Environmentally-Friendly, Heat-Resistant Profiles

Development of Materials Tailored to Process

Bioplastics are considered to be eco-friendly and are currently used mainly for packaging and food contact applications. By optimizing the heat resistance of PLA-based systems, which can be achieved by targeted crystallization of semi-finished parts during the manufacturing process, the Fraunhofer ICT aims to enable their use in technical applications as well.

In the long term an increasing demand for bioplastics and particularly for bio-based plastics is expected. Biopolymers form the basis of sustainable development, and stand for an effective and economical use of raw materials. Reasons for the significant interest in biopolymer materials include economic aspects but also continuous improvements in their property profiles as well as optimized processing conditions for bioplastics.

At present the preferred and most promising bioplastic is polylactic acid (PLA). PLA is widely available and at the same time has a reasonable market price. In the light of predicted price hikes for petroleum-based plastics, these developments will make PLA even more attractive in the future. It can be assumed that due to future shortages in raw materials and the associated higher purchasing and environmental costs, petroleum-based standard plastics will be increasingly replaced with bioplastics.

Profile made of polylactide (figures: ICT)

Material with Special Properties

Lactic acid is the basic material of PLA, and can be produced by means of fermentation processes using plant products. Polymerization is mostly carried out via polycondensation or ring-opening polymerization [1]. Thanks to comprehensive optimization measures in the manufacturing process over the past years, the sales price of PLA could be reduced from more than 10 EUR/kg to approx. 2 EUR/kg. For the future, experts expect a further reduction in prices.

Researchers at the Fraunhofer ICT in Pfinztal, Germany, are developing a new polymer blend portfolio with individually tailored properties for many application areas. Compared to other biopolymers PLA can be readily modified and is therefore highly variable and adaptable regarding its properties. In general, commercial PLA has an E-modulus in the range of 3,400–3,900 MPa and a tensile strength of 45–60 MPa. This puts it at the same level as other thermoplastic polycondensates. Similar to PET, PLA has a particularly high scratch resistance and is optically transparent in an amorphous state. In addition, even without the use of additives, PLA exhibits good oxygen barrier properties and is easily printed [2].

Nonetheless, and in spite of its good strength parameters, unmodified PLA is still not suited for application in technical areas. This is primarily due to its low ductility, but also to the heat resistance of 55–60 °C. Moreover, special conditions »

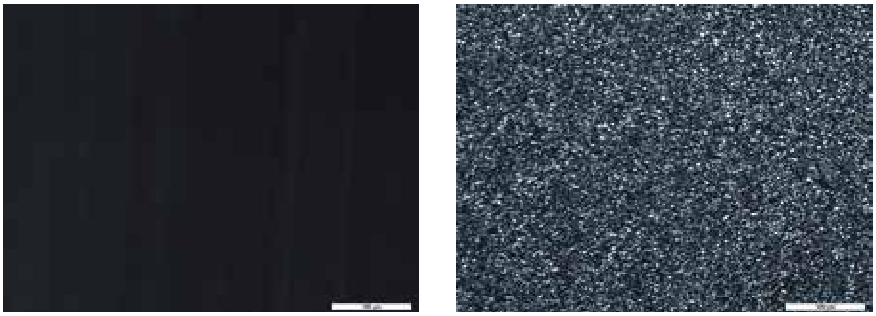

Fig. 1. Optical microscope image of microtome sections (10 µm): Amorphous PLA (left) and partially crystalline PLA (right)

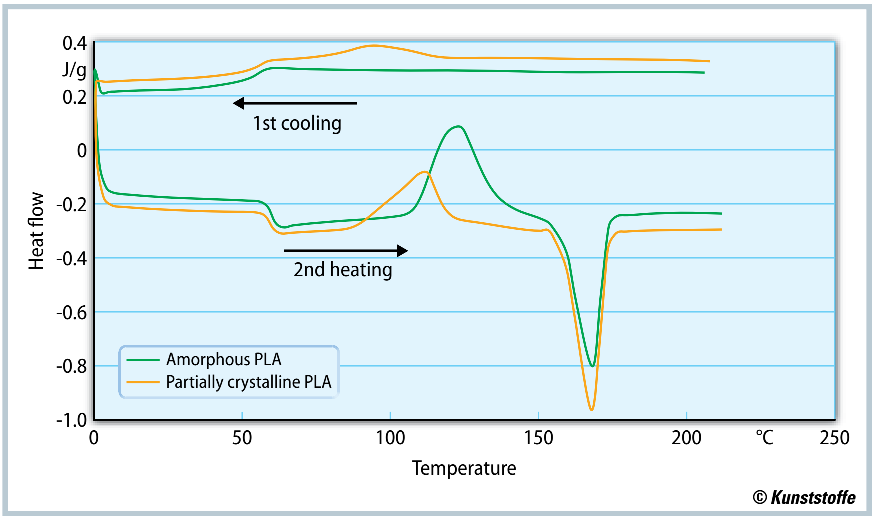

Fig. 2. DSC thermograph of amorphous PLA (green) and partially crystalline PLA (yellow)

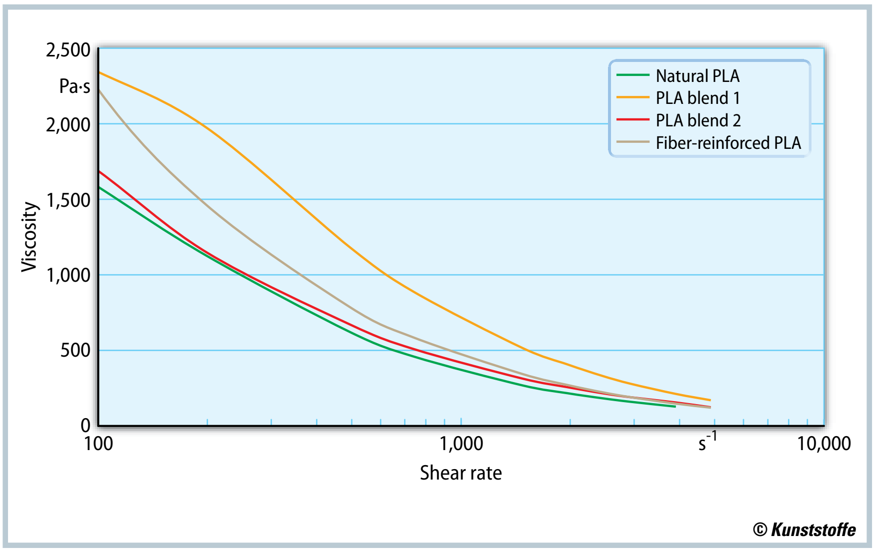

Fig. 3. Viscosity curves of PLA blends and PLA reinforced with natural fibers

must be followed when processing PLA. For example a drying stage is required before processing to ensure a maximum residual moisture of 250 ppm. A higher residual moisture during processing leads to hydrolytic decomposition and therefore damage to the polymer. As a result reduced material properties must be expected. Another challenge is the relatively low crystallization speed and the long cycle times that result during the injection molding processes. Compared with the very fast crystallization of PBT (within seconds), the crystallization time of PLA is counted in minutes.

From Film to Structural Component

Due to its outstanding biocompatibility PLA has already been used in medical technology for decades, e.g. as a drug carrier or material for implants. As a polymer blend with other bio-based materials, PLA has now become the first-choice bio-based plastic in the packaging field, and is already established as an alternative material for PE or PP in many areas. Other interesting markets for PLA-based systems are office and decorative articles and recently also children's toys [3]. All conventional technologies used in plastics processing can be used for PLA, such as extrusion, injection molding, blow molding, film production, and fiber spinning [4]. Another special application field for PLA involves compound materials. In combination with fibers – natural fibers in particular – the mechanical properties of PLA can be increased efficiently to levels that make them suitable for use in technical applications. Apart from the crystallization of PLA, the addition of natural fibers is a proven method for increasing the material's temperature resistance, thereby opening up the possibility of using PLA for technical applications.

More Crystalline – Better Heat Resistance

Contrary to crystalline PLA (opaque), amorphous PLA is transparent and exhibits a heat resistance of 55–60 °C. Components made of amorphous PLA are therefore not suitable for technical applications with temperatures above 60 °C. However, by realizing a regular arrangement of the molecular chains by means of crystallization, PLA can become more heat resistant [5]. Depending on the degree of crystallization, this approach allows an optimized heat resistance that may be higher than 100 °C [6]. Unfortunately pure PLA crystallizes relatively slowly compared with other polymers, even under optimum crystallization conditions. Conventional cooling times and mold temperatures are therefore not adequate for the production of crystalline PLA. This problem can be solved by introducing nucleating agents into the polymer matrix. Nucleating agents reduce the free enthalpy required for the crystallization of PLA and consequently lead to an

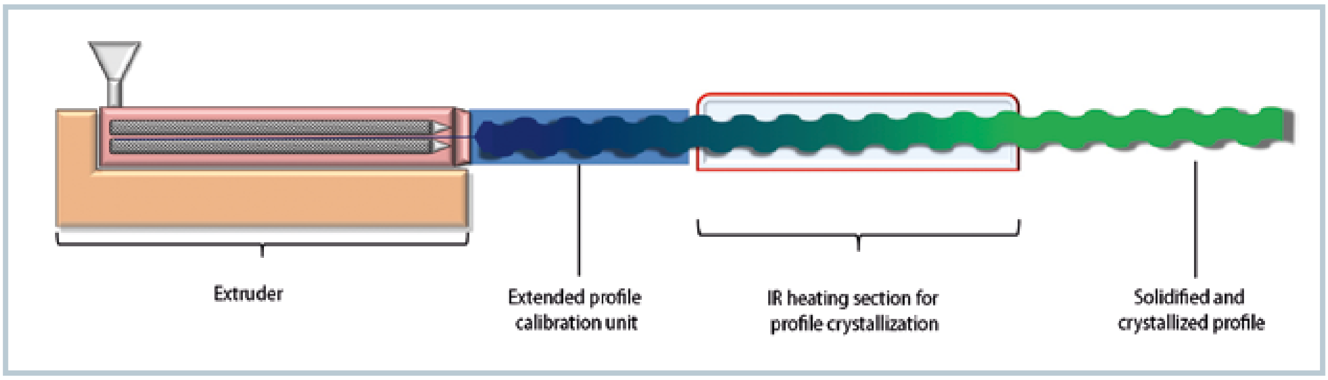

Fig. 4. Schematic representation of the direct crystallization process with variothermal tempering

earlier start and more intensive course of the crystallization process [7].

However, apart from an optimized nucleating system, the process conditions necessary for crystallization must also be optimized for the economical production of crystalline components made of PLA. It is this precise interaction between material and process development that leads to the required results regarding the degree of crystallization in manufactured components and the resulting material properties [6]. After injection molding, the component's crystallinity can be checked easily and reliably, e.g. by means of an optical microscope with crossed polarizers. If the examined material samples exhibit crystalline structures (spherulites), the plane of polarized light waves is changed. The result is that light waves are not completely extinguished when using crossed polarizers in the microscope, and spherulites become visible in the form of Maltese crosses. **Figure 1** shows an optical microscope image of amorphous PLA (left, black), and crystalline PLA (right, degree of crystallization about 40 %). Alternatively DSC analysis is also a fast and cost-effective procedure to determine the crystallization properties of polymers, and permits additional findings, e.g. concerning the kinetics of the processes involved and the occurrence of phase conversions. **Figure 2** shows a typical DSC curve for amorphous (green line) and partially crystalline PLA (yellow line).

Increase of the PLA Profile Crystallinity by Using a Temperature-Controlled Calibration Unit

Materials to be processed in profile extrusion have to fulfill additional material demands. One of the decisive factors for extrudability is to ensure adequate melt strength with simultaneous good flow characteristics. Plastics processed in profile extrusion (structural profiles) are mostly PVC, ABS, and polypropylene. Commercially-available PLA grades are not suitable to be processed in profile extrusion due to their low viscosity. Based on comprehensive investigations in material development, researchers at the Fraunhofer ICT have succeeded in developing PLA-based systems that exhibit an adequate melt strength and therefore meet the demands of profile extrusion. **Figure 3** shows the viscosity curves of PLA blends that have been produced at the Fraunhofer ICT and that have already been processed successfully in profile extrusion.

Regarding a direct crystallization during extrusion of PLA, researchers at the Fraunhofer ICT are realizing a strategy comparable with the Variotherm technology in the injection molding processes. The emerging profiles are passed through a temperature-controlled calibration unit, which permits the formation of crystal structures from the component surface down to the core. **Figure 4** shows a schematic representation of the new profile extrusion process.

With a technical plant (type: CMT 35, a conical counter-rotating dual-screw extruder; manufacturer: Cincinnati) adapted to the needs of application-related research, the Fraunhofer ICT is in a position to put the theoretically developed methods into practice in-house, and to optimize them continuously – both in terms of material and processing. Thanks to the new processing technology and the use of biopolymers as alternative material systems the researchers of the Fraunhofer ICT succeeded in widening the range of available materials and properties of structural and decorative profiles.

Summary

Researchers of the Fraunhofer ICT showed that the newly-developed PLA based materials can be processed on conventional profile extrusion plants. Furthermore they successfully demonstrated that the utilization of the Variotherm-like processing approach additionally increases the temperature resistance of the produced parts due to their increased crystallinity. ■

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