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Od Redakcji / Editorial Note

Niniejszy zeszyt „Polimerów" jest poświęcony kompozytom polimerowym.
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This issue of „Polimery" is devoted to the subject polymer composites.
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Biobased composites

Dedicated to the 20th anniversary of the Fraunhofer IAP**)**

Summary — Biobased thermoplastics, such as poly(lactic acid), have attracted much attention in recent years as an alternative to oil-based plastics both in academia and industry. Based on renewable raw materials these polymers offer advantages in terms of decreased dependence on fossil resources and reduced CO_2 footprint in accord with sustainability ideas and climate protection. In order to improve the properties of these materials, reinforcement with biobased fibers represents a promising option. An alternative route to glass and natural fiber reinforcement was taken and intensively investigated. The novel approach is based on the use of cellulose man-made fibers, in particular rayon tire cord yarn, as a biogenic reinforcing component. It was demonstrated that short fiber rayon reinforcement leads to dramatic improvements in the mechanical properties of various biobased and partially biobased matrix materials. While stiffness is easily enhanced also with natural fibers, the use of rayon results in considerable improvements in strength and impact properties in contrast to natural fiber reinforcement. For example, an enhancement of more than 500 % was observed in notched Charpy impact strength of poly(lactic acid). In the present contri-

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bution results concerning composite mechanical properties will be presented for various biobased matrix materials with special emphasis on the role of the fiber-matrix interphase. By reactive extrusion this interphase can be tailored from being weak (anti-coupling), intermediate (no modification) or strong (covalent coupling). Implications for the composite properties as a function of matrix stiffness will be discussed. Other factors influencing the composite properties such as fiber length and fiber diameter will be considered as well. Finally, some general conclusions will be drawn concerning future work and industrial prospects.
Keywords: biocomposites, interface, poly(lactic acid), cellulose fibers, mechanical properties.

BIOKOMPOZYTY

Streszczenie — Termoplastyczne biopolimery, np. poli(kwas mlekowy), w ostatnich latach skupiają uwagę zarówno ośrodków naukowych, jak i przemysłu, stanowiąc alternatywę dla materiałów wytwarzanych z produktów petrochemicznych. Biopolimery otrzymywane z surowców pozyskiwanych ze źródeł odnawialnych pozwalają na zmniejszenie zależności od zasobów paliw kopalnych, wpisują się też w ideę zrównoważonego rozwoju i ochrony środowiska. W celu poprawy wytrzymałości mechanicznej tego rodzaju polimerów stosuje się dodatek wzmacniających biowłókien jako zamienników dotychczas używanych włókien szklanych lub włókien naturalnych. W niniejszym artykule omówiono wpływ dodatku krótkich włókien regenerowanej celulozy (rayon) na mechaniczne właściwości kompozytów na osnowie całkowicie lub częściowo biologicznych polimerów. Zastosowanie naturalnych włókien w charakterze wzmocnienia biopolimerów prowadzi do zwiększenia sztywności materiału matrycy, użycie natomiast włókien rayon pozwala na polepszenie wytrzymałości mechanicznej i udarności [np. dodatek celulozy rayon do poli(kwasu mlekowego) powoduje wzrost o 500 % udarności z karbem wg Charpy'ego]. Określono wpływ różnorodnych czynników na wytrzymałość mechaniczną biokompozytów wzmacnianych włóknami rayon, m.in. oddziaływań międzyfazowych włókno-matryca polimerowa. Na drodze reaktywnego wytłaczania można otrzymać kompozyty o różnej sile wiązania włókien z matrycą polimeru. Omówiono także zależności właściwości biokompozytów z dodatkiem włókien rayon od sztywności bazowego polimeru jak również od długości i średnicy wykorzystywanych do wzmocnienia włókien.
Słowa kluczowe: biokompozyty, interfaza, poli(kwas mlekowy), włókna celulozowe, właściwości mechaniczne.

INTRODUCTION

The reinforcement of conventional oil-based thermoplastics with short fibers (up to 2 mm in length) is a classical method to improve the mechanical properties of the matrix material. Well known examples are glass fiber reinforced polypropylene (PP) and polyamide (PA). Injection molded items from these materials are much stronger and stiffer than their unreinforced counterparts, often more than hundred or even several hundred percent. On the other hand, biobased thermoplastics have attracted much attention in recent years as an alternative to oil-based plastics [1]. Based on renewable raw materials these polymers offer advantages in terms of decreased dependence on fossil resources and reduced CO_2 footprint in accord with sustainability ideas and climate protection. Still being a niche market, growth rates of 17.8 % per year are expected according to a recent Ceresana Research study [2]. Many of the big polymer producers (BASF, Bayer, DuPont, DSM, Arkema, Braskem, *etc*.) have biobased or partially biobased products in their portfolio. Pioneer work in this respect has been done by NatureWorks, now a joint venture of Cargill and Teijin, the world's largest producer of poly(lactic acid) (PLA) with a nominal capacity of 140 000 tons per year. Fiber reinforced types of PLA are not available on the market and standard formulations are not defined yet. Rather cellulosic and lignocellulosic fibers (wood, flax, hemp, abaca, recycled paper, *etc*.) have been employed with limited success especially in terms of strength and impact strength (for the case of PLA see, *e.g.*, [3]).

Retaining the advantages of natural cellulose fibers, cellulose man-made (spun) fibers, in particular rayon, have been used for reinforcement [4—7]. Starting with (oil-based) PP as a widely used commodity polymer *e.g.* in the automotive industry, it could be shown that rayon produces composites with excellent mechanical properties reaching and partially surpassing the level of glass fiber reinforcement [4, 8]. The natural next step was to use biobased and/or biodegradable matrix materials with PLA as the most obvious first choice [8]. Other research groups followed and fully confirmed the results [9, 10]. Other biobased and partially biobased matrix materials have been the subject of further investigations together with a targeted modification of the fiber-matrix interphase. From the industrial side, the approach has been supported by the rayon manufacturer Cordenka and the automotive tier one supplier Faurecia with special

emphasis of the latter on rayon reinforced PP. Prototypes of rayon – PP door panels and dashboards have been manufactured and validated in cooperation with Faurecia. Meanwhile, Cordenka offers PP-Rayon and PLA-Rayon for industrial applications [11].

In the present paper first the reinforcing rayon tire cord yarn and the biobased and/or biodegradable matrix materials investigated will be introduced and the latter will be cover a broad range of stiffness values. After a brief account of compounding techniques, results for composite mechanical properties will be presented with special emphasis on the role of the fiber-matrix interphase. By reactive extrusion this interphase could be tailored from being weak (anticoupling), intermediate (no modification) or strong (covalent coupling). Implications for the composite properties as a function of matrix stiffness will be discussed and some general conclusions will be drawn.

EXPERIMENTAL

Materials

Rayon tire cord yarn

The reinforcing fiber mainly used in these studies is the rayon tire cord yarn Cordenka®RT 700 which is produced by Cordenka GmbH, Obernburg, Germany, on a several thousand ton scale. The main application is carcass reinforcement for high speed and run flat tires. 1.350 filaments of 1.8 dtex corresponding to a diameter of 12 μm are joined in a yarn and wound around a bobbin resembling a glass fiber roving.

The mechanical properties of single filaments of rayon and other cellulose spun fibers have been characterized in some detail by own measurements [12, 13]. Some results are given in Table 1 in comparison to glass fibers. With 830 MPa the Cordenka fiber has the highest tensile strength among commercially available man-made cellulose fibers. Compared to standard viscose, strength and modulus are roughly doubled. Compared to glass fibers the properties are considerably lower, however, as will be presented later, property levels of the composites are in the same range and, moreover, rayon has a series of advantages over glass fibers.

T a b l e 1. Mechanical properties of single filaments of rayon tire cord yarn, standard viscose and E-glass

Fiber	Strength MPa	Modulus GPa	Elongation %
Cordenka® RT 700*)	830 ± 60a)	20 ± 1	13 ± 2
Enka® Viscose*)	308 ± 15	11 ± 4	24 ± 1
E-glassb)	1400…2600	75	

*) Determined by own measurements.
a) Standard deviation.
b) Data from literature [6].

First, the density of rayon with 1.5 g/cm^3 is lower than the glass density of 2.5 g/cm^3 bearing potential for light weight constructions. Then the wear of the processing equipment is much reduced owing to the „softer" character of the fiber (anisotropy) and the thus low abrasiveness. Less fiber shortage is experienced during repeated compounding for the same reason giving advantages at recycling operations. And finally incineration is facilitated due to the organic nature of the fiber. On the down side, besides low stiffness there is the reduced thermal processing window, posing difficulties for higher melting thermoplastics, say, above 250 °C. At this temperature chain scission of cellulose accelerates significantly resulting in a high number of pyrolytic products (*e.g.* levoglucosan) and therefore reduced fiber properties [14—16]. Finally, composite preparation might be affected by the hydrophilic nature of rayon.

Matrix materials and additives

A selection of matrix materials studied in combination with rayon fiber reinforcement is given in Table 2.

Completely biobased PLA and PHB are supplemented by the potentially partially biobased polyesters

T a b l e 2. Matrix materials and additives used in this study

Material		Tradename	Producer
PLA	poly(lactic acid)	NatureWorks® PLA-7000 D/4042 D	Cargill Dow
PA 6.10	polyamide	Vestamid Terra HS	Evonik Industries
StPrAcLau	starch propionate acetate laurate	—	Fraunhofer IAP [14]
PHB	poly(3-hydroxybutyrate)	Biomer® P 226	Biomer
PBS	poly(butylene succinate)	Biocosafe 1903	XINFUPHARM
PBSA	poly(butylene succinate adipate)	Biocosafe 1803	XINFUPHARM
PBAT	poly(butylene adipatetherephthalate)	Biocosafe 2003	XINFUPHARM
HMDI	hexamethylene diisocyanate	Hexamethylene diisocyanate	Sigma Aldrich
PP-*g*-MAH	maleic acid anhydride grafted polypropylene	Fusabond® MD353D	DuPont

PBS, PBSA, and PBAT to cover a broad range of stiffness, as shown in Table 3. StPrAcLau is a mixed starch ester with propionate as the major substitution component developed in this institute [17].

T a b l e 3. Selected mechanical properties of matrix polymers[*)]

Material	E GPa	σ_{max} MPa	ε_B %	a_c kJ/m^2	a_{cN} kJ/m^2
PLA	3.01	68.7	3.1	17.1	2.4
PA 6.10	2.00	64.6	25.7	n.b.[**)]	3.8
StPrAcLau	1.50	29.2	2.4	6.2	0.5
PHB	1.45	27.4	7.9	n.b.	4.8
PBS	0.75	40.4	230.5	n.b.	5.0
PBSA	0.36	31.0	250.3	n.b.	16.0
PBAT	0.08	17.8	130.1	n.b.	n.b.

[*)] E — Young's modulus, σ_{max} — tensile strength, ε_B — elongation at break, a_c and a_{cN} — Charpy unnotched and notched impact strength, respectively.
[**)] Not broken.

Compounding methods and injection molding

In contrast to glass fibers, where established methods for incorporating the fibers into the polymer melt exist, the feeding of organic fibers, in the present case rayon filaments, is not straightforward. On the one hand, direct feeding of the endless fiber rovings into a twin screw extruder equipped with suitable mixing and kneading elements is not successful owing to the high ductility of the fibers compared to glass fibers which are much more prone to breakage. On the other hand, rayon fibers which are cut prior to feeding into the extruder tend to be very fluffy and pose dosage problems due to the very low bulk density and for not being free-flowing.

A simple method on a small lab scale (300 g) is the use of an internal mixer (Brabender kneader W350) in combination with short cut fibers, usually 4 mm in length. Polymers and fibers were thoroughly dried overnight in vacuum at 55 °C and 100 °C, respectively and mixed for 5 min with starting temperatures of 170 °C (PLA), 165 °C (PHB), 160 °C (StPrAcLau) and 120 °C (PBS, PBSA, PBAT). Test specimens were produced on a Haake mini-jet injection molding machine according to ISO 527, type 5A (tensile experiment) and ISO 179 (Charpy impact strength).

For continuous manufacture a two-stage compounding method has been developed [4] as shown schematically in Fig. 1.

In the first step, the fibers are taken from a creel and fed into a coating die, covering the fiber bundles with thermoplastic matrix material. After cooling in a water bath, the strand is cut with a commercial pelletizer to give pellets G1.

After drying, these pellets are fed into a twin screw extruder (Rheocord 9000 PTW 25) with optimized screw configuration (mixing and kneading elements) for homogenization and final water removal to give the pellets G2 which are then used, after drying, for injection molding (Arburg Allrounder 270 M 500-90). With this method, very homogeneous composites are obtained, as shown in the optical micrograph for a PP-rayon test bar in Fig. 2.

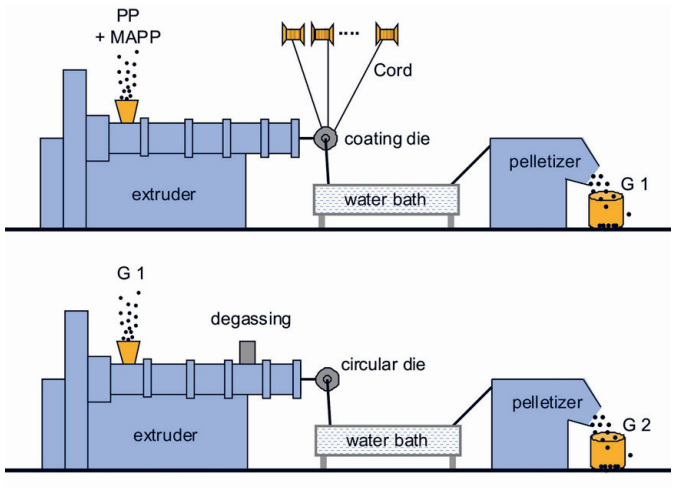


Fig. 1. Two stage compounding with coating step (above) and homogenization step (below)

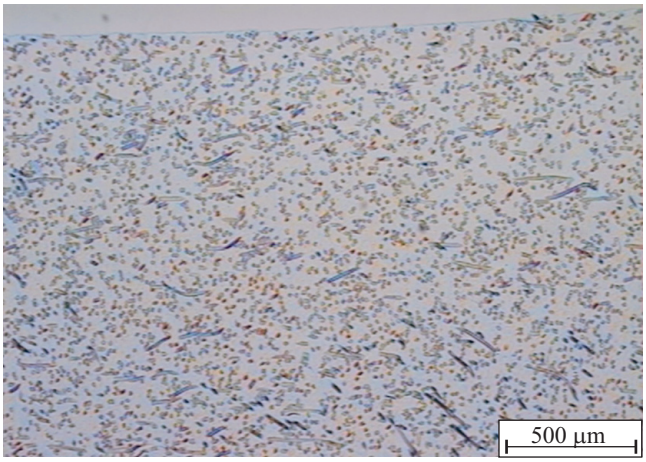


Fig. 2. Optical micrograph of 10 µm slice of PP-rayon composite test bar

In order to simplify the procedure above, a one-stage technology has been developed together with the fiber producing company Cordenka, based on direct feeding of short cut fiber pellets into the extruder [18]. The actual novelty in this respect is presented by the pellets themselves, since pure short cut rayon fibers cannot be fed into the extruder by usual techniques due to their wadding-like structure and thus low bulk density. Therefore, the fibers were coated with a special sizing to provide fiber adherence and pellet formation. This sizing has to comply with a series of partly contradicting requirements: a) fiber adherence as to provide pellet formation, b) pellet opening during compounding down to the sin-

gle filament level, and c) avoiding negative effects on composite properties. Moreover, due to technological reasons, only water borne systems were to be reasonably taken into consideration.

Successful experiments were performed with starch/starch derivatives, cellulose derivatives, polyvinyl acetate, polyvinyl alcohol and mixtures of them. Suchlike pellets can easily be fed into the extruder with common screw feeding systems. The pellet opening down to the filament level during extrusion was demonstrated [4].

Methods of testing

Mechanical properties

The mechanical properties, *i.e.* tensile strength (σ_{max}), Young's or tensile modulus (E) and elongation at break (ε_B) were determined under *quasi*-static stress in accordance with standards DIN EN ISO 527 and 178 on a Zwick 1445 tensile testing machine from Zwick GmbH & Co. KG. The impact properties, *i.e.* Charpy impact strength (a_c) and notched impact strength (a_{cN}) at room temperature as well as in frozen state ($a_c^{-18\,°C}$, $a_{cN}^{-18\,°C}$) were determined as per standards DIN EN ISO 179 on a pendulum impact tester manufactured by Wolfgang Ohst, Rathenow, Germany. All test specimens were conditioned for a defined period in a climate-controlled test laboratory at 23 °C and 50 % relative humidity.

Scanning electron microscopy (SEM)

Cryo-fractured surfaces were generated by breaking the test bars under liquid nitrogen conditions and subsequent sputtering with platinum with a thickness of 4 nm. The fracture surfaces of the samples were analyzed with a SEM Jeol JSM 6330 at 5 kV acceleration voltage.

RESULTS AND DISCUSSION

In this section important parameters related to the fiber and fiber matrix interaction influencing the composite properties will be discussed in turn and examples will be presented corroborating the general ideas.

Fiber content

Fiber content is the first important and simple factor influencing the composite properties. For PP-rayon composites this was investigated in some detail [8]. While for tensile modulus, strength and notched Charpy impact strength a pronounced positive, roughly linear correlation with a positive intercept was found, unnotched Charpy values were roughly constant on a high level of 80 kJ/m^2. Fiber contents of up to 42 wt. % were realized before processing became prohibitively difficult. This correlates to 30 vol. % fiber which for glass fiber reinforcement would have unusually high weight fraction of 55 %.

For PLA results have been published in [3]. Processing becomes difficult at fiber fractions above 30 wt. %, *i.e.* 26 vol. % (notice the higher density of PLA with 1.25 g/cm^3 *vs.* PP with 0.9 g/cm^3). The corresponding glass fiber weight fraction would be 40 wt. %. Up to that point, as expected, there were detected fairly linear positive correlations between the fiber content and tensile strength, stiffness, notched and unnotched Charpy values, also at low temperatures. Different from the PP case, intercepts close to zero were found, probably due to the higher starting level of the PLA matrix properties.

In what follows, fiber content is fixed to a level of 20 wt. % equal to a volume fraction of 17 % which in turn corresponds to a (hypothetical) glass fiber content of 30 wt. % (for a matrix density assumed to be 1.25 g/cm^3). This is a typical value for commercial glass fiber reinforced plastics.

Fiber-matrix interphase

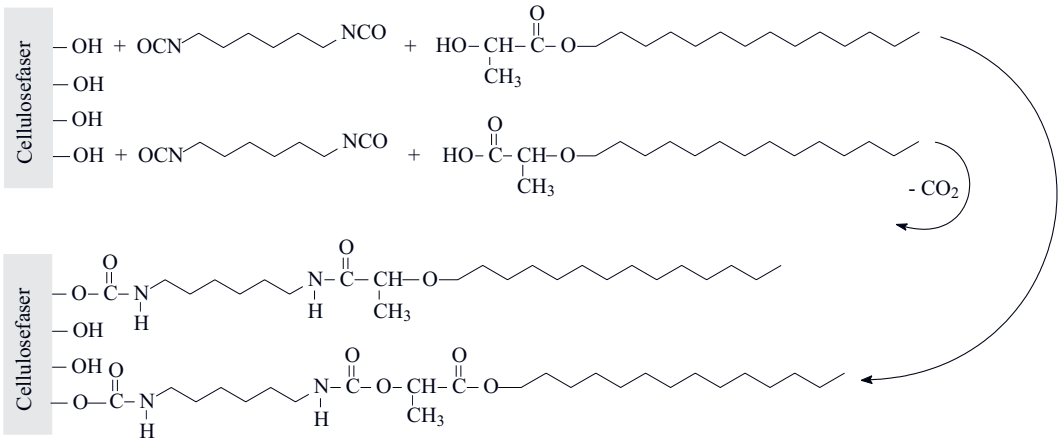
Strong interphase mechanism

Obviously composite properties will be influenced by the strength of the fiber-matrix interphase: strong, preferably covalent bonds between fiber and the matrix will lead to a good stress transfer to the fibers also at high deformations and even close to the sample failure and thus improve the composite strength, especially tensile strength, which will be discussed. The method employed for the polyesters used here is based on diisocyanate coupling agents, namely hexamethylene diisocyanate (HMDI) 1 % of which was added during compounding. The proposed coupling mechanism is shown in Scheme A.

Ideally, the plentiful hydroxyl groups at the fiber surface react with the isocyanate moieties such that the fiber surface is functionalized with the isocyanate groups which in turn can react with either hydroxyl or carboxyl groups at the PLA chain ends to give urethane or amide linkages, in which the latter chemical reaction is preferred. For a similar material system the proposed coupling mechanism is confirmed by NMR measurements by Ohkita *et al.* [19]. In that way covalent bonds are established between cellulose fibers and the matrix material. Side reactions such as H_2O with -NCO groups can be avoided as far as possible if the polymers and fibers are pre-dried before compounding. Results will be discussed in a later section in comparison with weak and moderate coupling.

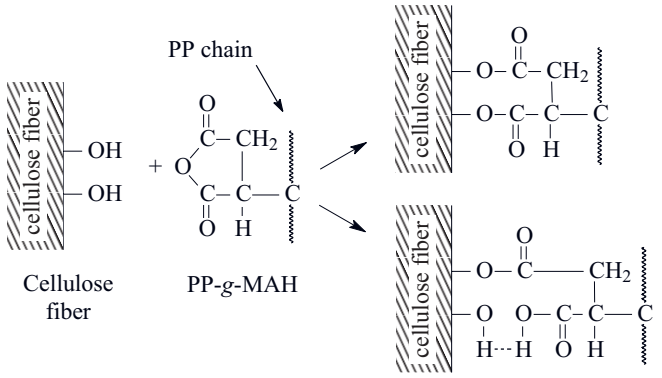
Weak interphase mechanism

Less obvious and opposed to strong covalent coupling, a weak interphase capable of producing an energy absorbing mechanism by fiber pull out during the fracture event can cause considerable improvements in impact properties, in particular notched impact strength without compromising stiffness and with minor losses in



Scheme A. Possible mechanisms of fiber-matrix coupling through a reaction with hexamethylene diisocyanate during reactive compounding

strength [20]. In the matrix materials from Table 2, this can be brought about by hydrophobizing the fibers during the compounding process. A simple method to accomplish this is to add small amounts (3 wt. %) of commercially available maleic acid anhydride (MAH) grafted PP (PP-*g*-MAH) to the matrix polymer and using the esterification reaction between cellulose hydroxyls and the acid groups of MAH as shown schematically in Scheme B.



Scheme B. Coupling scheme between cellulose fiber and maleic anhydride grafted PP according to Felix and Gatenholm [21] (with permission from Wiley)

The slightly grafted (maximum 1.5 %) hydrophobic PP chains are fixed to the fiber surface and render the fiber hydrophobic compared to the more hydrophilic polyester matrix. Finally, when no additional modifiers are used, the interphase turns out to be in between the two extreme cases described above.

Structure

Scanning electron microscopy micrographs of cryo-fractured composite test bars are shown in Fig. 3 PLA matrix as an example. Obviously, the HMDI-coupling (Fig. 3a) was successful and the fibers are covered with matrix material.

Moreover, no fiber pull-out is observed and fracture is the dominating fiber failure mechanism. In contrast, the weak interphase produces long fiber pull-outs and the fibers are not covered with matrix material. Similar observations have been made for the other matrix materials listed in Table 2.

Mechanical properties

PLA

Industrially, PLA is one of the most important bio-based and biodegradable thermoplastic materials which entered larger scale production in 2003 making this polymer widely available. The inherent brittleness can be overcome by rayon reinforcement without compromising strength or stiffness as demonstrated in Fig. 4 for unmodified fiber-matrix interphase and the small scale kneader technique.

With 20 wt. % rayon reinforcement, strength increases by 40 %, stiffness by 60 %, and unnotched and notched Charpy impact strength by 220 % and 140 %, respectively at room temperature. At -18 °C the Charpy values are reduced somewhat but remain on a high level. Interphase modification by reactive compounding as described above leads to the mechanical properties shown in Fig. 5 for the tensile and Fig. 6 for the Charpy impact experiments. Some improvement is noticed for strength and strong coupling, while the modulus is not affected due to the small deformations involved.

More apparent effects are seen for the impact properties in Fig. 6. Especially the weak interphase modification causes the mentioned energy absorbing effect through fiber pull-out in the notched experiments where the crack is forced to form in the notch root and the fibers act immediately. In contrast to that for the unnotched experiments the impact strength is less influenced by the investigated interphase characteristics.

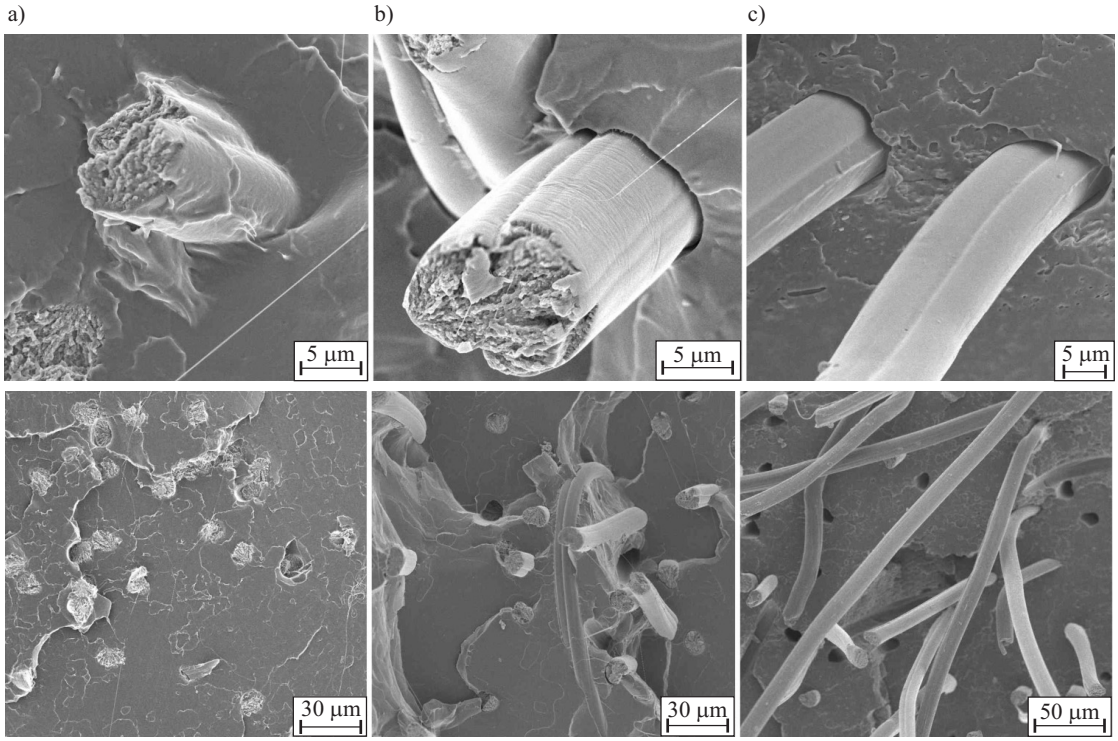


Fig. 3. SEM cryo-fracture micrographs of PLA-rayon composites with strong (a), moderate (b), and weak (c) interphase

This can be different for less stiff matrix materials as shown in Fig. 7 for PBS. Here, the unnotched Charpy value benefits from the strong coupling compared to the weak interphase. Similar to the unreinforced matrix the composite does not break at all. Likewise, strength is improved considerably to more than 80 MPa.

Other polyesters

Composite stiffness *vs.* matrix stiffness for the polyesters investigated is shown in Fig. 8 for the strong interphase. Since coupling does not influence the modulus (see above) the same values are found for both the weak and strong interphases.

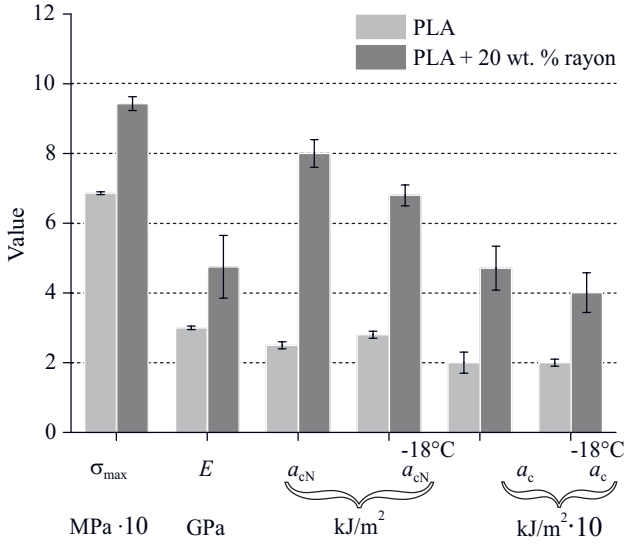


Fig. 4. Selected mechanical properties of PLA-rayon composites with unmodified interphase

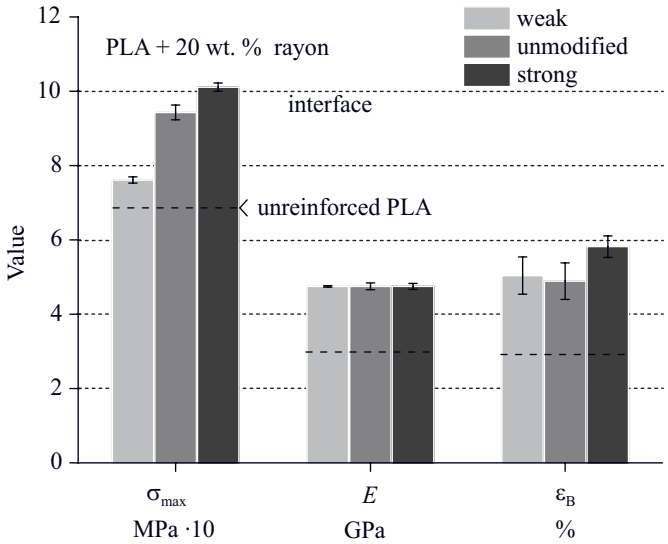


Fig. 5. Tensile properties of PLA-rayon composites with tailored interphase

Contributions above the straight line are caused by the 20 % rayon reinforcement and amount to between 1000 and 1500 MPa. A rough description would be that the fibers add a constant value to the respective matrix modulus, indicating a parallel coupling of the two phases, *i.e.* matrix and fiber (Voigt average, see, *e.g.* [22] for the concept).

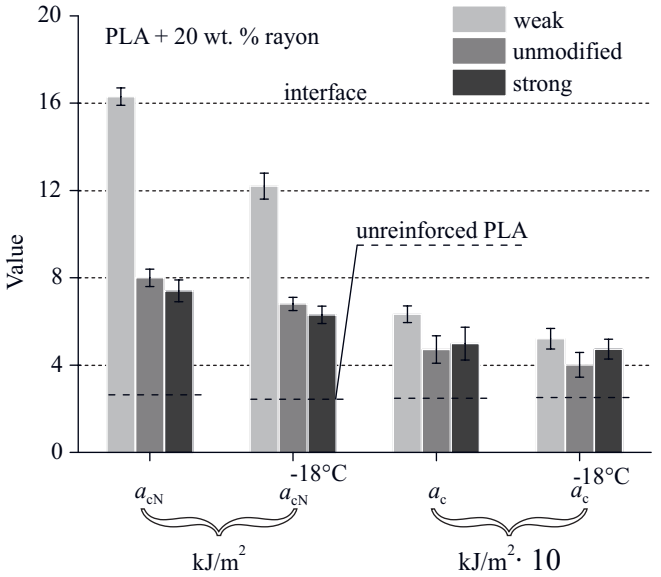


Fig. 6. Impact properties of PLA-rayon composites with tailored interphase

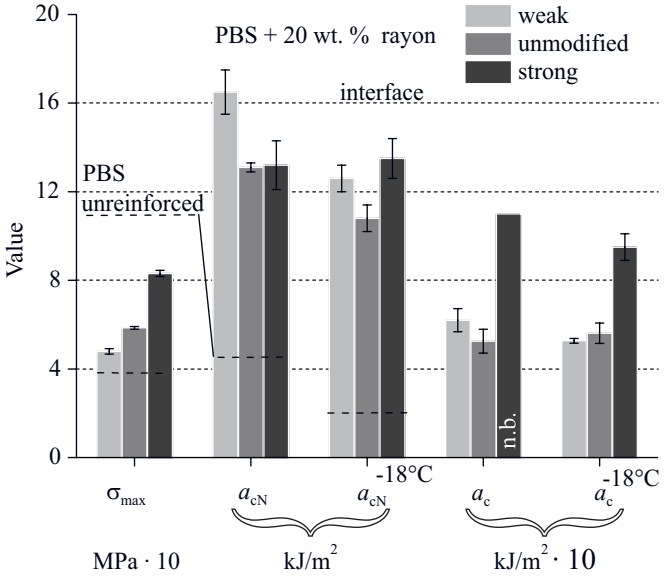


Fig. 7. Strength and impact properties for PBS-rayon composites with tailored interphase

A similar behavior is found for the composite strength of the (best performing) strong interphase systems as a function of the matrix strength, as depicted in Fig. 9.

While stiffness is easily increased by almost any filler material, such clear improvements in strength are less common especially in comparison to other cellulosic or lignocellulosic fibers [3].

Finally, rayon reinforcement in connection with weak interphases proves particularly useful for improving impact strength [23]. This is demonstrated in Fig. 10 where the composite notched Charpy impact strength is displayed vs. matrix modulus.

In comparison to the matrix values from Table 3 in particular the stiffer matrix materials experience substantial improvements: PLA is 6 times tougher, StPrAcLau

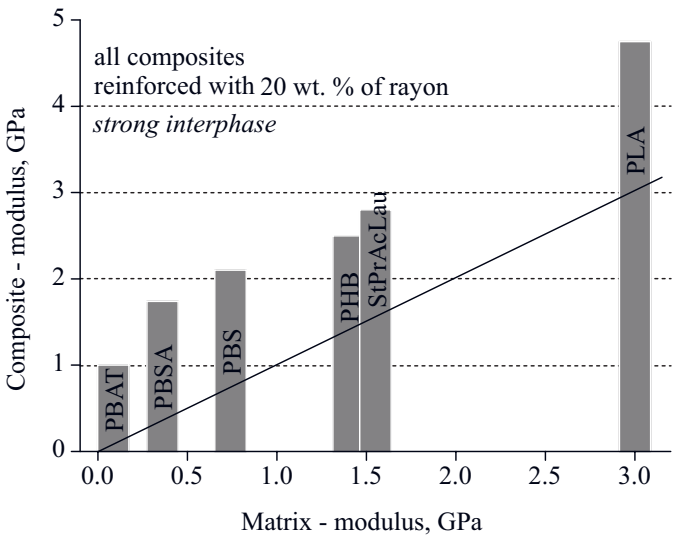


Fig. 8. Composite vs. matrix tensile modulus for biopolyesters

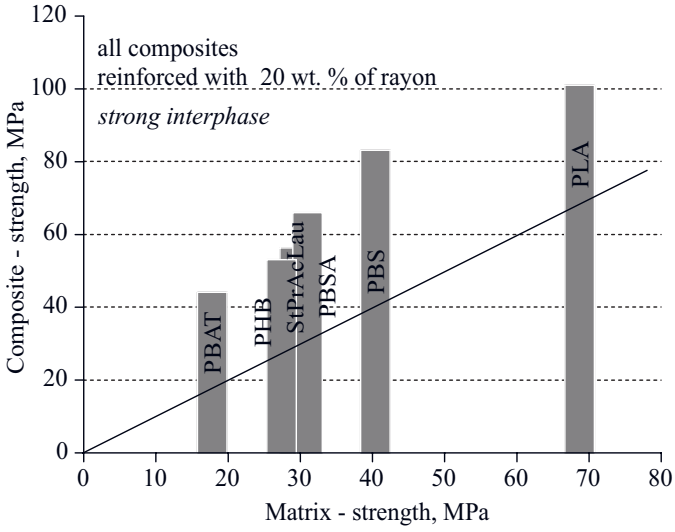


Fig. 9. Composite vs. matrix tensile strength for biopolyesters (strong interphase)

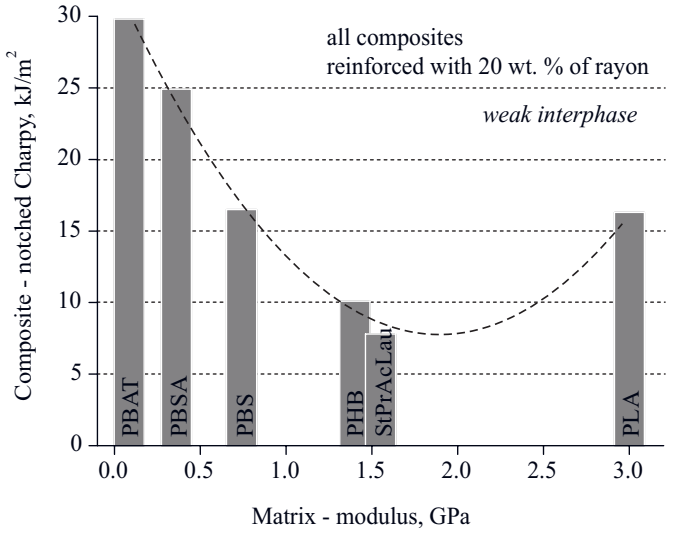


Fig. 10. Composite notched Charpy impact strength vs. matrix modulus for biopolyesters (weak interphase)

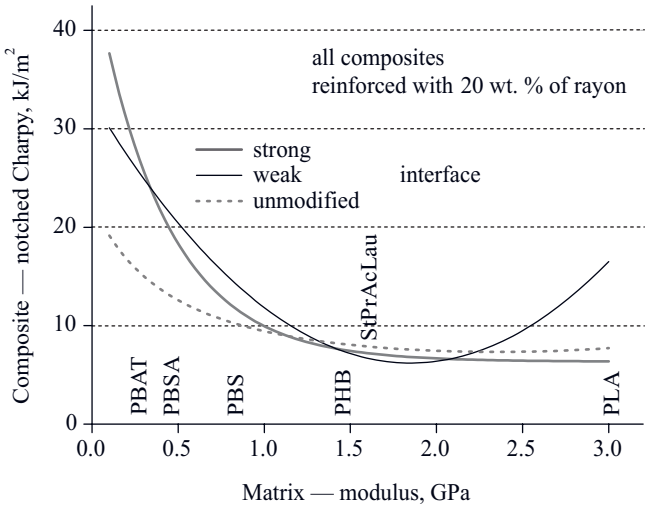


Fig. 11. Sketch of composite notched Charpy impact strength vs. matrix modulus for biopolyesters with varying interphase

even 14 times. Remarkable in this respect is the behavior of the notched impact strength for different interphase types as shown schematically in Fig. 11.

Below, say, 1500 MPa matrix modulus, *i.e.* the more flexible materials, both weak and strong interphase modification is advantageous. For the weak interphase the fiber pull-out mechanism mentioned earlier is activated, while for the strong interphase the movement of the matrix covered fibers acts likewise. This is not possible for a stiff matrix as PLA and only the pull-out of the bare fibers leads to the desired effect.

Fiber length distribution

Fiber length or more precisely, fiber length distribution plays an important role for the final composite properties. After removal of the PA 6.10 matrix by formic acid these distributions can be evaluated by optical microscopy of the remaining fibers. The two fiber length distributions shown in Fig. 12 represent two strongly different cases for a PA 6.10-rayon composite.

T a b l e 4. Characteristic values of fiber length distribution of PA 6.10 composites reinforced with 20 wt. % of rayon after different processing regimes

Processing	Fiber length, μm			
	by number average	median	by volume average	median
High shear	790	480	1620	290
Low shear	2040	1640	3300	1300
Without	~7000		~7000	

These distributions are generated by two different processing variants in the homogenization step of the two-step compounding. The distribution with the number average fiber length of 0.8 mm (Table 4) stems from the standard twin screw process with high shear and therefore severe fiber shortage. The other distribution with an average of 2 mm is obtained with low shear processing on a single screw extruder.

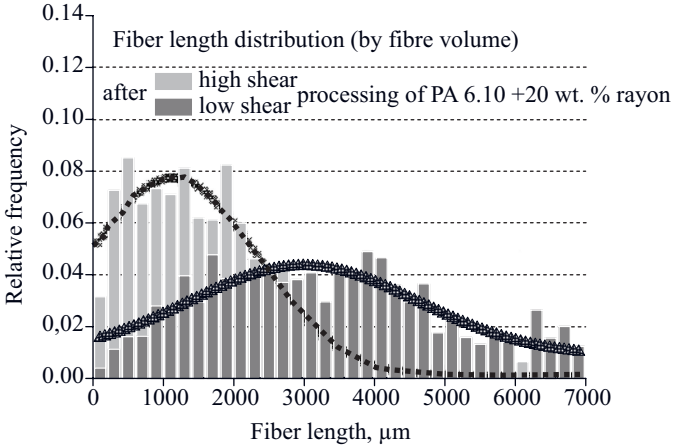


Fig. 12. Two strongly different fiber length distributions for PA 6.10-rayon composites

The implications for the mechanical properties are considerable as shown in Fig. 13. While the modulus stays the same and the tensile strength is only slightly enhanced, the impact properties display tremendous improvement. Unnotched Charpy strength at the room temperature is roughly doubled and notched impact strength increased almost five times. These results indicate that the average fiber length strongly influences the impact properties of the final composites.

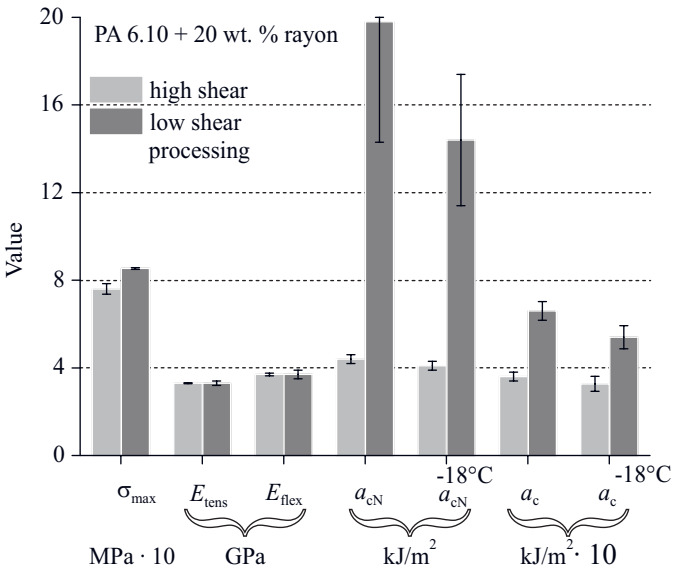


Fig. 13. Selected mechanical properties of PA 6.10-rayon composites with shorter and longer fibers

Fiber diameter

For a given amount of fiber, the surface area is inversely proportional to the fiber diameter. Thus for thinner fibers the fiber-matrix interaction will increase accordingly, an effect widely utilized in nano reinforcement. Moreover for thinner fibers the probability of fiber material defects is reduced (according to Weibull statistics) which generally results in improved mechanical fiber properties. For strongly coupled PP-rayon composites these effects have been investigated previously with fibers of varying diameter (titer) and similar modulus and strength but different elongation at break [13]. It turned out that composite modulus and strength increased for finer fibers, while elongation at break and impact properties decreased. The increase is in accord with the enhanced interaction and the decrease was attributed to the reduced elongation at break for the finer fibers.

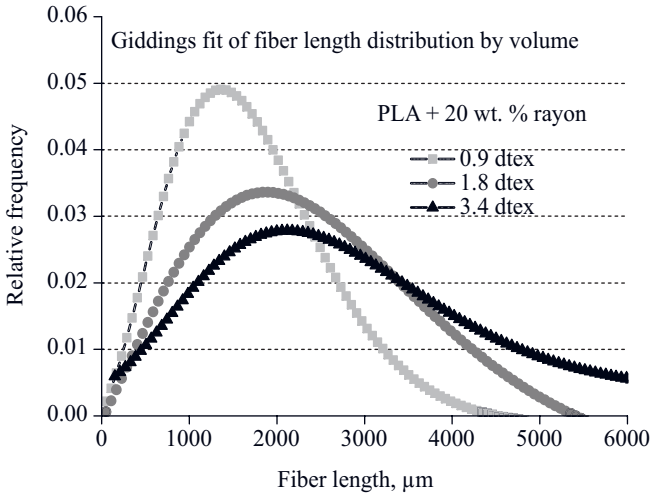


Fig. 14. Fiber length distribution for PLA composites reinforced with 20 wt. % of rayon fibers of varying titer after processing

However, a second effect must be taken into account which was investigated in more detail for PLA-rayon composites recently [24]. During compounding, fibers are shortened by the shear forces exerted by the mixing and kneading elements of the extruder in the homogenization step. In this process, finer fibers are more prone to breakage than thicker fibers as it is shown in Fig. 14 for three PLA-rayon composites. The titer of the fibers corresponds to 9 μm (0.9 dtex), 12 μm (1.8 dtex), and 17 μm (3.4 dtex). Fibers were extracted by the Soxhlet method using chloroform as the solvent.

Average fiber lengths and medians are presented in Table 5. Number averages range from 1.2 mm for the finest fiber to 1.9 mm for the thickest.

Irrespective of titer, all fibers have practically the same strength of 52 cN/tex or 780 MPa. However, the induced forces a single filament can withstand (as calculated from filament strength and titer) during compounding decrease from 17.6 cN for the thickest to 4.6 cN for the finest resulting in shorter average fiber length for the latter one.

T a b l e 5. Characteristic values of fiber length distribution of PLA composites reinforced with 20 wt. % of rayon fibers of varying titer after processing

Fiber titer (dtex)	Fiber length, μm			
	by number average	median	by volume average	median
0.9	1210	1080	1750	970
1.8	1660	1440	2260	1230
3.4	1910	1610	2760	1340
Initial fiber length	~7000			

Selected mechanical properties of the PLA composites with 20 wt. % fibers of the three titers are presented in Fig. 15.

Similarly to the PP case composite strength increases for finer fibers, while notched Charpy impact strength decreases. The behavior of unnotched impact strength is less distinct. It shows an optimum at the medium fiber diameter. Differently from the PP case, the modulus decreases and elongation at break increases.

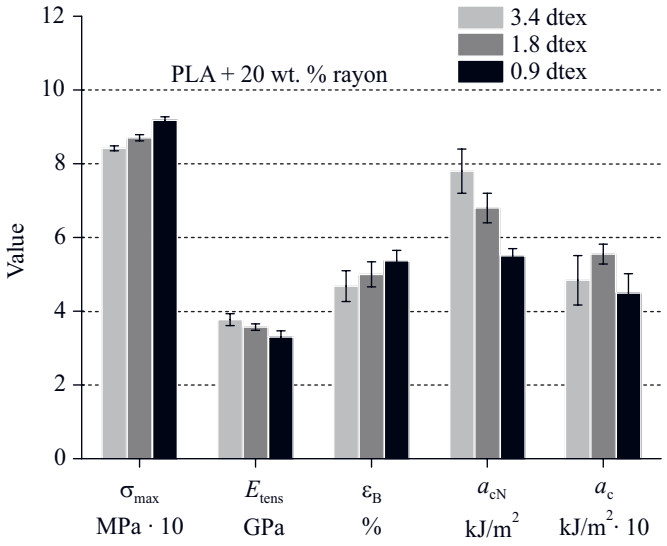


Fig. 15. Selected mechanical properties of PLA composites reinforced with 20 wt. % of rayon fibers of varying titer

Two contrary effects have to be taken into account: the enhanced fiber-matrix interaction for finer fibers and their shorter length compared to the thicker ones. The tremendous influence of the fiber length on impact properties has been proven explaining the improvements in notched impact strength for the thicker fibers here. For

the unnotched case the two contrary effects might influence on optimum for medium length fibers and medium interaction.

The reason for the increase in elongation and the decrease in modulus is not clear. It could be connected with differences in fiber orientation for this uncoupled system as compared to PP-rayon.

Other factors influencing the composite properties

As hinted at in the preceding paragraph, other factors like fiber orientation, homogeneity, fiber dispersion, flaws and voids but also thermal history influence the composite properties. Most of them are related to processing and can be controlled by appropriate techniques and handling.

Fibers have to be thoroughly dried before processing, in particular when combined with polyester matrices. An optimum has to be found between fiber dispersion and fiber length reduction during processing by an appropriate extruder screw design and processing regime. In this respect also matrix viscosity plays an important role in generating shear forces transferred to the fibers, which are higher for more viscous melts thus improving mixing efficiency. Matrix specific interactions, often caused by residual substances in the matrix, can lead to reduced properties and have to be eliminated by suitable chemical means. Moreover, differences in fiber and matrix polarities influence the wetting behavior during compounding and thus the mixing efficiency. High temperatures and residence times for processing and injection molding cause discoloration and for too high temperature or residence time, fiber damage with impacts on composite properties occurs. Even for intact composites the thermal history is important in terms of matrix crystallization. This is a well known effect for PLA which is amorphous after normal injection molding, yielding low heat distortion temperatures (*HDT*). Crystallized samples have much better *HDT*.

Fibers have been used without treatment before compounding in this study. Nevertheless, an appropriate surface or bulk treatment can offer additional possibilities for tailoring the composites. However, in doing so economic effects have to be taken into account.

CONCLUSIONS

The reinforcement of biobased and/or biodegradable matrix materials with man-made cellulose fibers, in particular rayon tire cord yarn, leads to remarkable improvements in mechanical properties. The cellulosic nature of the fiber retains the biobased and/or biodegradable nature of the matrix material in the final composite. In contrast to reinforcement with natural fibers, strength and especially impact properties benefit from the rayon reinforcement. Simultaneously, stiffness is improved in contrast to other techniques to improve toughness. Fiber-matrix interphases have been modified in the compounding process, and economic advantage over separate fiber treatment before processing.

First prototypes have been manufactured in cooperation with the automotive tier one supplier Faurecia Interior Systems, albeit with polypropylene as the matrix material. Constant efforts have been and are being made by the fiber producer Cordenka to introduce PLA- and PP-rayon composites into the market.

So far, some basic mechanical properties have been studied and a first, in some aspects detailed picture of this new class of short fiber reinforced materials has emerged and structure property relations have been elucidated. It has to be amended by investigations into long term behavior, including stability, biodegradation, the use of processing aids, flame retardants, color additives and recipe developments adapted to each specific application in question. These applications can be in the automotive sector, household appliances, toys, furniture industry or any other branch dealing with demanding injection molded parts.

For the man-made cellulose fiber producers, the foundations have been laid to enter a potential market, in particular in combination with biobased and/or biodegradable matrix materials. For the polymer producers a route has been opened up to widen their portfolio of biobased and/or biodegradable materials by reinforced types with improved mechanical properties.

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