

# The mechanical properties of polyethylene-terephthalate (PET) and polylactic-acid (PDLA and PLLA), the influence of material structure on forming

T Horvath<sup>1</sup>, M Kalman<sup>2</sup>, T Szabo<sup>3</sup>, K Roman<sup>4</sup>, G Zsoldos<sup>5</sup> and M Szabone Kollar<sup>6</sup>

<sup>1</sup> Research and Development Engineer at ÉMK LTD, Sajóbábony, Hungary

<sup>2</sup> Professor of Institute of Ceramic and Polymer Engineering, University Of Miskolc, Miskolc-Egyetemváros, Hungary

<sup>3</sup> Associate Professor and Director of Institute of Ceramic and Polymer Engineering, University Of Miskolc, Miskolc-Egyetemváros, Hungary

<sup>4</sup> PhD student, University Of Miskolc, Miskolc-Egyetemváros, Hungary

<sup>5</sup> Senior Lecturer of Institute of Ceramic and Polymer Engineering, University Of Miskolc, Miskolc-Egyetemváros, Hungary

<sup>6</sup> Senior Lecturer of Institute of Ceramic and Polymer Engineering, University Of Miskolc, Miskolc-Egyetemváros, Hungary

E-mail: horvath.tibor@emkkft.hu

**Abstract.** Those plastics that have been used by food industry as packaging (especially in sweet industry) have strict requirements. Most of these plastic constructions are primary or secondary packaging with direct or indirect contact with foodstuff. Over the appropriate mechanical properties, these packagings need to be safe enough to be used as direct contact material without any dangerous material migration or transfer. Recently the polyethylene-terephthalate (PET) is that material which is widely used for this kind of purpose and application. To substitute the PET, only that kind of alternative material which are fulfilling the requirements of applications and compliant to the relevant regulations can be applied.

The cost-efficient application of plastics strongly depends on the mechanical properties of the material. In light of these facts, both types of polylactic-acid (PDLA, PLLA) and the PET were tested. Comparing their mechanical properties PLA could be used as a real alternative of PET.

## 1. Introduction

In the new generation of packaging materials the environmental friendly approach is more highlighted than in the last few decades. Over that, the growing importance of food safety initiated new requirements and regulations to the packaging materials. Although the traditional packaging still can be used but new alternatives need to be found which is more suitable to the getting stricter regulations. The scoped field is the sweet industry which uses a huge amount of plastic as primary (those packagings which is part of individual product) or secondary (use for logistic purposes) packaging construction with non-food contact/indirect food contact/direct food contact types.

Regarding the plastic packaging constructions due to the new challenges the best alternatives could be the bio-sourced biodegradable plastic types.



“In general the biobased polymers can be divided into three main categories like a.) Polymers directly extracted/removed from biomass; b.) Polymers produced by classical chemical synthesis using renewable biobased monomers; c.) Polymers produced by microorganisms or genetically modified bacteria. With classical chemical synthesis (category b.) a wide spectrum of bio-polyesters can be produced” [1]. The polylactic-acid (PLA) is one of these numerous alternatives.

From environmental performance point of view the PLA (compared to PET) has lower values in almost all impact categories (CO<sub>2</sub> emission, human toxicity, fossil energy demand) except of eutrophication and acidification potential [2].

As the scoped company mostly uses virgin polyethylene-terephthalate (PET) a special alternative was requested to be found with appropriate mechanical properties. The lactic acid based PLA is a linear aliphatic thermoplastic polyester. The lactic acid can be obtained from fermentation of plant sourced starches. The extracted starches chemically converted into dextrose that fermented to lactic acid followed by polycondensation or Ring Opening Polymerization (ROP) process to produce polylactic-acid. Two stereoisomers exists for lactic as L and D isomers, therefore three PLA alternatives distinguished as PDLA made from D lactic, PDLLA which contains both L and D isomers, and pure L isomer built PLLA. The PLA is biodegradable, renewable, environmental friendly material and has good thermal processability so it seemed to be a potential substitute of PET but to verify the usability of PLA, the mechanical properties of both materials had to be compared [3, 4].

**Table 1.** Physical and chemical parameters of the PLA and PET foils [5]

Properties	PDLA	PLLA	PDLLA	PET
Crystalline structure	Crystalline	Semi crystalline	Amorphous	Amorphous and semi-crystalline
Melting temperature (T <sub>m</sub> )/ °C	180	180	variable	260
Glass transition temperature (T <sub>g</sub> )/ °C	50-60	50-60	variable	67-81
Half-life in 37°C normal saline	4-6 month	4-6 month	2-3 month	700 year
Elongation at break/ (%)	20-30	20-30	variable	230
Breaking strength/ (g/d)	4-5	5-6	variable	5,3

## 2. Experimental

### 2.1. Material and methods

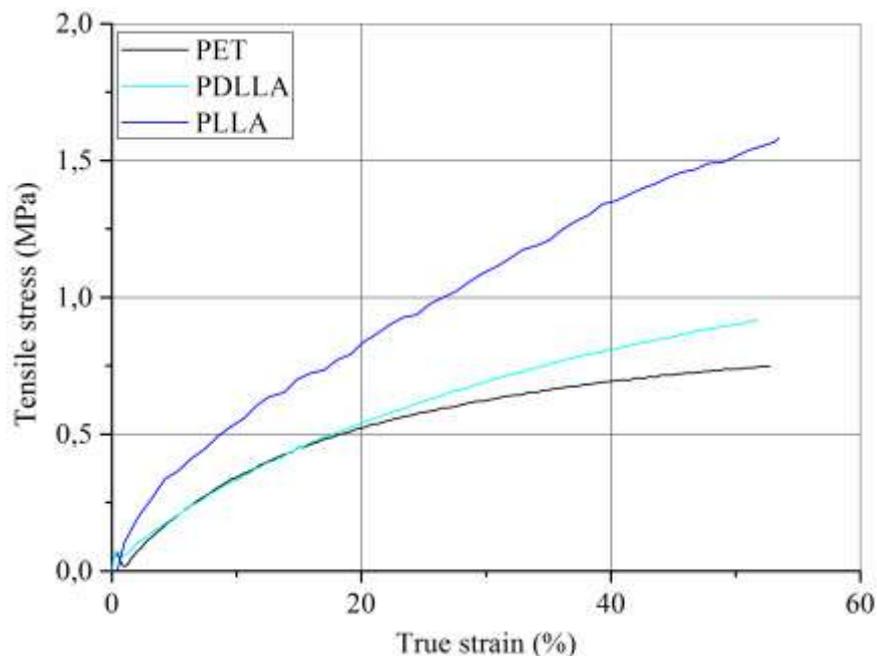
PET (virgin and recycled) and PDLLA samples were provided by Pro-Form Kft. and the PLLA sample was purchased from Goodfellow Cambridge Ltd. The thickness of the preformed PDLLA and preformed PET film were 300 µm, in case of PLLA foil the thickness was 50 µm. The glass transition temperatures (T<sub>g</sub>) of materials have been preliminary determined by DMA analysis with results as 57°C for PDLLA and 62°C for PLLA as well as 82°C for polyethylene terephthalate. For visual examination and follow up of deformation range the PET film surface screen was printed with a 1 mm splitting grid. In case of PDLLA film a 10 mm splitting grid was used. In the pre-conditioning phase of test all samples have been pre-heated. The pre-treatment temperatures (to release the remained forming stress in material) were slightly above the specific transition temperatures, 100°C for PET, 70°C for PDLLA and PLLA.

The preheating time was 2 minutes for all of three samples. After the pre-treatment the mechanical measurements were carried out at room temperature.

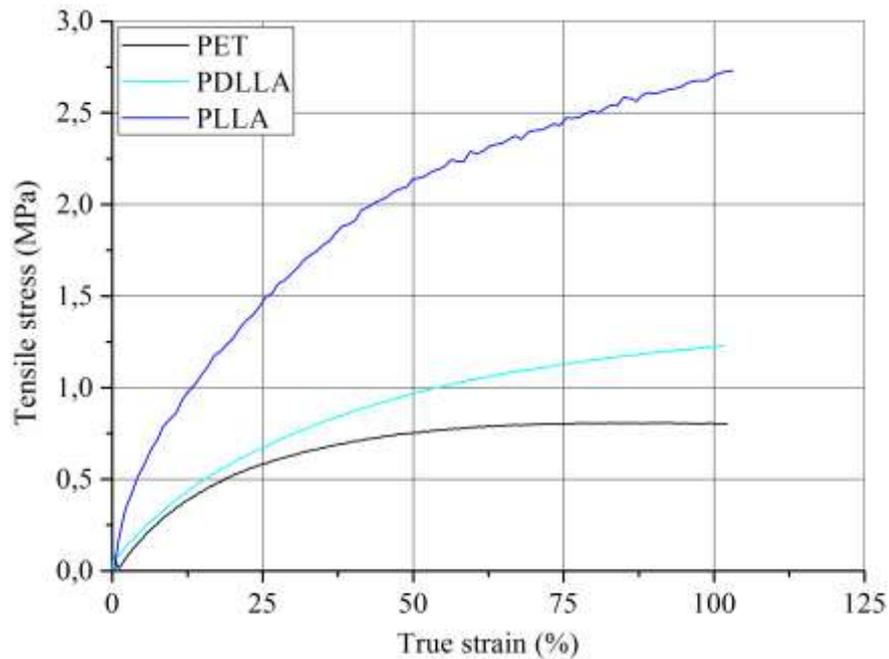
The mechanical properties were determined with tensile test. The test performed on INSTRON 5566 testing machine. The measurements procedure followed the ASTM D389 standard. The test speed was 100 mm/min at room temperature ( $23\pm 1^\circ\text{C}$ ). During the tests the 150%, 200% and 250% stretching levels were determined and adjusted. For purpose of further characterization of the materials DSC131 evo machine was used with  $10^\circ\text{C}$  as heating/cooling rate.

## 2.2. Comparison of mechanical properties of polyethylene terephthalate and polylactic acid

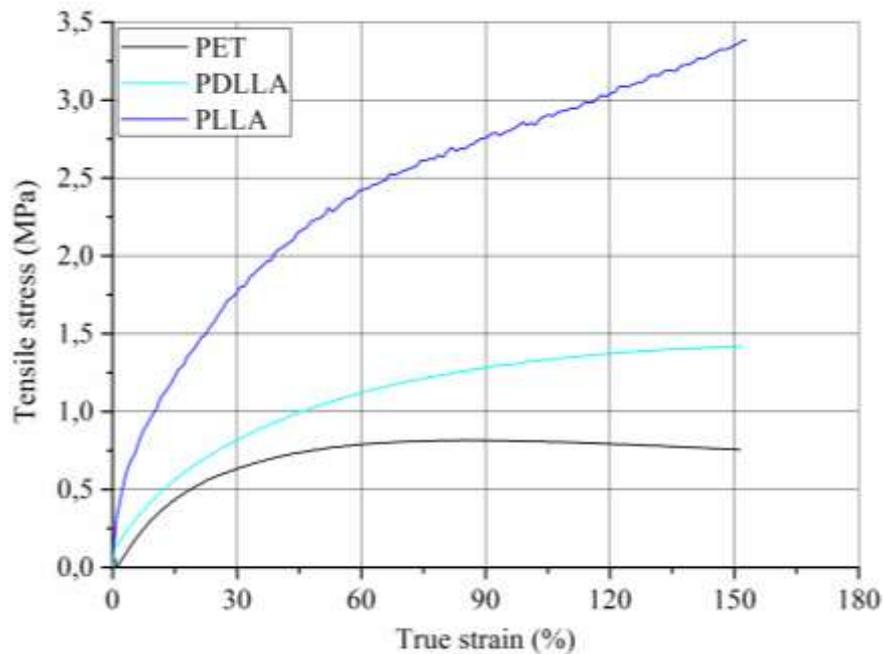
During the mechanical tests, the PET, PDLLA and PLLA samples were initially formed in a relatively high force range. In the first stage of the shaping the weak secondary bonds that cross connected the molecular chains are progressively disrupted and the collapsed molecular chains were oriented in the direction of forming force. This orientation process could be also observed in the further stages of tests but to ensure the adjusted stretch value smaller force was sufficient to realize it. At higher forming ratios (deformation from 200% up to 250%) the molecular chains reached the maximum of possible orientation. The final stage of mechanical test was the plastic material's creeping which was realised by the movement of mass centre of molecular chains. At lower forming ratio only the shorter molecular chains' mass centre could be moved (PET) while the longer ones (PLLA, PDLLA) stayed in positions. It was concluded that the PET material permanent creeping at lower forming force was caused mainly by the structure that built by shorter molecular chains.



**Figure 1.** Results of tensile test of PET, PDLLA and PLLA foils at deformation of 150%



**Figure 2.** Results of tensile test of PET, PDLLA and PLLA foils at deformation of 200%



**Figure 3.** Results of tensile test of PET, PDLLA and PLLA foils at deformation of 250%

The result of tests defined that the PLLA required the highest forming force. The PLLA needs 224% (average) of force, the PDLLA needs 52% (average) higher forces to reach the same deformation value compared to PET.

**Table 2.** Average molar mass of PET [6], PDLLA [7] and PLLA [8] foils

Properties	PET	PDLLA	PLLA
Average molar mass ( $M_w$ )/ g/mol	30 000 – 80 000	100 000 – 180 000	100 000 - 300 000

This referred to longer molecular chains as well as better filling of amorphous parts.

It can also be caused by the partially crystalline structure. Larger filler amorphous molecules and highly folded crystalline parts need greater forces to form orientation.

**Table 3.** Tensile stress maximums of PET, PDLLA and PLLA foils

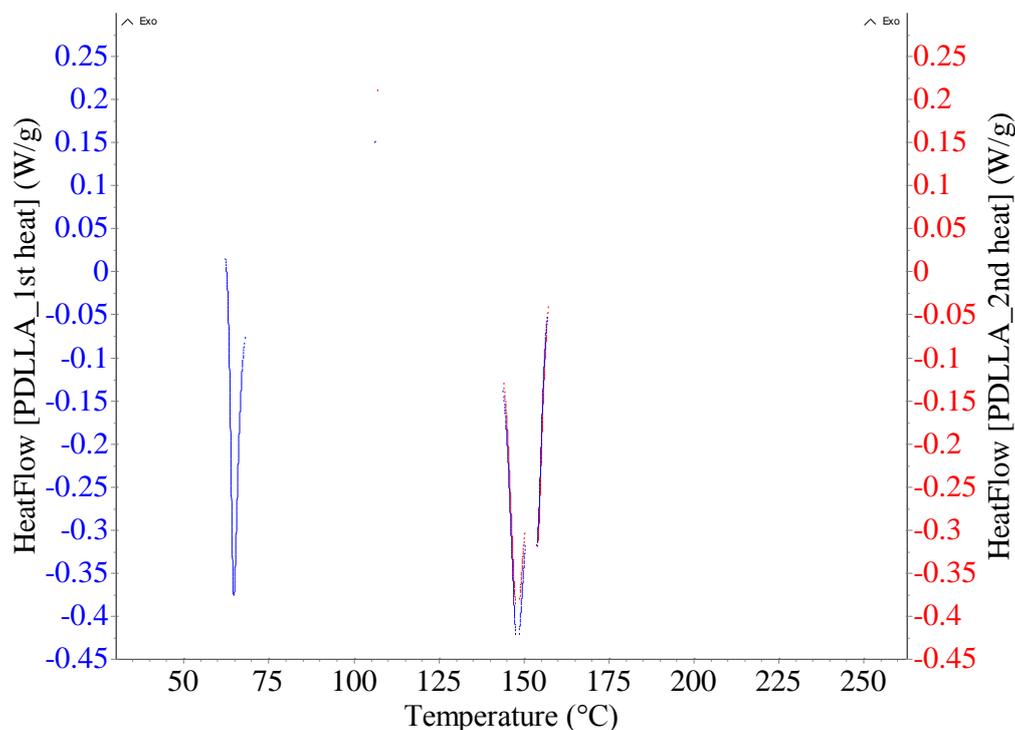
Strain %	PET (MPa)	PDLLA (MPa)	PLLA (MPa)
150	0.74	0.90	1.51
200	0.80	1.22	2.71
250	0.78	1.42	3.36

### 2.3. DSC analysis of polyethylene terephthalate and polylactic acid

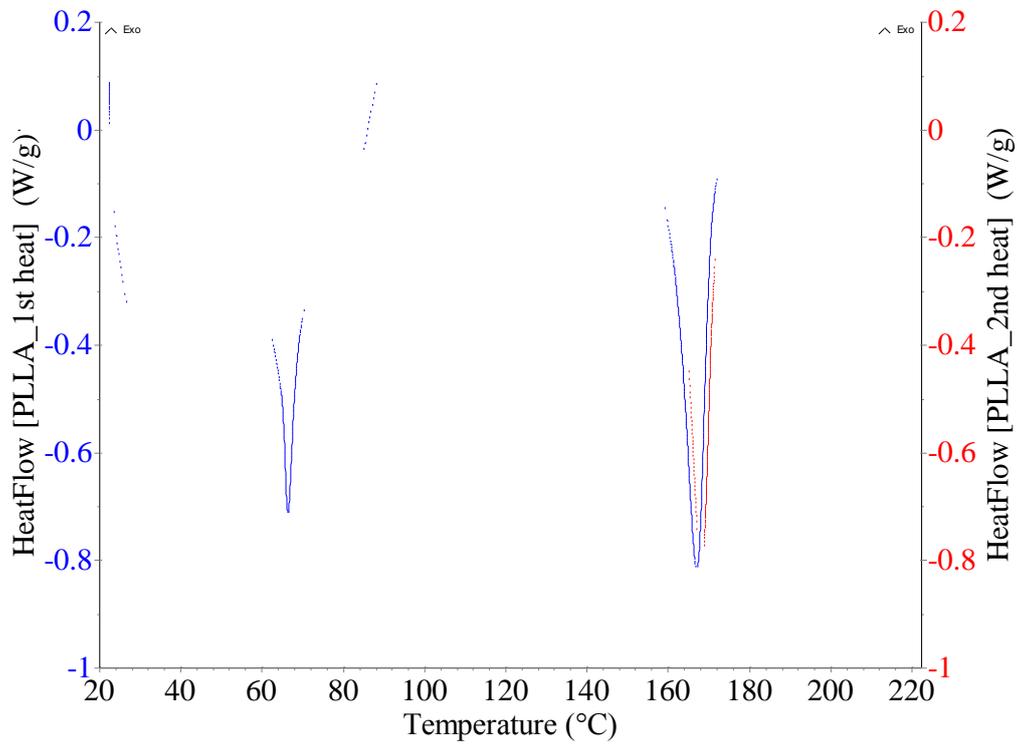
During the function analysis the PET and PDLLA and the pure L isomer built PLLA samples were tested on DSC131 evo machine. Regarding the PDLLA this material contains both D and L lactic acid isomers and constructed dual crystal structure under appropriate conditions. However, this dual crystal structure is also disadvantage of the material, as the different isomers cannot build a homogeneous crystal structure. It makes crystallization difficult and the whole process slow.

**Table 4.** DSC measurement data of analysis of PET, PDLLA and PLLA foils

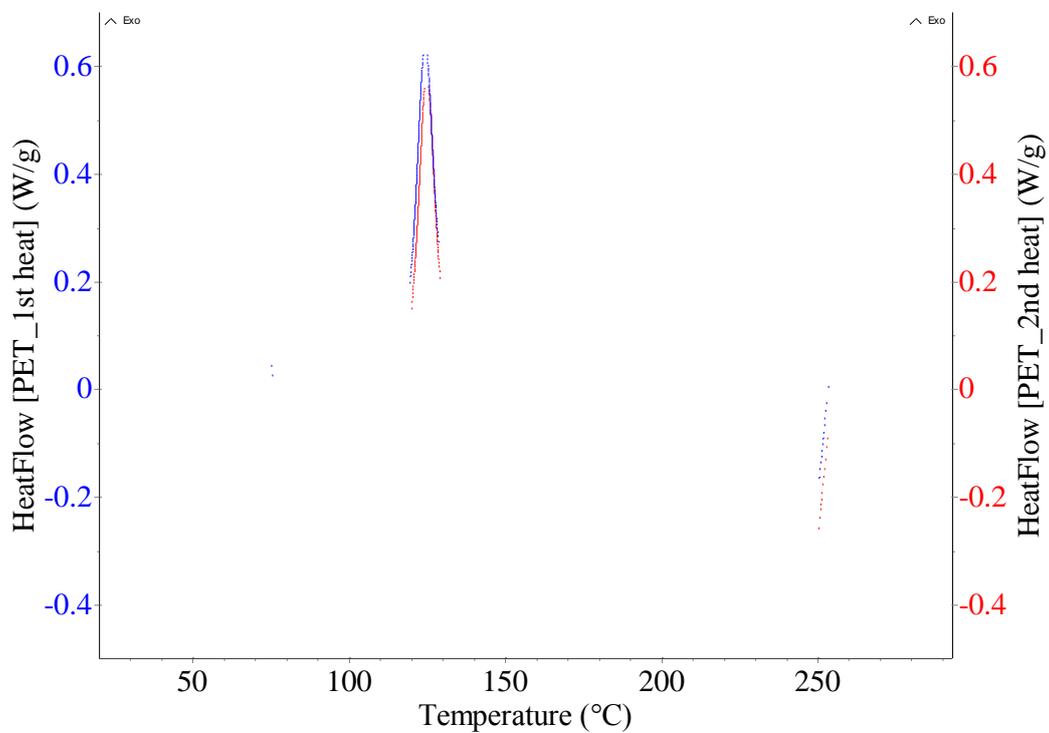
Material Type	PET	PDLLA	PLLA
Heating/Cooling ratio (°C/min)	10	10	10
Heat Range (°C)	25 - 275	25 - 275	-125 - 245
Heat Ramp	Linear	Linear	Linear



**Figure 4.** DSC curves of PDLLA foil (section I. first heating run section II. second heating run)



**Figure 5.** DSC curves of PLLA foil (section I. first heating run section II. second heating run)



**Figure 6.** DSC curves of PET foil (section I. first heating run section II. second heating run)

The measurements showed that the material contained two distinct crystalline fractions of heterogeneous crystal structure. This is confirmed by the two sub-functions obtained as a result of the separation and partitioning of the decomposition curve. During the DSC analysis, it was also found that the crystalline fraction of the material is constantly changing in proportion due to the degree of deformation. Theoretically the purity of the material (proportion of virgin / recycled material contents) also significantly influences the crystal structure of the material but this aspect is going to be investigated only at further stage of recent research [9].

**Table 5.** Results of DSC analysis of PET, PDLLA and PLLA foils

<b>Material Type</b>	<b>PET</b>	<b>PDLLA</b>	<b>PLLA</b>
Heat of crystallisation (J/g)	-27.03	-23.55	-24.07
Onset temperature of crystallisation (°C)	130.54	101.47	80.44
Heat of decrystallisation (J/g)	38.19	26.80	37.03
Onset temperature of decrystallisation (°C)	230.56	143.06	159.77
Percentage of crystallinity (%)	7.97	3.5	13.94

The pre-forming of the material has effect on the material's structure as due to the stretch, the collapsed molecules are oriented towards the moulding force. However, the mentioned orientation supports the formation of a crystalline structure at appropriate heat level, but above a boundary the crystalline structure also breaks down as the folded molecular chains are partially oriented in the axis of the forming force.

The rate of cooling also highly influences the degree of crystallization because the high rate cooling prevents the crystallization. With lower cooling speed, higher the ratio of the crystalline fraction. Thus, by stretching the material, orientation can be evolved in the material structure, which supports the formation of the crystalline structure during the cooling [10-14].

### 3. Results

Mechanical- and structural properties of the PET and PLA foils (PDLLA, PLLA) were tested and determined by mechanical and DSC analysis. Based on the experimental analysis, the PLA's (polylactic-acid) better material structure is confirmed to ensure better mechanical properties to forming it in higher load range compared to the PET. Regarding the material structure it was found that the PLLA and PET structures were more stable than the PDLLA. As results of DSC analysis the PDLLA contains both lactic-acid (L and D) isomers, which causes irregularity of molecular chains that highly influences to the final material structure and physical properties. In case of PLLA the crystallization process is more easily controllable as this material contains only L type of lactic-acid isomers. Due to this the physical cross-linking between the molecular chains ensuring more stable material structure of PLLA. That is why the mechanical properties (tensile strength, stiffness) of PLLA are higher compared to PDLLA.

Recently the PET is the most popular plastic in the packaging area of sweet industry. The mechanical analysis confirmed that the PDLA and PLLA can be used as a packaging material for foodstuff because this PLA material is fulfilling the complex requirements of primary and secondary packagings of sweet industry. As the PLA plastic is synthesized from bio-sources, its degradation time is relatively shorter, it is more environmental friendly solution compared to the PET.

#### 4. Conclusion

The PLA as bio-sourced and biodegradable material was found as applicable alternative of recently and widely used PET material in food industry area. Due to the different material structures which have been confirmed during the analysis, the PLA has better mechanical parameters than PET material does as the PLLA needs 224% (average) of force, the PDLLA needs 52% (average) higher forces to reach the same deformation value compared to PET. In addition the PLA's environmental performance is better compared to the PET as the PLA has lower overall environmental impacts.

In case of PLA, the PLLA which contains only L type of lactic-acid isomers was found as more advantageous material compared to the L and D type isomers built PDLLA. The reason of difference is the basic structures diversity of materials as the percentage of crystallinity was 13.94% for PLLA and 7.97% for PDLLA which ensuring better mechanical parameters to PLLA. The sweet industry mainly uses the polymers as primary (direct/indirect food contact) and secondary (indirect food contact) packagings of the products therefore both types of PLA can be used for the same purpose and application.

#### References

- [1] Weber C J, Haugaard V, Festern R, Bertelsen G 2002 Production and applications of biobased packaging materials for the food industry *Food Additives and Contaminants*, 172-177
- [2] Papong S, Malakul P, Trungkavashirakum R, Wenunun P, Chom-in T, Nithitanakul M, Sarobol E 2014 Comparative assesment of the environmental profile of PLA and PET drinking water bottles from a life cycle perspective *Journal of Cleaner Production*, **65.**, 539-550
- [3] Buzási L 2016 A műanyag csomagolószerszám gyártás helyzete Magyarországon *Polimerek*, **2. évf, 9 szám.**
- [4] Muller J, González-Martínez C, Chiralt A 2017 Combination of Poly(lactic) Acid and Starch for Biodegradable Food Packaging *Materials (Basel)*, **10 (8)**, 952-974
- [5] Xiao L, Wang B, Yang G, Gauthier M 2012 Poly(Lactic Acid)-Based Biomaterials: Synthesis, Modification and Applications, *Biomedical Science, Engineering and Technology*, 247-282
- [6] Dr. Bánhegyi Gy 2005 Poli(etilén-tereftalát) (PET) újrafeldolgozása a tulajdonságok javításával – *Műanyagipari szemle* **5.**
- [7] [http://www.bmg-inc.com/en/prod\\_and\\_res/bio\\_degmer/pdlla.html](http://www.bmg-inc.com/en/prod_and_res/bio_degmer/pdlla.html)
- [8] Ikada Y, Tsuji H 2000 Biodegradable polyesters for medical and ecological applications, *Macromol. Rapid Commun.* **21**, 117–132
- [9] Ehrenstein G W, Riedel G, Trawiel P 2004 Thermal Analysis Of Plastics *Carl Hanser Verlag GmbH & Co.KG, Munich.* 236-275
- [10] Dr. Czél Gy, Kollár M 2008 Anyagvizsgáló Praktikum *Sunplast*,
- [11] Bodnár I 2002 Potenciálisan biodegradábilis, politejsav bázisú polimerek szintézise és vizsgálata - Doktori (Ph. D.) értekezés *Debreceni Egyetem, Alkalmazott Kémiai Tanszék, Debrecen*
- [12] Pukánszky B 1995 Műanyagok *Budapesti Műszaki Egyetem Vegyészmérnöki Kar, Műegyetemi Kiadó*
- [13] D. Battezzore, S. Bocchini, A. Frache 2011 Crystallization kinetics of poly(lactic acid)-talc composites *eXPRESS Polymer Letters* **5 (10)**, 849-858
- [14] Zsoldos G 2012 UHMWPE - Biopolimer Felületének módosítása polimerizációs technológiákkal – PhD értekezés *Miskolci Egyetem*