Processing of Bioplastics
– a guideline –

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FNR
Fachagentur Nachwachsende Rohstoffe e.V.

Preface

For more than 20 years, the Federal Ministry of Food and Agriculture (BMEL) has been promoting, via its project co-ordination agency FNR (Fachagentur Nachwachsende Rohstoffe e. V.), the research and development of energy and products based on renewable raw materials.

Bioplastics have always been a major priority in this context. Their promotion has, however, never been closer to real practice than with the collaborative project "Kompetenznetzwerk zur Verarbeitung von Biokunststoffen" (Competence network for the processing of bioplastics), which has been supported financially by the BMEL since the beginning of 2013.

With the establishment of four regional centres of excellence for the material-related processing of bio-based polymers, research funding has left the laboratories and placed itself at the side of the user. The goal of the project is, on the one hand, to accelerate the transfer of know-how from research and development to the processors of bioplastics and, on the other hand, to address and resolve the suggestions, questions and problems of, in particular, the many medium-sized companies who genuinely want to pursue innovative approaches. In the past three years, the four alliance partners have moved much closer to this goal.

An important result of this work is the brochure which you are holding in your hands today. The brochure provides an overview of the data compiled over the last three years concerning the processing of bioplastics. The brochure primarily represents a showcase which will encourage you to look deeper, as the specific technical data concerning the materials and the processing can be found on the Internet in the corresponding database. The brochure and the database are important building blocks which facilitate the way forward for bioplastics on the market; above all, they are intended to show you new and innovative approaches for a transition towards a bio-based economy.

The collaborative project will continue to be funded until 31.01.2018. Should you have any questions regarding the processing and application of bioplastics, please do not hesitate to contact the consortium partners.

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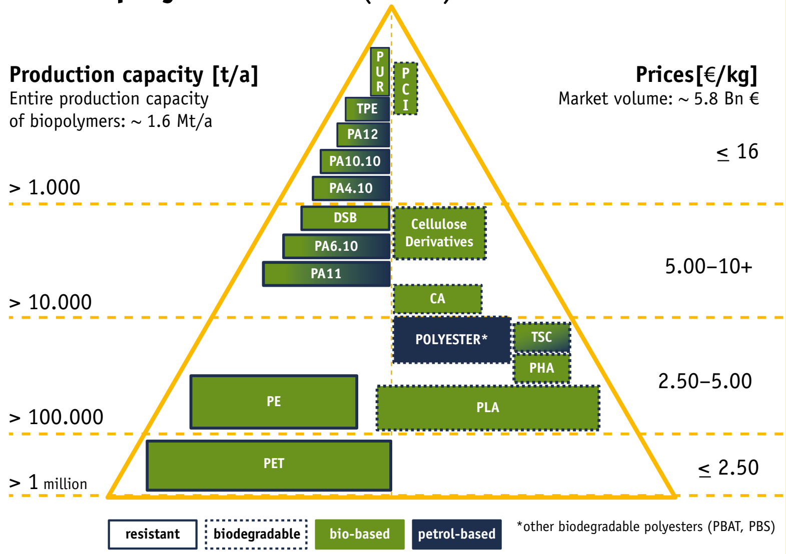
Bioplastics – chances and possibilities

Bioplastics

Everyday life without plastics is inconceivable today. In almost all areas of life, such as medical applications, packaging, office items, toys, sports equipment and household articles through to technical applications, for example in the automotive industry, they have proved effective and established themselves everywhere. However, most plastics are based on a finite resource – crude oil. The consumption of crude oil is significantly higher than its regeneration, which inevitably means that this raw material will no longer be available at some point. Bio-based plastics offer an alternative here. Furthermore, consumers are becoming more environmentally-conscious in their consumer behaviour, which means that sustainable bio-based materials are being increasingly implemented in place of conventional plastics.

In order for this to succeed, the plastics industry must provide information which enables the uncomplicated application and trouble-free processing of these bio-based plastics.

The biopolymer market (2014)



CA – cellulose acetates
PE – biopolyethylene
PHA – polyhydroxyalkanoates
DSB – resistant starch blends
PA – biopolyamides
PET – biopolyethylene terephthalate
PLA – polylactide
PUR – biopolyurethane
TPE – biothermoplastic elastomers
TSC – thermoplastic starch-composite materials

Source: IfBB

This is where the project for the processing of bioplastics, funded by the Federal Ministry of Food and Agriculture with project management by the FNR, comes in.

The motivation of the project partners for this collaborative project is the closure of the gaps in the information concerning the processing of bioplastics. Non-existent material data sheets or inadequate processing-relevant information impede the industrial processing of bioplastics and lead to non-optimal product results. Here, the project provides a remedy through the work of the alliance partners by determining and graphically representing this missing data, which is de facto helpful for the industry as concerns processing.

In principle, the range of available bioplastics can already cover many fields of application today.

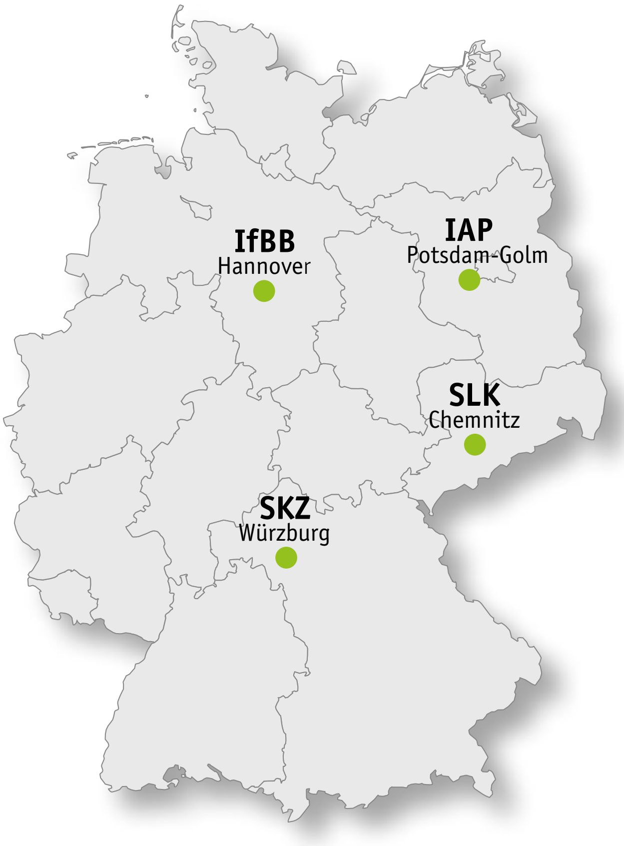
In practice, however, processing problems often still arise, even if only small information gaps are apparent. In order to facilitate the transition from a petrochemical material to a suitable bioplastic, these gaps must be closed and the relevant information for the processors must be made available in an easily-accessible form. This is the purpose of the project, as only then can the market penetration of bioplastics be significantly increased.

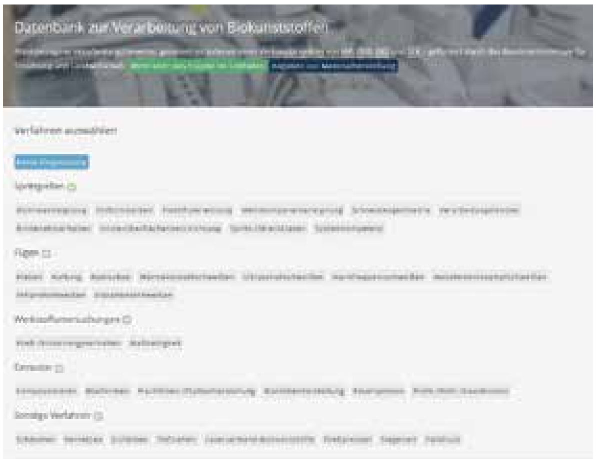
In summary, the following applies: the market volume of biopolymers is still low. Predictable production volumes on the part of the material manufacturers contribute to more consistent and, with increasing material quantities, declining prices. In order for bioplastics to play a significant role in the bio-economy process of the federal government and society, it must be ensured that the processing procedures are simple to implement in practice.

Close co-operation between practitioners and researchers is the prerequisite for this point: questions arising through practice were closely examined by the alliance partners and subsequently processed in such a way that each practitioner is able to use them as support in the processing area. Within the framework of the project, marketable materials such as PLA, PLLA, Bio-PE and PBT were therefore deployed. The detailed breakdown of the individual materials can be obtained from our processing database and excerpts will be referred to in the respective following chapters.

For the collaboration between the industry and the project partners, attention was initially focussed on the regional affiliation of the industrial partner. Furthermore, however, a close co-operation took place between the partners as regards processing-relevant issues and knowledge-sharing.

Ultimately, the results of this project have flowed into a database that quickly and easily demonstrates which processing-relevant measures must be observed for which procedure.





The brochure contains important basic instructions and information on many of the relevant processing methods and the potentially suitable bioplastics. It also provides an initial exemplary impression of what the database offers in a detailed presentation of results.

Should you have any questions, please do not hesitate to contact one of the partners.
(See addresses on the back of the brochure.)

The results database

The extensive experimental data, containing in excess of 12.000 data sets on marketable bioplastics from the four project partners, is clearly arranged and freely accessible on the Internet. The database offers the user the possibility of addressing the processing of bioplastics from a material-technological or procedural point of view. In the first case, the processor is familiar with his conventional material and embarks on a search for a bioplastic which fulfils his demands as regards the material and through which his conventional plastic can be replaced. In the second case, the processing procedure is predetermined for the practitioner and he seeks a suitable bioplastic for this process variant.

For a swift orientation, the first evaluations are carried out for database users by means of a traffic light system. Once the database user has used this to make a pre-selection, he can then delve deeper into the subject by calling up the data determined during the project. In the form of reports, data can be transferred by the user to his own machine.

Derived from the thematic focus of the project, the widely-varying processing characteristics such as, for example, the blow-mould suitability or the deformation behaviour in injection moulding, are covered. The data is founded on both scientific laboratory experiments and test setups in practice. It serves the user as a guideline in the processing of bioplastics and will be further supplemented.

www.biokunststoffe-verarbeiten.de

Compounding

– constitutes, following the production of the base polymer, the first preparation process for the refining and modification of plastics by means of extrusion. Through preparation, the characteristics profile of the plastics can be selectively altered and thus adapted to the subsequent process and the desired product characteristics. For this, the plastic is melted in the extruder, whereby it is mixed with additives, fillers, reinforcing materials or a combination thereof. After homogenisation and degassing of the compound, it is formed – usually as strands – using a tool, then cooled and processed into plastic granules.

Materials

The bioplastics examined in the section Compounding are the material classes named in Table 1. At this point, no type-specific naming of the applied bioplastics will be made. The results shown below are intended as general processing guidelines in accordance with the material class and were determined using a wide basis of data.

Table 1: Overview of the materials examined in the section Compounding

Material class	Type
CA	cellulose acetate
PA	polyamide
PBS	polybutylene succinate
PBS blend	polybutylene succinate blend
PE	polyethylene
PHBV	polyhydroxybutyrate-cohydroxyvaleriate
PLA	polylactic acid
PLA blend	polylactic acid blend
PLLA	poly(L-lactic acid)
TPS	thermoplastic starch
TPS blend	thermoplastic starch belnd

In the compounding process, numerous influencing factors arise before and during processing. Depending on the type of plastic, these factors are evident to varying degrees and affect the mechanical, thermal, (chemical) and rheological properties. The following results are therefore to be understood as an orientation and decision-making guide. In the case of information being provided by the material manufacturer, it is recommended that this processing data is used. However, as this is often not yet the case for bioplastics, basic instructions for processing-relevant points for common bioplastics are listed in Table 2.

Table 2:
Process window and processing instructions for bioplastics

Material	Processing instructions	processing temperature range[°C]	drying time	drying temperature [°C]	max. moisture [%]
CA	• Start of depolymerisation at T > 230 °C (vinegar odour, smoke formation) • Moisture > 0.15 % → foaming • Moisture < 0.15 % → flowability sinks	160–230	2–4 h	60	< 0.15
PA	• Pre-drying in closed extruder necessary • The processing temperature should be chosen depending on the type used • Rule of thumb: The higher the type number, the lower the processing temperature. Example: The processing temperature for PA 11 is 180 °C, whereas for PA 4.10 it is approx. 250 °C • Partially crystalline Bio-PA → drying after extrusion in the crystalliser	200–208	4–6 h	80	< 0.05
PBS	No data available				
PBS blend	No general statement, as high number of combinations possible				
PE	• Extrusion-technical processing identical with petrol-based PE • The processing temperature should be chosen depending on the type used	150–190	3–4 h	90	–
PHBV	• Storage in a cool (T < 50 °C) place at low humidity • Pre-drying necessary → hydrolytic degradation • Light thermal decomposition → small processing window • At T < 190 °C thermal damage • Adjustment of housing temperature to processing temperature • High heat storage capacity → under-water granulation • After extrusion → drying in crystalliser	130–180	2 h	100	< 0.025
PLA	• Pre-drying necessary → hydrolytic degradation • At humidity > 0.025 % H20 influence of hydrolysis increases; the material becomes more flowable through chain degradation (low viscosity) • Smaller fusing range • Sharply-defined fusing zone • Tiered temperature profile → Fast + gentle fusing (good for fibre incorporation) • After extrusion → drying in crystalliser	180–200	6 h	80	–
PLA blend	• No general statement, as high number of combinations possible • Dependent on miscibility, a relatively sharply-defined mixing zone should be chosen				
PLLA	• Processing comparable with PLA	190–220	6 h	80	< 0.025
TPS	No data available				
TPS blend	• No general statement, as high number of combinations possible • TPS proportion leads to hydroscopic properties (moisture absorption)				

Material pre-drying compared to process degassing in the compounder

Similar to the conventional plastic PET, bioplastics also contain materials for which special attention must be paid to their residual moisture content, as they tend to absorb moisture (they are hydrophilic). In order to be able to process these materials by means of compounding, two different methods are generally available:

- material pre-drying in terms of the drying of solid matter using appropriate drying equipment and
- process degassing during the compounding procedure.

Investigations into the drying influence itself are very extensive for bioplastics susceptible to hydrolysis. The following table therefore uses the bioplastic type PLA (Ingeo 3251D from the company NatureWorks) to provide an exemplary presentation as to the extent to which pre-drying of the material is necessary for subsequent processes and how effective the process degassing in the compounder can be. For the investigation, a portion of the material („EXTR dry") is dried for 16 hours at 80 °C prior to extrusion. The other part („EXTR wet") is processed undried (prior storage under standard atmospheric conditions at 23 °C and 50 % r.h.).

Table 3: Conditioning of Ingeo 3251D prior to extrusion and rheometric measurement

Designation	Conditioning prior to extrusion	Conditioning prior to rheometric measurement	water content prior to rheometric measurement [%]
EXTR dry (80 °C)	Dried 16 h, 80 °C	Dried 16 h, 80 °C	0.0182
EXTR dry (23 °C, 50 % r.h.)	Dried 16 h, 80 °C	storage at 23 °C, 50 % r.h.	0.3517
EXTR wet (80 °C)	storage at 23 °C, 50 % r.h.	Dried 16 h, 80 °C	0.0187
EXTR wet (23 °C, 50 % r.h.)	storage at 23 °C, 50 % r.h.	storage at 23 °C, 50 % r.h.	0.3482

The result of the investigation was that the water content of the examined PLA prior to processing has no significant influence on the process and the resulting material quality if the contained water can be discharged at an early stage via appropriate degassing zones during the preparation. The hydrolysis and the consequent degradation of the polymer chains is thereby reduced and, under optimum processing conditions, prevented almost entirely.

Summary

Compared to conventional plastics, drying prior to processing is recommended more often for bioplastics. Investigations during the project have, however, shown that for hydrophilic bioplastics, appropriate process adjustments and suitable degassing during compounding often eradicate the need for pre-drying. Unfortunately, manufacturer's instructions for processing are not always available. If, however, the processing recommendations (if available) are adhered to, the examined bioplastics can be processed like comparable conventional plastics. In order to reduce the information deficit, the project results serve as a support aid.

Additional and detailed results can be found in the online database for this joint project at:
www.biokunststoffe-verarbeiten.de

Injection moulding

– is the most frequently-used processing procedure for plastics. Extremely small components through to large plastic mouldings can be inexpensively manufactured in large quantities for direct usage. The plastic is thereby melted in the injection moulding machine and injected under high pressure into a injection mould. Factors which affect the manufacturing process – and thus the workability and quality of the materials and products – are shown in the following figure. Within the framework of the project, the listed influencing factors for the bioplastics were examined.

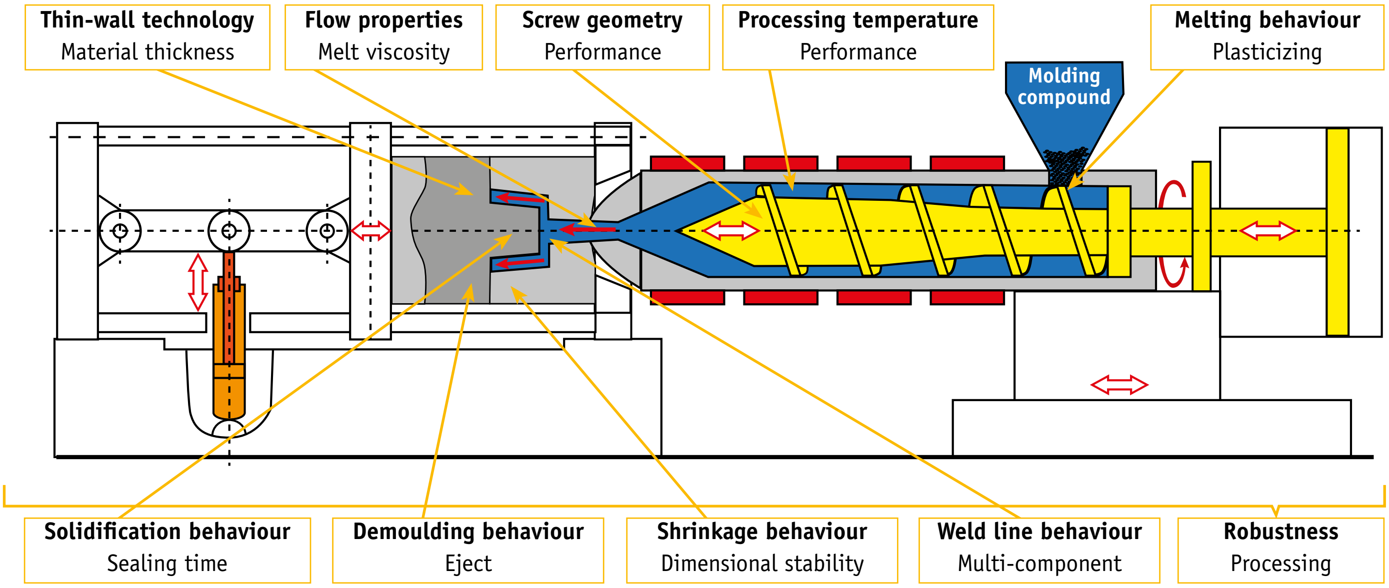


Figure 1: Factors which affect the injection moulding process

Materials

The bioplastics examined in the section Injection moulding are commercially-available bioplastics with appropriate market relevance. The examined materials are listed in Table 1.

Table 1: Overview of the materials examined in the section Injection moulding

Material class	Manufacturer	Type
PLA	NatureWorks	Ingeo 3251D
PLA	NatureWorks	Ingeo 6202D
PLA	NatureWorks	Ingeo 3052D
PLLA	Zhejiang Hisun Biomaterials	Revode 190
PBS	Showa Denko	Bionolle 1020MD
Bio-PA 6	Evonik	Vestamid Terra HS16
Bio-PE compound	Jelu	WPC Bio PE H50-500-20
PLA compound	Jelu	WPC Bio PLA H60-500-14
PHB	Metabolix	Mirel P1004
Bio-PE	FKuR	Terralene HD 3505

Plasticising capacity

At the beginning of each injection moulding cycle, the material feed for the following material entry is in the machine and is influenced by granule size and geometry. As regards the plasticising capability, the mass temperature and the viscosity have a significant influence on the achievable cycle time and should therefore occur within the residual cooling time of the previous moulding.

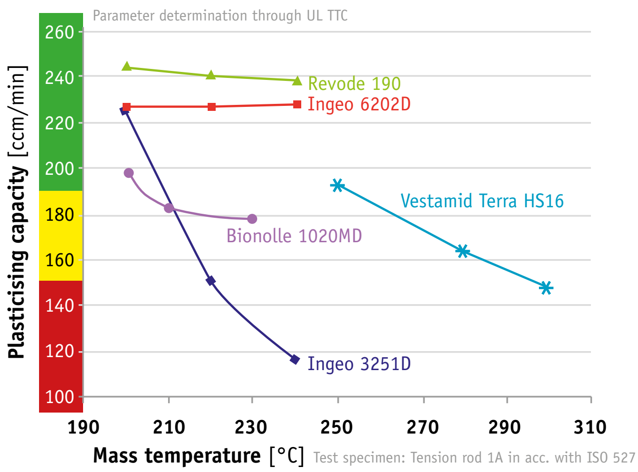


Figure 2: Plasticising capacity of bioplastics

A slow material feed causes process delays and leads to uneconomical production costs. The bioplastics examined here exhibit, compared to established conventional petrochemical plastics, a good-to-sufficient plasticising capacity. It must, however, be noted that the process temperatures play a decisive role in optimal processing. The plasticising capacity depending on the mass temperature as well as the temperature recommendations determined through DSC analysis (Differential Scanning Calorimeter) for the investigated materials are shown here. As a rough guide, the processing temperature is approx. 30-40 °C above the melting temperature and the cavity temperature is approx. 30 °C below the glass transition temperature T_G.

Dimensional stability

Once the sealing time is completed, the cooled part is ejected from the cavity. Due to material and tooling reasons, demoulding problems can hereby arise which can generally be rectified with a material-appropriate cavity and, on the part of the material, with the help of demoulding additives. An important aspect which must be observed when changing from a conventional plastic to a bioplastic – this also applies when changing to a different petroleum-based plastic – is the different shrinkage characteristics of the various materials. The component shrinkage allows significant statements to be made concerning the compatibility of the selected material with the existing cavity and as to whether component distortion must be expected. If the material which is to be substituted exhibits strongly-differing shrinkage behaviour, this usually leads to processing problems and requires a corresponding adjustment of the cavity. It is therefore not possible to make the sweeping statement that a slight shrinkage is „good" and a large shrinkage is „bad". As a general rule, if the cavity cannot be constructed to suit the material, the bioplastic should exhibit a similar shrinkage behaviour to that of the petrochemical material which is to be substituted. In addition, with bioplastics – as with conventional plastics – widely-differing shrinkage properties along and across the direction of flow lead to component distortion. The examined bioplastics shown in Table 1 exhibit an isotropic, i.e. similar shrinkage behaviour along and across the direction of flow. The risk of distortion is therefore slight.

Demoulding behaviour

The final step of each injection moulding cycle is the demoulding of the moulded part from the cavity.

Via actuators (pins, plates etc.), the moulding is thereby released from the mould wall and ejected from the cavity or taken over by a handling system. In order to ensure a secure production process, it is important that the demoulding is executed smoothly and that no moulded parts remain in the cavity after ejection. The forces which thereby act upon the ejector are dependent on the shrinkage, the coefficient of friction between the injection moulding and the cavity wall as well as the stiffness of the material. As a rule, draft angles and shrinkage dimensions for an injection mould are conceived for one plastic. If other plastics are used which have a different shrinkage behaviour, demoulding problems are often the result. As existing cavity are often initially used for the purpose of mould-proving for bioplastics, problems during demoulding are not uncommon. Due to increasing demoulding forces, ejection pins can, for example, pierce thin parts or be pressed too deeply into the surface. In the course of the research project, different demoulding agents were used in order to reduce resultant demoulding forces. These agents were incorporated into the PLA through tumbling and compounding. The demoulding forces arising in the testing tool could be significantly reduced, depending on the demoulding agent. Particularly the demoulding agents based on N,N'-ethylenbis (stearamid) showed very good results. Furthermore, the demoulding behaviour of PHB, Bio-PE, PLA and Bio-PA was examined.

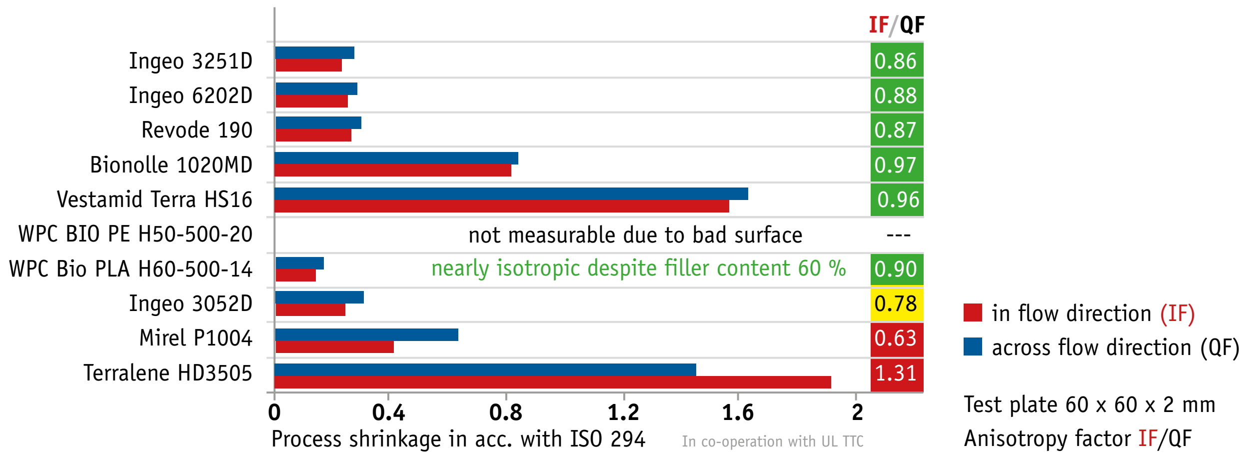


Figure 3: Shrinkage and distortion of bioplastics

Table 2: Temperature recommendations for processing
(Method: DSC/test device: Mettler DSC822e/Standard: IEC 1006)

Type	T_G [°C]	T_S [°C]	Recommendation $T_{Processing}$ [°C]	Recommendation T_{Cavity} [°C]
Ingeo 3251D	59	164	200	**30**
Ingeo 6202D	59	166	200	**30**
Revode 190	58	174	200	**30**
Bionolle 1020MD	44	113	180	**30**
Vestamid Terra HS16	119	223	250	**80**

Once the material has been plasticised and brought to the correct processing temperature, the injection process takes place. The rheological properties (flow properties) of the examined bioplastics are thereby comparable to those of petroleum-based plastics. Once the injection process has been completed, the cooling process of the material begins in the cavity, which can be described by means of the sealing time („solidification time“). The sealing time is strongly dependent on the present mass temperature and the solidification behaviour of the material itself and has, as does the plasticising capacity, a significant influence on the achievable cycle times.

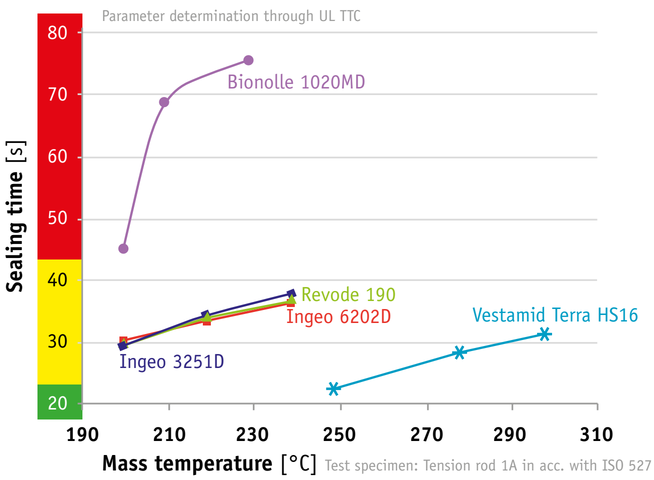


Figure 4: Sealing times for bioplastics

With the exception of PBS, the examined bioplastics lie within a range which can be evaluated as acceptable. The examined bioplastics achieve results which are only slightly worse than the average of the established bulk plastics.

Systems expertise

A holistic view of the injection moulding process shows that for the bio-based polyesters such as PLA and PHB, a high residual moisture in the material during processing in the injection moulding machine has the greatest effect on the mechanical and rheological behaviour. The increasing melt index and the decreasing mechanical values during the processing of moist material can be attributed to the molecular weight degradation through hydrolysis. The parameters of peripheral screw speed, screw advance speed, dynamic pressure, injection temperature, cavity temperature and cooling time, however, demonstrate no significant effect; a shear and temperature-insensitive behaviour for PLA can therefore be presumed. Solely the PHB exhibited measurable effects on the flow behaviour from a processing temperature of 200 °C and is therefore slightly more sensitive than PLA as regards higher processing temperatures. Hot runner processing is also possible.

Multi-component injection moulding

This is a method which is being increasingly applied due to the growing complexity of technical plastic mouldings. The suitability of bioplastics has not yet been examined within this process. As part of the research project, an experimental arrangement was developed for so-called “hard/hard” composites and a compatibility matrix for the application of bioplastics in multi-component injection moulding was thereby compiled. Furthermore, relevant influencing parameters (e.g. cavity temperature, melt temperature) were determined on the bond strength of bio-based 2-component mouldings. As an example, the bio-based polyesters PLA and PHB as well as the cellulose esters are cohesively combinable in multi-component parts. Based on this, the application of bioplastics in sandwich injection moulding was tested. Prior to this, the methods of chemical and physical foaming were examined with specific regard to the processing characteristics of bio-based polyesters.

Weld seam problems

Due to the increasingly complex designs of technical components and their manufacturing processes, this subject should not be neglected.

The trend towards the integration of different manufacturing procedures in one single complex manufacturing process remains unaltered. The back injection of organic sheets which have been previously formed in the same injection moulding tool is a well-known example. A result of this is that the flow paths of the plastic are increasingly more branched and progressively more weld seams are created in the structural components which significantly influence the mechanical properties. In addition, weld seams impair the appearance when they occur in a visible area.

Through adjustment of the process parameters, it could be demonstrated that the weld seam formation with bio-based plastics – just like petroleum-based plastics – can be positively influenced and that the same measures lead here to success.

Inline surface coating

With this method, thermoplastic carrier materials are coated with scratch-resistant polyurethane paints during an injection moulding process. The procedure is applied in order to manufacture high-gloss, scratch-resistant components in the visible range. Until now, bioplastics have not been used as a carrier material for polyurethane coatings. Within this research project, comprehensive system competence in the inline surface coating process during the processing of bioplastics was acquired, during which the suitability of different bioplastics as carrier material for polyurethane coating systems was investigated. The compatibility of different bio-based thermoplastics with these coatings was quantified through examination of the surface soundness. In addition, microscopic investigation of the interface between the carrier material and the coating layer was carried out. Polylactic acid (PLA), polyhydroxybutyrate (PHB) and diverse cellulose esters proved to be suitable carrier materials for the polyurethane coating.

Summary

The investigated bioplastics are commercially available and, as regards the field of injection moulding, mostly exhibit processing characteristics which are comparable with their petroleum-based counterparts. It is important that the cavity design and the processing properties of the new material are compatible with the petroleum-based predecessors. Crucial for the optimal processing of bioplastics is also the choice of the correct process parameters (particularly temperature), as some bioplastics have a slightly smaller process window. The reason for this is the more sensitive reaction to thermal loading compared to conventional plastics. During the further investigations into machinability and in relation to the use of a standard screw, the investigated bioplastics demonstrated good workability. Only a few materials require the use of special screw geometries. From a processing point of view, bioplastics provide an interesting alternative to petroleum-based plastics in injection moulding and have the potential to substitute these. The process and cavity parameters need only to be adapted to the bioplastic as a new material – exactly the same as when changing from one petrochemical polymer material to another petrochemical polymer material.

Additional and detailed results can be found
in the online database for this joint project at:
www.biokunststoffe-verarbeiten.de

Multi-component injection moulding

– Composites from thermoplastic elastomers (TPE) and hard thermoplastics are everywhere. Their application can be found in particular in areas where a soft-touch effect, grip or protection against slipping are necessary. For components which are in contact with liquids or moisture, TPEs are frequently used in seals in order to inject seal geometries directly in one manufacturing step. Furthermore, the progressive material development and optimisation of TPEs enables their increasing use in other application areas such as, for example, vibration and damping elements, which were previously reserved for cross-linked elastomers.

For all these applications, an application-specific, sufficient adhesion between the hard and soft components is necessary. The adhesion formed between the contact partners and the properties exhibited by a composite cannot generally be adequately estimated in advance due to a number of potentially effective adhesion mechanisms. A reproducible and absolutely comparable method for determining the composite properties is therefore of great importance in both the field of material development and the selection of material combinations for serial processes/products.

Materials

The bioplastics investigated within the course of this work are commercially-available bioplastics with appropriate market relevance. The materials investigated are listed in Table 1.

Table 1: Overview of the hard components examined in the section Multi-component injection moulding

Material class	Manufacturer	Type
PLA	NatureWorks	Ingeo 3251D
PLA	FKuR	Bio-Flex S 9533
PHB	Metabolix	Mirel P1004
PLA	Tecnaro	Arboblend 2628V
Lignin	Tecnaro	Arboblend LV100
PLA	RTP	RTP 2099 X 124790 E
CA	Albis	Cellidor B500-10
CP	Albis	Cellidor CP 400-10
PA 1010 (100 % bio-based)	Evonik	Vestamid Terra DS16
PA 410 (bio-based)	DSM	EcoPaXX
PE (bio-based)	Braskem	Green PE SHC7260

Table 2: Overview of the soft components examined in the section Multi-component injection moulding

Material class	Type
TPE-S 01	TPE-S, modified for PC/ABS adhesion
TPE-S 02	TPE-S, modified for PLA/CP/CA adhesion
TPE-S 03	TPE-S, modified for PA10/10-4/10 adhesion
TPE-V	TPE-V, modified for PC/ABS adhesion
TPE-E	TPE-E, standard type
TPE-E 01	TPE-E, partly bio-based
TPE-E 02	TPE-E, partly bio-based
TPE-U	TPE-U, partly bio-based
Bio-TPE 01	Bio-based TPE, polar
Bio-TPE 02	Bio-based TPE, non-polar

Investigation

The evaluation of the workability and compatibility of the applied plastics combinations was made possible by means of a 2-component peel test specimen which was developed, together with the corresponding injection moulding tool, specially for such issues. For the testing method, a peel test with carriage guide was implemented which, in addition to the measurement of the elongation-superimposed peeling force (crosshead travel of the tensile testing machine), additionally recorded the actual peel path (slide path).

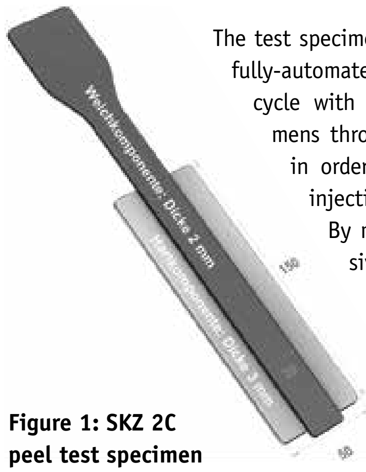


Figure 1: SKZ 2C peel test specimen

The test specimens were produced in a fully-automated injection moulding cycle with removal of the specimens through a handling device in order to ensure a constant injection moulding process. By means of a comprehensive in-tool sensor technology and an inline thermographic system, high process stability and reproducibility could be ensured.

In addition to components from a 2C cycle and the overmoulding of separately-produced „cooled hard parts“, tests with variothermic tempering for influencing the adhesion of the bond were also an integral part of the injection moulding work. The determination of the characteristic values was carried out after 24 hours and after 240 hours of storage under standard conditions and after warm storage of the specimens, in order to evaluate the long-term behaviour of the produced bondings.

Table 3 shows an excerpt from the results after 24 hours of storage.

Table 3: Excerpt of tested hard/soft combinations after 24-hour storage

Hard components		Soft components									
Commercial name	**Type**	**TPE-S 01**	**TPE-S 02**	**TPE-S 03**	**TPE-V**	**TPE-E 01**	**TPE-E 02**	**TPE-E 03**	**TPE-U**	**Bio-TPE 01**	**Bio-TPE 02**
		TPE-S hfmod. PC, ABS	TPE-S hfmod. PLA, CA, CP	TPE-S hfmod. PA10/10 & 4/10	TPE-V hfmod. PC, ABS	TPE-E	TPE-E partly bio-based	TPE-E partly bio-based	TPE-U partly bio-based	bio-based polar	bio-based non-polar
Ingeo 3251D	PLA										
Mirel P1004	PHB										
Arboblend 2628V	PLA-based										
Arboform L V100	Lignin-based										
Bio-Flex S 9533	PLA-blend										
Vestamid Terra DS16	Bio-PA 10/10										
RTP 2099 X 124790-E	PLA + talcum										
Cellidor B 500-10	cellulose acetate butyrate										
Cellidor CP 400-10	cellulose propionate										
EcoPaXX	Bio-PA 4/10										
Braskem SHC7260	Bio-PE										
Arboblend 2649VB	Bio-X, non-polar										

- < 10 N no adhesion
- 10–20 N poor adhesion
- 20–60 N good adhesion
- > 60 N very good adhesion

Summary

To date, several hundred conventional material combinations and test series have been successfully produced and tested at the SKZ within the framework of research and industrial projects. The work within the FNR project included more than 80 further pairs of materials in which at least one bioplastic per combination was deployed. The results show that there are already a large number of possible hard/soft combinations with bio-based plastics and that these, as regards their (adhesion) characteristics, exhibit similar behaviour to that of composites formed from conventional, freely-available thermoplastic/TPE combinations.

A great advantage in the evaluation of the measured peel force/path curves proved to be the measurement of the slide path (actual peeling path), with which the work could be carried out much more efficiently and more accurately than with the crosshead travel. In particular, the comparability of very different material combinations (e.g. with strongly-differing strength levels and/or strains) is provided by the slide path measurement. A further advantage is the possible direct local allocation of adhesion alterations/effects along the overmoulded area.

Of particular interest are the results for the partly bio-based soft components TPE-U and TPE-E. TPE-U, which is based on succinic acid, exhibited very good adhesion on all materials. With conventional TPE-U types, this strength is not – or only with difficulty – achievable. In contrast, no adhesion was achievable with the investigated TPE-E-types which, like the PLAs, belong to the polyester group.

Variotherm tempering of tools or tool sections, which can be applied for the moulding of microstructures, for improving the surface finish of foamed or fibre-reinforced components and for improving weld lines, is also suitable for increasing the bond strength of multi-component parts. Depending on the material combination, a significant improvement can be thereby realised.
Further studies on the workability and the (performance) characteristics showed that the bio-based polymers available on the market provide a meaningful alternative for future products. These materials are now in the third and fourth development generation; earlier restrictions, such as the shear sensitivity, thermal damage (retention time), flowability and demouldability, no longer pose a problem. Similarly, the material prices – particularly for PLA-based materials – have now stabilized at a competitive level, with a further downward trend.

Foaming

– of plastics is a processing method which is used in order to reduce the material weight and/or the density. Furthermore, foam structures exhibit insulating properties. With foaming, a propellant is added to the plastic during processing, which results in the material/component having a specific, two-phase foam structure. As bio-based plastics have, to a certain extent, a higher density than petroleum-based plastics, it would be logical to exploit density-reducing possibilities in order to develop improved properties. For the project, a theoretical consideration of the foamability of bioplastics was conducted. The process-technical features and difficulties regarding the foaming of bioplastics are primarily mentioned here, which is the reason why specific bioplastic types are not addressed.

Possibilities and requirements for biopolymers

Fundamentally, biopolymers on the basis of renewable raw materials can also be processed in a foaming procedure through the targeted use of functional additives. The thereby achievable foam depends on the minimum attainable density and quality of the biomaterial. For the foaming of (bio-) polymers, the following guidelines apply:

- The more molecular branches a material exhibits, the better it can be foamed. In this regard, the melt strength of the material plays an important role.
- If the material exhibits a high degree of crystallinity, its processing window is reduced. Foam generation in crystalline areas is impossible.

As for biofoam, compared to petroleum-based counterparts, largely identical – or at least very similar – characteristics profiles are necessary, no significant mechanical engineering enhancements must be made to the plant technology. The optimization scope includes solely formulation adjustments and the influence of relevant process parameters such as temperature and pressure.

Hydrolytic effect of chemical propellants on biopolymers

Whilst for physical foaming largely „pure“ propellants are applied and their reaction to the polymer melt can be theoretically determined, this is probably far more difficult with the application of chemical propellants. In addition to the active propellant gas, the decomposition reaction of chemical propellants also leaves behind decomposition residues such as NH_3 or H_20, which have a negative effect on the polymer matrix which is to be foamed. A deterioration in characteristics can be due to the chemical reaction between the polymer and the decomposition products or to the composition of the chemical propellant. The chemical propellant would accordingly contain carrier materials; this is unproblematic as regards petrochemical polymers but would, however, definitely have a negative effect on biopolymers.

Degassing and pre-drying

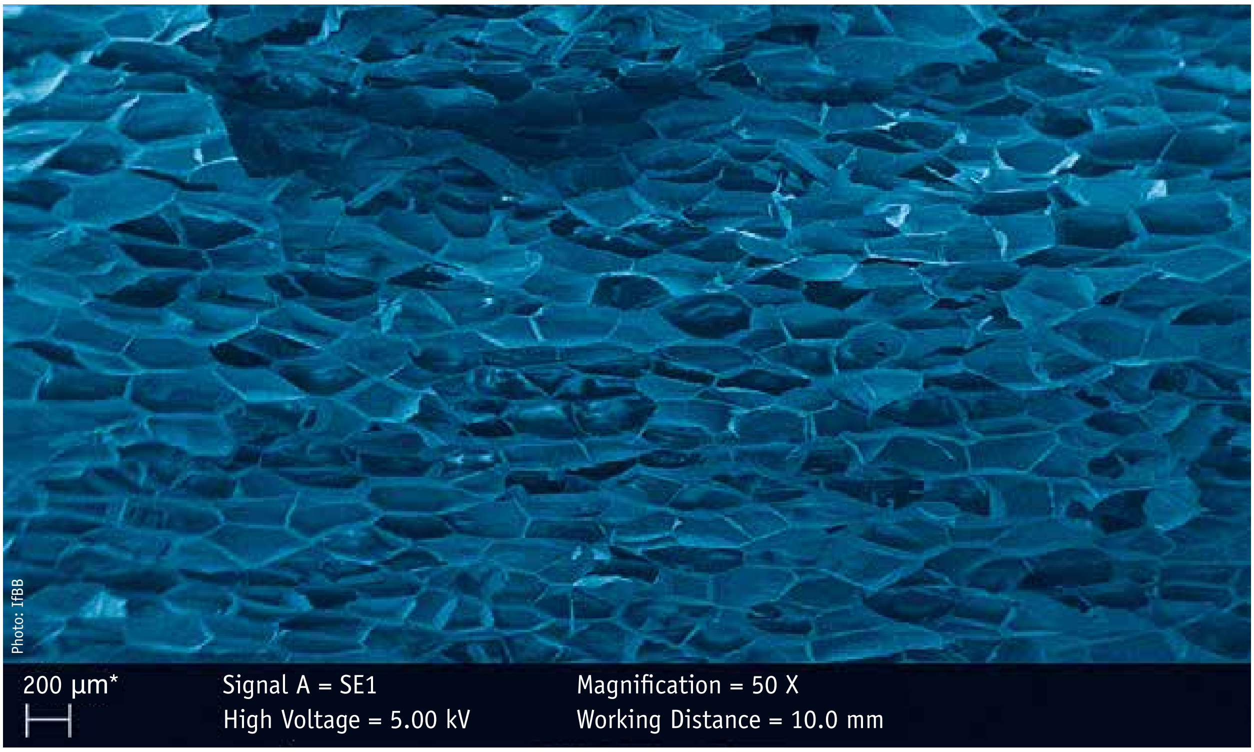
As, in principle, degassing cannot be carried out during chemical plastic foaming, regardless of the system technology, a pre-treatment in the form of an effective pre-drying should be additionally resorted to in the processing of hygroscopic bioplastics. This problem can only be avoided in physical foaming if a system with two interconnected extruders – a so-called tandem system – is used for foaming. It is thereby possible to effectively de-gas prior to the introduction of the physical propellant into the primary extruder.

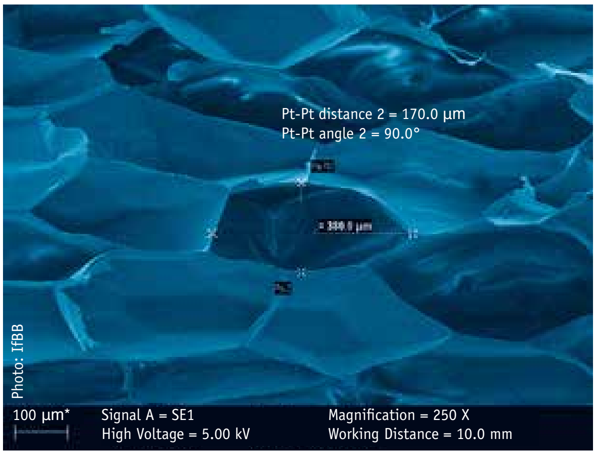
Thermal sensitivity and degradation behaviour

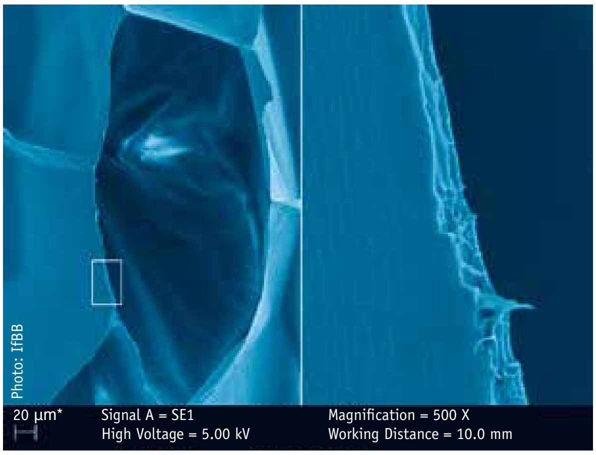
In order to prevent thermal damage and/or degradation mechanisms during the foaming of bio-based plastics, considerably more care must be taken with the process settings and the process build-up. This applies firstly in the case of raw materials being utilised which are not pressure and temperature-stable. For the same reason, a long process development should also be avoided. In addition to requiring lower operating temperatures, starch-based bioplastics can be relatively well-foamed; however, due to their relatively high tendency to absorb moisture, they exhibit a very unfavourable degradation behaviour. This behaviour significantly limits the application range of such foams.

Starch-based packaging material

Scanning electron microscope images of foam structures

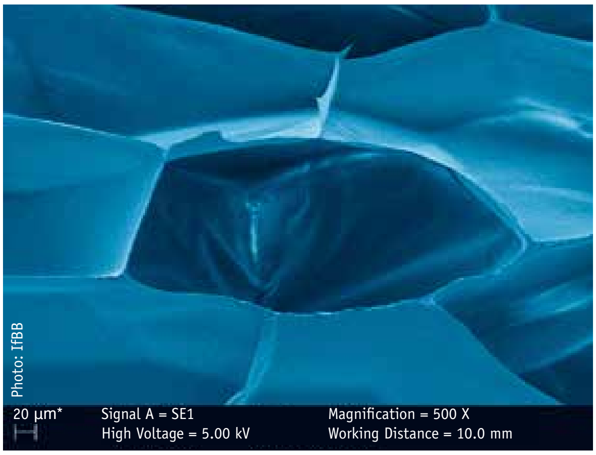






Summary

The foaming of plastics is a complex process; this also applies to the utilisation of bioplastics. Bio-based plastics are generally similarly-foamable to conventional plastics and do not require enhancement of the system technology. However, in this sector there is still too little generally-accessible processing information available. The processing procedure is further complicated through specific features exhibited by some biopolymers. Stable foam structures can therefore only be created if a compatibility/tolerability exists between the bioplastic and the respective effective propellant. Furthermore, bioplastics which tend to absorb moisture through their specific degradation behaviour cannot be utilised permanently for long-term applications.



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Cross-linking

– is a conceivable approach for the enhancement of plastics through high-energy radiation. With this, the re-combination of radiation-induced radicals enables a three-dimensional chain-branching and thereby an improvement in the material properties of the cured plastic. The various polymers react differently to radiation, particularly as regards cross-linking in comparison to chain scission. These reactions are, in addition to the irradiation parameters and the environmental conditions (presence/absence of oxygen, temperature), dependent on the chemical structures of the polymers which, in turn, can be roughly divided into three groups:

1. **the cross-linking type,**
2. **the degradation type and**
3. **the radiation-resistant type.**

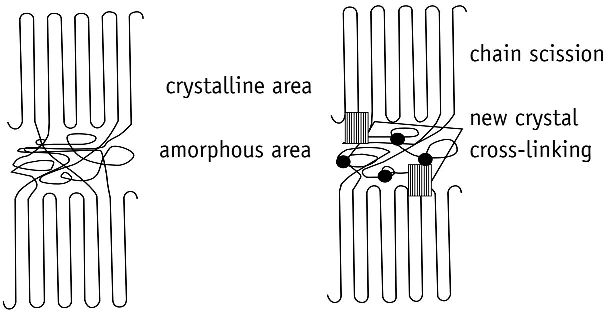

Figure 1: Effect of irradiation cross-linking on the morphology of a non-irradiated and an irradiated semi-crystalline polymer

Materials

Within the framework of the project, the possibility of cross-linking of bioplastics was investigated. For this, a research enquiry was carried out in order to evaluate the probability of a cross-linking of the biopolymers based on their chemical structure and physicochemical properties. Table 1 contains information concerning the reaction of commercially-available bioplastics to electron irradiation.

The cross-linking of a thermoplastic plastic material alters its polymer structure so that it resembles that of a thermoset. Furthermore, for purposes of practical research, a PLA was selected in order to demonstrate the changes compared to pure PLA injection moulding types as well as the effect of cross-linking agents. The investigated PLA showed changes in the mechanical and thermal properties through electron irradiation. Figure 2 shows the influence of electron beam irradiation on PLA with and without a cross-linking agent (CLA) compared to the reference material. A large variation in mechanical and thermal properties for the PLA without VHM means that the irradiated material begins to degrade. In contrast, PLA with VHM shows improved mechanical properties, which was particularly visible in terms of flexural strength. The improved mechanical properties therefore allow the conclusion that the polymer chains experienced a cross-linking. This is confirmed by the DSC analysis: the irradiated PLA shows no signs of typical crystallisation areas and was therefore cross-linked.

Table 1: Reaction of bioplastics to electron irradiation

Bioplastic	Primary beam effect (virgin)	Effective cross-linking agent (PFM)	Cross-linking with PFM
PA 610	degradation/neutral	TAIC	light
PA 1010			
PA 410			
PA 11			
PBAT, PBST	cross-linking	no information	medium
PBS	cross-linking	TMAIC	light
PBT	neutral (stable prior to irradiation)	TAIC	light
PCL	cross-linking	TMAIC	light
PE	cross-linking	TAC, AMA (allyl methacrylate)	light
PET	neutral (stable prior to irradiation)	potentially TAIC	heavy
PHAs (PHB/PHV)	degradation	no information	medium, lighter for co-polymer PHBV
PLA	degradation	TAIC, di-, triacrylate	light
PPA	neutral	no information	medium to heavy
PVOH	degradation/cross-linking water-soluble	no information	heavy

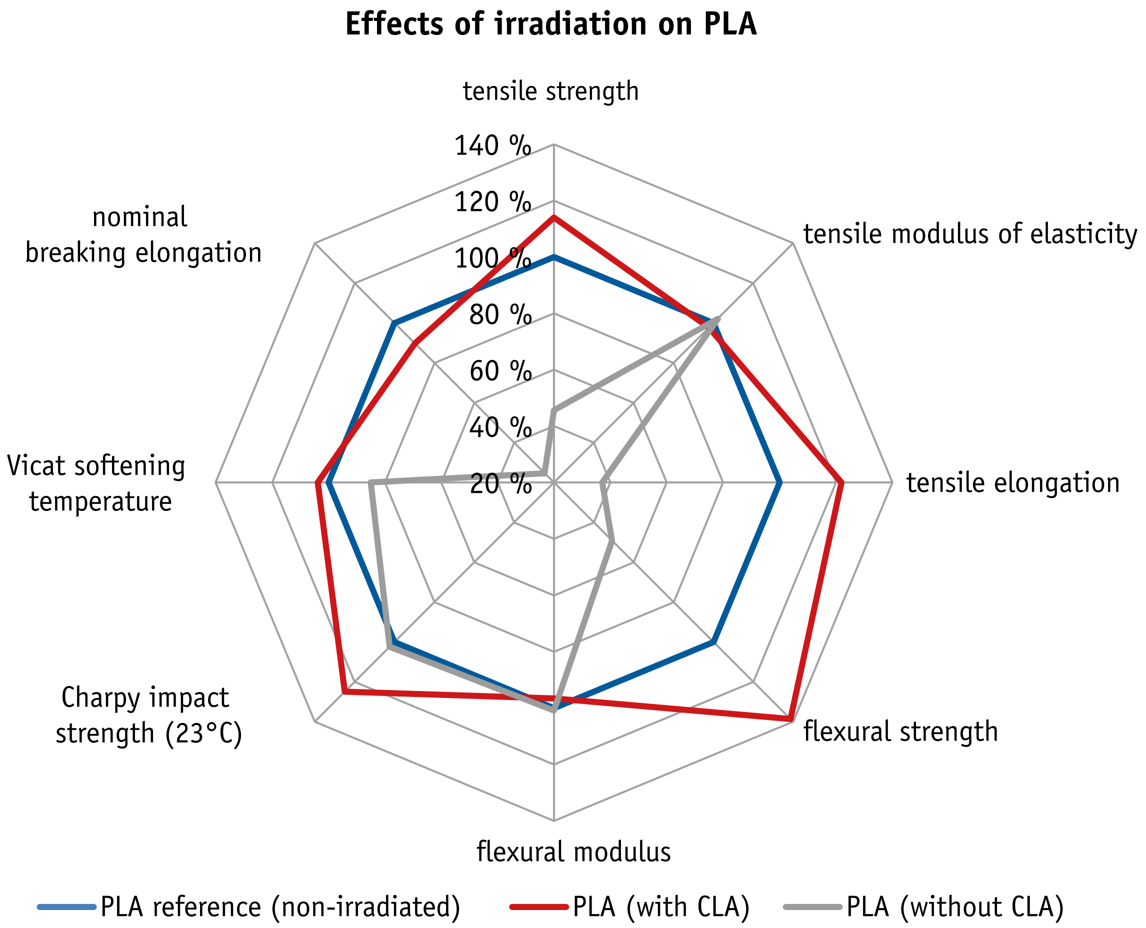

Figure 2: Effects of irradiation on the characteristics of PLA

Summary

The investigations confirm that the crosslinking of biopolymers is possible and can lead to significant alterations in the properties. The extent to which the properties alter depends on the irradiation dosage and the associated change in the macrostructure of the material. For successful crosslinks, a polymer-specific crosslinking agent is, however, often necessary. Material irradiation in the absence of CLA results in a degradation of the material and reduces the material properties.

Compared to other crosslinking procedures, the electron irradiation of polymers fundamentally offers many advantages. The degree of crosslinking can be easily controlled by the dosage. It is a clean process which, due to the reduced (or omitted) usage of additives leaves behind hardly any – if at all – undesired residues in the product. This is of particular importance in the medical field. In addition, the irradiation also simultaneously results in sterilization of the material. Irradiation is a stark contrast to conventional thermomechanical cross-linking, for which even ambient temperatures trigger reactions. However, electron irradiation is generally more expensive than silane or peroxide cross-linking. The profitability of the industrial electron irradiation procedure and the corresponding added value of the product can only be guaranteed with a high product throughput.

Colouring

– is just as important for bioplastics as for conventional plastics. There are virtually no plastic products which are not coloured. One of the main reasons for this is to increase the product appeal, which in turn leads to higher sales numbers. In the field of bioplastics, however, hardly any relevant findings have been available until now.

Colouring variants and colouring agents

When colouring plastics of any kind there are, depending on the shape and dosing options, a number of variations. The most common are listed here.

Table 1: Colouring variants for plastics

Masterbatch	Liquid colourants	Powder colourants
granulate form	liquid/paste	powder form
• Direct dosage possible • Pigments are incorporated into the carrier polymer • Addition of approx. 1–5 wt%	• Direct dosage possible • Pigments/dyes are bound in the liquid • Addition of approx. 0.01–1 wt%	• Direct dosage not possible, prior dispersion in a mixer necessary
		

An important factor when colouring is the nature and quality of the colouring. According to DIN 55943, the term „colouring agent" covers all colouring substances. These in turn are divided into the groups „dye" and „pigment", and may be of organic or inorganic origin. Dyes are soluble in the application medium and pigments are insoluble. Some colouring agents are thereby more resistant than others. Red colouring agents, for example, are generally less resistant to UV effects. The colouring of plastics is usually carried out during extrusion or in the injection moulding process.

Materials

The bioplastics investigated in the section Colouring are commercially-available materials with appropriate market relevance. The materials investigated are listed in Table 2.

Table 2: Colouring variants for plastics

Material class	Manufacturer	Type
PLA	NatureWorks	Ingeo 3251D
Bio-PE	FKuR	Terralene HD 3505
PLA+PBT	BASF	Ecovio IS 1335
PHB	Metabolix	Mirel P1004
PLA	FKuR	Bio-Flex S 9533

The applied colourants were liquid colourants with the following specifications:

Table 3: Applied liquid colourants

Colour	Colour name	Code	Density [g/cm^2]	Light-fastness
	White	DLC 0.1212	1.32	8
	Black	DLC 9.1214	1.03	8
	Yellow	DLC 1.1215	1.32	8
	Orange	DLV 2.1216	1.07	7
	Warm Red	DLC 3.1217	1.21	6
	Red	DLC 3.1218	1.19	6
	Rubin Red	DLC 3.1219	1.37	6
	Rhodamine Red	DLC 3.1220	1.30	7
	Purple	DLC 4.1221	1.07	8
	Violet	DLC 4.1222	1.43	6
	Blue	DLC 5.1223	1.50	7
	Reflex Blue	DLC 5.1224	1.52	8
	Process Blue	DLV 5.1225	1.32	8
	Green	DLC 6.1226	1.20	7

Investigations

In order to examine the entire colour palette of the available liquid colourants, the selection was limited to three bioplastics as the matrix polymer. These three materials were processed with each of the available colours in a proportion of 0.1 wt%. The objective was to obtain comprehensive statements regarding the workability, the optical behaviour and the influence of colouring on the mechanical characteristic values. The materials were processed using an injection moulding machine from KraussMaffei, Type 50-180AX, to form colour plates with the dimensions 90 x 55 x 2 mm. These plates were implemented in the subsequent investigations.

Workability

The liquid colourants could be easily incorporated into the bioplastics PLA Ingeo 3251D and Bio-PE Terralene 3505 HD during the injection moulding process. For this, a colour concentration of only 0.1 wt% was expended, which sufficed for an opaque colouring of the Bio-PE. Due to its translucent properties, the PLA did not attain complete opacity. One challenge proved to be the colouring of the bioplastic PLA+PBT. This exhibited an inhomogeneous and weak colour which could only be improved by increasing the colour concentration to 0.5 wt%. A great advantage of the liquid colourants can be recorded in the areas of dosage and colour change, as only ten cycles were needed in order to change from one colour to the next. This is not possible with the masterbatches usually used. Table 4 shows the injection moulding parameters which were used for the production of the colour plates.

UV stability

This investigation provides an insight into the impact of the incorporated liquid colours on colour changes in the material following UV irradiation. For this, ΔE indicates the value for the colour distance between the non-irradiated and the irradiated samples. From a ΔE value of 2 the eye generally recognises a deviation in colour; deviations in grey tones are detected much earlier. At a value of 4 the deviation is classified as immediately recognizable. Figure 1 shows the colour distance of all the liquid colours in combination with the utilised bioplastics.

The coloured PLA and Bio-PE exhibit colour deviations which can be predominantly evaluated as "normal" for 14-day UV irradiation. It is conspicuous that some colours (White, Black, Rhodamine Red, Purple, Process Blue) have a UV-stabilizing effect compared to the native (non-coloured) bioplastic. Colours such as Yellow, Warm Red, Red, Rubin Red, Violet, Blue and Reflex Blue, however, exhibit significant deviations and should therefore be furnished with UV stabilizers when used for mouldings which are exposed to strong sunlight.

Table 4: Injection moulding parameters for the production of the colour plates

PLA injection moulding parameters

Time	[s]
Injection time	1.5–2
Cooling time	32–36
Cycle time	54–58
Pressure	**[bar]**
Injection pressure	1200
Dwell pressure	450–480
Force	**[kN]**
Tensile force	470–485
Velocity	**[mm/s]**
Injection velocity	40
Temperature	**[°C]**
Entry/Zone 1/ Zone 11	50/180/240
Tooling temperature	2 x 25

Bio-PE injection moulding parameters

Time	[s]
Injection time	1.5–2
Cooling time	25–28
Cycle time	44–47
Pressure	**[bar]**
Injection pressure	1200
Dwell pressure	600–625
Force	**[kN]**
Tensile force	485
Velocity	**[mm/s]**
Injection velocity	70
Temperature	**[°C]**
Entry/Zone 1/ Zone 11	30/155/195
Tooling temperature	2 x 45

PLA+PBT injection moulding parameters

Time	[s]
Injection time	1.2
Cooling time	14–16
Cycle time	27–30
Pressure	**[bar]**
Injection pressure	900
Dwell pressure	630
Force	**[kN]**
Tensile force	485
Velocity	**[mm/s]**
Injection velocity	75
Temperature	**[°C]**
Entry/Zone 1/ Zone 11	60/155/210
Tooling temperature	2 x 25

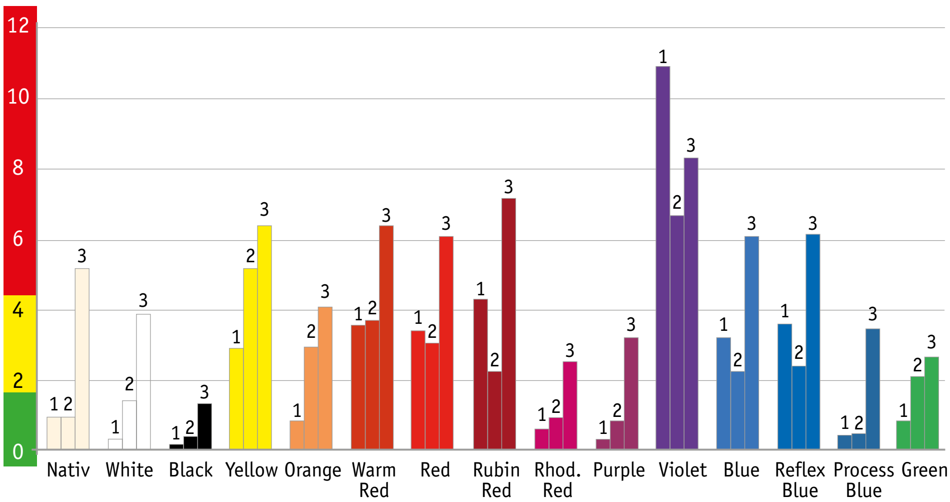

Figure 1: Colour distance after 14-day UV irradiation
Colour measurement in accordance with DIN EN ISO 5033-4; D65/10°; n=9
Measurement sequence: Ingeo 3251D (1), Terralene HD 3505 (2), Ecovio IS 1335 (3)

Mechanical properties

The evaluation of the mechanical properties is carried out based on the Charpy impact strength test following 14-day UV irradiation, as the bioplastics Bio-PE and PLA+PBT produced no fracture in the untreated state. For this test (DIN EN ISO 179/2), the force is determined which is needed in order to penetrate a test specimen. The test was conducted on selected colours.

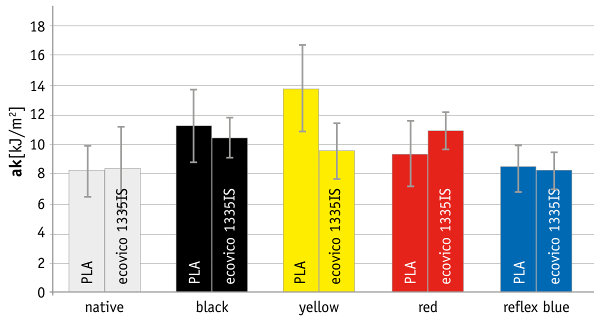

Figure 2: Impact strength results following 14-day UV irradiation
Impact bending test in accordance with DIN EN ISO 179/2; Type 2;
5J pendulum; n=12
Ingeo 3251D and Ecovio IS 1335 + 0.1 % colouring

Conspicuous in the investigations performed is that all liquid colours lead to characteristic value increases in the Charpy test. A positive effect on the resistance of these bioplastics can therefore be recorded.

Colouring with masterbatch

In order to compare the different colourisation methods, the two materials NatureWorks Ingeo 3251D (PLA) and Metabolix Mirel P1004 (PHB) were coloured respectively with a blue and a green masterbatch. The masterbatch was based on PLA, is commercially available and complies with the Standard EN 13432 with respect to the biological degradability.

During the processing of Ingeo 3251D, slight colour streaks occurred on the surface when a standard three-zone screw without mixing elements was used. A substantial improvement in the colour homogeneity, which led to the elimination of the streaking, was achieved through the application of a screw with additional toothed disc mixing parts before the non-return valve. A higher dynamic pressure also resulted in a reduction of the streaking. The processing parameters showed overall only a slight effect on the resultant colour. Solely an increase in the mass temperature resulted in a slight alteration in colour, but this was significantly below the visible threshold of perception. Ingeo 3251D therefore showed itself to be robust against potentially colour-changing factors in the injection moulding process.

Although the materials PLA and PHB are relatively similar in their molecular structure, an incompatibility with the carrier material of the masterbatch was determined during the colouration of Mirel P1004. The cause lay in the different viscosities of the two materials. This resulted in very strong streak formation on the component when the standard three-zone screw was used. By using a screw with mixing elements, the components became visually substantially more homogeneous; the colour measurements, however, showed significant scattering in the running process. The colouration had no influence on the mechanical properties.

Summary

The investigated bioplastics produce good results as regards colouring. The workability of the liquid colours used could be easily implemented in the injection moulding process. A colour content of as little as 0.01 wt% produced good results in the bioplastics PLA and Bio-PE. For PLA+PBT, however, the colour effect was less pronounced and a good result was only possible from a colour proportion of 0.5 wt%. Particularly positive is the low number of cycles needed for a colour change. In the coloured state, the investigated bioplastics exhibit a „typical behaviour" as regards their UV stability. In combination with colours such as red, significant colour variations are recognisable following prolonged UV irradiation, whereas colouring with e.g. black leads to UV stabilization. Particularly interesting is the fact that colouring with liquid colours noticeably increases the resistance of the examined bioplastics.

Overall, it should be noted that for the colouring of bioplastics with liquid colours, this is indeed possible without the use of special or additional measures and leads to good results.

When colouring with masterbatch, bioplastics exhibit the same process difficulties as conventional thermoplastics. A standard three-zone screw without mixing elements can therefore cause colour streaks due to insufficient homogenization. If the carrier material of the masterbatch is not compatible with the plastic which is to be coloured, no reproducible colour tone can be generated. This applies equally to bioplastics and conventional plastics.

Additional and detailed results can be found
in the online database for this joint project at:
www.biokunststoffe-verarbeiten.de

– plays a role, for example, as regards the printing of plastics. A high-quality print is just as important for bioplastics as it is for conventional plastics, in order to decorate the products following the production process and to increase product appeal. One important market here is the packaging industry, which requires basic information concerning the printability of bioplastics in order to utilise them. For the toy industry, a subsequent refinement is also essential in order to increase product appeal.

Materials

The bioplastics investigated in the section **Printing** are commercially-available materials with appropriate market relevance. The materials investigated are listed in Table 1.

Table 1: Overview of the materials investigated in the section Printing

Material class	Manufacturer	Type
PLA	NatureWorks	Ingeo 3251D
PHB	Metabolix	Mirel P1004
PLA	FKuR	Bio-Flex S 9533
PLA	Tecnaro	Arboblend 2330 M
PLA	Tecnaro	Arboblend 2628V
PLA	Tecnaro	Arboform LV100
PLA	RTP	RTP 2099 x 124790 E
Bio-PA	Evonik	Vestamid Terra DS16

Investigation

The printability is significantly determined through the wettability of the surface and is dependent on the chemical composition of the substrate. The determination of the surface energy through a contact angle measurement enables conclusions to be drawn concerning the printability of plastics. Due to their relatively high polarity, bioplastics – in particular PLA and PHB – exhibit in principle good wettability with paints and varnishes. Good results have already been achieved in pad printing through 1-component colour systems. Table 2 shows the surface tension of a number of bioplastics and their polar fraction.

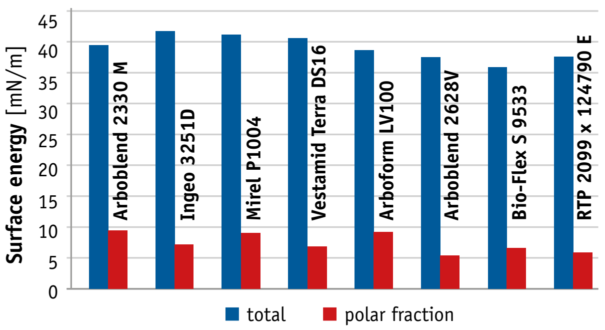

Figure 1: Surface energy

– also plays a role in the mechanical processing of plastics. In the manufacture of injection-moulded plastic parts, an additional machining processing step is often necessary, for example for the removal of sprues. The final form of many semi-finished products made from plastic is often achieved through machine processing methods such as turning, drilling or milling, although few special cutting tools are available on the market. Frequently tools are used which are also suitable for the processing of aluminium or steel.

Materials

The bioplastics investigated in the section **Mechanical processing** are commercially-available materials with appropriate market relevance. The materials investigated are listed in Table 2.

Table 2: Overview of the materials investigated in the section Mechanical processing

Material class	Manufacturer	Type
PLA	NatureWorks	Ingeo 3251D
PHB	Metabolix	Mirel P1004
PLA	FKuR	Bio-Flex S 9533

Investigation

In order to investigate the suitability of bioplastics for machining processes, the surface roughness of turned parts was measured in dependence on the rotational speed U, feed v(f) and infeed f of the lathe machine. Measurement of the temperature increase occurring at the plastic surface during processing was performed using a thermographic camera. Despite the high surface temperatures of up to 120 °C, roughness values of 4 µm were achievable when cutting with aluminium and steel materials. The bioplastics did not smear during processing. The average roughness of a cylindrical object made from the material Ingeo 3251D is shown exemplarily for varying processing parameters and tooling in Figure 2.

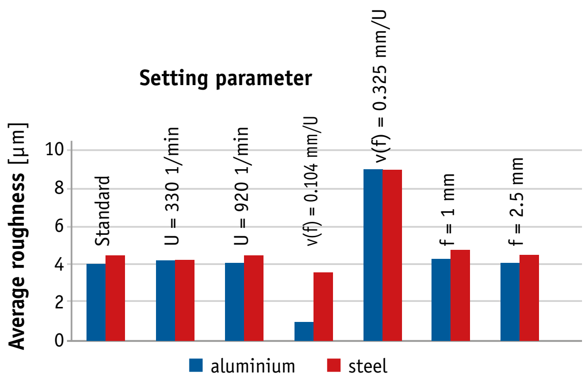

Figure 2: Average roughness of Ingeo 3251D in dependence on the setting parameters

Extrusion blow moulding

– is one of the standard methods for the production of hollow plastic technical mouldings (canisters, fuel tanks, air ducts in motor vehicles, etc.) and in the packaging sector (in particular plastic bottles and containers, etc.). For this procedure, the plastic melted in the extruder is extruded as a tube, the so-called preform, and inflated by means of compressed air in a hollow mould. The material solidifies on the cooled wall of the cavity and the article can be removed. Despite the vast potential application field for bioplastics in blow moulding, only a small amount of experience has been gained through their application until now. A simple substitution of a conventional material through a bioplastic is not generally possible, as a specific adjustment of machining and process parameters (temperature control, etc.) is necessary.

Materials

The bioplastics investigated in the section Extrusion blow moulding are commercially-available materials with appropriate market relevance. The materials investigated in co-operation with the Dr. Reinold Hagen Stiftung (charitable foundation) are listed in Table 1.

Table 1: Utilised materials

Material class	Manufacturer	Type
Bio-PE	Braskem	GreenPE SFG 4950
Bio-PE compound	FKuR	Terralene LL 1303
Cellulose blend	FKuR	Biograde 9550
PA 4.10	DSM	EcoPaXX Q170E
PA 4.10	DSM	EcoPaXX Q-X07633
PBAT+PLA	BASF	Ecovio F Blend C2224
PBAT+PLA	BASF	Ecovio FS 2224
PBAT+PLA	BASF	Ecovio T2308
PLA	NatureWorks	Ingeo 4043D
PLA	NatureWorks	Ingeo 4060D
PLA blend	FKuR	Bio-Flex F 6510
TPS blend	Novamont	Mater-Bi CF06A
TPS blend	Novamont	Mater-Bi DI01A
TPS blend	Novamont	Mater-Bi EF05B
TPS blend	Novamont	Mater-Bi EF05S

Extrusion behaviour

An evaluation of the basic properties and a classification as to whether a material is generally suitable for blow moulding is carried out based on standardized tests using a laboratory blow-moulding machine and a laboratory extruder. The focus is placed upon the formation of the preform. This is the basic input variable for the inflation procedure and therefore decisive as regards the properties of the moulded article. Key parameters are the melt stiffness (extensional viscosity) and the swelling and sagging behaviour. The tests provide information on the anticipated processing temperature and processing time window and thereby also on the necessary technical equipment. Many low-viscosity materials require the use of an accumulator head, as this enables processing times which are considerably shorter than for continuous extrusion.

Bio-PE very suitable | **PLA-blend** suitable | **TPS-blend** less suitable

Figure 1: Preform-formation in extrusion test

Production tests

Further product tests were conducted on suitable materials by means of a series production facility. The aim was to optimize the blow moulding process and to identify the main processing and performance characteristics of selected articles. Processing parameters for a number of bioplastics were thereby summarized. From four TPS blends, three could only be processed to a limited extent and one could not be processed at all. The processing temperatures in blow moulding are generally lower than the temperatures in injection moulding. A sufficient melt stiffness is necessary, but excessive stiffness during the inflation process can lead to the formation of cracks. Some materials can therefore only be produced using an accumulation head. With this, the melt is initially conveyed into an annular storage chamber and then ejected at a relatively high speed. The use of an accumulator head is necessary when the melt stiffness is too low. Due to the short time period between the preform extrusion („ejection") and the inflation process, sagging and possible tearing of the preform is avoided. Furthermore, an accumulator head should be used when the material solidifies too quickly – i.e. within a too-small temperature window – and can therefore no longer be shaped. The evaluation of the processing behaviour of the investigated bioplastics is shown in Table 2.

Table 2: Overview for processing by means of blow moulding in cooperation with RHS

		PLA blend	Cellulose blend	PA 4.10	PBAT+PLA	Bio-PE	Bio-PE-compound	TPS-blend
Preform-formation								
Article production								not yet investigated
Processing parameters extrusion tests								
Temperature feed zone	°C	145	145	200	145	140	140	160
Temperature profile extruder	°C	175–170	215–200	270–260	170–165	195–190	150–155	165–155
Temperature head	°C	170	200	260	165	190	155	155
Material drying		yes	yes	yes	yes	no	recommended	yes
Component shrinkage (averaged) Length/width; tooling temperature 15 °C	%	0.46	0.49	0.5	0.49	1.66	2.5	–
Comments All details refer to a specific material type			article very hard and brittle		heavy wall-thickness swelling			blow-moulding ability dependent on material type

Material suitable

Material suitable with restrictions
Use of an accumulator head is necessary

Material unsuitable

Summary

It can be fundamentally stated that the processing parameters and the necessary adaptations to the extrusion blow moulding process for bioplastics lie within the framework of the requirements necessary for conventional plastics (e.g. substitution of a polyolefin through a co-polyester). However, in the group of bioplastics there are few types of materials which have been optimised with respect to the blow moulding process. Almost all of the investigated materials are film or extrusion types. The material manufacturers must therefore carry out and offer adjustments – then nothing would stand in the way of the extrusion blow moulding of bioplastics.

Additional and detailed results can be found
in the online database for this joint project at:
www.biokunststoffe-verarbeiten.de

Flat film production

– is a widely-used procedure for the production of bio-based or compostable plastic films which are now part of our everyday lives. Shopping bags with bio-based or seedling symbols are offered by almost every major supermarket and chemist chain. A further example is rustling "florist's film", which is made from transparent bioplastics. Last but not least, there is also the compostable mulch film which, ploughed into the soil, is almost completely degraded between two vegetation periods.

Figure 1: Three-layer film extrusion system

A recent analysis of the bioplastics market shows a wide variety of bioplastics which have been specifically designed for film applications and which can be processed with standard systems engineering. However, a tendency is also evident – above and beyond the aforementioned simple product applications – which seeks to penetrate the market segments with more demanding products which are currently occupied by petrochemical standard plastics. These include, for example, thermoformed packaging for dairy and meat products. From a technical perspective, the material property deficits such as inadequate barrier properties or insufficient puncture and tear resistance of bioplastics are often responsible for a limited market penetration in the higher-value packaging segment. An effective aid can hereby be achieved through a multi-layer film structure, in which the positive characteristics of differing bioplastics are combined with one another.

In the film sector, the production of multi-layer films with 3, 5, 7 and, in some cases, even 9 layers, is the latest state of technology. The reasons for this are the potential cost savings which can be achieved through the combination of inexpensive and cost-intensive plastics or through the use of regranulates as well as the significant improvement in gas, vapour and aroma barriers and the improvement of the mechanical properties. Through a multi-layer structure, the visual appearance, the feel, the sealability and the printability can be precisely configured.

In order to be able to offer the potential user the broadest possible spectrum of procedural information regarding single and multi-layer film extrusion of bioplastics, market-relevant bioplastics were comprehensively investigated, both analytically and process-specifically, within the framework of the project. The focus was placed upon bio-based plastics such as PLA, Bio-PA 11 and Bio-PE. However, compostable co-polyesters, such as PBS, PBAT and PBSeT, which have a petrochemical raw material basis but are nevertheless included in the bioplastics, as well as biodegradable additives and binders based on polyvinyl acetate (PVAc) were also characterised. Last but not least, the alteration in the properties of bioplastics through blending with other bioplastics and additives was investigated. As a representative example, the PLA-PVAc blend must be highlighted. A relatively small addition quantity of 10 wt% PVAc effected in PLA a significant increase in the breaking elongation with a moderate lowering of the tensile strength. Positive alterations can also be recorded for the energy intake through abrupt stress and for tear resistance. With a mixing ratio of 7 parts PLA to 3 parts PVAc, a product is formed which can compete with HDPE and which is 70 % bio-based.

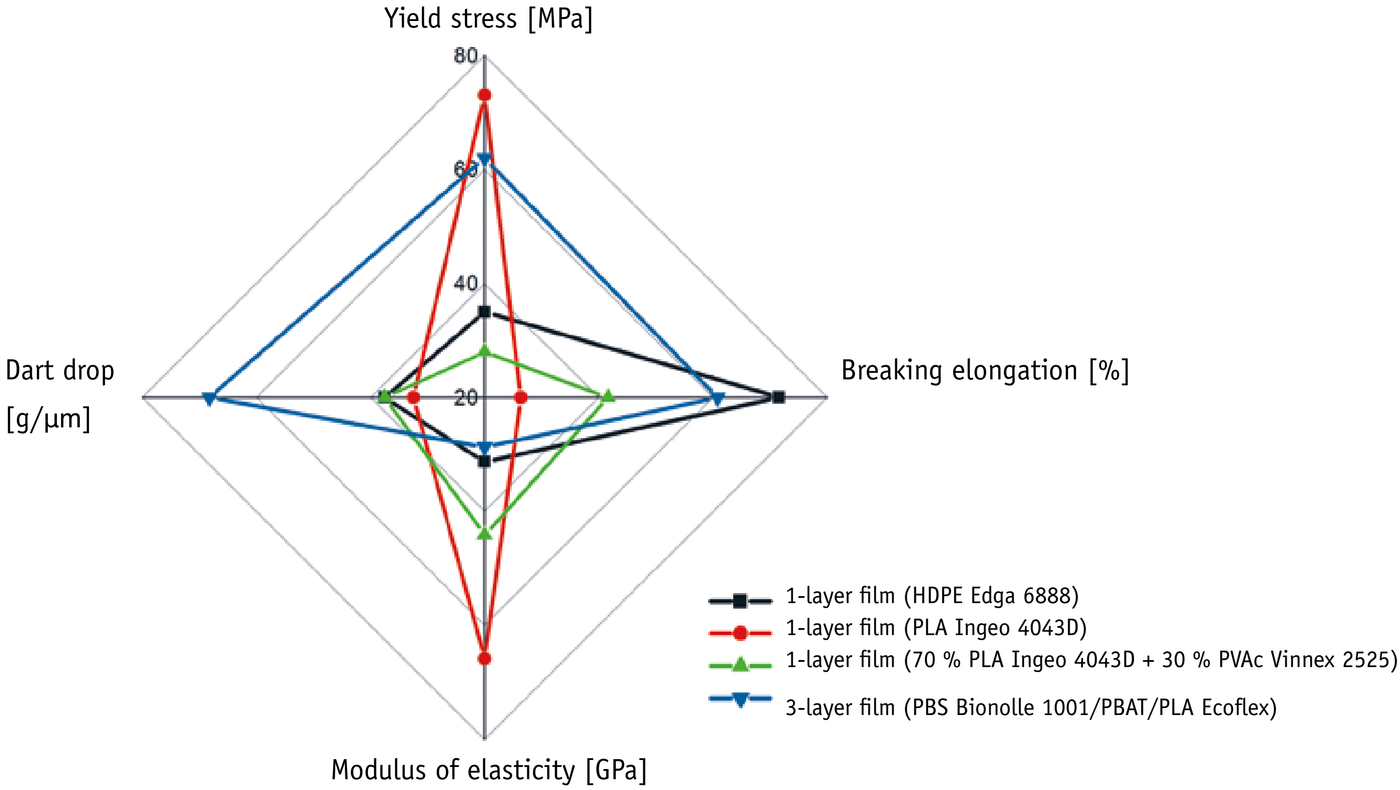

Figure 2: Comparison of the characteristics of modified and non-modified bioplastic films

The investigations show that the field of application for bioplastics can be considerably expanded through the multi-layer technique. The ability to combine differing bio-based co-polyesters with interesting mechanical properties to form a 3-layer composite which does not require the use of adhesive layers offers, thanks to the resulting strength, potential for reducing the thickness and therefore a minimization of the product cost. PBS thereby functions as the outer layer, due to its feel (similar to PE) and good printability. The inner layer can be made from softer and flexibly-composed PBAT/PLA for applications in which LDPE is currently used, or from harder and barely-stretchable PBAT/PLA types for HDPE applications. The breaking elongation thereby increases significantly and the puncture behaviour of the composite can be substantially improved (factor 7-10). Compared to PE films, the high oxygen permeability is considerably reduced. Due to the equal polarity of the applied plastics, an excellent adhesion between the individual layers is achieved even without bonding agents. Through this combination, expensive conventional 5-layer films, consisting of 3 layers of polymer (e.g. outer layer made from PE, inner layers from PA) and 2 layers of bonding agent (e.g. EVA), can be substituted if the described strengths should be achieved through a PA inner layer in connection with PE outer layers with conventional raw materials. In addition, the higher material costs for bioplastics can be compensated through efficient production and the elimination of the expenses for bonding agents.

A further investigated aspect is the re-use of salvaged bioplastic production waste. In this case, it was also possible to demonstrate that all bioplastic regenerate can be admixed to the new material in quantities typical for production of up to 10 wt%, without any negative impact on the quality or the mechanical properties of the semi-finished film product.

Summary

The performed investigations confirm that the processing of bioplastics to flat films and their performance spectrum can be increased to a significant extent through the addition of additives. Particularly effective with PLA is the polyvinyl acetate-based binder. For both single and multi-layer film extrusions, a significantly more ductile material behaviour can be achieved – without a significant reduction in the stiffness of the material. In multi-layer flat film extrusion, numerous meaningful combinations exist for polar bio-polyesters and blends thereof. Particularly worthy of mention here is the (PLA-PVAc)/(PLA-PBAT) combination. The mechanical properties, particularly puncture resistance and breaking elongation, are higher by a factor of 7 to 10 than with single-layer films of comparable film thickness. The elimination of adhesive layers also results in an enormous savings potential.

Thermoforming behaviour

– plays a role in the further processing of flat films to packaging in the food industry, which is very often carried out through thermoforming. With this highly-efficient forming procedure, bowls, cups and other containers can be produced. It is also possible to combine the production of the containers, the filling, sealing and packaging in one inline process. Outside of food packaging, blister packs are particularly well-known for all kinds of small items. Thermoforming offers the opportunity to adapt the packaging to the often complex geometry of the articles to be packaged. A modern packaging can thereby be produced in which, for example, small electronic devices can be safely stored and transported without additional padding.

Thermoforming tools can be made from aluminium or even from wood and are, due to the one-sided mould-contact with the film, very inexpensive to produce. Particularly for small and medium-series production, thermoforming offers an economical alternative to injection moulding.

Materials

The thermoplastic bioplastics existing on the market are, in principle, all suitable for thermoforming. Differences arise regarding the degree of stretching, wrinkling and punching properties. The selection of the suitable material depends on the application and must primarily be oriented on the required properties of the thermo-moulded components which are to be produced, such as transparency, stiffness and permeability. Through combinations of materials in multi-layer systems and/or the incorporation of additives, the characteristics profiles can be specifically adapted to the application. Synthetic, non-bio-based materials such as polyvinyl alcohol can thereby be used, for example in barrier layers, provided they – due to the small proportion – do not contradict the concept of bioplastics.

Highly-transparent thermoforming films can be produced from pure PLA, but they are extremely brittle and can therefore only be used in a few cases. Through the modification of PLA with a softening binder such as PVAc solid resin (Vinnex 2525) and the combination with a PA11 middle layer, highly-transparent and also highly-resistant films can be produced.

For the application of bioplastics in the sector of food packaging, the barrier properties play a major role with respect to water vapour, oxygen, flavouring agents, oils and fats. In addition to the aforementioned possibility of using multi-layer films, these properties can also be improved through coatings. The experiments within the framework of the project have demonstrated that the oxygen permeability of PLA can be decreased by around a hundredfold through the application of a layer of nanocellulose which is only a few micrometres thick.

The low softening temperature of the PLA is, on the one hand, a processing advantage; on the other hand, however, it restricts the scope of application to cold packaging. The question as to whether high-temperature-stable stereo complex PLA is also suitable for film production and subsequent thermoforming has not yet been sufficiently researched.

In the production of thermo-moulded parts, attention must be paid to the stretching of the material, particularly in multilayer films. Due to the shape, the material usually stretches unevenly. The result is a reduction in the wall thickness of the deformed part in a number of areas, which can influence the barrier properties of the layer structure. The thickness of the starting film, the layer thicknesses of the individual components and the degree of stretching must be adjusted accordingly.

Summary

As mentioned in the section on film production, multi-layer films made from bioplastic seal well. The combination of the layers should be selected with a view to well-sealable outer layers. The printability was better for all the investigated bio-materials than for films made from PE.
The production residues such as punching scrap, clamping rims, etc. can be easily ground and fed back into the processing cycle for the production of flat film.

The thermoforming process is predestined for the application of bioplastics in the packaging market, including for thin-walled packaging. Good, application-specific co-ordination between film manufacturers or suppliers and the thermoformer must therefore be achieved.

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Fibre reinforcement

– is suitable for significantly improving the mechanical and thermomechanical properties of polymer materials. With this concept, a complex chemical modification of the polymers is rendered unnecessary and new application areas for polymer materials can be developed. This, of course, applies equally to biopolymers. If the principle of sustainability is to be followed, focus should be placed upon plant-based natural fibres and bio-based fibre materials. Glass fibres or high-performance fibres such as aramid or carbon fibres can also be used for the reinforcement of biopolymers, but are not examined further here.

Materials

Fibres for the reinforcement of thermoplastic biopolymers must possess good mechanical properties, be infusible and have a high aspect ratio. Natural fibres have the disadvantage that their properties depend largely on the fluctuating growth conditions.

The commercially-available regenerated cellulosic fibre Cordenka CR is excellently-suited as a reinforcing fibre. It is available as an endless high-performance fibre and, up until now, has mainly been used for carcass-reinforcement of tyres approved for speeds of over 190 km/h.

The Cordenka CR fibre supplied by the manufacturer is comprised of 1350 filaments with a total titre of 2440 tex. In contrast to a glass fibre, such a fibre cannot be fed directly into an extruder and then crushed during compounding. For the production of staple fibres, the Cordenka CR had to be cut with a special fibre-cutting head. The smallest cutting length (equivalent to the highest number of blades) was 1.5 mm. Based on this, the cutting length was doubled respectively and staple fibres were produced with lengths of 3 mm, 6 mm and 12 mm.

For the matrix polymer, PLA injection moulding type Ingeo 3251D was used. Compounding was carried out with a twin-screw extruder, model Leistritz ZSE 18HP. This extruder has a screw diameter of 18 mm and a processing section length of 50 D. Through a special temperature control, it could be ensured that the PLA was completely melted in the first four extruder zones. The dosage of the fibres took place in zone 5. This is in order to achieve a gentle incorporation of the fibres into the polymer melt. The screw configuration of the extruder was also designed to enable gentle fibre processing. The staple fibres were added to the PLA at a barrel temperature of 180 °C.

In total, four PLA-rayon compounds with a fibre content of 20 % were formed under the same extrusion conditions. The granulate was subsequently processed to produce standardised test specimens using a BOY 22A injection moulding machine.

Influence of the fibre length distribution on the characteristics profile of the compound

Through the processing of the cellulose fibres in the extruder and the subsequent granulation of the strand, the fibres are shortened. Table 1 shows the median of the optical fibre length determination for the respective compound. It is noticeable that with an increasing initial length, the fibres are more strongly shortened through the processing procedure. With the device configuration selected here, the output fibre length of 3 mm was the best-preserved.

Table 1: Average fibre length distribution

Sample no.	Fibre length prior to compounding [mm]	Fibre length in test specimen [mm]
342	1.5	0.5
340	12	1.1
339	6	1.5
343	3	1.9

Table 2 shows the mechanical properties determined for the test specimens in dependence on the average fibre length in the test specimen. The Cordenka fibres have a significant reinforcing effect, which is particularly evident in the impact strength of the un-notched specimens. All the other characteristic values also improve with increasing fibre length. The effects are not so severe as regards strength; for the modulus of elasticity, an increase of 50 % was achieved.

Table 2: Mechanical properties as a function of on the fibre length

Fibre length [mm]	Charpy un-notched [kJ/m²]	Charpy notched [kJ/m²]	Strength [MPa]	Modulus of elasticity [GPa]	Elongation [%]
Without fibres	20	2	70	2.9	3.8
0.5	43	5	79	3.9	5.6
1.1	51	7	84	3.9	3.0
1.5	54	8	85	4.0	4.4
1.9	61	9	87	4.0	6.1

Further improvements in the mechanical properties of the compounds can definitely be achieved through the application of bonding agents.

Summary

Bio-based staple fibres produced from the cellulose cord Cordenka CR are excellently-suited for improving the impact strength of PLA and provide the opportunity of a long-term stable production and an equally long-term stable characteristics profile for the composite material. Depending on the intended use of the fibre-reinforced biopolymer, the appropriate reinforcing fibre and suitable additives can be selected.

– has achieved nowhere near the diversity offered by conventional plastics, even though the variety of bio-based raw materials which are suitable for blown film production – and which are available in permanently-consistent quality and in sufficient quantities on the market – exhibit excellent properties and application possibilities which make them attractive for use in the film market. Currently, this market is dominated by non-degradable, fossil-based films. As is usual in the conventional field, necessary adjustments to the material properties can be achieved to a significant extent through specific applications or targeted Improvement, for example of mechanical strengths through raw material modifications, through mixtures of differing raw materials or through multi-layer structures.

Processing behaviour

The available bioplastics which were examined within the framework of the project were, without exception, easy to process. Commonplace and non-modified processing systems were thereby used, such as are used for conventional materials. Many similarities were obvious between the processing of conventional and bio-based plastics; in the following, the focus will therefore be placed upon the differences between these raw material classes.

Fundamentally, it should be emphasized that all bioplastics could be extruded smoothly; the melt homogeneity was evidently good. The use of melt sieves is recommended in order to reduce the frequency of nibs.

All the materials could be easily flushed with LDPE following production; over the entire period, there was no significant contamination of the screw, the cylinder or other melt-carrying parts, even though a very large quantity of widely-differing materials was processed.

Materials

Table 1: Overview of the bioplastics examined in the section Blown film production

Material class	Manufacturer	Type
PBAT/PLA	BASF	Ecovio F 2341
PBAT/PLA	BASF	Ecovio F Mulch C 2311
Co-polyester/starch	Novamont	Mater-Bi CE 01 B
Co-polyester/starch	Novamont	Mater-Bi CF 06 A
Co-polyester/starch	Novamont	Mater-Bi EF 51 L
PBS	Mitsubishi Chemical	GS Pla FD 92 WD
PBS	Mitsubishi Chemical	GS Pla FZ 91 PD
PBS	ShowaDenko	Bionolle 1001MD
PLA	NatureWorks	Ingeo 4043D

The production of regenerate from production waste and its addition in the range of 10 % or higher was possible without any problems.

Differences to conventional materials were determined in the windows for the processing temperatures, which are smaller for biopolymers than for the well-known conventional raw resources. For example, for PLA a range of +/- 5 °C must be observed, whilst PBS types required +/- 10 °C. This temperature sensitivity was also observed in subsequent processing steps such as the sealing of the produced films.

Through mixing PLA with PVAc, however, the described processing window was enlarged and the melt stability was so improved that production was problem-free.

A drying of the biomaterials is generally recommended for production operations (80 min at 50 °C in a dry-air dryer); however, it must be reported that for non-dried materials from dry internal storage in closed containers, no disadvantages were observed whatsoever. They are generally delivered pre-dried. The moisture content was, in this case, less than 0.1 % and therefore within the suitable range for processing.

For the application of the bioplastics PLA and PBS, the achievable blow ratios remained behind those of conventional PE or the commercially-available and established PBAT/PLA co-polyesters. For pure PLA, blow ratios of a maximum of 1:2.4 were realisable; with PBS, 1:3.3 was nevertheless achieved.

Mechanical properties of films made from bioplastics

Important findings in relation to the applicability of the produced films result from the tensile tests – (Table 2 and Figures 1-3).

In the diagrams, a selection of films made from bioplastics is compared against two simple reference films (films A and B) which are made from PE. The biofilms are either mono films made from pure material types, mixtures or compounds or, in the case of films M to Q, 3-layer films.

The tensile strengths vary across a wide range. With the 3-layer films, strengths are obtained which go beyond the level of the mono films made from biopolymers, with no loss of elasticity thereby. The modulus of elasticity of these films thereby remains within a well-serviceable range.

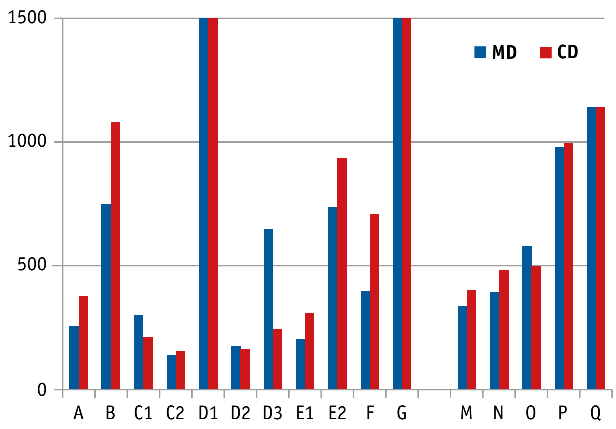

Figure 1: Module of elasticity [MPa]

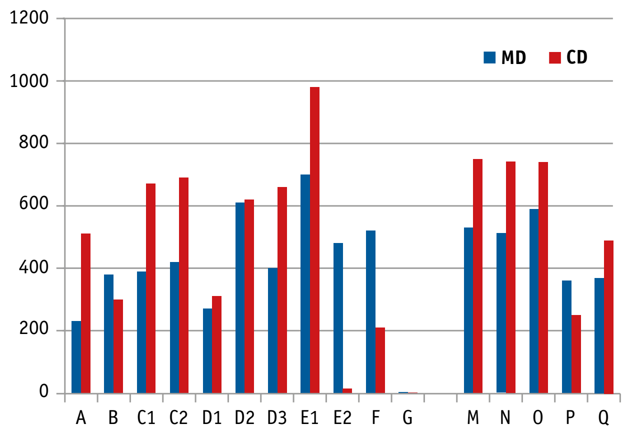

Figure 3: Breaking elongation [%]

With a reduced thickness, these films can be utilised in applications where today simple standard PE films are used. The same rates of increase also apply to the puncture resistance.

In many cases, PBAT/PLA co-polyester and also pure PBS (C1. D3. E1. F) offer high tensile strengths; these are, however, accompanied by high values for the breaking elongation and a low modulus of elasticity. These films exhibit a correspondingly soft behaviour, which restricts the application range.

If it is determined that the breaking elongation in the longitudinal direction (MD) exceeds the breaking elongation in the transverse direction (CD), this would indicate the PLA-typical low tear resistance which is, however, also recognisable in HDPE (film B).

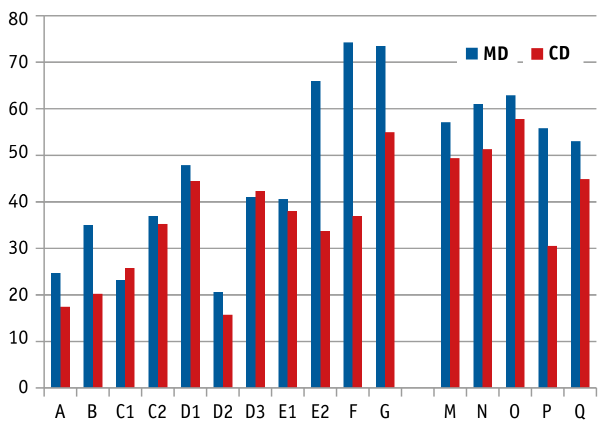

Figure 2: Maximum tensile strength [MPa]

Summary

Bioplastics can be easily processed into blown films which offer useful fields of application. The achievable film properties cover a wide range of possibilities.

However, this is not sufficient for challenging applications with high demands as regards, for example, the film strength. In such cases, PE blends are now being utilised using LLDPE or mLLDPE.

Through the combination of biomaterials, in particular by means of a suitable 3-layer structure, the film strengths can, however, be increased to a significant extent without the flexibility or the modulus of elasticity of the films leaving the customary range. In this way, the current application fields for bio-films are being extended, even though there is still need for development as regards achievement of the very high strengths.

Fibre production in melt spinning process

– is by far the most frequently-used method for the production of synthetic fibres, such as those found in the clothing, filtration and automotive industries. With a share of almost 60 %, these synthetic fibres, which are manufactured from fossil raw materials, distinctly dominate the worldwide fibre market. The role of bio-based and partly-bio-based alternatives is, however, expanding continuously due to their sustainability and the growing environmental awareness. Bio-based and partly bio-based thermoplastics can be easily-processed using conventional industrial equipment and, through their good characteristics profile, are suitable for numerous applications in the textile and furniture industries.

Materials

The bioplastics listed in Table 1 were processed within the project framework in a semi-industrial melt spinning machine from the company „Fourné Polymertechnik GmbH“ and were examined regarding their suitability for spinning and the resulting mechanical properties.

Table 1: Overview of the materials examined in the melt spinning process

Material class	Manufacturer	Type
PLA	NatureWorks	Ingeo 6201D
PLA	NatureWorks	Ingeo 6400D
PA 11	Arkema	Rilsan BMNO TL
PA 4.10	DSM	EcoPaXX Q170E

Figure 2: Fourné melt spinning machine

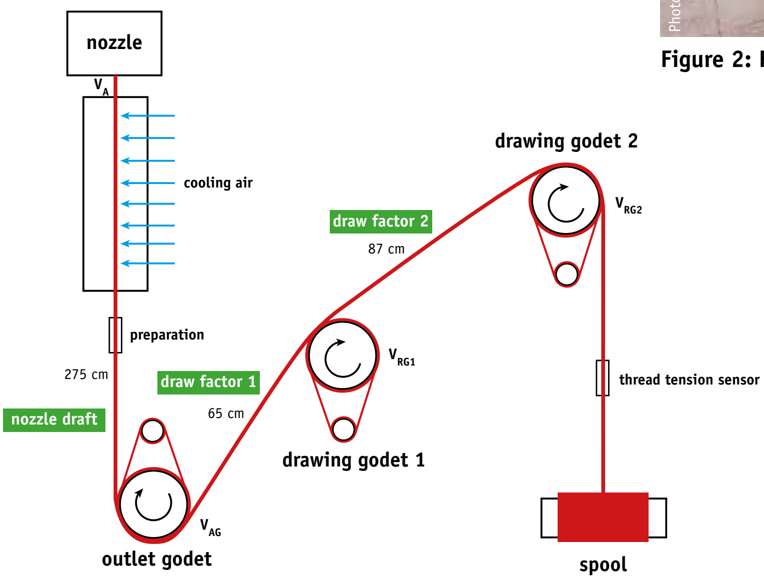

Figure 1: Filament yarn course in the spinning process

Processing behaviour

All the examined materials exhibit good extrusion properties and allow a uniform and continuous feed process. With flow rates of up to 3 kg/h and godet speeds of up to 1800 m/min and with diverse nozzle geometries (32 – 120 hole), processing windows could be identified which permit a stable filament yarn manufacturing process.

In order to ensure a stable process, the granulate should be dried prior to processing in order to achieve a moisture content of 0.01-0.1 % (24 h at 50-120 °C/vacuum drying oven). The polyamides exhibit a particularly strong dependence of the viscosity on the moisture content. For very dry granulate (~ 0.01-0.03 %), it is therefore recommended to perform the spinning process in higher processing temperature ranges in order to counteract the increase in viscosity. In order to realise uniform mechanical properties in the filaments, the material should therefore be brought to approximately the same initial moisture content prior to spinning. Even if the other process parameters are held constant, a decrease in viscosity through increased temperature or higher moisture content results in alterations in the filament properties and thus to inconsistencies in the produced yarn. This generally contributes to an increase in the breaking elongation and a change in the tensile strength and the modulus of elasticity.

A further difficulty in the spinning process of polyamides is posed by the electrostatic charging of the filaments. The resultant destabilizing spreading of the filament bundle on the yarn-guiding elements can be counteracted without extensive technical outlay through the utilisation of a suitable spin preparation. The stretching of the filaments on drawing godets should take place for all materials above the glass transition temperature (see Table 1). A decrease in the yarn tension not only serves the stabilisation of the drawing process but also enables higher degrees of drawing and ultimately leads to an improvement in the mechanical properties.

In order to counteract the thermal degradation of PLA, it is recommended that the extrusion speeds and flow rates are set as high as possible. The good flow properties of the melt allow this without problems. Alternatively, a lower processing temperature (215-220 °C) could also be selected.

Table 2: Temperature recommendations for the processing (Method: DSC/test device: Perkin Elmer DSC 7)

Type	T_G [°C]	T_S [°C]	Recommendation $T_{processing}$ [°C]
Ingeo 6201D	55	168	230–240
Ingeo 6400D	55	171	230–240
Rilsan BMNO TL	45	192	230–240
EcoPaXX Q170E	60	248	280–290

Mechanical properties of the filament yarn

With the system-specific dimensions (2 m clearance between nozzle and outlet godet), the following total drawing of the extruded filaments could be achieved: factor 330 for Ingeo PLA 6400D, factor 530 for Ingeo PLA 6201D, factor 400 for Rilsan PA 11 and factor 450 for EcoPaXX PA 4.10. The larger dimensions of the equipment used in the industry for filament yarn production would certainly exceed these values and enable a further optimisation of the mechanical properties.

The achieved mechanical properties for the individual filaments are shown in Table 3.

Table 3: Achieved mechanical properties for the individual filaments (Method: tensile test)

Type	Tensile strength [cN/tex]	Modulus of elasticity [cN/tex]	Breaking elongation [%]	Titer [dtex]
Rilsan PA 11	≤ 52	≤ 576	≥ 27	≥ 0.6
EcoPaxx PA 4.10	≤ 44	≤ 301	≥ 36	≥ 0.9
PLA Ingeo 6201D	≤ 28	≤ 465	≥ 34	≥ 0.8
PLA Ingeo 6400D	≤ 43	≤ 624	≥ 29	≥ 1.5

Summary

To summarise, it can be said that the bio-based and partly bio-based polyamides represent virtually equivalent alternatives to the customary spin types of PA 6 and PA 6.6 with respect to the processing and the resulting mechanical properties. The properties profile for the lactic acid-based polyesters achieved values which enable application in the textile sector. At the same time, these values and the thermal stability of PLA fibres are currently too low to be used in technical applications. In view of the present biodegradability of PLA and the environmental benefits resulting therefrom, an optimistic forecast for the future of this class of materials in textile applications is realistic.

Joining technology

– at this point covers the welding and adhesive bonding of plastics. Bioplastics find application primarily in the packaging industry, in gardening and landscaping and in medical technology. Their range of applications and their market share is, however, growing progressively. They are also increasingly in demand as resistant polymer materials for technical applications. In order to successfully apply bioplastics both as packaging and as technical materials, these materials must exhibit, amongst other attributes, good welding and adhesive bonding characteristics.

Materials

The bioplastics investigated in the section Joining technology are commercially-available bioplastics with appropriate market relevance. The materials investigated are listed in Table 1.

Table 1: Overview of the materials examined in the section Joining technology

Material class	Manufacturer	Type
PLA	NatureWorks	Ingeo 3251D
PLA	NatureWorks	Ingeo 4032D
PLA	NatureWorks	Ingeo 4043D
PLA	NatureWorks	Ingeo 4060D
PLA	Simona	SimoGreen natural
PLA	Simona	SimoGreen green
PHB	Metabolix	Mirel P1004

Welding

Plastics can generally be bonded to one another through various welding methods, such as thermal contact welding, ultrasonic welding, high-frequency welding, infrared welding, etc. In most cases, the choice of procedure is determined by the materials to be welded and the resulting costs, as each procedure has material and application-specific advantages and disadvantages.

There are a multitude of factors which can affect the weld seam quality. Primarily, the material properties such as modulus of elasticity and melting temperature as well as the welding parameters should be mentioned here. For perfect welding, the German Welding Society (DVS) has recommendations for most petrochemical-based plastics. For bioplastics, however, such recommendations are completely absent. Basic welding parameters for selected bioplastics are therefore listed in Tables 2-6 below.

Table 2: Heated element butt welding

Heated element butt welding						
Material*	Heating element temperature [°C]	Alignment time [s]	Alignment pressure [MPa]	Heating-up time [s]	Welding pressure [MPa]	Cooling time [s]
SimoGreen green	190 … 250	2	0.05	15 … 50	0.05	100
Ingeo 3251D	190 … 250	2	0.25	10 … 50	0.25	100
* Investigated sample geometry: 170 x 15 x 5 mm (parallel tensile bar)						

Table 3: Thermal contact welding

Thermal contact welding			
Material*	Welding time [s]	Welding pressure [MPa]	Heating element temperature [°C]
Ingeo 4060D	0.1 … 0.9	1.0 … 3.5	95 … 140
Ingeo 4032D	0.1 … 0.9	1.0 … 3.5	95 … 150
Ingeo 4043D	0.1 … 0.9	1.0 … 3.5	110 … 150
* Investigated sample geometry: film with a thickness of 50 µm			

Table 4: Ultrasonic welding

Ultrasonic welding			
Material*	Welding time [s]	Welding force [N/mm]	Amplitude [µm]
Ingeo 4060D	0.1 … 0.5	1.2 … 1.6	15.8 … 22.1
Ingeo 4032D	0.1 … 0.5	0.6 … 1.6	15.8 … 28.4
Ingeo 4043D	0.1 … 0.7	1.2 … 1.6	15.8 … 25.3
* Investigated sample geometry: film with a thickness of 50 µm			

Table 5: High-frequency welding

High-frequency welding			
Material*	Welding time [s]	Welding pressure [N/mm]	Voltage on the electrode [V]
Ingeo 4060D	0.4 … 0.9	0.8 … 3.2	700 … 1.200
Ingeo 4032D	0.4 … 0.9	0.8 … 3.2	700 … 1.100
Ingeo 4043D	0.4 … 0.9	0.8 … 3.2	700 … 1.100
* Investigated sample geometry: film with a thickness of 50 µm			

Table 6: Infrared welding

Infrared welding				
Material*	Performance [%]	Heating-up time [s]	Cooling time [s]	Joining pressure [MPa]
SimoGreen green	50 … 80	25 … 60	30	0.05
Ingeo 3251D	50 … 70	40 … 60	30	0.80
* Investigated sample geometry: Test specimen Type 1A in accordance with DIN EN ISO 527-2				

Adhesive Bonding

Due to their relatively high polarity, the surface of the bioplastics PLA and PHB exhibits in principle a good wetting with paints, coatings and adhesives. By selecting the right adhesive or coating, good adhesion and a correspondingly high bond strength can be achieved.

If the user is committed to using a particular paint or a particular adhesive, the surface of the bioplastics can be selectively modified. The bioplastics PLA and PHB can thus be easily activated with conventional surface pre-treatment systems such as Corona, atmospheric-pressure plasma or low-pressure plasma. This allows the resulting adhesion and the bonding between the bioplastic and the adhesive or the paint to be significantly increased.

Within the framework of the performed investigations, four different bioplastics (three different PLA types and one PHB) were tested regarding their bonding properties. Considering the relatively high strength of the PLA plastics used (Ingeo 3251D, SimoGreen natural and SimoGreen green), structural adhesives should, in principle, be considered advantageous in application. Mirel P1004. in contrast, exhibits a slightly lower tensile strength and higher ductility. For adhesive applications with Mirel P1004. a flexible adhesive would therefore be preferable.

The adhesive processes in plastics technology are comprised essentially of four processing steps:

- Preparation (cleaning, adapting, etc.)
- Pre-treatment (application of specific pre-treatment methods or primers)
- Bonding (application of the adhesive and joining)
- Curing

At the beginning, the utilised materials were therefore tested regarding compatibility with typical cleaning agents. It was thereby determined that cleaning agents with ketone groups such as, for example, methyl ethyl ketone or acetone can cause a change in the substrate surfaces through solvent effects. These should therefore be considered as critical for cleaning purposes. In contrast, the typical alcohol-based plastic-cleaning agent showed good suitability as regards degreasing the surface to be bonded and should therefore be utilised for this task.

The utilised adhesives, which were pre-selected, based on the requirements and the measured surface energy, could be used without surface treatment with varying degrees of success. The performed investigations have demonstrated that, for example, the utilised bioplastics can be bonded with a relatively high strength (at least 5.5 MPa) using two-component room-temperature-curing polyurethane adhesives without pre-treatment. For the utilised two-component room-temperature-curing methacrylate adhesives, the determined strengths were actually in the area of 8.3 MPa. These high strengths could also be documented with corresponding fracture patterns (cohesion or substrate fracture in accordance with DIN EN ISO 10365).

The applied physical surface pre-treatment methods (atmospheric-pressure plasma and low-pressure plasma) led to a significant increase in the surface energy and an improvement in the adhesive strength for two-component room-temperature-curing epoxy adhesives (at least 5.3 MPa for PLA and 4.3 MPa for PHB). The test specimens broke thereby in the substrate. The use of atmospheric-pressure plasma additionally led to a significant improvement in the mechanical tensile shear strength of the PHB bond with silane-modified polymer adhesives (MS polymers) from 0.6 to 1.7 MPa. A cohesive fracture pattern could be observed hereby.

Sanding (as a method for improving the mechanical adhesion), however, showed no distinct improvement in the mechanical properties within the framework of the performed investigations. This method can therefore be considered as not recommended. In order to provide an unambiguous statement, further investigations must be carried out regarding this point.

Summary

The bioplastics available on the market can be securely bonded using conventional welding procedures such as thermal contact welding, ultrasonic welding, high-frequency welding, heated element butt welding and infrared welding. Fortunately, no special constructional modifications must be made to the welding machines. However, it should be noted that each material has its own processing window. If bioplastics are processed under welding conditions which are suitable for the material, this leads to an expedient bonding (a short-term welding factor of 1.0 can easily be achieved).

For the preparation of the adhesive surface of the bioplastics PLA and PHB, alcoholic cleaning agents should be used in order to avoid solvent effects. The bonding of PLA materials without surface pre-treatment can be carried out with polyurethane adhesives and with methyl methacrylate adhesives. When using epoxy adhesives, the substrate surface should be prepared using physical surface pre-treatment methods (such as Corona or plasma). For PHB, flexible adhesives (1-C polyurethane or MS polymers) may also be used in combination with physical surface pre-treatment methods, due to the material properties. In all cases, statistically-verifiable test bondings should be carried out, following the selection of the adhesive, in order to determine the mechanical properties and thereby to avoid, as far as is possible, undesirable effects such as „kissing bonds" or „weak layers".

Additional and detailed results can be found
in the online database for this joint project at:
www.biokunststoffe-verarbeiten.de

Profile extrusion, pipe extrusion and co-extrusion

– designates the continuous production of continuous products by means of extruders. Thanks to their substantial proportion of plastic applications, semi-finished products such as pipes or profiles which are manufactured through extrusion represent a mass market and are widespread in technology, construction and so on. In the extruder, the plastic is melted and thrust under pressure through a shaping tool. One of the reasons for the low market penetration of biopolymers is the insufficient viscosity and melt strength. Within the framework of the project, the relevant influencing factors for bioplastics were examined and modification concepts were developed in order to make biopolymers extrudable.

Materials

The bioplastics investigated in the section Extrusion are commercially-available bioplastics with appropriate market relevance. The materials investigated are listed in Table 1.

Table 1: Overview of the materials examined in the section profile extrusion, pipe extrusion and co-extrusion

Material class	Manufacturer	Type
PLA	NatureWorks	Ingeo 2003D
PLA	NatureWorks	Ingeo 8052D
PLA	NatureWorks	Ingeo 4043D
PLA	NatureWorks	Ingeo 7001D
PLA+Vinnex	NatureWorks	Ingeo 2003D + Vinnex 10, 20, 30 %
PBS	Showa Denko	Bionolle 1001MD
PBSA	Showa Denko	Bionolle 3001MD
PLA+PBA+Vinnex		
Green PE	Braskem	SHC 7260
Green PE	Braskem	SGD 4960

In the area of extruded plastic profiles, the search for bio-based alternatives is in vain, as the available starting materials rarely meet the requirements. Bioplastics are therefore mainly processed into packaging materials, such as, for example, PLA in injection moulding or film extrusion procedures. The profile extrusion itself is still in its infancy, as a result of which only products with a limited suitability for this process are available on the market. Initial attempts at the mono-extrusion of PLA to form profiles did not succeed. This was due to the limited flow properties as well as the weak melt stability. For the establishment of bioplastics in the production of semi-finished products, it was therefore in part necessary to counteract the negative trends through targeted modification and to thereby modify the plastics for extrusion.

Modification and extrusion

With the aid of chemical and physical modifications, the melt strength and viscosity of commercially-available PLA types could be significantly increased by a factor of up to 25 %.

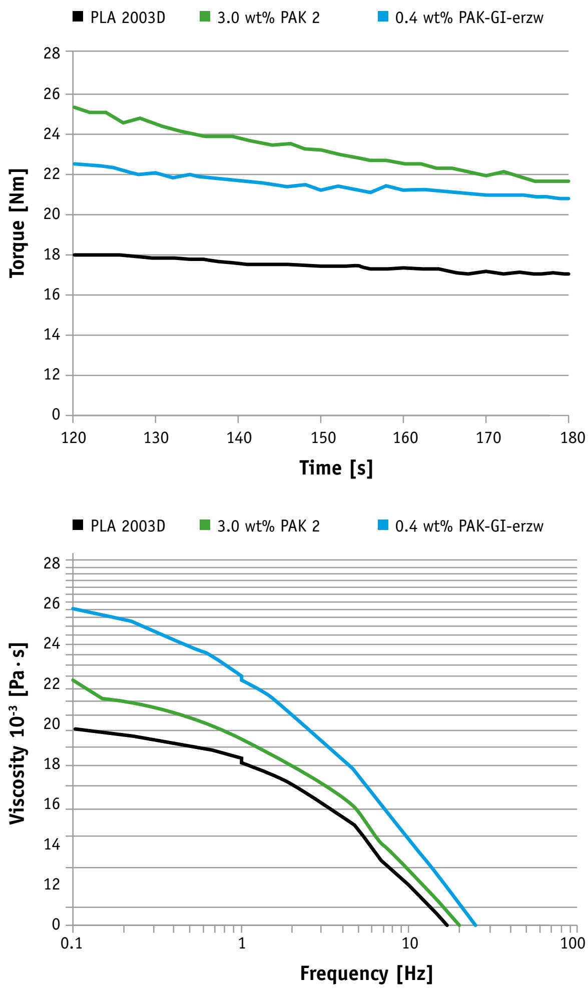

Figure 1: Rheological graphs for chemically and physically-modified PLA

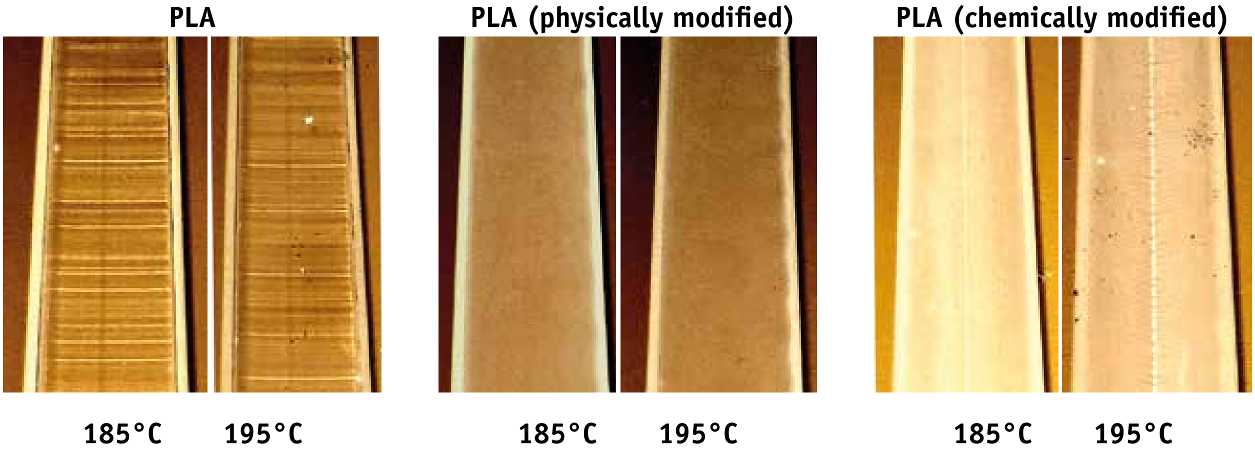

Figure 2: Extruded profiles from non-modified and modified PLA

With these modified materials and a gentle process management, profiles of a good quality could ultimately be produced.

In addition to the PLA modified in this way, further different commercially-available types such as NatureWorks Ingeo 2003D, 4043D, 7001D could be extruded, whereby the melt stability was not achieved and the pipe quality was poor. More promising proved to be the modification with the binder Vinnex, which yielded good results in differing percentage additions.

In addition to the most widely-used material PLA, further commercially-available bioplastics were also tested. For this, PBS (Bionolle 1001MD), PBSA (Bionolle 3001MD) and two types of Green PE (SHC 7260. SGD 4960) were tested, with which pipes of a suitable quality were produced.

Material tests

The quality of the materials could be confirmed using the most common analysis methods. For this, the pipes were analysed using DSC, plate-plate rheometer and MFI.

As regards mechanical tests, the pipes were subjected to tensile and bending stresses and the impact strength HDT (A/B) was determined. The results of the test series are available in the database.

Co-extrusion

The fast pace and the high demands of the pipe industry have made it additionally necessary to test not only the materials in the field of mono-extrusion. Intelligent pipe systems are multi-layer composites in which not only one type of material is utilised. Against this background, a 3-layer pipe head was produced, with which the co-extrusion of three layers is possible. The tool underwent flow optimisation in order to ensure a smooth melt flow.

Summary

Within the framework of this project, the potential of bioplastics in the field of extrusion could be demonstrated. With the aid of optimized plastics and processes, it is possible to establish bioplastics in this market segment. Although the number of commercially-available types of extrusion is small, the optimization and adjustment of the necessary properties is – analogous to conventional plastics – nonetheless possible.

Additional and detailed results can be found
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www.biokunststoffe-verarbeiten.de

Injection blow moulding and injection stretch blow moulding

– is applied under the umbrella term "injection blow moulding" for the economic production of hollow bodies and wide-neck containers with accurately-fitting outlet and sealing areas and a volume of 2 ml to 1 l. Common applications are containers in the cosmetics and hygiene sector (shampoo bottles, cream jars) and small bottles for liquid or pourable medicines.

Injection blow moulding is an efficient manufacturing process in which a preform is initially injection moulded and subsequently transformed into the end product using the residual heat. A classic injection blow moulding machine consists of three stations (see Figure 1). In the first station, the preform is produced and the cooled down to the thermo-elastic range of the respective plastic. After opening of the cavity, the injection moulded part remains on the so-called transport or blow pin and is transferred to the second station, the blow mould. In the blow mould, compressed air is used to actually form the finished part. Once the demoulding temperature has been reached, the finished blow moulded component can be removed from the third station.

In addition to the standard plastics (PE, PP, etc.), technical plastics (COC, PC and COP) are currently also being processed in injection blow moulding. Due to their insufficient viscosity, their workability in blow moulding is, however, limited. Experience has shown that the extrusion and thermo-forming types which are used in the packaging industry are particularly suitable for blow moulding. These materials generally exhibit a good extensional behaviour during the forming process, which is a decisive factor in the achievement of a constant wall thickness distribution. Due to a current low availability of bioplastic types which are suitable for injection blow moulding, appropriate extrusion or extrusion blow moulding types are being fallen back upon. An overview of bioplastics which are suitable for injection blow moulding is provided in Table 1.

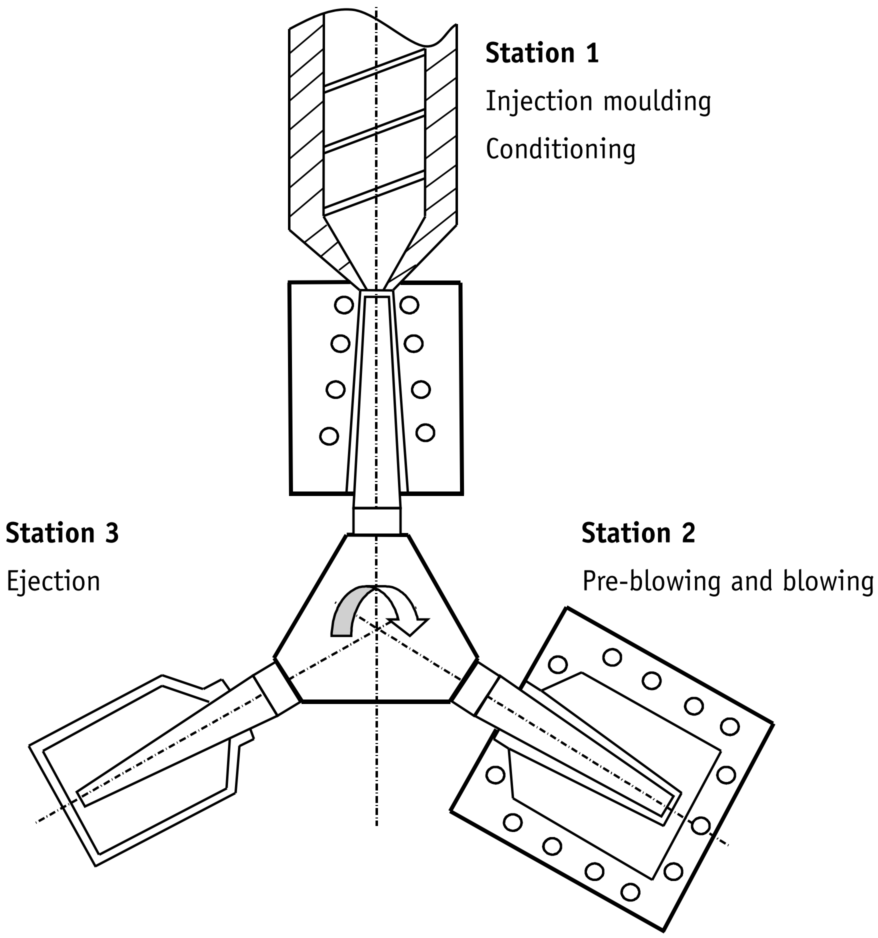

Figure 1: Injection blow moulding

Table 1: Investigated bioplastics which are suitable for injection blow moulding

Polymer	Manufacturer	Type	P [g/cm³]	MFI [g/10 min]
HDPE	Braskem	SGF 4960	0.961	0.6 (210 °C, 2.16 kg)
PLA	NatureWorks	Ingeo 7001D	1.23	14.7 (210 °C, 2.16 kg)
PBS	Showa Denko	Bionolle 1001MD	1.26	1.3 (190 °C, 2.16 kg)
PBSA	Showa Denko	Bionolle 3001MD	1.26	3 (190 °C, 2.16 kg)
PLA+PBAT	BASF	Ecovio T2308	1.26	7.8 (190 °C, 2.16 kg)

The investigations carried out on numerous bioplastics show that almost all types developed for film or blown film extrusion can be used in the injection blow process. Optimum temperature conditions in the injection moulding cavity are, however, necessary in order to achieve an optimum shaping of the preform to form the hollow body as well as a constant wall thickness distribution in the finished product. This can only be ensured through a rapid-response zone temperature control. The temperatures in the upper and lower form halves should thereby be zone-controllable, independent of one another. In the case of non-symmetric hollow bodies, a temperature profile muss be specifically embossed along the periphery in order to achieve a constant wall thickness distribution across the periphery.

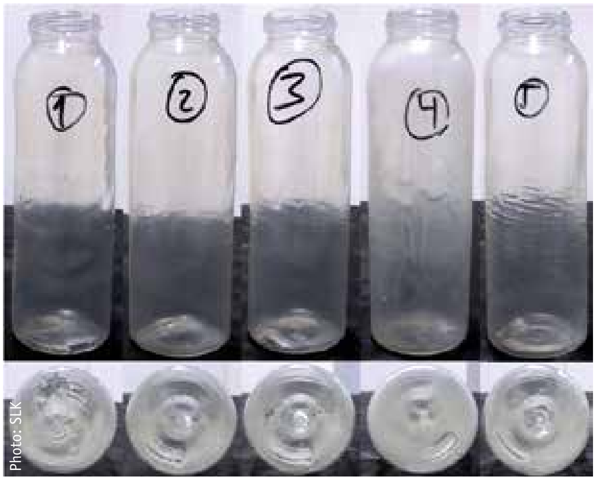

Figure 2: Injection blow moulded baby bottles made from bioplastics (from left to right: Bio-PE, PLA, PBS)

Additional difficulties in the injection blow moulding of bioplastics are posed by the relatively high specific heat capacity and low thermal conductivity of bioplastics, in particular for bio-based polyesters. The passive temperature-controlled transport pin continuously absorbs heat during the injection moulding process, but emits only a part of this heat into the cold blow air which flows in the second and third process steps. The remaining heat difference allows an almost constant pin temperature but is far higher than the temperature of the tool outer wall. This situation complicates the process control significantly and is reflected in the fluctuating temperature profile of the preform, an inhomogeneous distribution of the wall thickness and long process times.

Summary

Numerous highly viscous extrudable bioplastics can be processed into hollow bodies of good quality through the injection blow moulding process. Due to the relatively high permeability values for gases (CO_2 and O_2), flavourings and moisture as well as the lack of resistance to many organic solvents (ethanol, methylene chloride or chloroform), the application field for bio-based polyesters and their compounds is, however, severely limited. Current developments in injection blow moulding of bioplastics are therefore moving towards multi-layer plastic containers. With a thin intermediate barrier layer or inner layer from, for example, bio-based polyamide 11 and surface layers of soft or impact-modified PLA, a virtually fully-bio-based and transparent container can be produced, without adhesive layers, which could possess the potential to substitute bottles made from PC or COC. The contents of the bottle can thereby be safely protected from UV radiation, water vapour, O2 or CO2 and the performance additionally improved. Furthermore, the new multi-layer technology could open up perspectives for bioplastics in pharmaceutical and cosmetic applications in which chemical resistance as well as sterilising capabilities with hot steam, high-energy radiation or ethylene oxide are imperative.

Plastic extrusion

– serves the manufacture of long-fibre-reinforced thermoplastics.

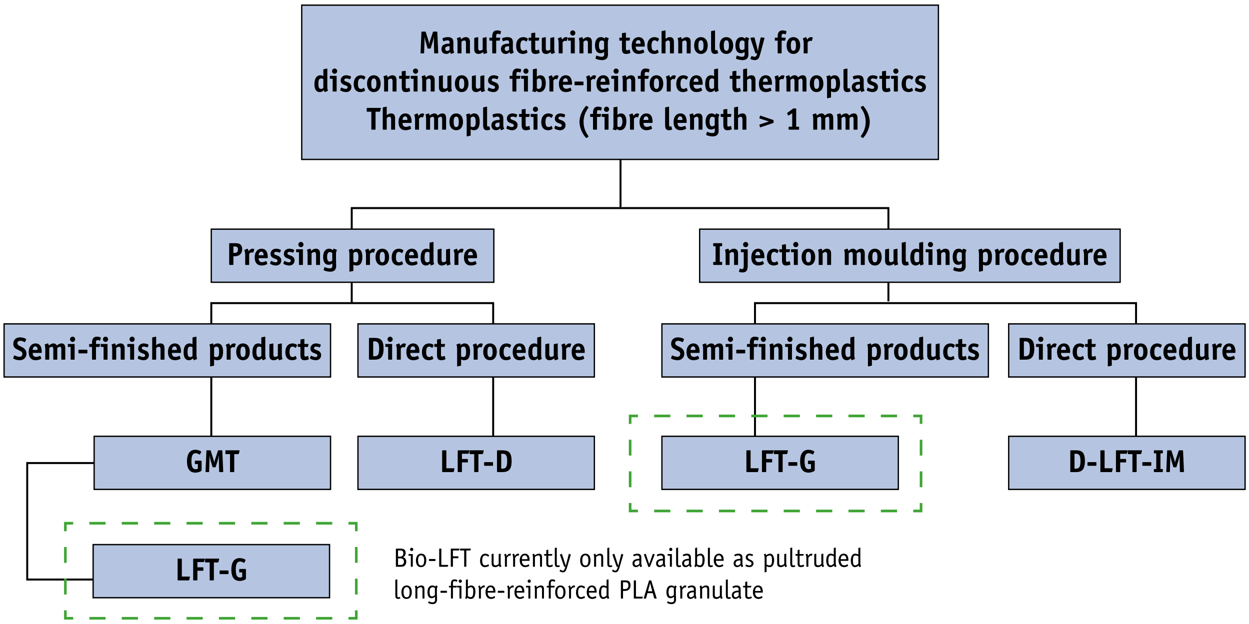

Figure 1: Structure of manufacturing technologies for long-fibre-reinforced thermoplastics

Fibre-reinforced thermoplastics can be found in many industrial sectors and applications and are increasingly gaining in importance due to the demand for lightweight construction and load-adapted component design. Of particular importance hereby are the long-fibre-reinforced thermoplastics, since they enable, more than any other class of materials, adjustable material properties and design freedom. Today they are already firmly established as a lightweight material for semi-structural components in the automotive industry. Long-glass-fibre-reinforced polypropylene, polyamide and ABS are currently being used in motor vehicle large components such as instrument panel supports (Mercedes Benz E-class), front-end carriers (Fiat Stilo, Škoda Fabia), underbody elements (Mercedes Benz A-Class) and spare wheel covers (VW Touran). Due to the low material price, the favourable material properties and the recycling advantages, PP is even displacing technical plastics.

Long-glass-fibre-reinforced thermoplastic components can be produced indirectly from semi-finished products or manufactured via the direct procedure. The semi-finished-based thermoplastic moulding materials include glass-mat-reinforced thermoplastics (GMT) and prefabricated rod-shaped pellets (LFT-G). Of particular industrial interest are, however, the direct procedures (LFT-D), such as the XRETM process (Faurecia) or LFT-D-ILC (Dieffenbacher). Due to the elimination of an additional processing step for the semi-finished products, LFT-D processes are economically advantageous.

Despite the development of the process technology, LFT extrusion has numerous advantages – but also disadvantages – compared to LFT injection moulding. The extruded components must be finished in an additional post-processing step. Passage openings can generally only be realised through subsequent punching; this results in production waste which causes additional material costs and higher recycling outlay. During extrusion, particularly in GMT or LFT direct processes, significantly higher fibre lengths can, however, be realised. In addition to improved strength and impact resistance, this has a positive effect on the deformation properties and dimensional stability as well as improved creep and fatigue behaviour of the components under thermal stress. Furthermore, the ratio of the component size to the tool investment falls in favour of the extrusion process.

Table 1: Comparison of the material properties of the LGF thermoplastics

	POLYFORT® FPP LGF 30	BIO-FED PLA LGF 30	testing standard
Modulus of elasticity [GPa]	7.5	11.4	ISO 524-1/-2
Tensile strength [MPa]	110	91.7	ISO 524-1/-2
Breaking elongation [%]	2.6	1.06	ISO 524-1/-2
Charpy impact strength [kJ/mm²]	60	22.3	ISO 179 / 1 e U
Charpy notched impact strength [kJ/mm²]	18	18.7	ISO 179 / 1 e A
HDT/A [°C]	149	60	ISO 75

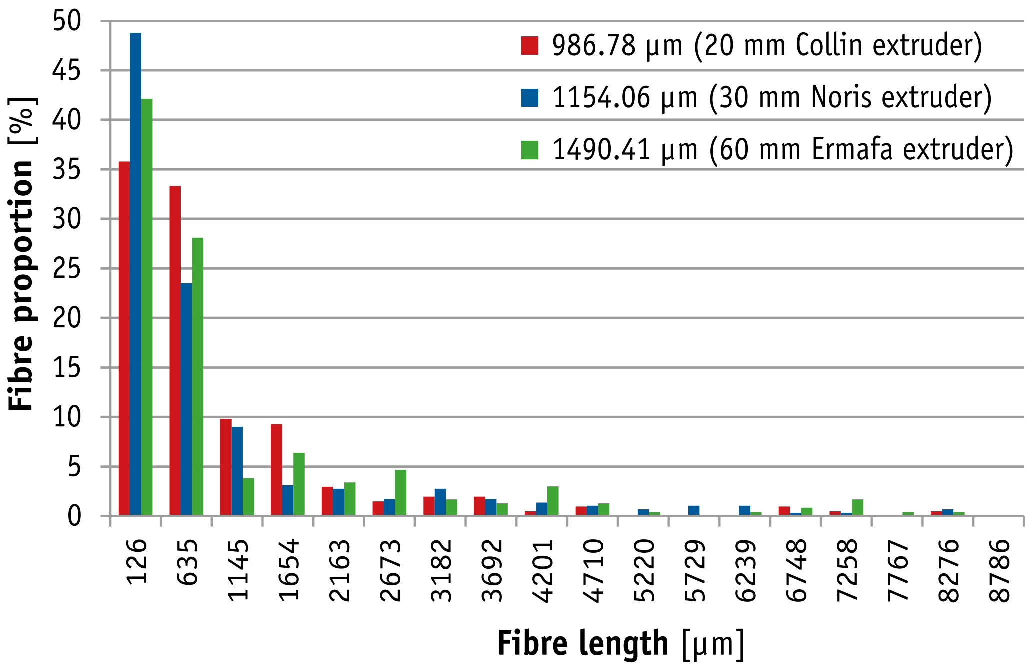

Figure 2: Fibre-length distribution and average fibre length in dependence on the screw diameter

High material prices and often inadequate material performance result in a lack in demand for Bio-LFT. It is, however, still in its infancy and requires, compared to conventional LFTs, a number of material-related and procedural developments. One of the few bio-based products currently available is the polylactide (PLA) LGF 30 which is offered upon request by the company BIO-FED GmbH as sheathed, rod-shaped granulate of 10 mm in length. This Bio-LFT-G is an injection-mouldable and extrudable PLA with 30 wt% LGF reinforcement. The optimum processing method for this material is plastification pressing. For this, the granulate is melted in an extruder, homogenized, then discharged in the form of a strand and pressed. Since for this type of granulate the dissolving of fibre bundles and the wetting of individual fibres takes place in the single-screw extruder, extruders with larger screw diameters (D > 60 mm) must be used in order to minimise fibre damage mechanisms. The fibres are damaged most strongly whilst the melt is filling the tool. Through a suitable design of the extrusion tool, the shortening of the fibres can be significantly reduced.

Summary

The potential of bio-based plastics is far from exhausted with this already-implemented and typical example. The applicability of PLA as a bio-based matrix material for competitive extruded LFT applications requires further efforts in research and development. Studies show, for example, that through the addition of further compatible bioplastics, in particular polybutylene succinate (PBS), the impact strength and the thermal stability of the composite can be significantly increased without any substantial loss in stiffness and strength in the material. In the future, a major role in extruded semi-structural applications will, however, be played by the non-degradable, bio-based polyamides and Bio-PP, as these possess a considerably wider range of properties which can be more easily optimised.

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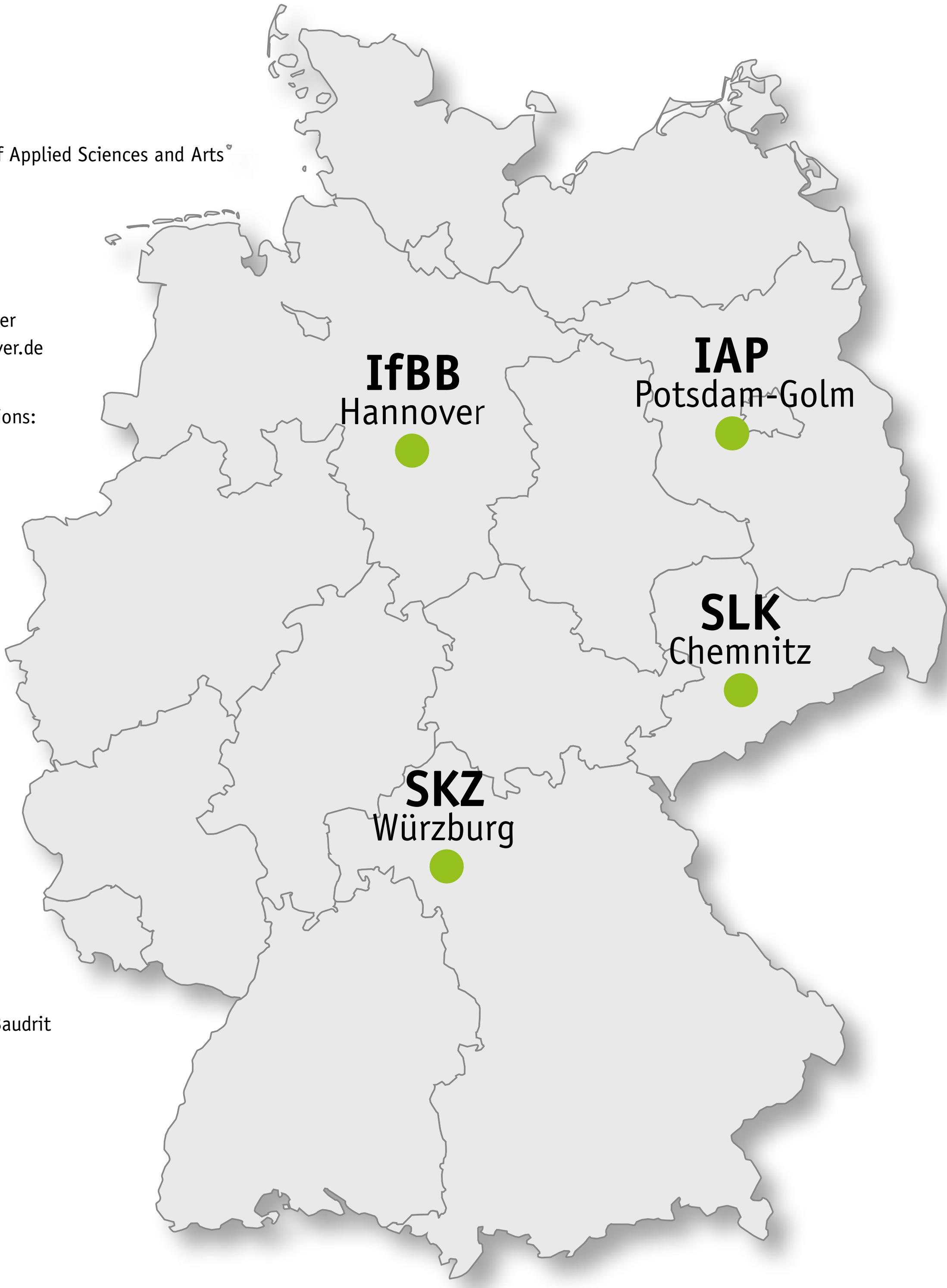

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