

Influence of Recycling of Poly(lactic acid) on Packaging Relevant Properties

Christian Hopmann, Sebastian Schippers, Christopher Höfs

Institute of Plastics Processing (IKV) in Industry and the Skilled Crafts at RWTH Aachen University, Pontstraße 55, 52062 Aachen, Germany

Correspondence to: C. Höfs (E-mail: hoefs@ikv.rwth-aachen.de)

ABSTRACT: The most promising representative of biodegradable plastics in packaging applications is polylactide (PLA). Despite this, there is only a small market of PLA in Europe. Reasons for that are the high price of PLA raw material and the lack of knowledge of the behavior in packaging applications. It has a number of peculiarities so producers of plastics packaging hesitate to use it. Like other polyesters, it can degrade at increased temperatures in the presence of moisture by hydrolysis whereby it loses its physical and chemical properties. In all production processes, production waste is generated (i.e., stamping grids or edge trim). In most cases, this waste is used. It is not known in detail, how an internal recycling process will influence the final product properties. One problem is hydrolysis by which the production waste is partially degraded. Target of this study is to analyze the recycling process of PLA within the context of necessary process adaptations and the effects upon ecological efficiency. Films for packaging containing multiple types and amounts of production waste will be produced by extrusion and tested concerning their mechanical properties. The analysis of the recycling behavior showed that internal PLA production waste is well suitable for recycling. The influence of the recycling on the molecular weight is negligible. The effect on the viscosity and thus on the extrusion process is higher. Packaging relevant properties like mechanical or optical properties are hardly influenced. Especially recycling with a recycling quota of up to 50% has an insignificant effect on the film properties. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41532.

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INTRODUCTION

Poly(lactic acid) or polylactide (PLA) is one of the most promising bioplastics, because it is commercially available in industrial scale and an appreciable number of established packaging applications are available on the market. It can be processed in all usual thermoplastic manufacturing processes of the plastics industry like extrusion, injection moulding, thermoforming, blow moulding, blown film extrusion, or foaming. Examples for major PLA products are extruded sheets for thermoformed products, bi-axially oriented films, blow moulded bottles, injection moulded products and fibres for apparel and nonwovens.¹

Nevertheless, PLA is used rarely for packaging application at the moment. An important fact is the lack of information about the influence of recycled PLA (r-PLA). Although the recycling of production waste and sorted postconsumer waste is state of the art in plastics industry the influence of r-PLA on the mechanical properties, packaging relevant properties such as optical, barrier, and migration properties, or biodegradability, and the processing behavior is unknown. Feedstock recycling^{2–4} and mechanical recycling^{5–8} are analyzed in science. Especially

mechanical recycling is suitable for converters. Technical requirements and process know how are low.⁹ Despite this, the internal recycling of PLA production waste is not established as it could be.⁵ Since it is not known in detail yet, how an internal recycling process influences the final product properties, internal waste is only disposed and not re-used.

Like every polymer, PLA is exposed to several degradation mechanisms. Thermal, mechanical, and hydrolytic degradation of PLA are analyzed in various publications.^{10–21} Mechanical recycled material is exposed to these degradation mechanisms multiple times. This so called down-cycling leads to a degradation of the polymer.²² Detailed information about the change of packaging specific properties as a function of the recycling quota and the influence of r-PLA's history like temperature and stress load, storing conditions, crystallising, or drying onto final product properties is an important prerequisite for a target-oriented reuse of PLA waste.

To set up polymer structure-property relationships and to understand the influence of different process parameters, the r-PLA films are characterized by different methods. Aim is to achieve an optimum product quality for packaging. Overall aim

is the reduction of production costs, raw material input, and an improvement of the ecological balance. In a consortium of four research institutes the recycling of pure PLA waste was investigated: The Flanders' PlasticVision, Kortrijk, Belgium, analyzed injection moulding and the Institute of Plastics Processing (IKV) analyzed the extrusion process. The chemical analysis of the recycled material was done by the Fraunhofer Institute for Structural Durability and System Reliability (LBF), Darmstadt, Germany. Celabor, Herve, Belgium, characterized the physical properties of the recycled products and executed a Life Cycle Analysis (LCA) for different recycling options.

EXPERIMENTAL

Materials

The study is conducted with Ingeo Biopolymer 2003 D. This PLA for sheet extrusion is made by Nature Works LLC, Minnetonka, USA. By using a PLA without blending, effects which occur during recycling can be traced back to the PLA itself. Any side effect of a potential blend partner is excluded. Ingeo 2003 D has a density of 1.24 kg/m^3 and a MFR of 6 g/10 min (210°C , 2.16 kg). Since PLA is a polycondensate it has to be dried before processing. A moisture content of less than 250 ppm is recommended by Nature Works. Usually the predrying is performed in a dry air dryer, which heats up the polymer and conveys dry air through a hopper, which stores the r-PLA. One problem is the low glass transition temperature of PLA. As r-PLA is normally amorphous, a temperature above 60°C leads to a crystallisation, which involves a clumping of the flakes. Due to that, the PLA has to be dried at temperatures below 60°C , which is time consuming. Alternatively, the r-PLA in this study is crystallised at 100°C before drying. Crystallised PLA can be dried at higher temperatures around 90°C and therefore faster and more efficiently. Nevertheless, drying is inflexible energy-, and cost-intensive. Within the experiments the PLA is processed at a processing temperature of 190°C and a mass throughput of 72 kg/h .

Extrusion Equipment

The extrusion trials are conducted using the extrusion equipment of IKV. The extrusion line produces flat films for thermoforming. It is equipped with a 60 mm extruder ($L = 38 \text{ D}$) and a 3-roll-calander stack (both Reifenhäuser GmbH & Co. KG Maschinenfabrik, Troisdorf, Germany). The extrusion line is equipped with a melt pump (Maag Pump Systems GmbH, Grossostheim, Germany) and a 400 mm coathanger extrusion die for flat films (Verbruggen nv, Temse, Belgium). The extruder speed is controlled so that the pressure at the melt pump inlet is constant. This is performed by means of a PID element. In addition, the line is equipped with a melt rheometer (Göttfert Werkstoff-Prüfmaschinen GmbH, Buchen, Germany). The rheometer consists of a melt pump, which enables the inline measurement of viscosity curves in relation to the shear rate. Since a correlation of complete viscosity curves is not possible, an average viscosity is calculated. This means, the viscosity is averaged over the viscosity at the shear rates of 8, 25, 33, 51, and 60 s^{-1} .

An infrared drum (Kreyenborg Plant Technology GmbH & Co. KG, Senden, Germany) is used for crystallising and a dry air dryer (Motan Holding GmbH, Isny, Germany) for drying the

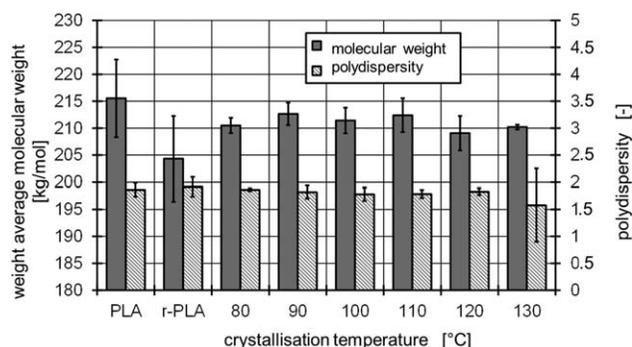


Figure 1. Influence of crystallisation temperature on weight average molecular weight of r-PLA.

r-PLA. The moisture of the PLA is controlled and measured continuously during the experimental tests with a Hydro Tracer (Aboni GmbH, Schwielowsee, Germany).

Aim of the experiments is to reproduce industrial recycling scenarios. Films produced from virgin PLA (Ingeo 2003 D) are used for the recycling trials. A shred mill (Heinrich Dreher GmbH & Co. KG, Aachen, Germany) processes these films to flakes, which are subsequently used as r-PLA. Blends of virgin PLA and r-PLA with varying recycling quota are used to produce films, which are analyzed regarding their chemical and physical properties. Either the r-PLA flakes are recycled directly or they are re-granulated to r-PLA granules. For the granulation a ZSK26MC twin screw extruder of Coperion GmbH, Stuttgart, Germany, is used.

Analysis Equipment

Size Exclusive Chromatography is conducted by LBF, Darmstadt, Germany, to measure the molecular weight distribution. The equipment is composed of pump 515 (Waters GmbH, Eschborn, Germany), autosampler AS100 (Thermo Separation Products) and a Waters 410 RI-detector. Three PSS SDV-column (106 \AA , 105 \AA , 104 \AA , each 5 \mu m , $L \times I.D. 30 \times 0.8 \text{ cm}$, polymer standards service (PSS), Mainz, Germany) are used for the separation. The Young's modulus is analyzed on a Zwick Z010 (Zwick/Roell GmbH, Ulm, Germany) according to DIN EN ISO 527 - 3 Type 2. Dart impact tests are conducted according to DIN EN ISO 6603-2 on a drop weight impact test system of CEAST 9350 (Instron Engineering Corporation, Norwood, USA). The color is measured within the CIELAB System (DIN EN ISO 11664 - 4) with a Spectro Guide (BYK Gardner GmbH, Geretsried, Germany).

RESULTS AND DISCUSSION

The typical recycling route of converters includes shredding, crystallising, drying, and reprocessing of the recycled waste to a new product. It can be shown that crystallising with infrared (IR) radiation leads to a change of the PLA properties. In addition to crystallinity and material moisture, the molecular weight is influenced as well. The weight average molecular weight of r-PLA flakes, which are prepared at different crystallising temperatures is shown in Figure 1.

The crystallisation time in the analyzed time frame of 10–40 min does not affect the molecular weight and is not further investigated in this study. The weight average molecular weight

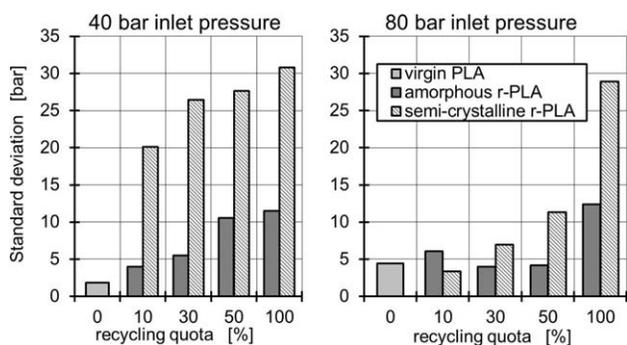


Figure 2. Standard deviations for two different melt pump inlet pressures.

of the PLA drops approx. 5% during processing to r-PLA flakes. By crystallising the r-PLA flakes the molecular weight is increased by ~4% again. The polydispersity stays constant. This means that the total molecular weight distribution is shifted to slightly lower weight average molecular weights. A slight increase of molecular weight is possible. By applying heat above the glass transition temperature T_g the mobility of the PLA chains increases. In addition, moisture is removed. These conditions enable a solid state polymerisation (SSP). The SSP is an equilibrium reaction. Because the SSP happens under atmospheric conditions instead of inert conditions and due to the lack of catalysts the effect is limited. The chain extension happens fast at the beginning of the crystallisation. Due to that and the limited mobility of the chains a reconnecting of chains is only possible, if chain ends are locally close by chance. Because of the ongoing crystallisation the chain mobility decreases and therefore also the SSP stops and is not time depending.

To prevent a strong down-cycling, typically the waste is not reprocessed to 100%. Instead it is reprocessed with a defined recycling quota. Depending on the packaging application, the recycling quota may be up to 50% of internal production waste. In the following five recycling quotas (0, 10, 30, 50, and 100% r-PLA) are analyzed. According to the recycling quota, flakes and virgin PLA in granule form are blended. Either amorphous flakes or crystallised flakes are used. Both are dried to moisture contents below 300 ppm. Crystallising before drying is performed at 110°C for 20 min. The crystallised r-PLA flakes have a crystallinity of 25% and the amorphous flakes have a crystallinity of 1%. The processing parameters are constant.

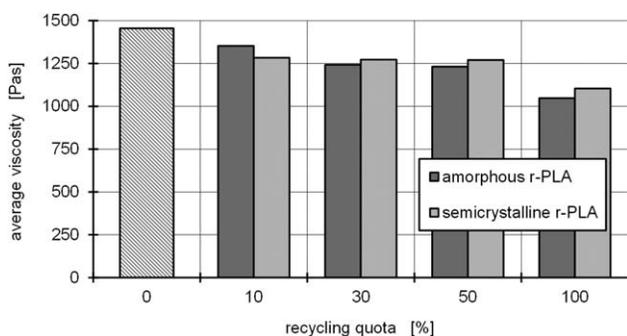


Figure 3. Average viscosity during recycling of r-PLA flakes.

Process Stability

The stability of the process is affected by the crystallinity of the r-PLA flakes. A stable process is characterized by a low standard deviation of the pressure at the pump inlet. Figure 2 shows the standard deviation of the pump pressure at the melt pump inlet for 40 and 80 bar.

The deviation during the extrusion of virgin PLA accounts for ~5% of the inlet pressure. The deviation for semi-crystalline r-PLA with almost 26% crystallinity is higher than for amorphous r-PLA. By increasing the pressure at the melt pump inlet a stabilisation of the process is achieved. This is visible through the decrease of the relative deviation for an inlet pressure of 80 bar. The increase of the average pressure leads to a decrease of the relative deviation. The deviation increases with increasing recycling quota. The processing of 100% amorphous r-PLA leads to a deviation of 28%. Semi-crystalline r-PLA causes deviations between 50 and 77%. In that case, a safe production is not possible anymore. The melt pump is not able to equalize the fluctuation of the pump pressure. The major reason for the increasing deviation is the rising amount of inhomogeneous flakes. Due to the inhomogeneous flake size the melting and conveying behavior is inhomogeneous. The geometry of the flakes handicaps the flow in the extruder. The flat flakes are compressed during extrusion so that the flat surfaces between two flakes are in contact. This leads to friction between the flat surfaces. In combination with the increasing compression the flakes block the screw channel. The material flow stops and the pressure at the melt pump inlet decreases rapidly. As result the control accelerates the screw speed, which builds up the pressure in front of the blocked section until the blocked section is released rapidly. The pressure in front of the pump increases again quickly. The effect is intensified for crystallised r-PLA. The creation of crystalline structures leads to a harder plastic. The blocking effect in the extruder is increased. By applying a higher pressure at the pump inlet the backflow of the melt is increased. Friction and interference of forward directed drag flow and backward oriented pressure flow are higher. The blockage is destabilised and, therefore, the process stabilised.

The average viscosity at varying recycling quotas is shown in Figure 3. Again, semi-crystalline and amorphous r-PLA flakes are used.

By using r-PLA the viscosity drops with increasing recycling quota. Due to the low difference of the absolute r-PLA content the difference in the range of a recycling quota of 10–50% is low: Up to a recycling quota of 50% the average viscosity decreases ~15% for amorphous or 13% for semi-crystalline r-PLA. Only by recycling 100% r-PLA the average viscosity drop accounts for 28% for amorphous respectively 24% for semi-crystalline r-PLA. Such a drop of viscosity affects the process. Although a drop of 28% does not affect the production of film on the laboratory line, the process window is changed. In general, machine components such as e.g., the die and the melt pumps are designed for a specific viscosity. A change in viscosity is therefore counterproductive and leads to a change in the process behavior and product quality. Apart from the 10% recycling quota, semi-crystalline r-PLA leads to a slightly higher

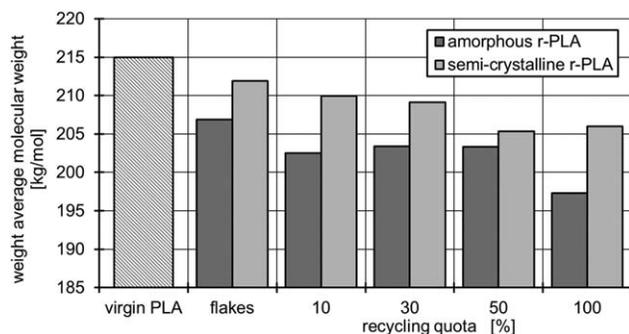


Figure 4. Weight average molecular weight for recycling of r-PLA flakes.

average viscosity. That confirms that the crystallisation affects the chain length positively. Due to the higher molecular weight (longer chain length) the viscosity is higher.

Molecular Weight

Figure 4 presents the molecular weight of the films, which are produced with varying recycling quota. The molecular weight of films with semi-crystalline r-PLA is higher due to the pretreatment with the IR crystalliser. The molecular weight for semi-crystalline r-PLA is 4% higher in average. Up to a recycling quota of 50% the molecular weight loss is marginal; 2% for semi-crystalline r-PLA, and 3% for amorphous r-PLA. Especially when considering the low difference to the molecular weight of film made of virgin PLA the difference is negligible. The results show that the viscosity is affected stronger as the molecular weight. The correlation found by Arraiza et al.¹⁷ implies that the viscosity shows dependence on the 3.4th power of the molecular weight. As shown the molecular weight is hardly influenced but the viscosity, as shown in Figure 3, is influenced significantly.

Instead of recycling flakes directly after shredding, they can be processed to granules before film extrusion. The geometry of the granules is similar to the geometry of the virgin PLA granules. Granules are advantageous since the material transport in e.g., pipes and dosing units is easier. In addition, the process behavior in the extruder during plastification is better. The melting process is more homogeneous than the melting of flakes. On the other side, an additional processing step with potential degradation has to be conducted. Virgin PLA delivered by the supplier is processed to flakes. The flakes are either crys-

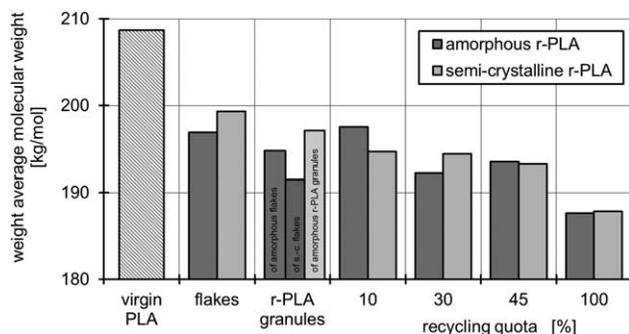


Figure 5. Weight average molecular weight at different processing steps for recycling of r-PLA granules.

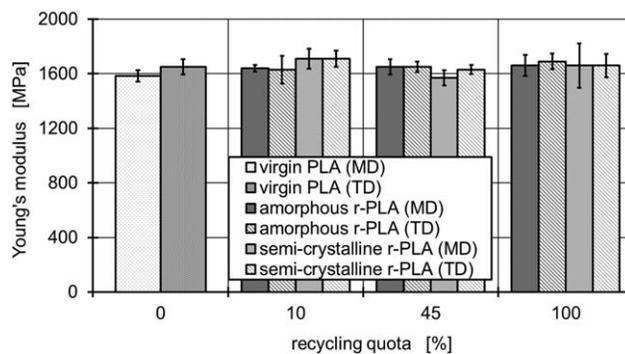


Figure 6. Young's modulus of films with varying recycling quota.

tallised and dried or only dried and then processed to granules. Granules produced from semi-crystalline r-PLA flakes are crystallised before reprocessing. The granules are re-processed with varying recycling quota. The molecular weight during these different processing steps is shown in Figure 5.

The shown molecular weights are in a narrow range. In general, the molecular weight loss is marginal and due to deviations of the measurements small effects are hardly significant. Virgin PLA loses molecular weight when processed to flakes. The molecular weight of amorphous r-PLA granules made of the semi-crystalline r-PLA flakes (second column) is lower than made of amorphous flakes (first column). One possible explanation is the different shearing in a co-rotating twin screw extruder. Since semi-crystalline r-PLA flakes are harder they are exposed to a higher shear in between the screws. Following, the shear induced thermal stress is increased. The degradation is increased during the granulation. The following crystallisation of amorphous r-PLA made of semi-crystalline flakes, represented by the second column, increases the molecular weight ~3% (third column). All in all, the molecular weight loss is marginal again. The difference in molecular weight between recycling quotas up to 45% and between semi-crystalline and amorphous granules is little (max. 5%). Only the processing of 100% r-PLA leads to a higher molecular weight loss. Due to the negligible difference the effect upon further film properties is expected to be negligible, too.

Packaging Properties

To evaluate the mechanical properties of the produced films tensile tests and dart drop tests are conducted. The recycling quota has no effect on the Young's modulus (Figure 6). Even eight times recycling of 100% r-PLA does not affect the Young's modulus. The change of the molecular weight or respectively the chain length is not significantly even for these recycling steps so that the Young's modulus is not influenced.

The results of the dart drop analysis are summarized in Figure 7. A recycling quota of 0% is only represented by amorphous r-PLA. Virgin PLA is only available as semi-crystalline material. The normalised maximum force varies between 112 and 140 N/mm. The films are brittle, which is confirmed by the low work load of the films between 0.2 and 0.33 J/mm. Films made of amorphous r-PLA resist a higher force, but a lower work load.

Due to the high brittleness of the films the standard derivation is high. Because of that only a slight tendency can be identified.

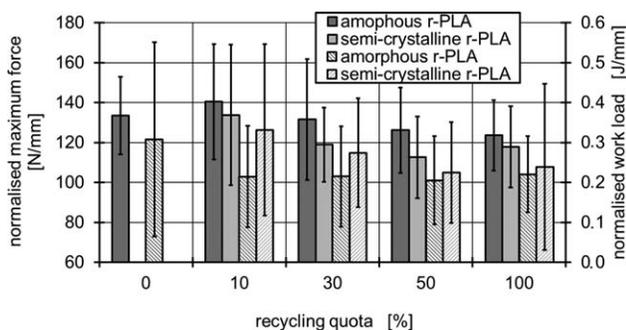


Figure 7. Dart drop analysis of PLA films with varying recycling quota.

Work load and maximum force decrease little during recycling of PLA. The already high brittleness increases. Due to the degradation of the polymer the concentration of monomers and oligomers with low molecular weight increases. These contents are not detectable by size exclusive chromatography but lead to a decrease of the viscosity and the mechanical properties under impact loading. At low concentrations low molecular ingredients are not working as plasticiser. This phenomenon is described by various scientists.^{23–26} Intramolecular bonds e.g., van der Waals forces, are increased. They function as cross link and increase brittleness.

In addition to viscosity, molecular weight and reaction on impact load the colour of the films changes. The analysis shows that only the colour b^* in CIELAB colour scale is affected. The colour b^* characterises the blue, respectively the yellow colour. An increase in b^* corresponds with a yellowing of the film. The development with varying recycling quota is shown in Figure 8.

Although the colour change is little, it is noticeable. Especially at high recycling quotas, the optical properties of the films decrease. For a recycling quota of 50% semi-crystalline r-PLA flakes, an increase of 6% respectively, 3% for amorphous flakes can be measured. Due to the unavoidable thermal degradation during processing and recycling yellowing occurs. At high recycling quotas the content of multiple processed and therefore multiple degraded PLA is higher. The higher thermal degradation through multiple processing leads to a chemical reaction: Carbonyl groups with conjugated double bonds are formed. They are responsible for a yellowing of the film.^{10,13,27} Films which are produced with a blend of semi-crystalline flakes are subjected to a stronger yellowing. Due to the thermal crystalli-

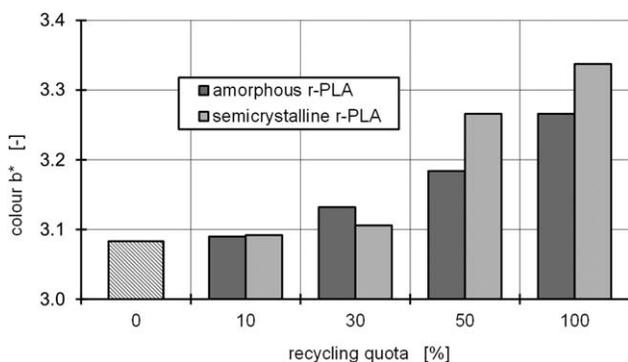


Figure 8. Colour b^* of films with varying recycling quota.

sation process the semi-crystalline flakes undergo a higher thermal degradation and therefore a higher yellowing takes place.

In addition to the mentioned film and melt properties of the PLA, other packaging relevant properties have been evaluated (e.g., coefficient of friction, surface energy, coefficient of permeation for hydrogen, and oxygen etc.). An influence of recycling on these properties cannot be identified.⁵

CONCLUSIONS

PLA is a promising biobased and biodegradable plastic used in packaging. Motivation for the use of PLA is its biobased feedstock. Therefore and due to its high prize recycling of PLA is necessary.

By crystallising PLA the molecular weight is increased by $\sim 3\%$. The total molecular weight loss is marginal up to a recycling quota of 50%. The mechanical and the optical properties of the produced films are hardly influenced. Only a little yellowing is recognisable. The influence upon the process properties is more significant. Viscosity decreases by ten percent and more with a higher recycling quota and the use of r-PLA flakes leads to high pressure fluctuations during extrusion and an adaption of the extrusion parameters is required.

In general, the results show that internal recycling is highly applicable for PLA. The product properties are hardly influenced. Recycling increases the competitiveness and allows an economical and environmental sustainable production of packages from PLA.

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