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Online observations and process analysis of chain extended polylactides during injection moulding

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ABSTRACT

The present work focuses on the processability and degradation control during injection moulding of two different polylactide grades after chain extension achieved using epoxidized and maleated chain extenders. In the first part of the contribution, the influence of chain extension and the resultant change in the viscosity on the processing parameters, such as injection pressure, melt temperature, or flowability, will be discussed. For this purpose, besides a normalized MFI test, a special investigation methodology, which included a flow-spiral test and the measurement of injection pressure, was employed for online observations. In regards of the flow behaviour, it was confirmed that the different functional groups of the used chain extenders play a dominant role in counteracting the degradation of polylactide. The second part deals with the mechanical performance of modified PLA. It was shown that the chain extension reaction leads to chain branching, and, thus, the crack stopping mechanism is influenced positively. As a consequence, the polymer toughness was affected and the mechanical behaviour improved.

1. Introduction

Melt processing of polylactides is complicated due to their low thermo-mechanical stability. Therefore, even low-shear (gentle) processing conditions can lead to serious degradation of polymer chains with formations of oligomers and others low molecular weight fractions. Consequently, a decline of the processability, and, finally, a catastrophic deterioration of the mechanical performance are observed. In addition, polylactide is characterised by a very low melt strength [1–5]. Kanev et al. investigated the flow behaviour of different PLA melts when subject to typical compounding conditions, and found an extremely low shear viscosity and a broad Newtonian-plateau [6].

With respect to the injection moulding process, the low melt viscosity leads to problems when setting up the back pressure at the front of the screw. The back pressure is needed to operate the needle valve nozzle or hot runners. Besides this, polylactide flows relatively poorly in close and long channels. Increasing the injection pressure in this case leads to mechanical damage and reduces the molecular weight [7]. Finally, the slow crystallization rates usually prevent suitable crystallization. Therefore, commercial PLA processed in conventional injection moulding process is mostly amorphous [8–11].

The present study deals with two different polylactides. The basis polymers were subjected to a chain extension reaction during compounding, and, afterwards, processed in a conventional injection moulding process. The effects of reactive extrusion were extensively analysed in the previous publication [12], thus they will not be discussed in the course of this contribution. The frame of this work includes an online investigation of processing parameters in injection moulding which were affected by structural changes and improvement of thermo-mechanical stability due to addition of a chain extender to the polylactide. Additionally, the impact of the polymer processing parameters, the polymer morphology and the resultant mechanical performance will be reflected.

2. Experimental section

2.1. Polymers and additives

Two polylactides from NatureWorks LLC/USA, PLA 3051D and PLA 4042D, were used. According to the processing guidelines [13,14], the polymers should be processed in the temperature range 190–205 °C. Both polylactides were supplied form of semi-crystalline pellets. Additional material parameters are summarized in Table 1.

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Table 1
General processing and structural properties of the employed PLA [13,14].

Property	Unit	PLA 3051D	PLA 4042D
Processing temperatures (entry to nozzle)	[°C]	20–165–195–205	45–180–190–200
Screw velocity	[rpm]	100–175	20–100
Melt temperature	[°C]	150–165	n/a
MFR (210/2,16)	[g/10 min]	13	6
D-lactide content	[%]	3,7–4,6	4,0–8,0
Residual monomer	[%]	0,30	0,30

PLA 3051D is predisposed for injection moulding applications, and it is characterized by a relatively high stiffness, low impact strength and good transparency. In contrast, PLA 4042D represents an extrusion grade polylactide. Both PLA 3051D and PLA 4042D can be processed on conventional processing machines as long as the moisture content in the pellet does not exceed 250 ppm.

In order to observe the behaviour of chain extended polylactide during injection moulding, two multifunctional chain extenders were used. Both reactive additives are based on a styrene-acrylic copolymer substrate with a different functionality. CESA-extend represents an epoxidized chain extender with an epoxy functionality of 9. This chain extender was provided by Clariant Masterbatches in form of a solid masterbatch composed of commercial polylactide as a carrier polymer and Joncryl 4368S from BASF as the epoxidized reactant [15,16]. The second chain extender was Joncryl 3229. This additive is functionalized with maleic acid anhydride reactive groups. The functionality of Joncryl 3229 equals 6. In this paper, the abbreviation "CESA" will be used for the epoxidized chain extender and "Joncryl" for the maleated additive.

2.2. Processing conditions

The addition of chain extenders was realized by compounding PLA with a predefined dosage of additives. The compounding conditions and resultant structural changes of the polymers are described in previous publication [12].

In the course of this study, the injection moulding machine Klöckner Ferromatik FM 85, manufactured by Klöckner Ferromatik, was used. The machine is characterized by a screw diameter of 40 mm and a clamping force of 850 kN. The *L*/*D* ratio is 21. The applied temperature profile was 50 – 180 – 190 – 200 – 190 °C from entry to nozzle, accordingly.

The injection pressure was 450 bar and the constant injection rate was realized using a constant injection velocity of 200 mm/s in accordance with ISO 294-1 standard. The injection speed was calculated in the critical cross-section of the sample as described in the above mentioned standard. Materials used for the study of processability and the characterization of mechanical parameters were dried at 110 °C overnight prior to injection moulding (moisture content < 100 ppm).

2.3. Flow behaviour of the melt and online observations of processability

The flow behaviour in injection moulding is usually assessed quantitatively by means of special constricted flow channels in the mould. For this purpose, either standardized tests, e.g., for estimation of the melt flow index, or practical experiments like the flow-spiral test can be used [17,18]. The melt flow index (MFI) of pellets compounded with CESA was measured in accordance with ISO 1133 at the testing temperatures 220 °C and 230 °C under 2.16 kg and 10.0 kg loads respectively. A capillary viscosimeter from Haake, type Meltflixer, was used for the measurements. Each experiment represents the double determination of ten separate measuring points.

The spiral test represents a practice-relevant comparison of the flow behaviour within a material group. Direct measurements are performed under real processing conditions. In contrast to conventional MFI, the results obtained during spiral testing describe the polymer's ability to flow, taking effects such as melt cooling, solidification, crystallization and boundary layer effects into account. The spiral length is used as a measuring parameter under specific injection conditions. In general, the filling of the mould increases with increasing flowability, as is schematically depicted in Fig. 1.

The applied injection mould was designed as a closed spiral mould with a maximum flow length of 1640 mm and a symmetric trapezoidal cross-section of 3.5 mm in height and 7.0 mm in width. The injection rate was varied between 200, 400 and 600 mm/s. Each result represents at least 6 independent repetitions. Flow-spiral experiments were completed using previously dried pellets. The injection pressure was kept constant at 80 bar for all recipes. The cavity pressure was not recorded due to the length of the spiral. Remaining processing parameters correspond with the description provided in the previous section.

In order to estimate the increase of injection pressure due to addition of chain extender, further experiments with a standardized mould according to ISO 294 were carried out. The mould design comprises a symmetric double cavity with a Z-melt distributor. The constant injection pressure of 450 bar was registered based on the hydraulic pressure exerted on the screw, whereas the resultant cavity internal pressure was measured directly by a piezoelectric sensor which was placed in the mould. For this purpose, the previously compounded pellets containing polylactide with a chain extender were processed on the injection moulding machine into standard test specimens with shoulders in line with ISO 527 (specimen type 1A). The cavity pressure was measured approx. 2 cm behind the gate entry of each dog-bone specimen.

The melt temperature was measured using a Hasco Z 251-2 (Type K – NiCr–Ni thermocouple) temperature sensor. First, approx. 3200 mm^3 of the melt were injected into a plastic box, and, immediately after the sensor was introduced about 5 cm into the volume, the melt temperature was recorded directly (immersion mode). The measurement was repeated three times.

2.4. Analytical and mechanical analysis

The analysis of the molecular weights was accomplished using gel permeation chromatography (GPC). First, the polylactides were dissolved in dichloromethane (total volume was 100 μL). Afterwards, the separation was conducted at room temperature. Two PLGel 5microns MIXD C-columns were used. In order to ensure a constant flow of the mobile phase, an isocratic pump, type Agilent

Fig. 1. Flow-spirals with varying form filling (arrow indicates higher flowability).