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Biodegradable Plasticized Poly (lactic acid) Films

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Abstract: **The effect various biologically compatible low molecular weight plasticizers (containing ester groups and hydroxyl groups) on stress-strain properties (modulus of elasticity, tensile strength, ultimate elongation, etc.) and the biodegradability (in phosphate buffer solution and in the soil) of the biodegradable aliphatic polyester - poly (lactic acid) (PLA) was studied.**

Films cast from the solution in chloroform (CPLA) as well subsequently thermally treated films (TPLA) were examined.

It has been found (DSC method) that CPLA is almost completely amorphous, while TPLA – highly crystalline. TPLA is less resistant and much more compliant: shows about three times smaller value of modulus and more than 30 times higher ultimate elongation.

Plasticizing leads to considerable increase of deformability CPLA. Significant drop of elasticity modulus with growth of plasticizers content was observed. Plasticizers effectively reduce the value of stress maximum, increase the ultimate tensile elongation and decrease the strength of CPLA. The glycerol triacetate (TA) with more similar molecule structure to PLA turned out to be a most efficient plasticizer.

A presence of plasticizers facilitates the degradation process of CPLA in the phosphate buffer solution and in soil, as well

Keywords: **poly (lactic acid), thermal behavior, strength-deformation characteristics, plasticization, biodegradation**

I INTRODUCTION

Poly (lactic acid) (PLA) is linear aliphatic thermoplastic polyester derived from renewable resources. Best known for its ability to biodegrade, the polymer can be processed to replace less environmentally friendly hydrocarbon-based polymers, such as polystyrene or polyethylene. Since PLA biodegrades, has some other desired properties (enough high melting temperature, good barrier characteristics) and can be easy processed, it finds applications in various fields – packaging, medicine and agriculture [1; 2; 3].

However, certain mechanical characteristics (mainly too high elastic modulus and low elongation at break) of PLA seriously restrict its application as films for packaging industry [4]. To improve the compliance and flexibility of the plasticized PLA systems have been made and investigated [5; 6]. Two tasks were raised for this study. Firstly, to compare plasticizing effect of number of selected plasticizers by analysis of strength-deformation characteristics of plasticized PLA films and, secondly, to assess the influence of these plasticizers on the biodegradability of films.

II MATERIALS AND METHODS

PLA *Biomer L9000* (U9000/03/2903) was used. The average molecular weight 109.55 kDa was determined by intrinsic viscosity measurements in chloroform at 30^{o}C.

Several, mostly branched, ester groups and hydroxyl groups containing low molecular compounds of rather narrow range of molecular weight (218 – 500) were used as plasticizers (Table 1).

Taking into account that PLA is a polymer with extremely high content of ester groups it might be expected that some of chosen compounds will turn out to be well compatible with the polymer. Melting point of all used compounds (- 15 to -78^{o}C) is sufficiently less than glass transition temperature of PLA (see Table 2 and Fig. 1), which could positively influence the drop of glass transition temperature of plasticized systems. Comparatively high values of boiling temperature for these compounds (256 – 300^{o}C), in turn, suggests the low volatility of these compounds. Most of used compounds are acknowledged as acceptable plasticizers for PS, PVC, PVA, etc. [3; 5; 6].

III PREPARATION OF FILMS

Plasticizers were introduced into polymer by mixing of polymer and plasticizer solutions in common solvent – chloroform. The total content of polymer together with plasticizer in all cases was 4 wt%.

Films were prepared by solution casting technique: 40 ml of solution were pored in glass Petri dishes (diameter 140 mm). Films with thickness 100 $\pm$ 5 μm were prepared by evaporation of solvent at room temperature (initial thickness of solution layer was 2.5mm): 24 h was enough to reach complete evaporation of the chloroform. Films with 10, 15 and 20 wt% of plasticizers were prepared and tested.

Part of plasticized PLA films was thermally treated. Films were inserted between 2 layers of PTFE coated glass fabric and steel sheets. The packet was placed between heated plates of press (hydraulic RONDOLL press) heated to 170^{o}C (the temperature which corresponds the maximum on melting peek, Table 2 and Fig. 1) and kept for 4 min at low pressure. Then films were cooled between cold metal plates (average cooling rate 50 ^{o}C/min).

TABLE 1

CHARACTERISTIC OF USED PLASTICIZERS

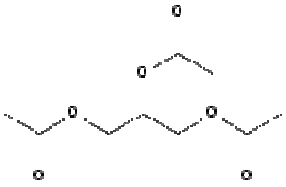
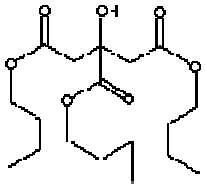
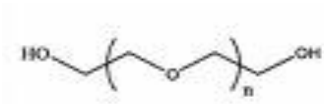
Name and designation	Molecular formula	Molecular weight, g/mol	Melting point, °C	Boiling point, °C	Use
Triacetine, glycerol triacetate, **TA**		218.21	-78	258	Used as a food additive (as a solvent in flavourings, humectant and others)
Tributyl citrate, **TBC**		360.45	-76	418	Used as additive for food contact, medical and pharmaceutical materials
Polyethylene glycol (PEG 300), **PEG**		300 (average)	- 15	250	Used in a variety of pharmaceuticals and in medications.
GRINDSTED® SOFT-N-SAFE, **GSNS**	fully acetylated monoglyceride based on castor oil	500.5	-21.5	>300 (at 1mm Hg)	Fully degradable food additive.

TABLE 2

DSC CHARACTERISTIC OF CASTED AND SUBSEQUENTLY THERMALLY TREATED PLA

Sample	Glass transition temperature, °C			Cold crystallization				Melting			
	initial	flexion	final	Temperature, °C			Heat effect, ΔH, J/g	Temperature, °C			Heat effect, ΔH, J/g
Cast	43	48	58	85	97	116	19	148	163	174	32
	Sharp, very evident peak										
Subsequently thermally treated	25	38	51	no				141	168	177	42
	Weakly expressed										

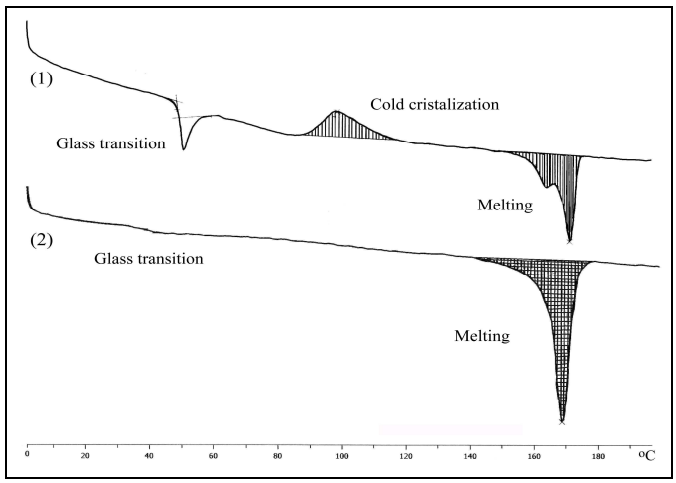


Fig.1. DSC curves of PLA: cast (1), subsequently thermally treated (2)

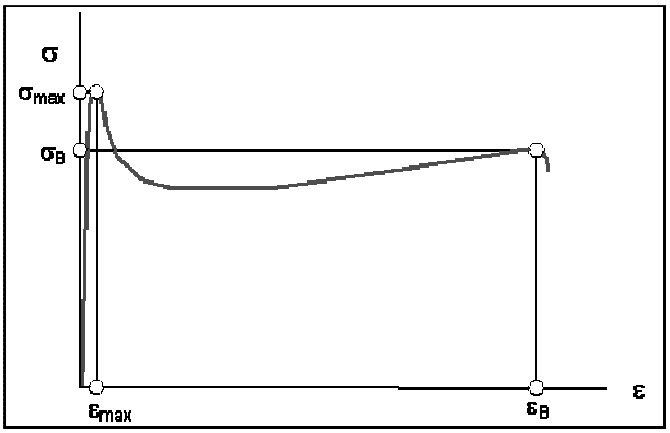


Fig. 2. Characteristics which were determined from tensile $\sigma(\varepsilon)$ curve: elastic modulus $E=\lim(d\sigma/d\varepsilon)|_{\varepsilon\to 0}$, σ_B – tensile strength, ε_B – ultimate elongation, σ_{max} – stress at the maximum, ε_{max} – respective elongation

IV STRENGTH-DEFORMATION CHARACTERISTICS

Double blade shaped samples of films were cut (width - 5 mm, length of working area – 10 mm).

The thickness of each sample was measured at 5 different points by a micrometer and the average was taken. Tensile test of the films was carried out at 20°C by use of Zwick Roell testing equipment according to requirements of LVS EN ISO 527-3:2000 [7] (the speed of the upper cross-head 10 mm/min). Stress (σ) - strain (ε) relationship was determined till the breaking of samples. A number of strength-deformation characteristics (Fig. 2) of films were determined from stress-strain curves. The results present the mean values of five independent measurements.

V THERMAL CHARACTERISTICS

Thermal analysis for films were carried out using a *METTLER TOLEDO STARe* 1 DSC at a heating rate of 10°C/min under nitrogen atmosphere. The sample weight was around 5 mg. The glass transition, cold crystallization and melting temperature regions were determined. Crystallinity of PLA was determined from the melting heat effect data of polymer crystalline phase, assuming that for 100% crystalline PLA this value is 93.1 J/g [8].

VI BIODEGRADABILITY IN THE PHOSPHATE BUFFER SOLUTION AND IN THE SOIL UNDER CONTROLLED LABORATORY CONDITIONS

Biodegradation of plasticized PLA films was tested in phosphate buffer solution (PBS) and in the microbiologically active soil under controlled laboratory conditions (25°C; pH 6.5).

Samples of size 30 x 30 mm were prepared and placed in glass dishes with phosphate buffer. Slightly alkaline phosphate buffer solution (pH = 7.2) was prepared by dissolving 9.49 g $Na_2HPO_4 \cdot 2H_2O$ and 1.81 g KH_2PO_4 in 1 L of distilled water in accordance with [9]. Three samples were taken from each plasticized system. All dishes were placed in the thermostat at 25°C.

Every week one sample from each system was removed from the glass dishes rinsed of with distilled water, dried 24 h at 32°C and aged for 72 h at 60°C in vacuum oven till the unchanged mass. Estimated weight loss of films during the period was calculated. The remaining samples were substituted with fresh PBS [9; 10].

Biodegradation in the soil was evaluated gravimetrically under controlled laboratory conditions at 25 ± 1°C in microbiologically active, moist garden soil (pH = 6.5). Film samples were placed in the soil in glass Petri dishes and kept in oven at 25°C. Every week 3 parallel samples from each system was taken out, washed in distilled water and dried at 105°C for 72h. The weight loss of the films was determined.

VII RESULTS AND DISCUSSION

Cast PLA (CPLA) films show tensile strength-deformation characteristics rather different from thermally treated (Fig. 3, Table 3). Values of strength σ_B and elasticity modulus E of cast polymer are comparatively high, while ultimate elongation ε_B is very low (close to 5 %). It become obvious, that CPLA needs to be plasticized in order to achieve required deformability of films. Unexpectedly, thermally treated PLA (TPLA) turned out to be less resistant and much more compliant polymer. It shows about three times smaller value of E and more than 30 times higher ε_B value. It seems that there is no acute necessity for plasticizing of TPLA. However, TPLA films likely are less attractive for packaging use, because of potentially more knotty processing technology.

Judging from DSC data (Table 2 and Fig. 1), CPLA in heating run shows cold crystallization (heat effect conform degree of crystallization 20%, followed by melting (degree of crystallization 34%). It means that crystallinity of CPLE does not exceed 14%. Namely CPLE is nearly amorphous and at tensile test temperature (more than 25°C below glass transition flexion temperature) behaves as typical amorphous glassy polymer.

On DSC thermogram of TPLA (Table 2 and Fig. 1) only one heat effect (melting of crystalline part of the polymer) occurs, corresponding to high crystallinity – 45%. Glass transition of amorphous part of thermally treated polymer is about 10°C lower, comparing with cast polymer. Seems, that structure of the amorphous part TPLA is less organized (comparing with CPLA) and is more friable.

TABLE 3

STRENGTH DEFORMATION CHARACTERISTICS OF PLA

PLA	E, MPa	σ_{max}, MPa	ε_{max}	σ_b, MPa	ε_b
Cast	1054	no	no	40	0,06
Subsequently thermally treated	370	15	0,05	9	1,97

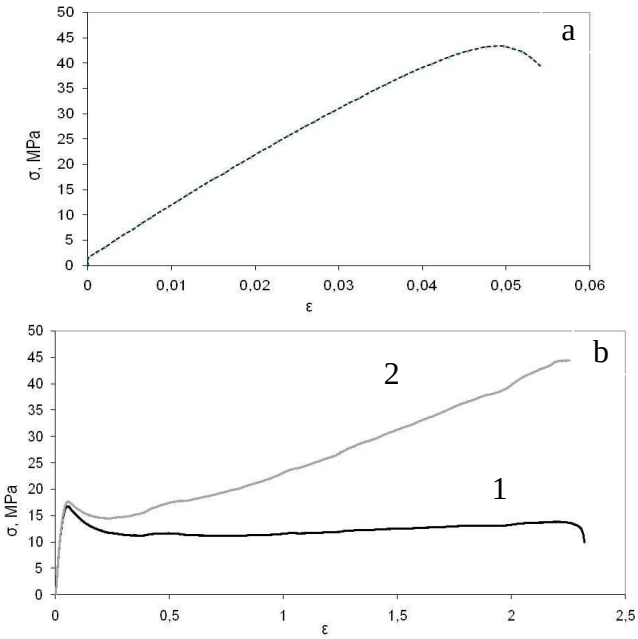


Fig.3. Tensile stress (σ) – strain (ε) curves of cast (a) and thermally treated PLA films (b): curve 2 – true stress

High deformability (large ε_B) of TPLA is a result of stress-induced "melting" and subsequent "recrystallization" of crystalline regions and their orientation along tensile direction, which is typical for crystalline polymers [11].

Maximum on the $\sigma(\varepsilon)$ curve (σ_{max}) most likely characterize the ultimate stress which is necessary to destroy the glassy amorphous framework and to release crystalline regions. It is a highest value on the $\sigma(\varepsilon)$ curve of TPLA. At the same time the value of σ_{max} (Table 3) is about three times smaller than σ_B value of cast polymer (it is the stress at which fully amorphous glassy structure breaks). Considerable orientation strengthening of TPLA can be observed: there is a gradual growth of stress with elongation after the maximum. The effect of orientation strengthening becomes more pronounced if instead of engineering stress σ true stress σ^* values ($\sigma^* = \sigma(1+\varepsilon)$) is used (Fig. 3, curve 2). Plasticizing leads to considerable increase of deformability of cast PLA.

Elastic modulus $E = \lim(d\sigma/d\varepsilon)|_{\varepsilon\to 0}$ characterizes the resistance of the initial structure of the polymer at low unite strain values, when structure transformations nearly have not yet occurred. Therefore directly modulus may serve as measure of the ability of certain plasticizer to weaken intermolecular interaction. There is significant drop of E values with content of various plasticizers (Fig. 4a). On $\sigma(\varepsilon)$ curves of plasticized CPLA σ_{max} peak appears. Plasticizers effectively reduce the value of σ_{max} (Fig. 5a).

There is significant increase of ultimate tensile elongation ε_B of CPLA with plasticizer content (Fig. 6a), as well. Typical undesirable effect of plasticizing is strength reduction of polymer. Really, σ_B values decreases when the plasticizer content grows (Fig. 7a). All observed tendencies (Fig. 4a - Fig. 7a) are the result of greater or lesser ability of certain plasticizer to weaken intermolecular bonds of polymer. As can be seen (Fig. 4a - Fig. 7a) most efficient plasticizer is TA (gray diamond markers). Comparing with other used plasticizers (Table1) the structure of TA molecule is more similar to the structure of CPLA. The consequence of this similarity is the best compatibility of TA with CPLA. As could be expected, less efficient plasticizer is PEG with less similar structure of the molecule (gray circular markers).

Effect of plasticizers on strength-deformation characteristics of TPLA differs from CPLA. Peculiar "antiplasticizing" impact can be observed in many cases. If the best plasticizer TA (and few others) show "normal" tendencies: decrease of E (Fig. 4b) and σ_{max} (Fig. 5b) values, as well increase of ε_B (Fig. 6b) values, then some other behave differently. Growth of E (Fig. 4b), σ_{max} (Fig. 5b) and σ_B (Fig. 7b) with increase of content of certain plasticizers (at small content values) likely is a result of structure ordering of TPLA. To confirm this assumption (which may turn out to be of practical interest), further experimental structure studies are necessary.

It was of particular interest to evaluate the influence of plasticizers on the character and rate of biodegradation (only CPLA systems with limited range of plasticizers were studied). There are significant visual changes of samples. Even during first week of aging in phosphate buffer solution shrinkage and bleaching of samples can be observed. Surface of some samples became callous. More likely the reason of it is the growth of crystallinity of plasticized polymer [13].

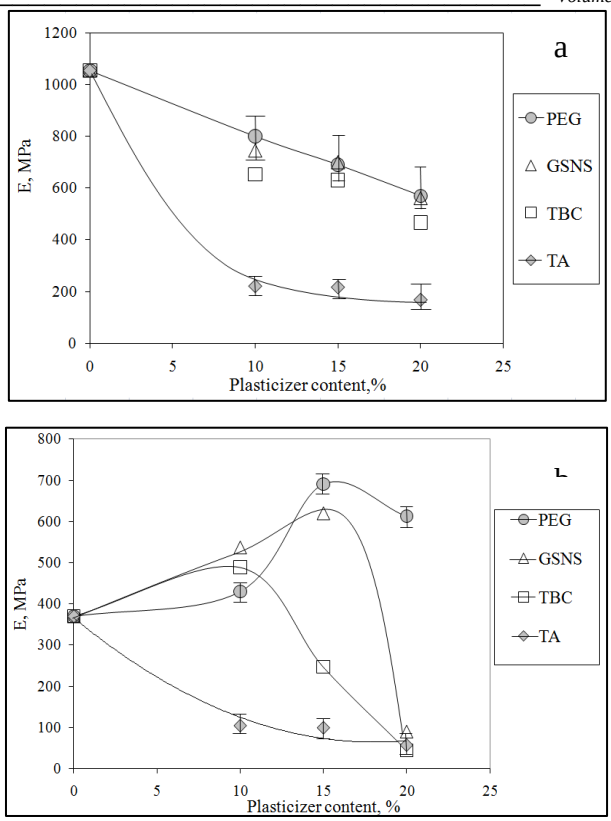


Fig.4. Modulus of elasticity of CPLA (a) and TPLA (b)

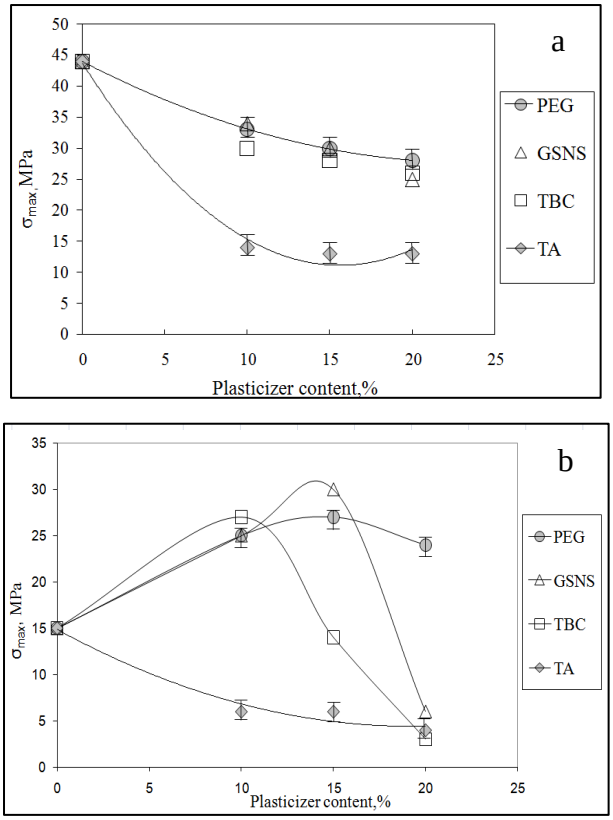


Fig.5. Stress at the maximum of CPLA (a) and TPLA (b)

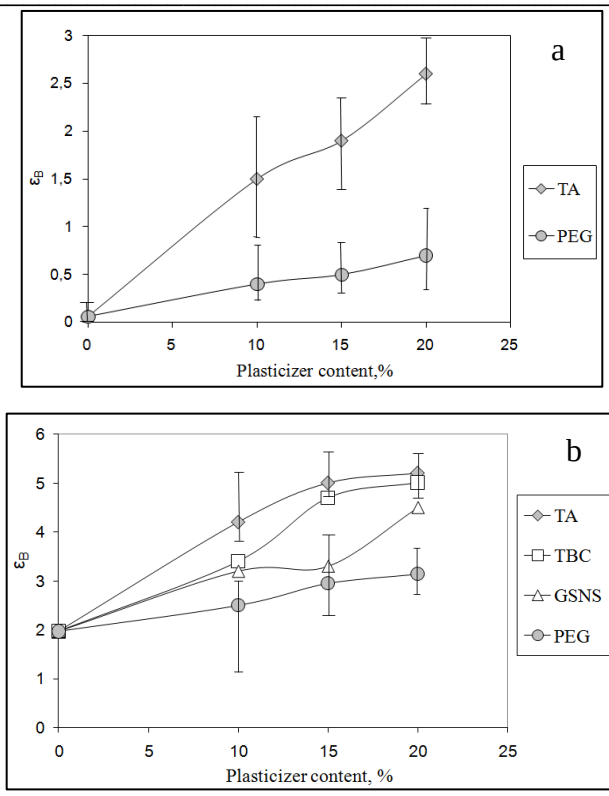


Fig.6. Ultimate elongation of CPLA (a) and TPLA (b)

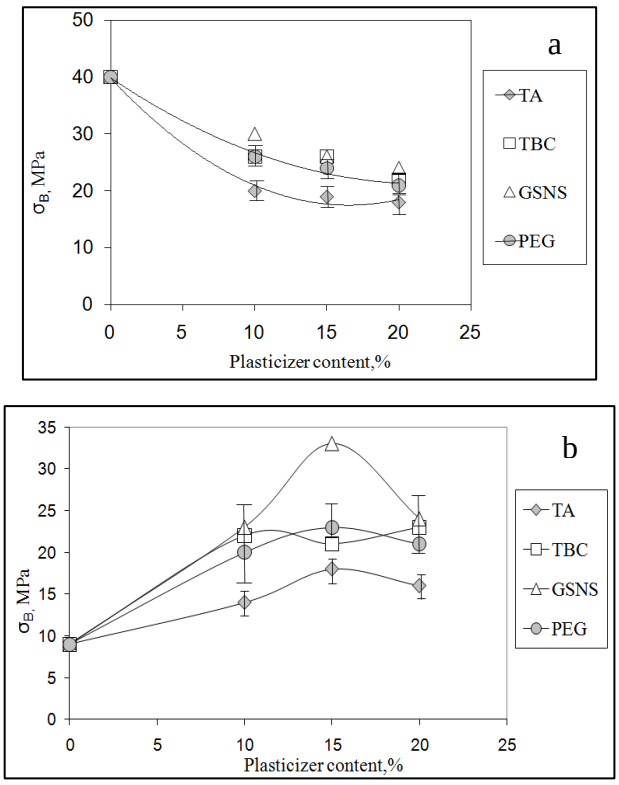


Fig.7. Tensile strength at break of CPLA (a) and TPLA (b)

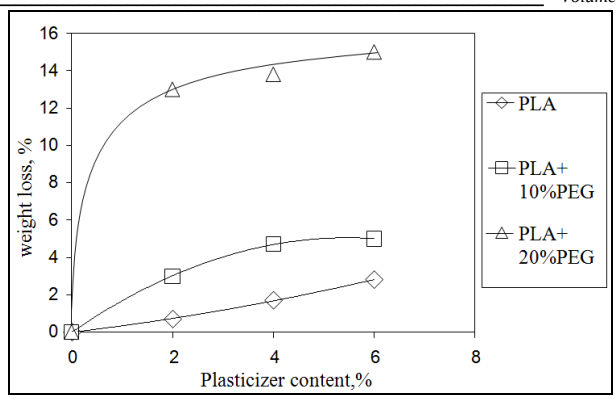


Fig.8. Weight loss in phosphate buffer solution for PLA plasticized with PEG

Presences of plasticizers facilitate the degradation process of CPLA in the phosphate buffer solution. Weight loss rate significantly increases with content of PEG in polymer (Fig.8). Similar trends can be observed also in a case of biodegradation in soil. Weight loss rate of samples increases with the raise of content of plasticizers: PEG and GSNS (Fig.9a).

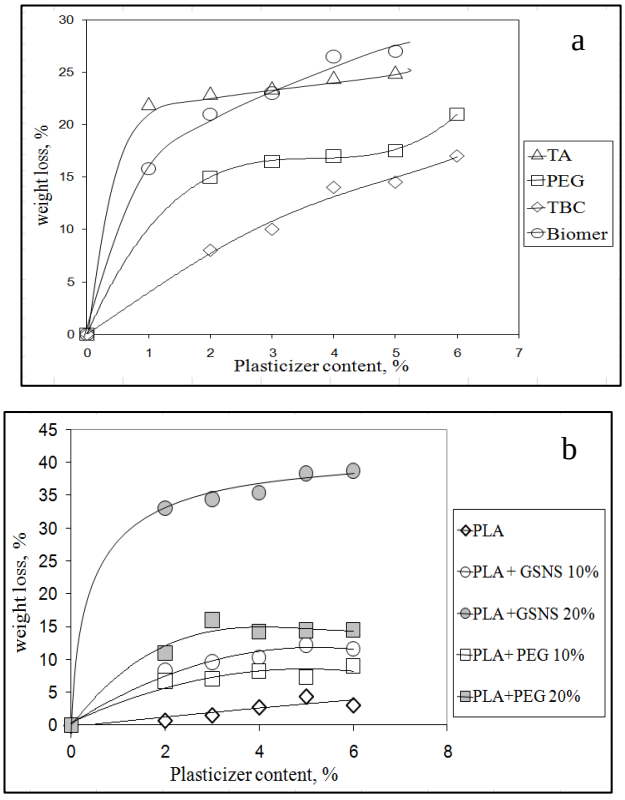


Fig.9. Degradation kinetics in the soil of plasticized PLA (a) and plasticized PLA with 20% of plasticizers

There is too little experimental evidence of the effect of chemical nature of the plasticizer on the rate of biodegradation. However, it is obvious that this characteristic is really important. Biodegradation proceeds faster in the range of plasticizers TBC < PEG < TA (Fig.9b). The degradation rate of TA containing CPLA reaches the degradation rate of recognized biodegradable starch biopolymer Biomer (Fig.9b).

It seems that the ability to affect the biological degradation depends not only on chemical nature of certain plasticizer, but also on its ability to alter the molecular arrangement of PLA. More detailed studies are necessary.

VIII CONCLUSIONS

Cast poly (lactic acid) (CPLA) is nearly amorphous and at tensile test temperature, which is more than 25°C below glass transition temperature, behaves as typical amorphous glassy polymer: shows high strength and elasticity modulus and vary low ultimate elongation. In order to achieve required deformability of films, necessary for packaging use, CPLA needs to be plasticized. Cast and subsequently thermally treated poly (lactic acid) (TPLA) is highly crystalline. Its glass transition temperature is about 10°C lower. TPLA is less resistant and much more compliant: shows about three times smaller value of modulus and more than 30 times higher ultimate elongation. High deformability of TPLA is a result of stress-induced "melting" and subsequent "recrystallization" of crystalline regions and their orientation along tensile direction. A number of mainly branched, ester groups and hydroxyl groups containing low molecular compounds of rather narrow range of molar mass were used as plasticizers. Plasticizing leads to considerable increase of deformability cast PLA. Significant drop of elasticity modulus, which characterizes the resistance of the initial structure of the polymer at low unite strain values, with growth of plasticizers content was observed. Plasticizers effectively reduce the value of stress maximum on the stress-strain curves, increase the ultimate tensile elongation and decrease the strength of CPLA. All observed tendencies are the result of greater or lesser ability of certain plasticizer to weaken intermolecular bonds of polymer. The glycerol triacetate (TA) turned out to be a most efficient plasticizer. Its molecule structure is more similar to the structure of PLA. The consequence of this similarity is the best compatibility of TA with CPLA.

The influence of plasticizers on the character and rate of biodegradation was studied. Presence of plasticizers facilitates the degradation process of CPLA in the phosphate buffer solution and in soil, as well.

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Zane Grigale, Martiņs Kalniņš, Anda Dzene, Velta Tupureina. Biodegradablas plastificētas polilaktīda plēves.
Pētīta vairāku atšķirīgu bioloģiski saderīgu estergrupas un hidroksilgrupas saturošu mazmolekulāru plastifikatoru (glicerīna triacetāts, tributilcitrāts, polietilēnglikols, acetilēts monoglicerīds uz rīcineļļas bāzes) ietekme uz biodegradabla alifātiska poliestera polilaktīda (PLA) stiprības-deformatīvo īpašību rādītājiem stiepē (elastības modulis, stiepes robežspriegums, trūkšanas pagarinājums u.c.) kā arī uz bioloģiskās noārdīšanās spēju (fosfātu buferšķīdumā un augsnē). Pētījumos tika izmantoti plēves veida PLA paraugi, kas iegūti atlejot no polilaktīda un plastifikatora šķīduma hloroformā (CPLA), kā arī pēc tam termiski apstrādāti paraugi (TPLA). Izmantojot diferenciālas skenējošās kalorimetrijas (DSC) metodi konstatēts, ka CPLA ir praktiski amorfs (kristāliskuma pakāpe nepārsniedz 14 %), kamēr TPLA – kristālisks (kristāliskuma pakāpe – 45 %).
TPLA ir ievērojami padevīgāks: uzrāda trīs reizes mazāku elastības moduļa vērtību un 30 reizes lielāku trūkšanas pagarinājuma vērtību, salīdzinājumā ar CPLA. Plastificēšana izraisa būtisku CPLA deformējamības (relatīvā trūkšanas pagarinājuma) palielināšanos. Elastības moduļa vērtības samazinās, palielinoties plastifikatora saturam. Plastifikatori efektīvi samazina sprieguma maksimumu vērtības, vienlaicīgi palielinot CPLA trūkšanas pagarinājuma un samazinot tā stiepes robežsprieguma vērtības. Konstatēts, ka glicerīna triacetāts, kura molekulas struktūra ar visvairāk līdzīga polilaktīdam, ir visefektīvākais CPLA plastifikators. Plastifikatoru klātbūtne būtiski sekmē polilaktīda sadalīšanos kā fosfātu buferšķīdumā, tā arī augsnē.

Зане Григале, Мартыньш Калныньш, Анда Дзене, Велта Тупурейна. Биоразлагаемые пластифицированные пленки полилактида.

Изучено влияние ряда биологически совместимых низкомолекулярных пластификаторов, содержащих сложноэфирные и гидроксильные функциональные группы (триацетат глицерина, трибутилцитрат, полиэтиленгликоль, ацетилированнй моноглицерид на базе касторового масла) на деформационно-прочностные свойства при растяжении (модуль эластичности, предел прочности, удлинение при разрыве, напряжения в максимуме и др.) и биоразлагаемость (потери массы и фрагментация в буферном фосфатном растворе и в почве) биоразлагающегося алифатического полиэфира – полилактида (PLA). Иссследовались пленочные образцы PLA, отлитые из раствора PLA и пластификатора в хлороформе (CPLA), а также впоследствии термически обработанные пленочные образцы (TPLA). Используя метод дифференциальной сканирующей калориметрии (ДСК), установлено что CPLA практически аморфен (степень кристалличности не превышает 14 %), в то время как TPLA – кристалличен (степень кристалличности 45 %). В сравнении с CPLA, TPLA значительно более податлив: обнаруживает в три раза меньшее значение модуля эластичности и в 30 раз большее значение удлинения при разрыве. Пластификация приводит к существенному увеличению деформируемости CPLA (росту относительной деформации при разрыве). Обнаружено значительное снижение значений модуля эластичности с ростом содержания всех пластификаторов. Пластификаторы эффективно снижают значения максимумов напряжения, вызывают существенное увеличение удлинения при разрыве, а также снижение предела прочности CPLA. Триацетат глицерина, имеющий наиболее близкое полилактиду строение молекулы, оказался наиболее эффективным пластификатором CPLA. Присутствие пластификаторов существенно ускоряет разложение PLA как в буферном фосфатном растворе, так и в почве.