Material structure particularity of polyethylene-terephtalate (PET) and poly-lactic (PLA)

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Abstract - The huge amount of synthetic plastics are used in the packaging area, especially in food packaging, because there have great effects in the environmental and alternative, more ecologic materials are being required. Poly-lactic acid (PLA) is one of the most significant biodegradable thermoplastic polymers. It is compostable and made it from renewable sources. The mechanical and optical property of PLA is very similar to the Polyethylene, but is more fragile, less heat-resistant and offer low resistance to oxygen permeation. In this work, two commercial PLA foils and one commercial PET foil properties were examined. The correlations between the mechanical, thermal and barrier properties were analyzed. From these measurements we can understand the PLA is a usable for packing applications, especially in the sweet manufacturing. Films were studied by tensile testing, differential scanning calorimetry and thermally simulated discharge analysis.

Keywords— PET, PLA, stretching, mechanical properties, TSD, DSC, crystal structure.

I. INTRODUCTION

The last few decades in the European Union, the environment protection is the most important, especially must be protected from the industrial and human contaminated. In the past years the depletion of the natural resources and environmental degradation threatens to the world. As a consequence, research efforts have been introduced at different levels to find alternative solutions. A specific concern is the field of packaging, which was producing huge amounts of non-degradable plastic in some critical areas. The non-degradable products can affect Europe’s and the planet’s natural resources. These problems caused further problems and the recycling costs of the products will be higher [1,2]. In Hungary the plastic industry is using only 36 percent from the PLA and PET foils such a packaging materials. Some industries worked on new biodegradable products. This material can become the part of nature, such microorganisms. There are already existing materials but their use is less prevalent because of their poor mechanical properties.

FIGURE I. PLA ROTATION IN THE NATURE [2]

Plastic materials can be found in the sweet industries to the most widely used plastic foil is the polyethylene-terephtalate (PET). The manufacture has special requirements; therefore the PET is a suitable material. A new material needs to be suitable for the seller, producer and consumer requirements and comply with the recent EU regulations. Alternative materials have to have similar set of properties. However, they need to be biodegradable following “environment friendly” approach. PLA is a renewable sustainable option to the packaging industry. It has high molecular weight. The PLA foils are colorless, glossy and rigid which is similar to the properties of PS materials.

The two isomers of LA can produce three distinct materials: poly (D-lactic acid) (PDLA), a crystalline material with a regular chain structure; poly (L-lactic acid) (PLLA), it is a semi crystalline, it has same regular chain structure as the amorphous of poly (D, L-lactic acid) (PDLLA).Three different stereo chemical forms exist for lactide: L-, D- or both L-, D- Lactide (meso-lactide), each one having their own melting properties. PLA has a degradation half-life in the environment ranging from 6 months to 2 years, depends on the size-, shape- and the isomers of the materials and the production temperature.

TABLE 1
PHYSICAL AND CHEMICAL PROPERTIES OF THE USED PLA AND PET FOIL [3].

Properties	PDLA	PLLA	PDLLA	PET
Solubility	All are soluble in benzene, chloroform, acetonitrile, tetrahydrofuran (THF), dioxane etc., but insoluble in ethanol, methanol, and aliphatic hydrocarbons			phenol, o-chlorophenol DMSO, nitrobenzene,
Crystalline structure	Crystalline	Hemicrystalline	Amorphous	Amorphous and semi-crist.
Melting temperature (T_m)/ °C	180	180	variable	260
Glass transition temperature (T_g)/ °C	50-60	50-60	variable	67-81
Decomposition temperature/°C	200	200	180-200	293-306
Elongation at break/ (%)	20-30	20-30	variable	230
Breaking strength/ (g/d)	4-5	5-6	variable	5,3
Half-life in 37°C normal saline	4-6 month	4-6 month	2-3 month	700 year

II. EXPERIMENTAL

2.1 Materials and methods

PET and PDLLA samples were obtained by Pro-Form Kft. and the PLLA sample was purchased from Good fellow Cambridge Ltd. the thickness of the PDLLA and PET film were 300µm, and the sample thickness of the PLLA foil was of 50 µm. In case of PET and PDLLA preformed films were used. The PET film surface was screen printed with a 1 mm splitting lattice and a 10 mm splitting lattice was used for the PDLLA film samples to follow the deformation ranges. The forming temperature of PET was 100°C. The forming temperature of PDLLA was 70 °C. The preheating time both of samples was 2 minutes.

The mechanical properties can be determined with tensile test. The test was 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±1°C). During the tests the 150%, 200% and 250% stretching was determined.

The DSC measurements were carried out by DSC131 EVo machine to determine the polymer structure. The heating/cooling rate was: 10 °C/min.

The structural differences were measured by SETARAM-TSC II TSD equipment. The measurement cooling and heating rate was 5°C / min.

2.2 Results and discussion

During the PET mechanical test, founded that the fluidized PET samples were initially formatted in a relatively high power range. At this stage, the weak secondary bonds connected the molecular chains are disrupted. In the amorphous material the increased kinetic energy of the collapsed molecular chains due to heating. It means that they were able to orient themselves in the direction of force in the direction of a sufficient degree of shaping force. This orientation process is also indicated by the fact that at a later stage of formatting, much smaller force was sufficient to further shape the sample. At higher forming (deformation between 200% and 250%) the molecular chains reached the maximum of orientation. The sample reached the threshold values, because the elongated molecular chains were smaller than the deformation. The center of gravity of shorter and smaller molecular chains moved, the material was been subjected to permanent flow.

From the mechanical test, the curves of poly-lactic acid (PDLLA) were significantly higher than the other samples. This can be explained by the forming force range is difference for different materials. From the result of tensile test of PET, forming was partially coupled with the long-running flow of molecular chains. In the case of PDLLA, the material was capable of absorbing even more loads without partial flow. This referred to longer molecular chains as well as stronger intramolecular interactions is in amorphous parts, but also caused by the partially crystalline structure. Larger amorphous molecules and highly folded crystalline parts need greater forces to form orientation.

In the process as a whole, it is very similar to that experienced for PET, because the PDLLA also required a higher rate of effort in the initial phase to initiate orientation. The process also started with the weak secondary cross linking of the chains, and the orientation of the amorphous and crystalline molecules happened.

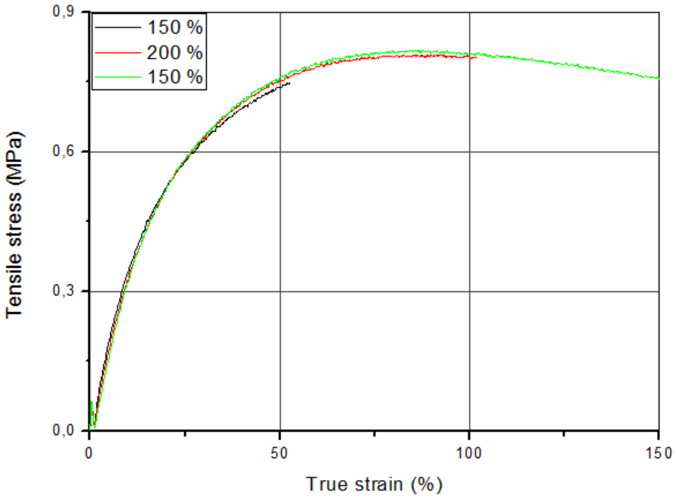

FIG. 2: RESULTS OF TENSILE TEST OF PET FOIL INN CASE OF DIFFERENT DEFORMATION RANGE

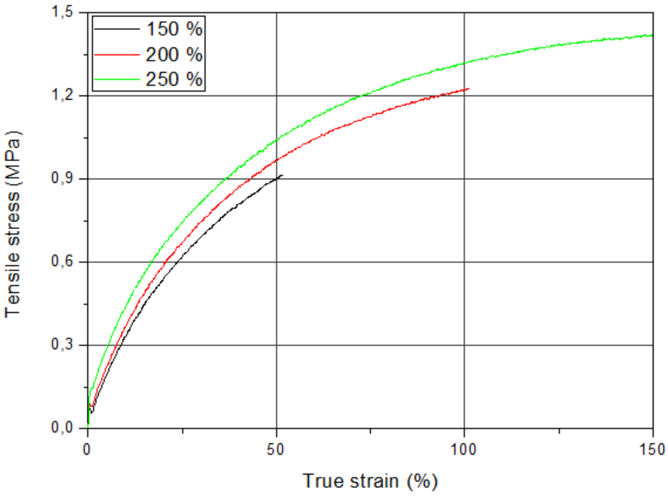

FIG. 3: RESULTS OF TENSILE TEST OF PDLLA FOIL IN CASE OF DIFFERENT DEFORMATION RANGE

During the function analysis, it became clear that both of L and D isomers of poly-lactic acid samples were tested. It formed crystalline structure under appropriate conditions. However, this dual crystal structure is also a disadvantage of the material, as the different isomers cannot build a homogeneous crystalline structure. It slows down and makes crystallization difficult. The measurements showed that the material contained two distinct crystalline fractions of heterogeneous crystal structure. This is supported by the two sub-functions obtained as a result of the resolution of the decomposition curve. During the DSC analysis, we also found that the crystalline fraction of the material is constantly changing in proportion to the degree of deformation and the purity of the material (including virgin / recycled material) also significantly influences the crystal structure of the material [4]. The former relates to the definition of the forming parameters (heating rate, forming force range, rate of decay, cooling rate). In the initial phase of deformation (0-150%), due to the one-axial stretching, the collapsed molecules are oriented towards the force.

This orientation favors the formation of crystalline structures. Above a boundary, the crystalline structure also breaks down, and like folded molecules, the folded molecular chains are partially oriented in the axis of the forming force, thus breaking down the polymer crystals. Of course, this is only true for deformations at temperatures above T_g, since only then is high enough the energy state of the molecule, which allows this deformation to be followed without structural damage and structural modification.

The required internal energy state is achieved by the surplus of energy input during the heat transfer. Of course, the rate of cooling also greatly influences the degree of crystallization because high speed cooling prevents crystallization, so the lower the cooling speed, the higher the ratio of the crystalline fraction. Thus, by heating the material, orientation can be applied to the material, which favors the formation of the crystalline structure during crystallization due to the cooling.

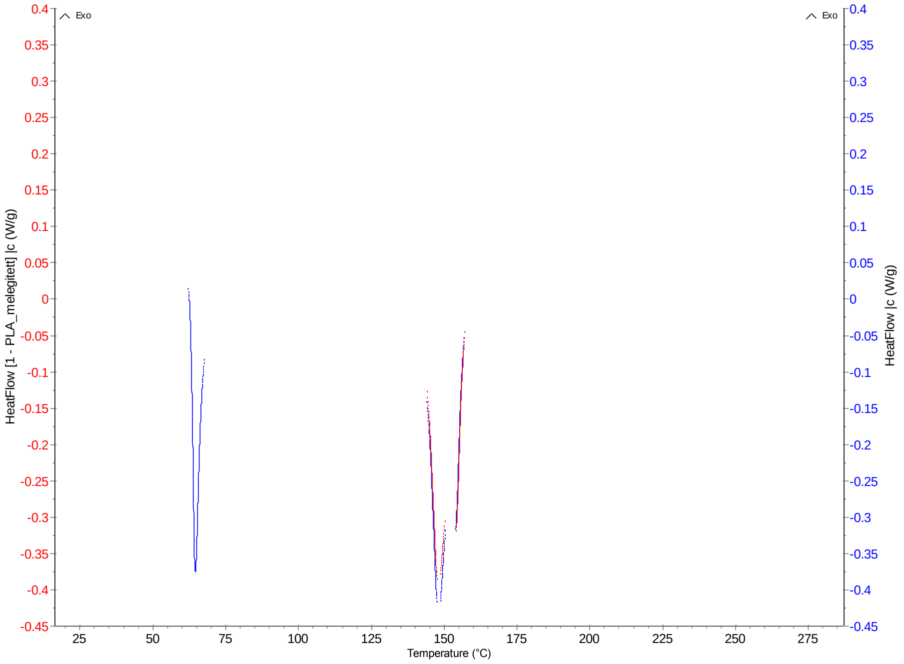

FIG. 4: DSC CURVES OF PDLLA FOIL (SECTION I. FIRST HEATING RUN; SECTION II SECOND HEATING RUN)

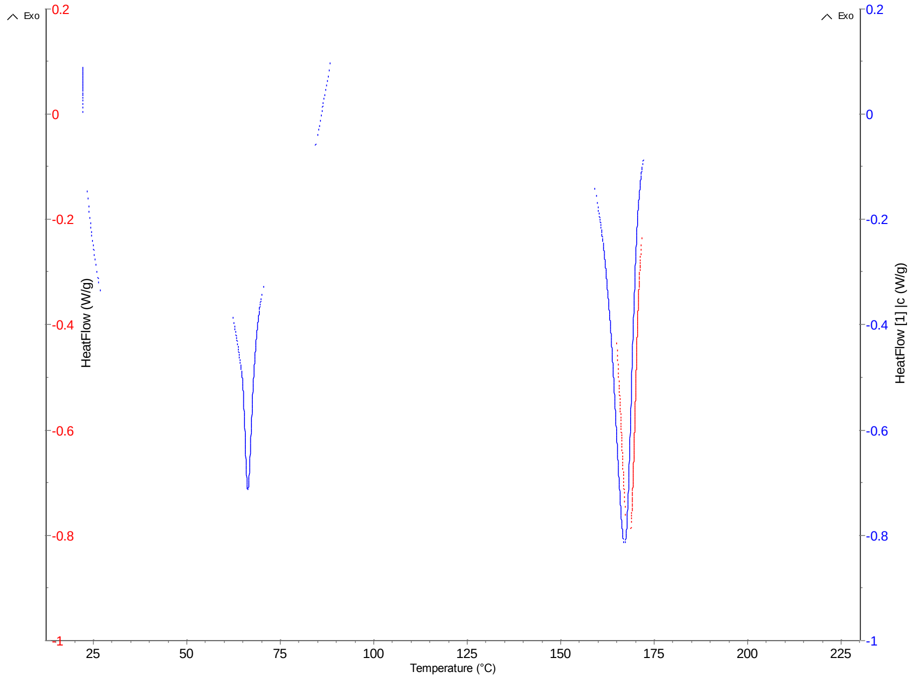

FIG. 5: DSC CURVES OF PLLA FOIL (SECTION I. FIRST HEATING RUN; SECTION II SECOND HEATING RUN).

The structural properties of PDLLA and PLLA were also investigated by TSD method. The measurements performed by SETARAM-TSC II. The polar groups of the diluted material were orientated by electrical field and then frozen in. Subsequently, with the slow rise of the temperature, we investigated the extent of the released current, which referred to the conformational movements that occurred, thus referring to the characteristics of the material structure.

The TSD test curve of PDLLA shows the relaxation process of the frozen polarization orientation. The range of temperature was about -100 to -50 ° C, the energy supplied by increased the temperature is sufficient to trigger the conformational rebounds. The mobile segments were already able to retard. These segments were usually located at the end of the chain, and may be more mobile side groups. The experienced phenomena could be split into three sub-processes, with segments of the same length and side groups for each sub process. The activation energy of which is almost the same.

If the temperature was raised more the Brownian-motion increased and appearances the greatest proportion of the glass transition. As at this stage enough energy is available for the polar groups in the main chain to recover.

TABLE 2
THE RESULTS OF PDLLA TSD MEASUREMENTS

Number of Peak	ϑ_{max} (°C)	I_{max} (pA)	A_e (kJ/mol)	Relax strength
1	-96.8	4.8	25	0.052
2	-73.6	5.5	25	0.079
3	-51	2.5	63	0.019
4	54	154	180	0.91
5	83.6	404	140	3.6
6	94.3	173	192	1.20

TABLE 3
THE RESULTS OF TSD ANALYSIS OF PLLA

Number of Peak	ϑ_{max} (°C)	I_{max} (pA)	A_e (kJ/mol)	Relax strength
1	-99	2.5	25	0.026
2	-73.6	4.2	30	0.052
3	-52	7.6	56	0.064
4	59.8	150	85	1.88
5	84.4	675	118	7.12
6	94.3	177	192	1.23

PLLA specimen TSD was also tested at low temperatures. The initial phase of the measurement - just in the case of PDLLA- was characterized by conformational rebounds. However, here we have also encountered an irregular process, which requires further measurements and tests to be identified.

Further temperature rising, also experienced a higher rearrangement near the T_g. The study was completed above the T_g, as no further relaxation process was expected.

During the examination, the generated orientation polarized part of molecular chains with an electronic field. This orientation has been fixed with cooling of the specimen. In the following step, slowly heated up the sample and measured the electron electricity. In this phase, the molecular disorientation was started to appear. This was correlated to the conformation movements and depends on the temperature [5].

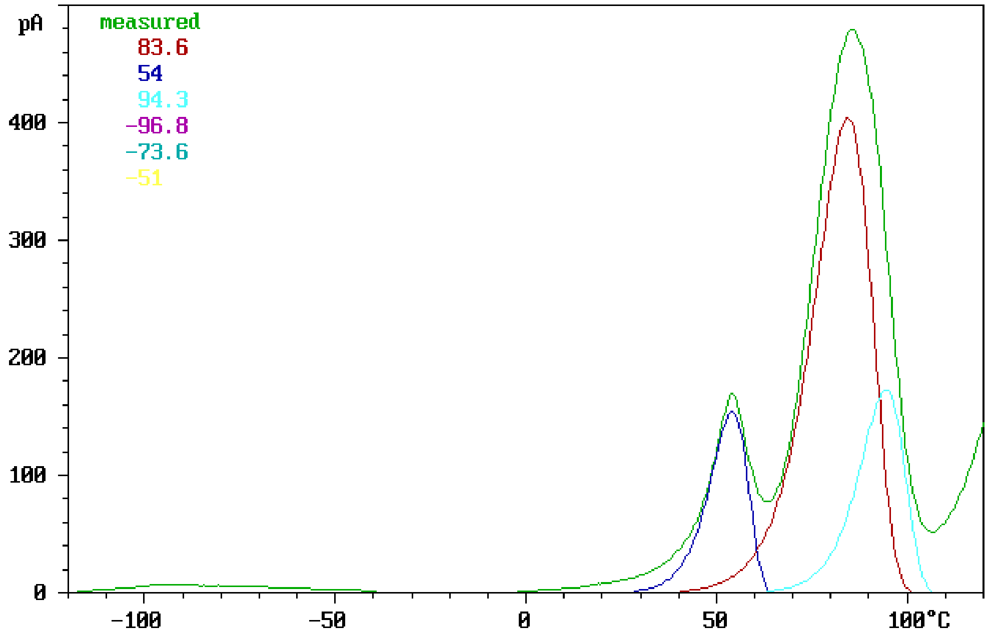

FIG. 6: TSD CURVES OF PDLLA FOIL (5K/MIN↓; 5K/MIN ↑)

In case of both materials (PDLLA and PLLA) the heat generated the molecule conformation movements. It has been started on relative low temperatures.

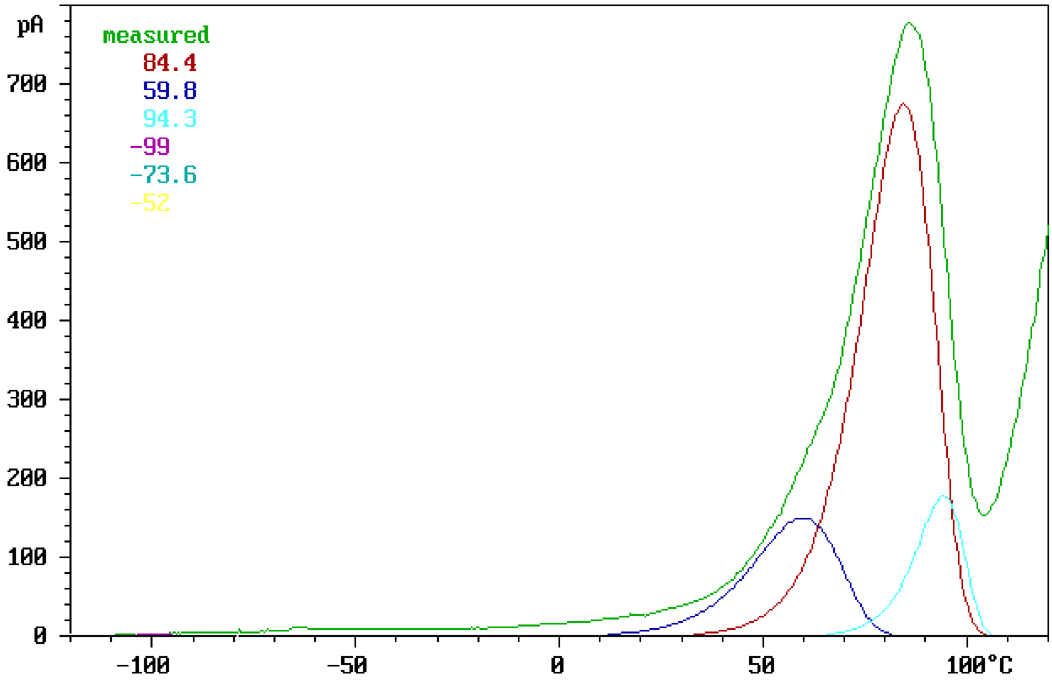

FIG. 7: TSD CURVES OF PLLA FOIL (5K/MIN↓; 5K/MIN ↑)

The temperature further changing causes the conformation movements. The rising heat was generated this movement. It means that the glass transition range was near the measurement result that the largest strength of the electricity's was determined. In this phase it was a quite available energy for polar parts of main chains to disorientate [5].

III. RESULTS

Mechanical- and structural's properties of the PET and PLA foils can be determined by mechanical-, TSD- and DSC analysis. The result of the TSD and DSC analysis is that the PLA (poly-lactic-acid) has special material structure, that ensuring better mechanical properties to forming it in higher load range compared to the PET properties. From the DSC and TSD analysis the PLLA and PLA have stabile materials structures, than the PDLLA. During the measurements of PDLLA contains L and D isomers, which is cause irregularity of molecular chains. This irregularity can be affected in the final structure. In case of PLLA the crystallization process is easier to control. As a result to the physical cross-linking between the molecular chains was more stable in the structure of final material. Finally, from the results can be confirmed that the PLLA can be used for as a packaging products in the sweet industrials, because this materials is compliance to the complex requirements.

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