction of the structural properties in the load-bearing part [18]. The main problems are very often a simplification of average energies and the conclusion that „the higher the impact energy the better impact strength". However, the crash behavior always depends on both force and deflection at the same time. Indeed, these two parameters contribute to the mean impact energy, but they must always be considered separately. Due to the high maximum force occurring during crashes, brittle and stiff materials can achieve exact the same impact energies as some very ductile and weak composites, because of their high deflection.

The experimental work in this study encompassed a comprehensive analysis of the fracture mechanic under dynamical load. The results of the material resistance against unstable crack propagation are depicted by load-deflection curves obtained from the instrumented Charpy impact test (Fig. 4). Besides the typical initial stage, in which the obvious elastic material behavior dominates, a somehow plastic deformation can marginally be seen in PP Cell composites. Apart from that, all composites fail with brittle fracture either with splitting (PLA) or without splitting (PP). The characteristic zig-zag bands are related to the resonance frequency of the investigated system. A further reason for the occurrence of this phenomenon is the test execution procedure. Here, the sample is hit at the moment of the first contact with the pendulum and accelerated to a higher velocity than the testing velocity. As a result, the contact is broken, and the force signal from the piezoelectric sensors decreases rapidly. In an instant, the pendulum hits the specimen again, and the second force signal is registered. This effect usually disappears after a short period of time, depending on damping properties of the tested material.

The PLA Cell composites are characterized by a significantly more brittle performance than PP Cell. In the case of PLA, the reinforcing fibers primarily contribute to the improvement of the breaking force, and, due to the friction on the interphase and pull-out effects, the deformation increases slightly. PLA composites achieve an apparently higher maximum force at a lower deformation-at-break value. However, in comparison to their PP equivalents they do not show any crack propagation regions. Thus, the impact energy is a function of only the first constituent, namely the elastic material behavior. For this reason, its average is lower than that of PP Cell composites (Table 2). Glass fibers increase the maximum force for both composites. However, the change in deflection takes place in PP GF only. It is certainly an effect resulting from extraordinary pull-out mechanisms, which are reflected in the SEM micrographs (Fig. 2). Consequently, an extended crack propagation region occurs, compensating the considerably lower force at the maximum level. Hence, the total impact energy (impact strength) equals nearly that of PLA GF (see Table 2).

In relation to tensile test, the abaca fiber composites demonstrate an improvement in their maximum force at a negligible increase of the deformation. The main reason

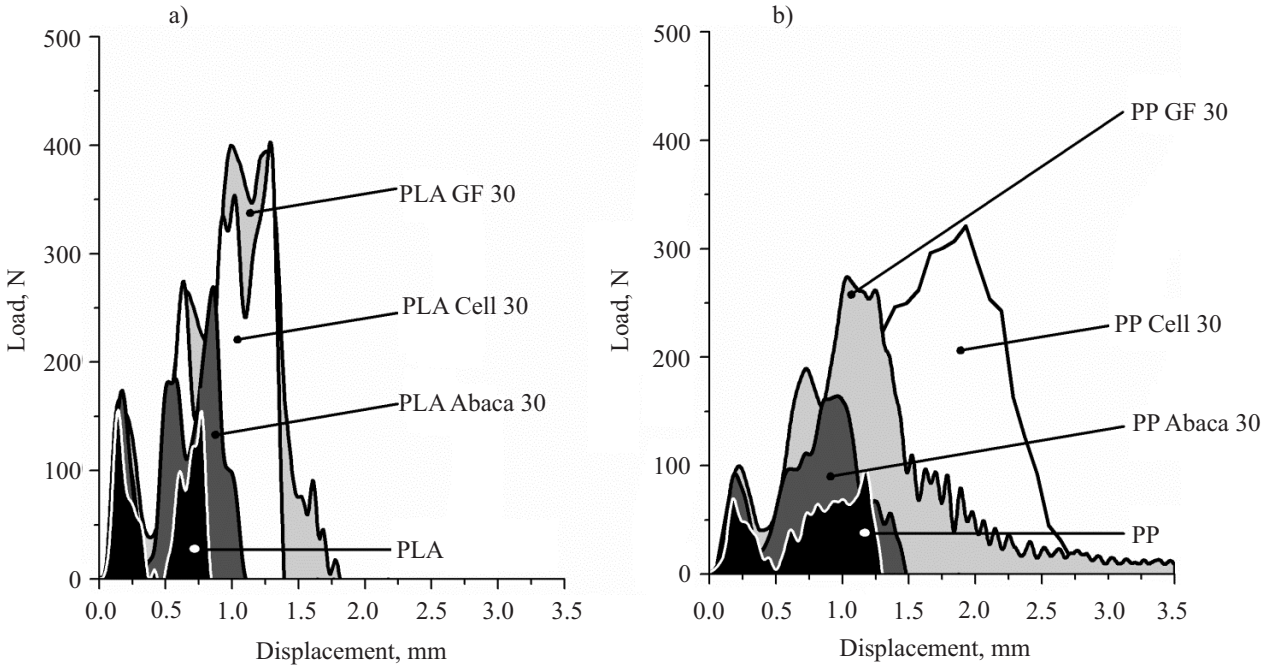

Fig. 4. Load-displacement diagrams from A-notch Charpy impact test (PLA — a, PP — b composites)

for this specific material behavior is the fiber mechanical performance combined with the non-favorable fiber aspect ratio, and visible fiber damage during processing [4]. Nevertheless, the impact strength can be enhanced by the factor 2, providing proof-of-concept with regard to the mechanical properties of natural fiber reinforced composites.

T a b l e 2. Mean values of A-notch Charpy impact strength (fiber content 30 wt. %)

	PLA				PP			
	—	Cell	Abaca	GF	—	Cell	Abaca	GF
Mean value of a_{cN}, kJ/m^2	1.6	8.2	3.7	10.1	1.9	16.1	3.7	8.6
Standard deviation	0.15	0.90	0.30	0.30	0.30	2.35	0.40	0.50

Further improvement in the crash resistance

As described above, one of the foreground failure mechanisms, which leads to an increase in the impact strength of short fiber composites, takes place when drawing the fiber out of the matrix. The reason for this is an enlarged path of initiated cracks that enables the cracking to be stopped better *via* energy dissipation, and higher energy consuming friction in the fiber/matrix boundary region [19]. Tailoring the interphase in this way leads to more frequent fiber pull-outs (weakening the interfacial bonding). Therefore, the impact strength must rise simultaneously. On the contrary, other mechanical properties, like strength and stiffness, will suffer a loss. Taking this into account, any modification of interphase must be carried out extremely carefully.

A very first example of this innovative approach contributes to the final focus of the presented study. The modifier used is a reactive additive from the BASF company. Joncryl ADR 3229 is an originally maleinated chain extender based on styrenic-acrylic copolymers with moderate polarity. The number of functionalities is 6. It has no significant impact on the processing or structural properties of PLA [4]. The additive was added during the first compounding step. The quantity was between 1 and 5 wt. % in relation to the fiber content. In contrast to the earlier part of this paper, the following section will describe PLA composites with only 20 wt. % of man-made cellulose.

The authors assume that the maleinated groups of Joncryl 3229 react chemically with the hydroxyl groups of the cellulosic fibers, and develop a thin additional film on the fiber surface. Therefore, the reaction leads to a closing of fiber-surface imperfections, making the fibers smoother and more slippery. Besides this, the presence of the new moderate polar layer on the surface disturbs the bonding with polyester. Both mechanisms induce a massive fiber pull-out, which can be seen in Fig. 5.

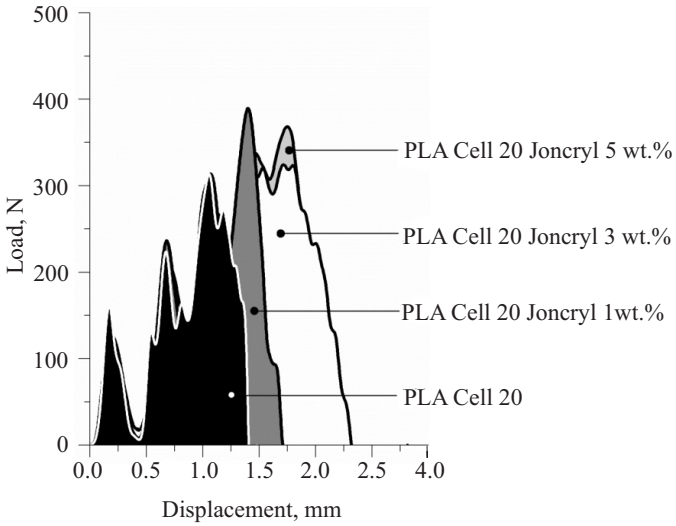

Fig. 6. Load-displacement curves for PLA 20 Cell modified with Joncryl 3229

Analyses of the load-displacement curves of those composites reveal a visible change in the material behavior compared to unmodified PLA (Fig. 6). The major difference is the somewhat increased maximum force, and

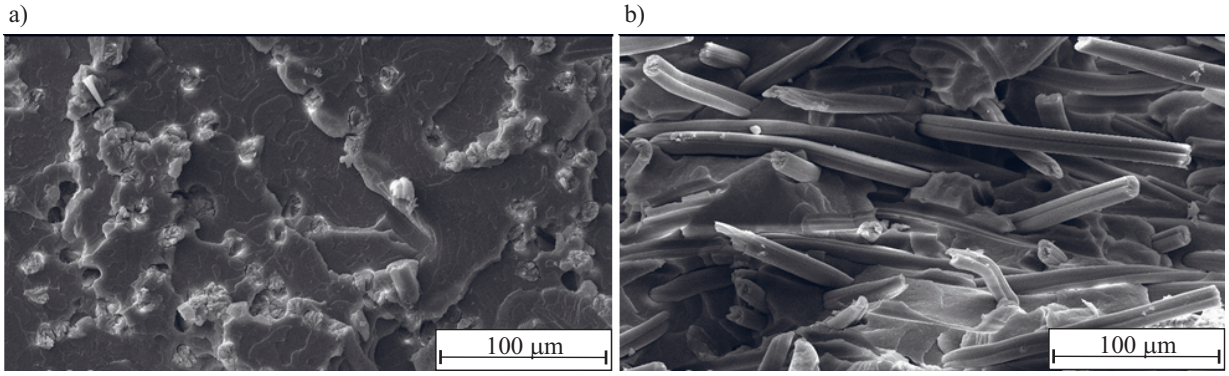

Fig. 5. Exemplary micrographs of PLA Cell 20 — a and PLA Cell 20 with 3 wt. % of Joncryl 3229 — b

an increased deflection with a higher Joncryl content. The strain doubles as early as at the content of 3 % Joncryl, whereas further increase of the additive content does not change the behavior significantly. Finally, the values of the impact strength have been improved from 6.7 kJ/m^2 to 9.1, 12.7 and 12.8 kJ/m^2 for 0, 1, 3 and 5 wt. % of Joncryl 3229, respectively. All in all, this equals an additional enhancement by approx. factor 2.

By means of this method, the impact strength of the brittle PLA man-made cellulose composites exceeded the impact resistance of its PP counterparts noticeably. In comparison, PP with 20 wt. % of man-made cellulose achieves the Charpy impact strength of merely 9 kJ/m^2.

CONCLUSIONS

In order to improve the mechanical properties of cellulosic fiber reinforced polymers, the combination of optimized processing conditions and customized additives is of significant importance. This compromised the main focus of the experimental work in this study. As shown in the paper, the majority of the investigated mechanical properties of biobased composites achieves or indeed exceeds the level of their petrochemical equivalents. The essential matter is the complex approach, including not only the discussion on mean values obtained in *quasi*-static tests, but a detailed analysis of the micro-mechanical material behavior. Thus, combining the analysis of the microstructure, the load-displacement curves, and finally, concluding the resulting impact on the macro-properties.

This study also proved that biogenic man-made cellulose can successfully be used as a reinforcing fiber. The performance of such composites corresponds to GF counterparts, while simultaneously leading to much higher impact strengths. Abaca fiber, here as an example of a fully natural fiber, is a great constituent adjusting positively the CO_2 footprint and, in some way, improving the mechanical performance. The most significant impact of abaca is on composite's stiffness. Nevertheless, further mechanical properties, such as the tensile or impact strength, can also be considerably enhanced if the appropriate processing parameters are provided.

The poor impact strength of the brittle PLA composites is still an issue, unlike for the PP equivalents, but can easily be avoided by tailoring the interphase. It has been proven that the maleinated additive Joncryl 3229 influences the interfacial region so that fiber pull-outs become the dominant mode of failure. As a consequence, the impact energy increases extraordinarily. The impact strength can be doubled already at a low additive content, evidently exceeding the impact resistance of PP-based composites.

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Received 26 VIII 2012.