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TITLE:

**Investigation of the thermoformability of various D-Lactide content  
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## **Abstract**

In this paper, we investigated the thermoformability of PLA films with various D-Lactide contents and therefore different crystallization properties, performing tensile and ball burst tests at various temperatures and testing rates. We found that the behavior of the PLA films tested above the glass transition temperature significantly differ due to the difference in D-Lactide content, and thus crystallinity. During tensile testing, elevated temperatures and mechanical stress caused the crystallization temperature to decrease and thus highly induced crystallization. At the same time, as testing speed was increased, the ability of the polymer to crystallize decreased. In ball burst tests, the PLA films crystallized more than during tensile testing. We described the differences found between tensile testing and ball burst testing, which latter better represents the conditions of thermoforming through inducing biaxial deformation.

## **Keywords**

Poly(Lactic Acid), thermoforming, ball burst test, D-Lactide content, crystallinity

# 1. Introduction

Nowadays, the production and usage of petroleum-based plastics receives an increasing amount of criticism, partly because petroleum is a limited resource and partly because not all plastic waste is recycled. This causes waste management and pollution problems—an enormous amount of plastics, mainly single-use, short-lifetime packaging plastics end up in landfills or even worse, in the ocean. As environmental consciousness and the need for sustainability grow, biopolymers receive more and more attention, since they have two extraordinarily properties, which may solve these problems. First, biopolymers can be produced from renewable agricultural resources instead of petroleum and second, they biodegrade into non-toxic materials like water, humus and carbon-dioxide. Therefore, the whole life cycle of a biopolymer fits into the cycle of nature [1-4]. Currently, a great deal of research is dedicated to developing biopolymers that have similar properties, processability and a reasonable price compared to conventional, petroleum-based plastics. Two decades ago, the entirely starch-based Thermoplastic Starch (TPS) was believed to revolutionize the plastic industry, but its poor mechanical properties and high water uptake still significantly limit its applicability, although these properties can be compensated either by blending [5] or reinforcing [6]. Currently, Poly(Lactic Acid) (PLA) is the biopolymer with the most potential to replace conventional plastics [7].

PLA is a thermoplastic, aliphatic, semi-crystalline polyester, which can be derived entirely from agricultural plants containing starch (corn, maize, rice, potato, etc.) or sugar (sugarbeet). In the first step, glucose is made from starch or sugar by hydrolysis followed by the production of lactic acid through the fermentation of glucose in the presence of lactic acid bacteria (*Lactobacillus*) [8]. Finally, PLA is produced from lactic acid. There are several ways to achieve this, but the most common method is to first synthesize the dimer of lactic acid called lactide and then perform ring-opening polymerization on lactide to produce the high molecular weight PLA [9]. As two stereoisomers exist, namely L-, and D-lactic acid, there are three types of lactides named L-, D- and D,L-lactide (or meso-lactide). Subsequently, PLA can be regarded as a copolymer of L-lactic and D-lactic acid. When PLA is made from only L-lactic acid or D-lactic acid, it is isotactic and is referred to as PLLA (Poly(L-Lactic Acid)) or PDLA (Poly(D-lactic Acid)), respectively [10, 11]. Usually, PLA grades containing 0-15% D-lactide are produced, depending on the given application, since the D-Lactide content highly influences the crystallization and thermo-mechanical properties of PLA [12-14]. PLA grades with higher D-lactide content crystallize very slowly, thus these grades are used when transparency is required. On the other hand, PLA grades with low D-lactide content including the optically pure and isotactic PLLA crystallize the fastest amongst PLA grades (but still slower than conventional plastics, such as like Poly(Propylene) (PP) or Poly(Amide) (PA)) and are usually used to produce crystalline PLA parts with an improved heat deflection temperature [15, 16]. PLA can crystallize into  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\eta$  (also called stereocomplex) crystal forms [17]. The most common and stable type is referred to as  $\alpha$  form, which develops during processing (both cooling from melt and annealing) or from solution [18, 19]. There is also a less ordered (disordered) crystal form called  $\alpha'$ , which has the same conformation but a loose packing manner and lower density compared to the  $\alpha$  crystal form [20-22]. Additionally, if the  $\alpha$  form is subjected to high drawing at a high temperature, the  $\beta$  form develops [23, 24], while the  $\gamma$  crystal form can be developed when, for example, a hexa-methylbenzene substrate is used and epitaxial crystallization is applied [25]. Finally, when the optically pure PLLA and PDLA are compounded, stereocomplex PLA develops [26-28].

The glass transition temperature of PLA is around 50-60 °C (depending on molecular weight [13]), its melting temperature is 150-175 °C (depending on D-lactide content [13]), a tensile modulus of 3-3.5 GPa and a tensile strength of 60-65 MPa. However, it is brittle, with a notched Charpy impact strength of only 2-3 kJ/m<sup>2</sup> and has a low heat deflection temperature (HDT ~50 °C) [29]. The latter property is evidently the result of the low crystallinity (due to slow crystallization) and the inherently low glass transition temperature of PLA. Based on its properties, PLA could readily substitute stiff, strong and transparent polymers, such as Polystyrene (PS) or Poly(Ethylene Terephthalate) (PET) and when modified, it can also substitute tough polymers as well like PP or Acrylonitrile Butadiene Styrene (ABS) [30]. PLA can be processed by conventional plastic processing technologies, such as extrusion, injection molding, thermoforming, compression molding, rotational molding, film or bottle blowing, and foaming. It can even be used as a filament in fused deposition modeling (FDM) [10], a widely used additive manufacturing technology. Accordingly, PLA is typically used for products like trays, bags, films (even with antibacterial properties [31]), cups, cutlery, agricultural and office utensils, foamed packaging [32] and medical implants; PLA is even suitable as matrix material in natural fiber [33] or talc-reinforced biocomposites [34] for automotive or electronic industry applications, where flame retardancy is crucial [35, 36]. PLA products are often made by thermoforming, which is a versatile process, since various molds can be used (e.g. plastic, wooden, steel, aluminum) cost-effectively for both small and large series production. Thermoforming can be used to produce yoghurt cans, trays, inner covers for fridges and similar products.

The quality of the preform (the film or sheet) largely determines the quality of the final product in thermoforming. At present, there is no deformability test that is fully suitable for characterizing the thermoformability of a polymer film. This is because thermoformability is difficult to infer from standard tests since the nature of stress is different. Generally, tensile tests at elevated temperatures, direct thermoforming tests (mold necessary), various burst tests [37], simulations [38], pneumatic deformability tests (when the polymer sheet or film is heated to the forming temperature and is inflated pneumatically) or the combination of these are applied to predict and investigate the behavior of a polymer film during thermoforming. The pneumatic deformability test, for example, follows the dynamics of the thermoforming process well, but it is difficult to obtain a qualitative index of thermoformability from it, while tensile tests only represent a uniaxial stress state. In contrast, the ball burst test is specially designed to test woven fabrics, whereas the penetration of a ball causes complex, biaxial deformation on a clamped fabric and thus this method better represents the biaxial conditions of thermoforming. For this reason, it is worth investigating the usability of the ball burst test for the prediction of the behavior of thermoformed polymer films, since it could provide thermoformability indices, such as force–displacement curves, temperature dependence and strain at break/force at break values, and the process is well traceable. Moreover, since the ball burst test represents biaxial stress conditions, it could play a key role in mold and process design. The deformability and thermoformability of PLA films is a rather new research area, therefore we investigated the thermoformability of PLA films with various D-lactide contents using ball burst tests and standardized tensile tests with various deformation rates and temperatures.

## 2. Experimental

### 2.1. Materials and processing

We used extrusion grade PLA types 4032D, 2003D and 4060D from NatureWorks (Minnetonka, MN, USA) with D-lactide contents of 1.4%, 4.3% and 12%, respectively (the D-lactide contents were provided by the manufacturer). All PLA grades had a density of 1.24 g/cm<sup>3</sup>, a glass transition temperature of 55-60 °C, a melting point of 155-170 °C (depending on D-lactide content) and an MFI of 6-7 g/10 min (at 210 °C, 2.16 kg). Prior to processing, the different PLA grades were dried with a hot air drier at 80 °C for 6 hours to remove moisture. 400 µm thin films were produced with a LabTech LCR 300 film sheet extruder equipped with a slit die set to a slit distance of 1 mm, while the roll temperature was set to 65 °C. The films were cooled at an ambient (room) temperature of 24 °C. The extruder was equipped with a 25 mm diameter, 30 L/D screw, and extrusion temperature was set to 190 °C–190 °C–185 °C–180 °C–175 °C–175 °C (from die to hopper). Screw rotation speed was 54 1/min and pulling peripheral speed was 1.0 m/min. 5 centimeters from each side of the films was removed and this way the specimens were cut from the middle of the films. A 54 mm diameter disk and ISO 527-3 standard dumbbell-shaped specimens were cut from the films for the ball burst test and the tensile tests, respectively.

### 2.3. Methods

The tensile tests of the PLA films were performed on a Zwick Z250 universal testing machine (Ulm, Germany) equipped with a Zwick BZ 005/TN2S force-measuring cell with a force limit of 5 kN. ISO 527-3 standard specimens were cut from the PLA films in flow-wise direction. The tests were performed at 25 °C (room temperature), as well as elevated temperatures of 65 °C, 70 °C and 75 °C (representing typical thermoforming conditions) with crosshead speeds of 50, 100, 200, 350 and 500 mm/min. A heat chamber provided the required temperatures for the tests. 5 independent tests were carried out for each temperature–crosshead speed setup.

A TA Instruments Q2000 calorimeter was used for the Differential Scanning Calorimetry (DSC) tests. 4–5 mg samples were tested with nitrogen as purge gas at 50 ml/min. In non-isothermal mode from 0 °C to 200 °C and with a heating and cooling rate of 5 °C/min, we determined the glass transition temperature ( $T_g$ ), the cold crystallization temperature ( $T_{cc}$ ), the enthalpy of cold crystallization ( $\Delta H_{cc}$ ), the melting temperature ( $T_m$ ), and the enthalpy of fusion ( $\Delta H_m$ ) of the samples from the heating scan and the crystallization temperature ( $T_c$ ), and their enthalpy of crystallization ( $\Delta H_c$ ) from the cooling scan. We calculated crystallinity from the first heating scan of the injection molded specimens using Equation (1):

$$X = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_f} \cdot 100 [\%], \quad (1)$$

where  $X$  [%] is the calculated crystallinity,  $\Delta H_m$  [J/g] and  $\Delta H_{cc}$  [J/g] are the enthalpy of fusion and the enthalpy of cold-crystallization, respectively, while  $\Delta H_f$  [J/g] is the enthalpy of fusion for 100% crystalline PLA (93.0 J/g) [39].

Ball burst tests were performed on a Zwick Z250 universal testing machine equipped with a Zwick BZ 005/TN2S force measuring cell with a force limit of 5 kN, a heat chamber and a ball burst head. The layout of the ball burst tester can be seen in Fig. 1.

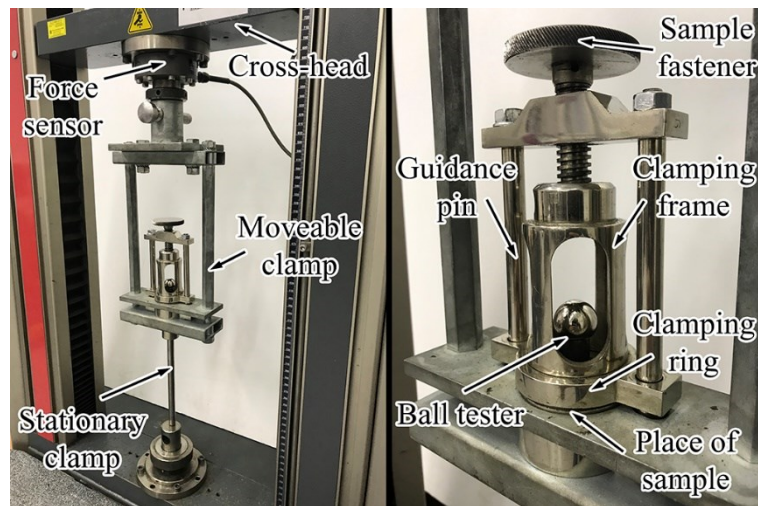


Fig. 1. Layout of the ball burst test

During the measurement, the clamping ring is opened (lifted up) with the sample fastener screw, and the specimen is placed. During this operation, the ball tester is located below the plane of the specimen. The specimen is fixed by the sample fastener and after the necessary temperature control, the measurement starts. Accordingly, the ball moves vertically in a uniform motion counter to the moveable clamp until the upper measuring limit, while force-displacement values are recorded. The clamping, inner hole and burst ball diameter were 54 mm, 25 mm and 19 mm respectively. Similarly to tensile tests, the ball burst tests were performed at 25°C (room temperature), 65°C, 70°C and 75°C by using a cross-head speed of 50, 100, 200, 350 and 500 mm/min on 60x60 mm area films cut from the extruded films. 3 independent measurements were performed for each temperature-cross head speed setup. 5 minutes waiting time was applied after putting the films into the heat chamber to ensure homogeneous thermal conditions. At all temperatures, the ball burst tests were also performed without using films to be able to determine the frictional properties of the test head. These force values were subtracted from the real measurement results. Although this measurement better represents the biaxial conditions of thermoforming compared to uniaxial tensile tests but has its own limitations, which comes from the limited strain rate (tensile testing machine capability), limited maximum drawing height (clamp design) and finally, ball burst test only represent the heating and drawing phase of thermoforming, but not cooling under vacuum. Nevertheless, to be able to determine thermoformability (force-displacement curves), the most important phases are the heating and drawing phases.

## 2. Results and discussion

Our investigation began with the DSC analysis of the untested, unaltered films (Fig. 2.).

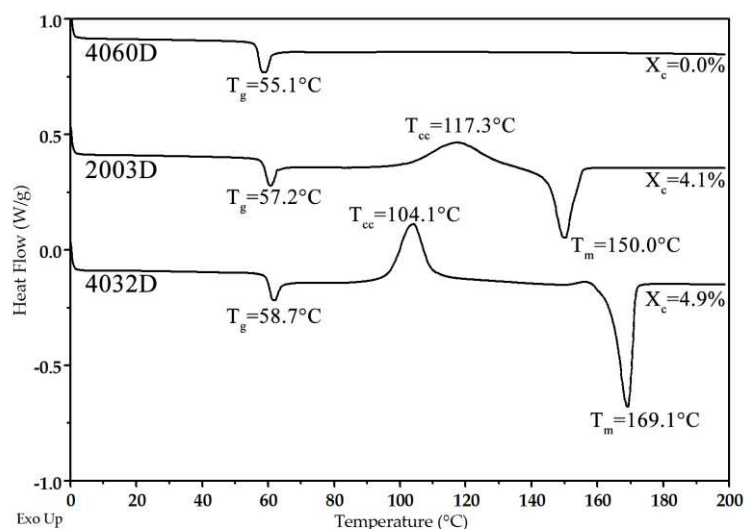


Fig. 2 The first heating DSC scan of the PLA films

The three PLA films with different D-lactide contents have different calorimetric properties. Although all PLA films investigated had a  $T_g$  between 55–59 °C, their crystallization behavior significantly differ. Namely, the lowest D-lactide content PLA grade (4032D) had the most potential to crystallize, and it had the lowest  $T_{cc}$  at 104.1°C with a sharp and narrow cold-crystallization exothermic peak. On the contrary, the 2003D PLA grade with 4.3% D-lactide content crystallized much more slowly. This is represented by a higher  $T_{cc}$  of 117.3 °C and a wide cold crystallization exothermic peak, while the 4060D PLA grade with the highest D-Lactide content of 12% did not even show a trace of crystallization. Accordingly, 4032D, 2003D and 4060D PLA films had a crystallinity of 4.9%, 4.1% and 0% respectively, which developed during processing. Lower D-lactide content meant a higher melting temperature. Accordingly, grades 2003D and 4032D had a  $T_m$  of 150.0 °C and 169.1 °C, respectively. PLA grade 4060D did not melt since it was unable to crystallize either during cooling after extrusion or during heating in the DSC test.

Our investigation continued with the tensile testing of the PLA films at 25 °C, 65 °C, 70 °C and 75 °C. The crosshead speed was also varied from 50 mm/min to 500 mm/min (Fig. 3).



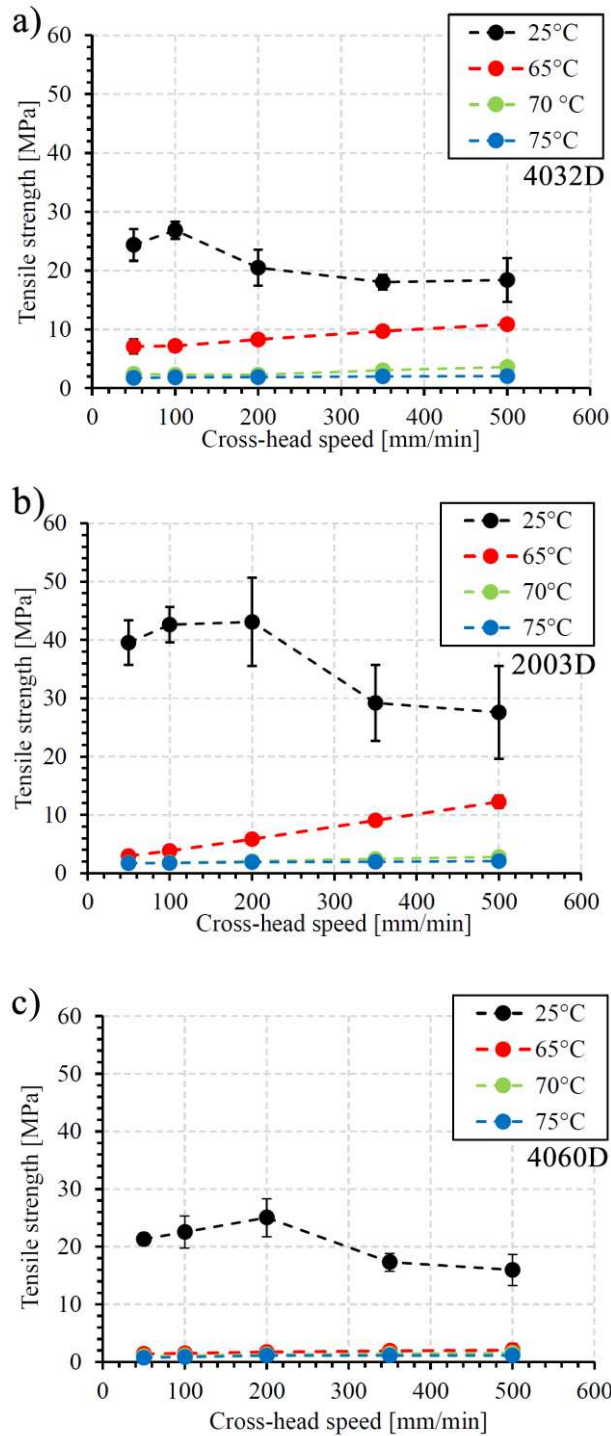


Fig. 3 Tensile strength as a function of the crosshead speed of different PLA films (a) 4032D, (b) 2003D and (c) 4060D

Naturally, the higher the tensile testing temperature was, the lower the tensile strength of the given PLA sample was, while it was expected that an increase in crosshead speed causes an increase in tensile strength as well. Interestingly, D-lactide content greatly affects the behavior of the specimens. The tensile strength of the highest D-Lactide content PLA grade (4060D) was practically independent of the temperature between 65 °C and 75 °C and the crosshead speed between 50 mm/min and 500 mm/min. Thus, a decrease in testing temperature from 75 °C to 65 °C resulted in only a minor increase in strength, which can be explained by the low crystalline ratio

(amorphous structure) of this grade compared to the other investigated grades. On the contrary, when we used the lower D-Lactide content grades 2003D (4.3%) and 4032D (1.4%), which have a greater ability to crystallize, both temperature and crosshead speed had more influence. For these two grades, tensile strength linearly increased with increasing crosshead speed, but only in the case of 65 °C; when the temperature was just above  $T_g$  and so the amorphous phase was in rubbery state, the crystalline phase could still have some influence on strength. Additionally, the difference between the testing temperature and  $T_g$  was lower for the 2003D ( $\Delta T=7.8$  °C) and for the 4032D ( $\Delta T=6.3$  °C) than for the 4060D ( $\Delta T=9.9$  °C), due to the different  $T_g$  values causing different viscosity at the rubbery state despite the same testing temperature. When the testing temperature was increased to 70 °C or 75 °C, crosshead speed had an even smaller effect on tensile strength, since the mobility of the amorphous phase increased so much that the crystalline phase alone could not have a significant influence. It also suggests that if crystallinity is increased, the specimen can be heated to a higher temperature, where crosshead speed still has an effect on tensile strength.

When the various PLA grades were tested at room temperature, as crosshead speed was increased, first tensile strength increased, then it started to decrease. This phenomenon still needs to be investigated more deeply, but a possible explanation is that above a certain testing speed threshold, the mechanical energy input generated so much heat in the thin films that the temperature rise increased the mobility of the polymer chains and eventually caused tensile strength to drop.

Our investigation continued with the crystallinity analysis of the tested films. Table 1 and 2 show the crystalline ratio of the films made from 4032D and 2003D and tested at various temperatures and crosshead speeds, and thus with various mechanical stress and thermal history can be seen. Every time a film sample was tensile tested at an elevated temperature, another film sample was also put in the heat chamber for annealing so that we had a non-tested reference sample with the same thermal history as the tested film.

Crosshead speed	Temperature			
	25 °C	65 °C	70 °C	75 °C
50 mm/min	5.6	18.6	44.0	47.6
100 mm/min	6.6	17.9	41.1	46.3
200 mm/min	5.1	18.8	39.8	47.5
350 mm/min	7.2	12.8	38.3	45.7
500 mm/min	4.6	13.0	36.7	46.6
Annealed, not tensile tested reference	5.2	6.6	6.1	6.2
Unannealed not tensile tested reference	5.2			

Table 1 The crystallinity of the 4032D PLA films tensile tested at various crosshead speeds and temperatures

Crosshead speed	Temperature			
	25 °C	65 °C	70 °C	75 °C
50 mm/min	0.1	1.7	31.0	35.7
100 mm/min	0.7	1.6	28.2	33.7
200 mm/min	0.8	0.4	22.5	32.7
350 mm/min	1.2	0.8	18.1	33.7
500 mm/min	1.6	0.5	8.5	33.1
Annealed, not tensile tested reference	1.2	1.4	1.5	1.2
Unannealed not tensile tested reference	1.2			

Table 2 The crystallinity of the 2003D PLA films tensile tested at various crosshead speeds and temperatures

Annealing the reference samples (neither annealed, nor tensile tested) caused crystallinity to increase slightly. However, these crystallinity values are still far from the possible maximum crystallinity, thus annealing at 65 °C, 70 °C or 75 °C did not cause a significant crystalline structure to develop in any of the PLA grades. At the same time, when samples of PLA grade 4032D were subjected not only to an elevated temperature for annealing, but to tensile stress as well, crystallinity increased very significantly; from 6.1-6.6% to 13.0-18.6%, 36.7-44.0% and 45.7-47.6% for the testing temperatures of 65 °C, 70 °C and 75 °C, respectively. The testing temperatures (higher than  $T_g$ ) increased molecular chain mobility. Additional mechanical stress increased the orientation and the chain folding aptitude of the polymer chains. This eased and accelerated crystallization. Interestingly, the higher the crosshead speed was, the lower the crystallinity developed. Increasing the crosshead speed from 50 mm/min to 500 mm/min decreased crystallinity from 18.6% to 13.0%. Despite decreasing crystallinity, tensile strength increased with increasing crosshead speed. For the 2003D grade, only testing temperatures 70 °C and 75 °C and mechanical stress were enough to significantly increase crystallinity. At 65 °C, the tensile tested specimens had similar, or, in the case of higher crosshead speeds, even lower crystallinity compared to the specimens subjected to heat treating only. The reason could be that the  $T_g$  of PLA grade 2003D is near 65 °C, causing the lamellae to slip and the chains to unfold. Finally, in the case of PLA grade 4060D, neither various temperatures nor different crosshead speeds caused a major change in crystallinity, which can be attributed to the high D-Lactide content of this grade.

In the first heating scans of PLA grade 4032D, there was no significant difference between the curves of the specimens tested at room temperature at various test speeds (Fig. 4/a). However, there were significant differences in the first DSC heating scans of the specimens tested at 65 °C at various test speeds (Fig. 4/b).

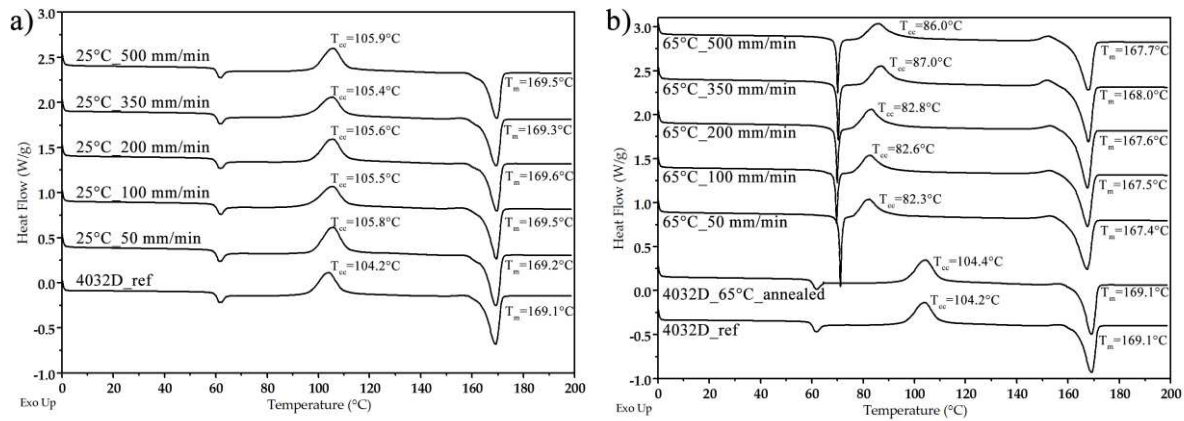


Fig. 4 The first DSC heating scan of 4032D PLA films tensile tested at 25 °C (a) and at 65 °C (b)

In the DSC curves of the specimens tensile tested at 65 °C, the cold crystallization peaks shifted to lower temperatures, which suggests that the polymer is more prone to crystallization. This is similar to the effect of nucleation [42], but in this case, this increased crystallization is caused by the oriented polymer chains and not by nucleating agents. Additionally, the tensile tested specimens had much lower crystallization enthalpy than the annealed specimens, due to the much higher crystallinity of the former. Also, the lower the crosshead speed was, the more the  $T_c$  shifted to lower temperatures, increasing crystallization (Tables 1 and 2). This can be explained by the fact that at lower crosshead speeds, the polymer chains have more time for orientation, and the polymer chains are less likely to unfold than in the case of higher crosshead speeds. PLA 2003D films exhibited a similar tendency, thus cold crystallization peaks shifted to lower temperatures and crystallization enthalpies became smaller, representing increased crystallinity (Fig. 5).

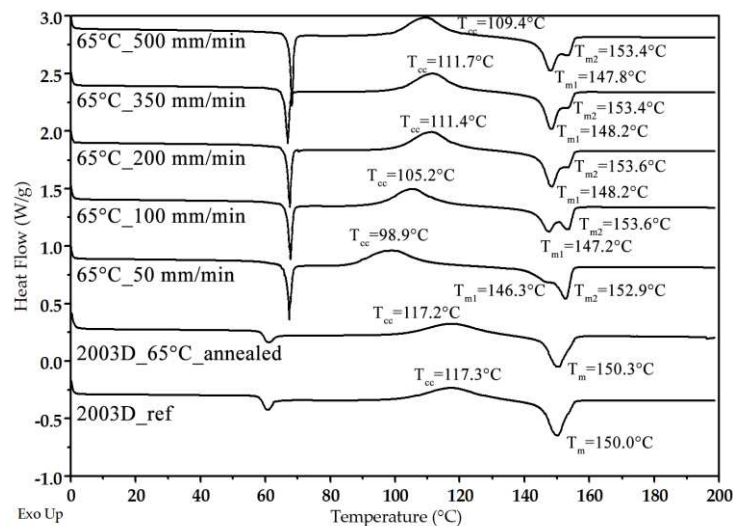


Fig. 5 The first heating DSC scan of 2003D PLA films tensile tested at 65 °C

Again, the lower crosshead speed was during tensile testing, the more the  $T_c$  shifted to lower temperatures, representing an increased tendency to crystallization and increased overall crystallinity. In this PLA grade, not only crystallinity, but also the ratio of the  $\alpha$  and  $\alpha'$  crystal forms change—this causes single or dual melting peaks [40, 41]. The higher crosshead speed was, the lower overall crystallinity was, but the  $\alpha$  crystal form was dominant.

Finally, due to the low crystallization rate of the 4060D grade PLA films, no crystallization peaks were visible either due to annealing or due to tensile testing at elevated temperatures.

Our investigation continued with the ball burst tests of the films. The relatively high deviation of the force values measured may be caused by the uneven crystallization of the specimens; this is the result of the biaxial stress state developed during ball burst tests. We found that the maximum force (required for forming) increased when the PLA films started to crystallize during the ball burst tests. Moreover, maximum force also increased with an increase in ball burst speed, in accordance with the tensile test results.

First, we tested the 4032D PLA grade films, with the lowest D-Lactide content of 1.4%. At 65 °C, the specimens only suffered fracture above a ball burst speed of 200 mm/min, while significant crystallization was present above a ball burst speed of 100 mm/min (Fig. 6.).

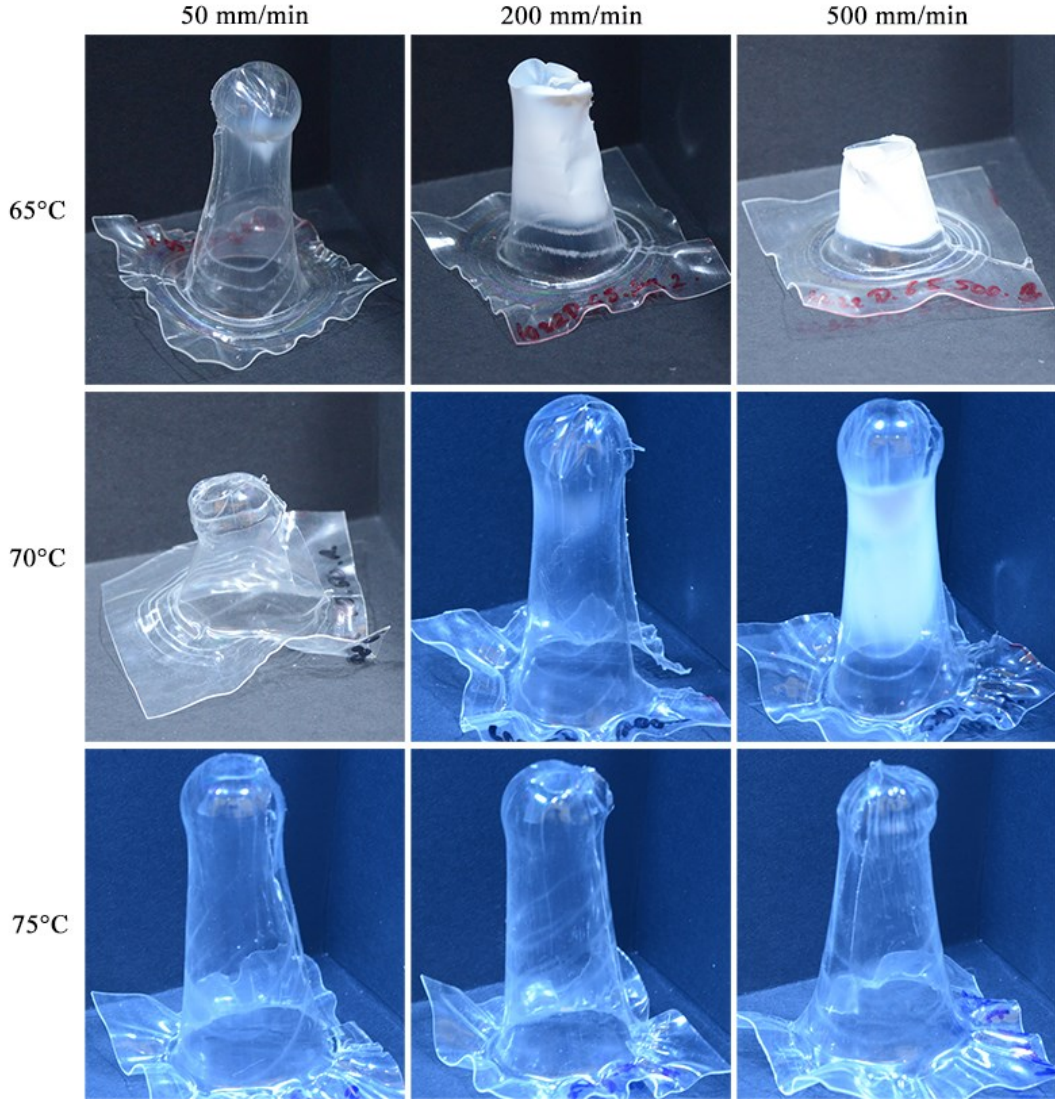


Fig. 6 The 4032D PLA film specimens after ball burst testing at various temperatures and ball burst speeds

At 70 °C, the crystallinity of the specimens still increased with increasing ball burst speed. However, due to the increased temperature, significantly crystallized specimens were only manufactured with a ball burst speed of 350 mm/min or higher. This is a major difference compared to the tensile test results. In tensile tests, the higher the crosshead speed was, the lower the overall crystallinity was—during ball burst tests, the higher the ball burst

speed was, the higher the overall crystallinity was. This is represented by whitish areas on the ball burst tested specimens, while the tensile tested specimens had no such areas. This difference may be due to the biaxial deformation caused by the ball burst test, which is much closer to real thermoforming conditions. Finally, at 75 °C, the testing temperature applied was so high above  $T_g$  ( $T_{\text{testing}} - T_g = 16.3$  °C) that none of the specimens suffered fracture during the test or was able to crystallize significantly. We investigated maximum force as a function of ball burst speed (Fig. 7) and found that at higher temperatures, lower force was necessary to form the specimens. This was in accordance with the previous tensile test results. Also, increasing ball burst speed increased deformation force.

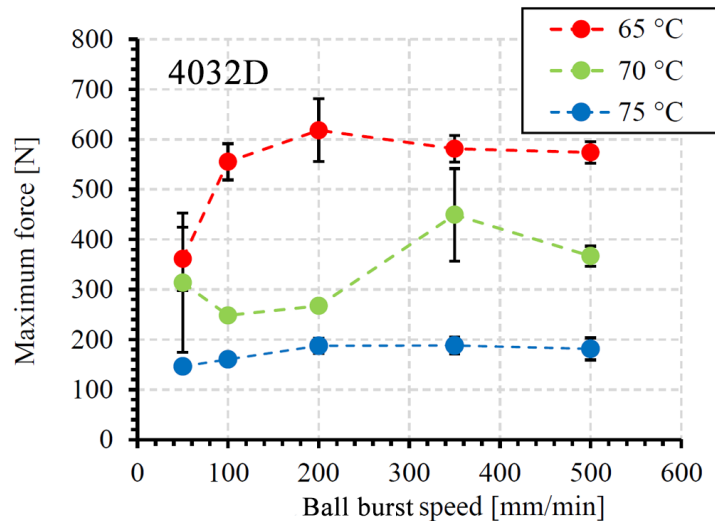


Fig. 7 The maximum force required to form the 4032D PLA film specimens during ball burst testing at various ball burst speeds

In this case, force increased with increasing testing speed not only at 65 °C, but also at 70 °C. This is probably due to the biaxial deformation caused by the ball burst test—the stress and deformation during the ball burst test are much closer to real thermoforming conditions than in the case of tensile testing. Next, the 2003D PLA films were tested with ball burst tests. At 65 °C, all the specimens highly crystallized at all of the investigated deformation rates (Fig. 8).



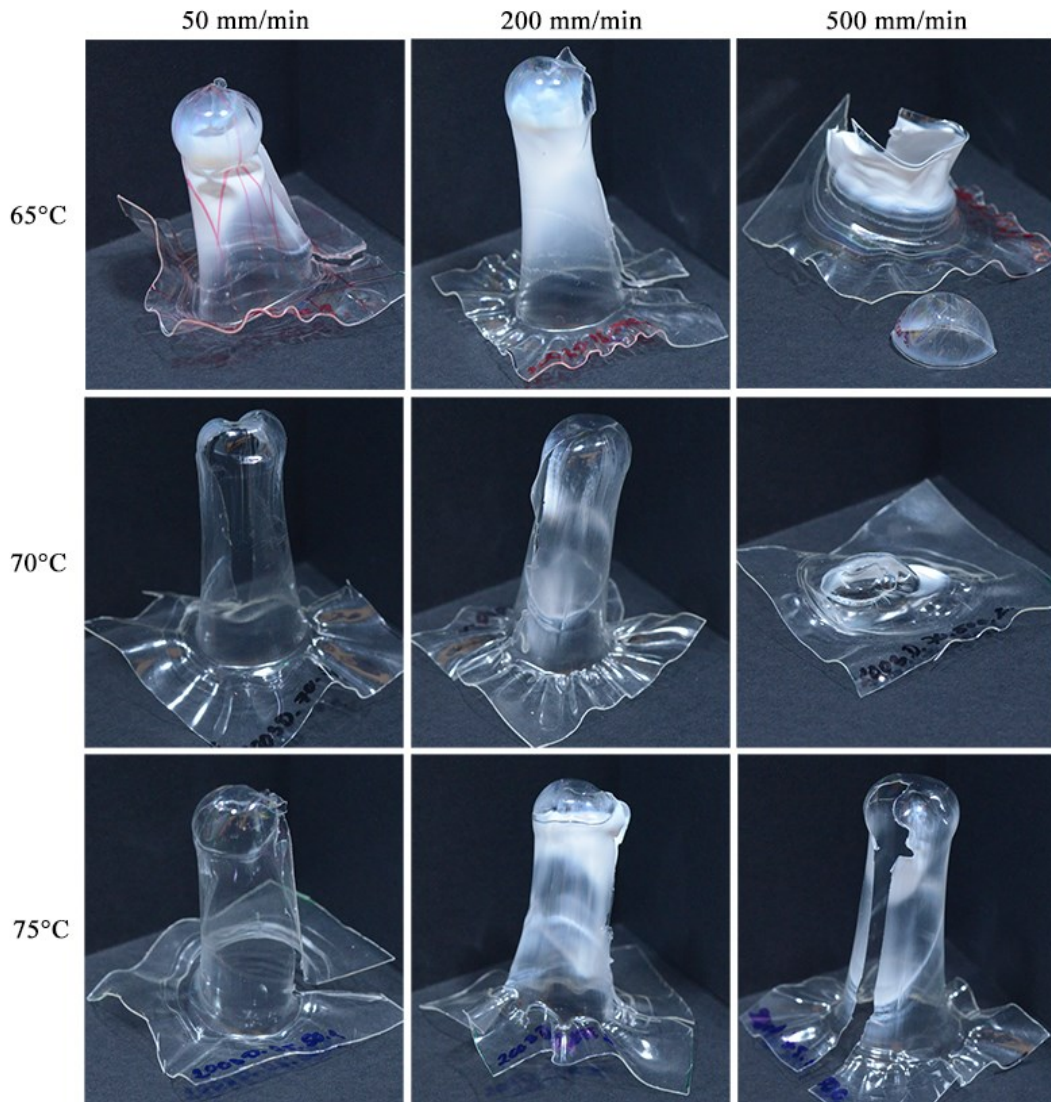


Fig. 8 The 2003D PLA film specimens after ball burst testing at various temperatures and ball burst speeds

On the contrary, at 70 °C and 75 °C, the specimens crystallized far more slowly, which is represented by the more transparent areas on the tested specimens. Similarly to the 4032D PLA grade results, the higher the temperature was, the lower the force required for forming was, while an increase in ball burst speed increased the deformation force as well (Fig. 9).

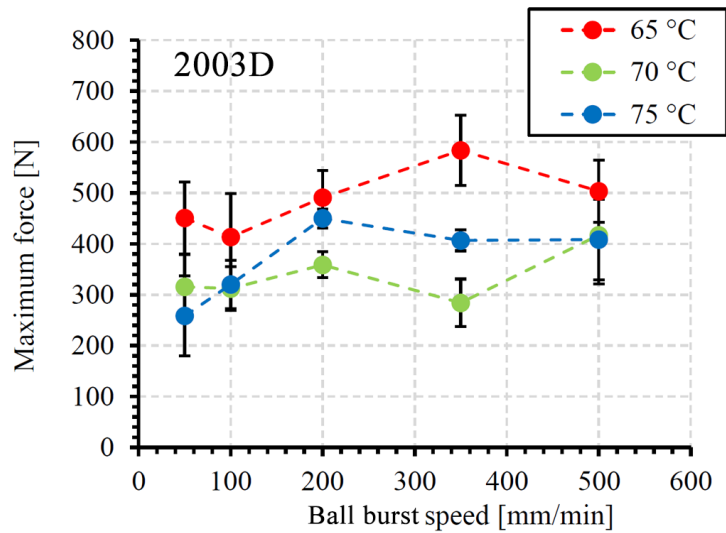


Fig. 9 The maximum force required to form the 2003D PLA film specimens during ball burst testing at various ball burst speeds

Finally, the 4060D PLA specimens representing the highest D-Lactide content were tested by ball burst tests. We measured the lowest force values for this grade, due to its very slow crystallization rate and low crystalline ratio. Despite the slow crystallization of this PLA grade, the thermal and mechanical stimuli caused some opaque/whitish areas on the specimens, representing a trace of crystallization in contrast to tensile testing, where no evidence of crystallization was found. Additionally, the very low crystallinity caused the specimens to collapse and thus the ball burst test head shape was not maintained on the specimens (Fig. 10).



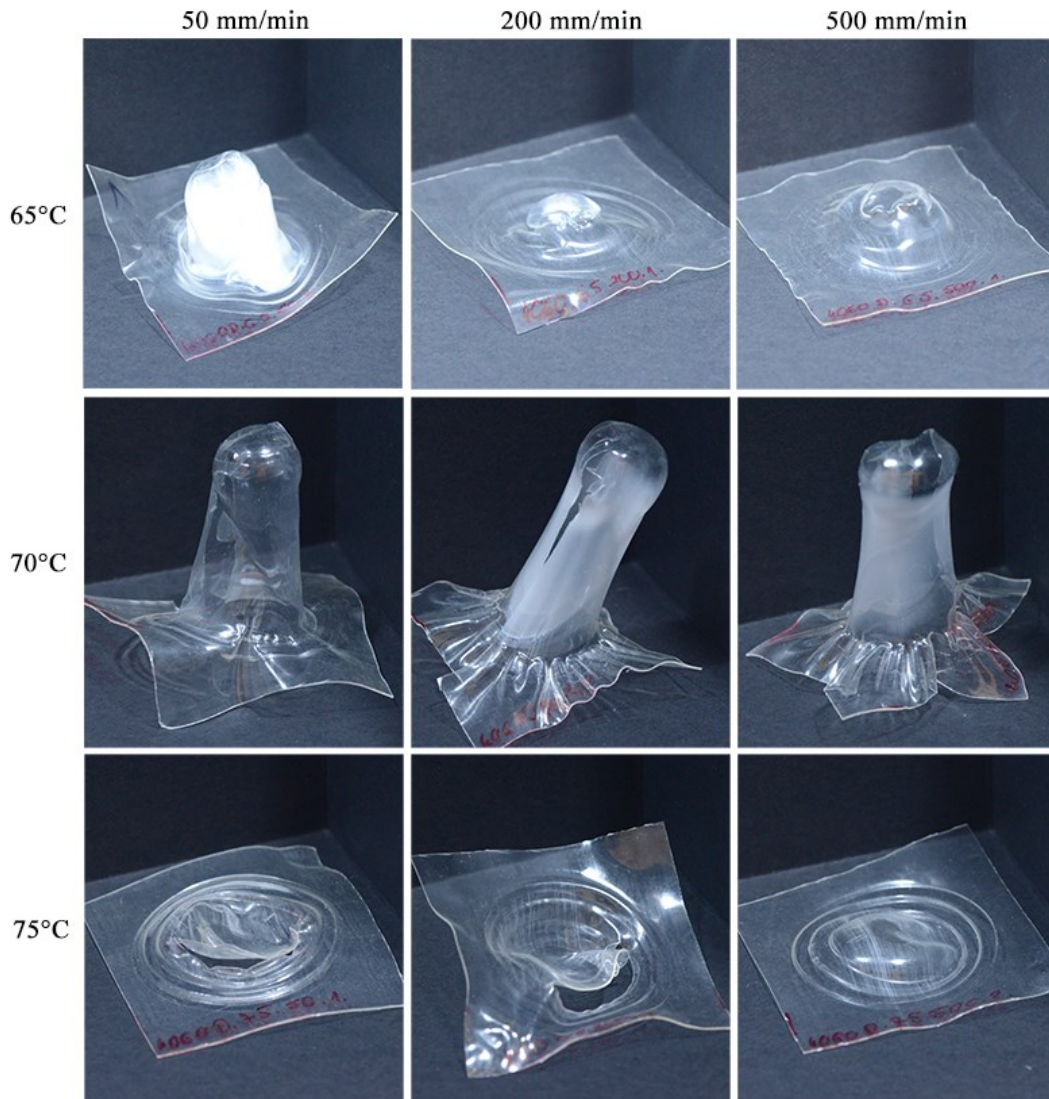


Fig. 10 The 4060D PLA film specimens after ball burst testing at various temperatures and ball burst speeds

Increasing the temperature to 70 °C and 75 °C resulted in only minor traces of crystallization. At 75 °C, many specimens were already damaged by the clamping frame, therefore it was not possible to perform the ball burst test. Finally, we investigated the deformation force–ball burst speed curves and found them to be similar to those of the other two PLA grades; the higher the applied temperature was, the lower the force values were. At the same time, the force did not increase significantly with ball burst speed, which could be explained by the insignificant crystallization during the ball burst tests compared to the other two investigated PLA grades. This is in accordance with the previous tensile test results (Fig. 11.).

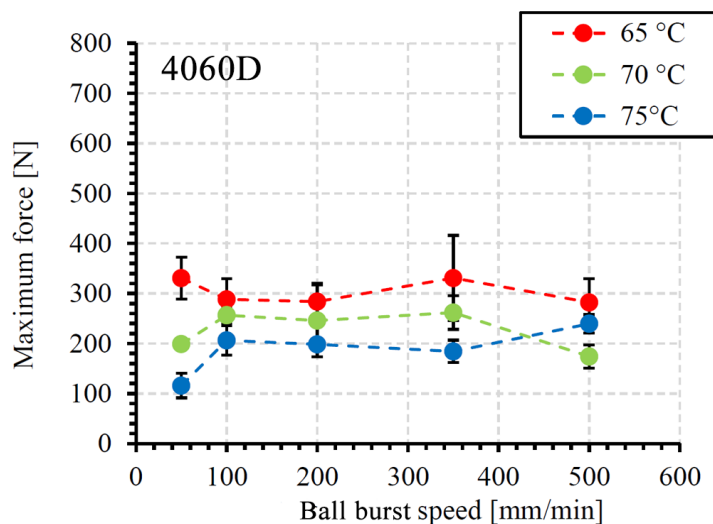


Fig. 11 The maximum force required to form the 4060D PLA film specimens during ball burst testing at various ball burst speeds

### 3. Conclusion

In this paper, we investigated the thermoformability of three different D-Lactide content (1.4%, 4.3% and 12%) PLA films representing different crystallization properties by means of tensile and ball burst tests conducted at various temperatures (25°C, 65°C, 70°C and 75°C) and testing rates (50-500 mm/sec). To the best of our knowledge, the ball burst test, which is widely used in the textile industry, has seldomly been applied on plastic films and has not been applied on PLA films yet in the investigation of thermoformability. However, the biaxial deformation induced during the ball burst test better represents real thermoforming conditions than the uniaxial deformation during tensile tests. The tensile behavior of the PLA films greatly differ due to the difference in D-Lactide content. Grade 4060D has a D-Lactide content of 12% and thus crystallizes slowly and has low crystallinity. Its tensile strength was practically independent of both temperature between 65 °C and 75 °C and crosshead speed between 50 mm/min and 500 mm/min. On the contrary, lower D-Lactide content grades 2003D (4.3%) and 4032D (1.4%) have a greater ability to crystallize, therefore their tensile strength linearly increased with increasing crosshead speed, but only in the case of 65°C. This testing temperature was just above  $T_g$  so the amorphous phase was in a rubbery state, but the crystalline phase still had an influence. The crystallinity of the tensile tested films was measured and compared to annealed reference samples, which had the same thermal history as the samples tensile tested at an elevated temperature. Annealing caused only a minor increase in crystallinity; at the same time, when the samples were subjected not only to an elevated temperature for annealing, but to tensile stress as well, crystallinity very significantly increased from 6.1–6.6% to 13.0–18.6%, 36.7–44.0% and 45.7–47.6% for the testing temperatures of 65 °C, 70 °C and 75 °C, respectively, in case of the 4032D PLA grade. This means that the additional mechanical stress superposed on already increased molecular chain mobility caused by the applied testing temperature higher than  $T_g$  increased the orientation and the chain folding aptitude of the polymer chains and this eased and accelerated crystallization. The DSC curves of the lower D-Lactide content PLA films tensile tested at 65 °C show that  $T_c$  shifted to lower temperatures, which suggests that the polymer is more prone to crystallization. Moreover, the lower the crosshead speed was, the more  $T_c$  shifted to lower

temperatures, increasing crystallization even more and representing even higher crystallinity. This can be explained by the fact that at lower crosshead speeds, the polymer chains have more time for orientation. Additionally, for the 2003D PLA grade not only crystallinity, but also the ratio of the  $\alpha$  and  $\alpha'$  crystal forms changed, namely, increasing crosshead speed increased the development of the  $\alpha$  crystal form. Finally, in the ball burst tests, increasing testing temperature decreased crystallinity, while increasing ball burst rate increased crystallinity. This was a major difference to the tensile test results, since during tensile tests, the higher the crosshead speed was, the lower overall crystallinity developed. The significantly crystallized regions are whitish areas on the ball burst tested specimens, while the tensile tested specimens had no such areas. For the 4060D PLA films, despite the slow crystallization of this PLA grade, the thermal and mechanical stimuli caused some minor opaque/whitish areas on the specimens, representing a trace of crystallization, in contrast to tensile testing, where no evidence of crystallization was found. We pointed out the differences between the tensile testing and ball burst testing; the latter better represents thermoforming conditions through inducing biaxial deformation.

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