Evaluation of some eco-friendly plasticizers for PLA films processing

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ABSTRACT: This study was conducted as a first step in order to obtain green materials for food packaging by using an eco-friendly bioplastic, polylactic acid (PLA), and nontoxic plasticizers. Different types of nontoxic biocompatible plasticizers/lubricants, both obtained in the laboratory, as well as commercial ones, were employed to modulate physical and mechanical properties of PLA. Melt compounding by means of a Brabender mixer led to obtaining of homogeneous materials. The incorporation of PLA oligomer, L-lactide, poly(ethylene glycol), and epoxidized soybean oil (USE) improved the melt flow and processability, increasing the hydrophilicity of the resulted plasticized PLA systems. USE significantly increased the elongation at break, reduced the glass transition temperature, and increased the PLA chain mobility. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43223.

INTRODUCTION

Nowadays, the interest in the use of biopolymers in different applications has increased due to their potential to substitute certain synthetic and petroleum-based materials. Also, the development and application of biocompatible plasticizers/lubricants are increasing in the last decades as a result of stringent regulations imposed on mineral oil-based lubricants with their nonbiodegradable toxic wastes. However, vegetable oil-based plasticizers/lubricants have poor performance characteristics such as thermal and oxidative instabilities.

Polylactic acid (PLA) is a thermoplastic polymer used in the packaging sector, as it has glassy transition temperature of approx. 60°C, higher than the temperature of use products. It performs like traditional plastics. It is resistant to solvents and fragrances used in food field and presents as well a good barrier to vapor and permanent gases.[1] Lactic acid is a nontoxic constituent of the human metabolic cycle, gives absolute biocompatibility to the PLA polymer. Polylactic acid/polylactide are nontoxic, biodegradable, biocompatible, bioabsorbable, compostable polymers obtained from renewable resources that could be thermally processed and find utilization in a variety of fields: packaging, medicine, agriculture, pharmacy, textile industry. It is approved by Food and Drug Administration (FDA). It is degraded through the mechanism of ester hydrolysis to return lactic acid, which is naturally consumed to yield carbon dioxide, water, and biomass. PLA can be also converted back to the starting material (lactic acid) which can then be purified and used to make virgin poly-

mer again, avoiding down cycling and preserving the value of the lactic acid through many cycles of use. It can help reduce greenhouse gas emissions. Compared with other petroleum based plastics such as polypropylene, and polyethyleneterephthalate (PET), PLA requires the least amount of energy to produce, and releases the least amount of carbon dioxide during production. Therefore the PLA is considered a greener alternative to PET and other plastics because its supply chain requires less transportation and thus contributes less CO_2 to the atmosphere. It is used as numerous materials such as non-woven fibers, oriented films, extrusion coating, flexible film, cast sheet, injection molding and foam. The prohibitive cost is one factor that has kept its application still mainly confined to the high-value, specialty applications.[2]

PLA use is limited in certain applications, although it is an eco-friendly bioplastic with excellent biocompatibility and processability. PLA presents poor toughness, being a very brittle material with less than 10% elongation at break that limits its use in the applications that need plastic deformation at higher stress levels.[3]

Although the stereochemical composition of the PLA has a significant effect upon its melting point, crystallization rate, extent of crystallization, and mechanical properties,[4] the flexibility of PLA may be modified by blending it with a second polymer or a plasticizer. A lower glass transition temperature, enhanced ductility and improved processability could be achieved by changing some of the plasticizer properties: molecular weight, polarity, and end groups.[5]

Table I. Some information on Ecological Plasticizers used in this Study

Plasticizer	Number average molecular mass (M_n)	Density (g/cm^3)
Epoxidized soybean oil (USE)	1000	0.99
Lactide (L)	144.13	1.34
PLA oligomer (S7)	8900 (DLS); 4475 (GPC)	1.20
PEG (PEG2)	2000	1.21 (20°C)
PEG (PEG4)	4000	1.09 (60°C)

Different biodegradable as well as nonbiodegradable plasticizers have been used as plasticizers for PLA, but for packaging, only nontoxic substances approved for food contact applications can be considered as plasticizing agents. The choice of plasticizers to be used as modifiers for PLA is limited by technical and legislative[6] requirements of the application in food packaging. Scientific literature contains some studies regarding the use of different plasticizers for PLA.[7–10] The selection of a plasticizer for PLA films is normally based on the compatibility and biodegradability of the plasticizer, the amount of the plasticizer required for plasticization, and the desired functional properties of the films. Therefore, new and old plasticizers should continuously be studied in the field of food-packaging materials.

The aim of the present study was to evaluate and compare the effect of different types of nontoxic plasticizers on the melt processing, mechanical, rheological and thermal properties, as well as on the changes of the surface properties of PLA.

EXPERIMENTAL

Materials

PLA used in this study was type 2002D from NatureWorks LLC (Minnetonka, MN), having a density of 1.24 g/cm^3, melt flow index (MFI) of 5–7 g/10 min (at 210°C/2.16 kg). It was obtained from renewable annual resources, with a D-lactide content of 4% (96% of L-lactide).

Soybean oil is a biocompatible multifunctional additive for lubricating oil because of its composition consisting in fatty acids (lauric acid, myristic acid, palmitic acid and stearic acid) and unsaturated acids (palmitoleic acid, oleic acid, linoleic acid, linolenic acid, gadoleic acid).[11] γ-tocopherol was the main isomer in soybean oil. Similar tocopherol contents and compositions were reported in the literature for wheat germ oil and soybean oil. Phytosterols as campesterol, sigmasterol and β-sitosterol are also present.[12]

The improved performance of epoxidized soybean oil over soybean oil was validated by Adhvaryu and Erhan.[13] They have shown that the epoxidized soybean oil can be considered as a potential source of high-temperature lubricants having also a significant content of antioxidant compounds. Epoxidized soybean oil is the result of the oxidation of soybean oil with hydrogen peroxide and either acetic or acid. It is a nontoxic, clear to yellow liquid that is used as a plasticizer and stabilizer in plastic materials, mainly PVC, replacing dioctyl phthalate. Epoxidized soybean oil is the most readily avail-

able in large volume and one of the lowest-cost vegetable oils in the world.[14]

The epoxidised soybean oil (USE) used in this work was synthesized by Mustaţă et al.[15] The soybean oil was epoxidised with peracetic acid and hydrogen peroxide, in the presence of glacial acetic acid/toluene. USE has epoxy equivalent 270/g.[16]

L-lactide (3,6 dimethyl-1,4-dioxane-2,5-dione) was purchased from Aldrich, has melting point (m_p = 116–119°C) and boiling point (b_p = 142°C). FDA classification of lactic acid is Generally Recognized as Safe (GRAS; 21 CFR, 180.1061) for use in food as long as good manufacturing practices are maintained.[17]

PLA oligomer (S7) was synthesized by solution polycondensation procedure of L-lactic acid (L-LA). The reaction product S7 was dried at 70°C for 24 h, under vacuum and finally ground. The reaction yield was about 73 wt %.[18] It is a nontoxic compound used in medical field.[19]

Poly(ethylene glycol) PEG 2000 (PEG2) and PEG 4000 (PEG4) were purchased from Sigma-Aldrich. PEG2 has average molecular weight M_n = 1900–2200, melting point = 50–53°C, 45 mol of ethylene oxide (EO), pH = 5–7, hydroxyl number: 51–62. PEG4 BioUltra in form of flakes, has an average molecular weight M_n of 3350 to 4000, has 93 EO, viscosity range of 110 to 158 cSt, melting point 55–60°C, pH 5.5–7.0, range of average hydroxyl number, 25–32 KOH mg/g. PEGs are neutral, water soluble, and nontoxic polymers, employed by the FDA for internal consumption and injection in a variety of food, cosmetics, medicines, and drug delivery systems.[20] The polymer is used as a lubricating coating for various surfaces.

Other information about the used plasticizers are presented in Table I.

Their chemical structures are represented in Scheme 1.

Compounding Method

Plasticized materials with PLA matrix and different plasticizers were obtained by melt compounding performed at 175°C for 10 min, with a rotor speed of 60 rpm, using a fully automated laboratory Brabender station (Duisburg, Germany). Because PLA could degrade by ester linkage hydrolysis, PLA pellets were dried in a vacuum oven for 12 h at 80°C before blend preparation when all traces of moisture were removed.

Specimens for the mechanical characterization were prepared by compression molding using a Carver press (175°C with a pre-pressing step of 2 min at 50 atm and a pressing step of 2 min at 150 atm). Dog bone shaped tensile testing specimens of 1 mm thickness and 80 mm length were obtained. All the obtained sheets presented a good homogeneity. For oxygen permeability test and ATR-FT-IR analysis, films were obtained by press moulding, using a pre-pressing step of 2 min at 50 atm and a pressing step of 2 min at 200 atm. The notations of the obtained composites are as follows:

- PLA/USE: PLA containing 15 wt % epoxidized soybean oil;
- PLA/L: PLA containing 15 wt % L-lactide (L).
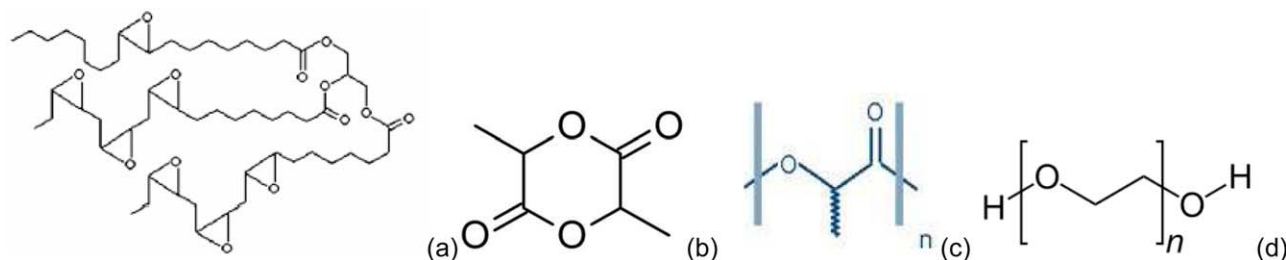
Scheme 1. Chemical structure of (a) USE, (b) lactide, (c) PLA oligomer (S7), (d) PEG2 and 4 have different *n* values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

- PLA/S7: PLA containing 7 wt % LA oligomer (S7)—low amount was used because it increases the material rigidity—see tensile properties;
- PLA/PEG2: PLA containing 15 wt % PEG 2000;
- PLA/PEG4: PLA containing 15 wt % PEG 4000.

Investigation Methods

All characterization tests were performed on samples prepared in the same conditions, namely one step of processing and another of compression moulding, in the last step only suitable pressure was used for sheets or films preparation. Drying was done only before processing as moulding was performed immediately after melt processing.

Processing Behavior. Melt processing behavior of the prepared blends was studied by evaluation of some parameters obtained from torque-time curves at different moments of melt processing in Brabender mixer.

ATR-FT-IR Spectroscopy. ATR-FT-IR spectra of composite materials were recorded using FT-IR spectrometer Bruker, Vertex 70 (Billerica, MA) equipped with ATR device (ZnSe crystal) with a 45 angle of incidence. Sixty-five scans were acquired with a spectral resolution of 2 cm^{-1}.

Differential Scanning Calorimetry Measurements (DSC). Thermal analysis of materials was carried out on a DSC analyzer TA Instruments Q20 Dynamic Scanning Calorimeter (New Castle, DE) and the thermograms were recorded at heating rates of 10°C/min from 20 to 200°C to and cooling rates of 5°C/min using a two-stage mechanical cooling system. Indium (m.p. = 156.6°C; ΔH_m = 28.45 J/g) was used as reference material to calibrate the temperature and energy scales of the instrument. 5 to 10 mg of sample was accurately weighed (± 0.01 mg) and encapsulated in 40 μL flat-bottomed aluminum pans. Empty pans were used as references. All measurements were performed under N$_2$ atmosphere. From DSC curves the glass transition temperature, cold crystallization, and melting temperatures (standard deviation in temperature is of ± 0.5°C) have been determined and corresponding crystallization and melting heats (standard deviation $\pm$ 1–2 J/g) have been evaluated. The degree of crystallinity of the PLA samples was obtained by dividing the melting enthalpy of the sample by 93.7 J/g which is the estimated melting enthalpy of a pure crystalline PLA.[21]

Scanning Electron Microscopy (SEM). Examination of the fracture surfaces of tensile specimens was done using a Scanning Electron Microscope (SEM, Hitachi/S-3500N, Japan) at an accel-

erating voltage at 20 kV. The SEM instrument was equipped with a Robinson detector. Magnification is given on each photo.

Tensile Properties. The tensile properties (tensile strength, elongation at break, the Young's modulus) were determined according to SR EN ISO 527-2/1996. An Instron (USA) 5 kN test machine operated at a crosshead speed of 10 mm min^{-1} was used for testing the specimens. At least five samples were tested for each composition, and the average value was reported. All measurements were performed at ambient conditions, i.e., a temperature of 23°C and a relative humidity of approximately 50%.

Dynamic Rheological Measurements. Oscillatory melt rheology tests have been realized on an Anton Paar (Austria) rheometer equipped with CTD450 device with an in plate–plate geometry with 25 mm diameter, oscillatory mode, at a testing temperature of 175°C.

Oxygen Permeability Tests. Permeability tests were performed with a PERMETM OX2/231 Permeability Tester from Labthink Instruments Co., Ltd. (Jinan, China), using oxygen as test gas (RH ~50%), at a temperature of 23°C. Nitrogen was used as oxygen carrier. The oxygen flow rate was fixed at 20 mL/min, while that of nitrogen was 10 mL/min.

Water Contact Angle Measurements. The samples were kept 48 h at 50% RH before being tested in static conditions on an AdveX Instrument (Brno, Czech Republic). A 2.5 μL droplet of water was applied on the film surface. The evolution of the droplet shape was recorded by a video camera and image analysis software was used to determine the contact angle values. The contact angle value reported is the average of 10 measurements; PLA was used as a reference for the contact angle measurement.

Thermogravimetry. The thermogravimetry (TG) analysis was performed on a Paulik-Paulik-Erdey type Derivatograph MOM Budapest (Hungary) from 25 to 700°C at a heating rate of 12°C/min, in open Al$_2$O$_3$ crucible using an air flow of 30 cm^3/min, sample weight being of 50 mg.
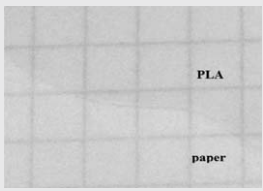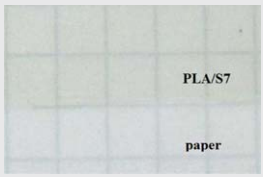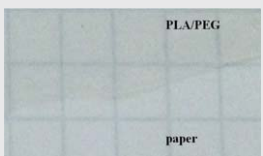
RESULTS AND DISCUSSION

Processing Behavior

Some of the processing parameters obtained from the torque-time curves during compounding of PLA/plasticizer blends are presented in Table II.

The processing behavior of the obtained blends was evaluated from the following characteristics: torque at different processing times and at the end of mixing, as well as from the specific

Table II. Processing Parameters for Melt Processing of PLA and Plasticized PLA

Sample	TQ_{max} (Nm)	TQ_{1min} (Nm)	TQ_{5min} (Nm)	TQ_{fin} (Nm)	$Emix_{fin}$ (J/g)	Sample images
PLA	66.4	17.2	13.3	12.6	225	
PLA/USE	20.9	7.2	4.9	4.6	84	
PLA/S7	32.1	12.7	8.2	7.5	139	
PLA/L	17.0	7.9	5.3	4.4	82	
PLA/PEG2	13.7	3.0	6.5	5.9	111	
PLA/PEG4	12.9	0.9	7.3	6.5	117	

TQ_{max}, maximum torque; TQ_{1min}, torque after 1 min processing time; TQ_{5min}, torque after 5 min processing time; TQ_{fin}, torque at the end of processing time; $Emix_{fin}$, specific energy at the end of processing.

energy at the end of processing considered as energy required to process a unit mass of material, calculated by multiplying torque with rotor speed and and 9.087×10^{-3} and divided by processed mass of material.[22]

Due to its semicrystalline structure, PLA shows the highest viscosity in melt state, with increased values of torque up to the end of melt processing in Brabender mixer. The specific energy of mixing at the end of processing showed also the greatest value for PLA matrix. As the different plasticizing agents have been incorporated in the PLA matrix, a general decrease of the processing parameters was observed, depending on the type of the plasticizers. The lower is the torque level, the less mechanic energy is necessary for processing a material. The decreased torque values at different moments of mixing were recorded for all modified materials, explaining thus the improvement of flow and melt processing behavior of the resulted blends compared with neat PLA matrix. The growth of TQ_{1min} to TQ_{5min} for PLA/PEG2 and PLA/PEG4 could be explained by the tendency of PEG to increase the toughness of the blends (see rheology results).

The increase of material's flexibility and flow in melt state led to low specific energy consumption, the values of $Emix_{fin}$ generally decreased for all obtained PLA/plasticizer blends that should mean that at least some of them act also as lubricants. The

torque values and Emix increase with molecular mass of plasticizers with the same chemical nature. The lowest value of torque at all recorded mixing times and of the specific energy at the end of processing being recorded for PLA/L blend, possibly explained by a good miscibility of the components.

It is also worth to mention the good transparence of the films (thickness 0.5 mm) which is a requirement for food packaging applications.

FT-IR Analysis

The effect of the used plasticizers on the FT-IR spectrum on PLA is presented in Figure 1, while Table III shows the main characteristic peaks of plasticized PLA related to neat PLA.

PLA exhibits the main bands at 957 cm^{-1} (O-H vibration of carboxylic acid), 1041 cm^{-1}, 1084 cm^{-1} (C-O stretching), 1128 cm^{-1}, 1182 cm^{-1} (C-O stretching), 1360 cm^{-1} (C-H stretching of -CH$_3$; symmetric deformation), 1454 cm^{-1} (C-H stretching of -CH$_3$; asymmetric deformation), 1749 cm^{-1} (C=O stretching); 2999 cm^{-1} (C-H stretching of -CH$_3$).

The effect of epoxidized soybean oil plasticizer on FT-IR spectrum of modified PLA is plotted in Figure 1. The spectra show four main regions: -CH stretching at 3000–2850 cm^{-1}, C=O stretching at 1750–1745 cm^{-1}, C-H bending at 1500–1400 cm^{-1} and -C-O stretching at 1100–1000 cm^{-1}.[23] The FT-IR spectrum
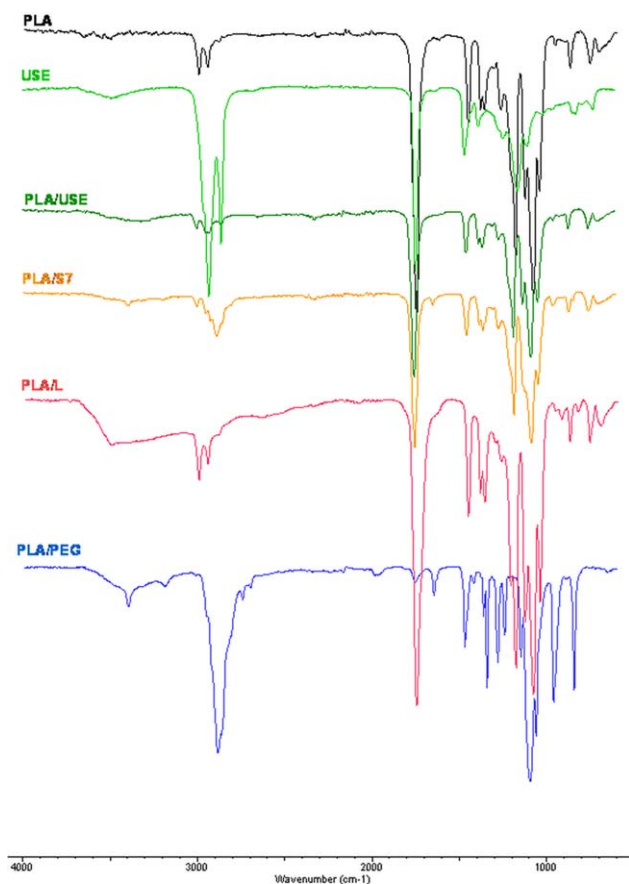
Figure 1. FT-IR spectra of PLA and PLA/plasticizer systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

for modified soybean oil (USE) presents some important bands as follows: 2846-2904 cm^{-1} attributed to the terminal groups CH, CH$_2$ and CH$_3$, 1745 cm^{-1} and 1160 cm^{-1} assigned to esteric groups absorptions, while the bands specific to the epoxidic groups are located at 825 to 840 cm^{-1}. The decrease of the absorption bands from 3380 cm^{-1} and 1650 cm^{-1} characteristic to the unsaturated acids confirm that the epoxidation reaction took place.

In the FT-IR spectrum of PLA/USE, an important change was found for 3200–3600 cm^{-1} region where a broad O–H stretching absorbance was observed. A small amount of hydroxyl group (O–H) in the blend could be attributed to the possible hydrogen bonding between the ester group or terminal hydroxyl groups of PLA and the oxirane group of USE. The shift of the bands is a proof of special interactions between components whish assure a good compatibility of components and homogeneity of the materials.

Some interactions between PLA and plasticizer were recorded by shifts of the specific bands at 1749 to 1753 cm^{-1}, 1180 to 1176 cm^{-1}, 1128 to 1126 cm^{-1}, 1084 to 1080 cm^{-1}, 2995 to 2945 cm^{-1}. An efficient plasticizer must contain two types of structural components; the polar and nonpolar components. According to G. Wypych, polar groups in a plasticizer improve mechanical properties and are essential for good compatibility.[24]

Hydrolysis induced by moisture is the primary mechanism of PLA degradation and also environmental factors as temperature and bacterial attack on the fragmented residues lead to PLA biodegradation. The structural integrity of PLA based materials decreases as the molecular weight drops, but high molecular weight PLA products are stable under typical use and storage conditions. The presence of plasticizers blocks the reactive functional groups of PLA by

Table III. Assignment of Characteristic Bands of PLA/Plasticizer Films

| Peak wave number (cm^{-1})	Assigned to	Characteristic bands of plasticized PLA (cm^{-1})					
		PLA	USE	PLA/USE	PLA/L	PLA/S7	PLA/PEG
954	O—H vibration of carboxylic acid	956	960	957	953	961	960
1043	—C—O— stretching vibration in —O—C=O	1045	1016	1043	1043	1043	1059
1078	—C—O— stretching vibration in —O—C=O	1080	–	1082	1081	1081	1093
1128	—C—O— stretching vibration in —O—C=O	1128	1103; 1157	1130	1127	–	1146
1186	C—O stretching	1182		1182	1181	1181	–
1375	C—H stretching of -CH$_3$; symmetric deformation	1361; 1382	1383	1360; 1383	1359; 1384	1359; 1383	1341; 1359
1454	C—H stretching of -CH$_3$; asymmetric deformation	1452	1462	1453	1453	1452	1466
1748	C=O stretching	1748	1742	1751	1749	1749	1752
1267	C=O bending	1267	1261	1267	1266	1272	1280
2994	C—H stretching of -CH$_3$	2945;2995	2855; 2924	2996/2927; 2944	2946; 2996	2997	2883
	$I_{Crystalline}/I_{Amorphous}$	0.95	–	1.04	–	1.16	1.15
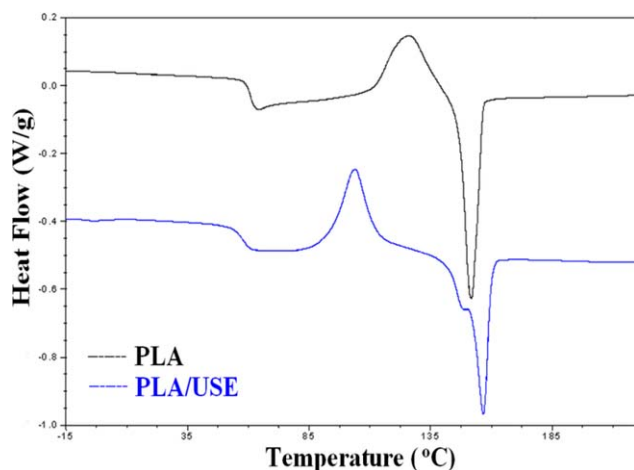
Figure 2. DSC thermograms for neat PLA and PLA/USE blend (first heating). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. DSC Data for Neat PLA and PLA/USE (First Heating)

Sample	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_m (J/g)	X_m (%)
PLA	60.7	125.9	151.6	22.9	24.6
PLA/USE	57.4	103.7	148.2; 156.7	24.0	30.1
PLA/S7	57.8	107.7	148.3; 156.6	19.8	22.7
PLA/L	58.2	108.5	149.0; 154.6	20.8	26.1
PLA/PEG	52.4	105.6	147.5; 151.6	22.5	28.3

Glass transition temperature (T_g), cold crystallization temperature (T_{cc}), melting temperature (T_m), melting enthalpy (ΔH_m), and crystallinity degree (X_m).

formation of covalent bonds, so these blends should have an extended stability.

The oxirane oxygen content (OOC) (epoxy ring absorptions at 1270 cm^{-1} and 877 cm^{-1}) in USE represents the polar component other than the carbonyl group of carboxylic ester functionality and it seems that by interactions both of them assure a better compatibility of components.[25]

With incorporation of the plasticizers in PLA blends is observed that characteristic bands appear at slightly increased frequency. A small shift of C-O stretching peak from 1080 cm^{-1} (neat PLA) to 1082 and 1093 cm^{-1} and in C=O stretching from 1748 cm^{-1} to 1753 cm^{-1} in both PLA/USE and PLA/PEG were observed. These shifts in the absorption bands indicate the miscibility and interactions of PLA and the plasticizers[23] mainly with USE and PEG. The bands at 868 and 754 cm^{-1} are associated with amorphous and crystalline phases of PLA, respectively. The ratio between the normalized intensities of these bands is proportional with crystallinity index and the corresponding values for studied samples are given in last row of the Table III. A slight increase of this ratio is evident in case of PLA/biocompatible plasticizers/lubricants blends. This indicates a modification in morphology of the systems containing plasticizers because of increase of chain mobility. These results are in accordance with variation of some thermal properties.

Thermal Properties

Thermal analysis of PLA and its blends has a great technological importance in flexible food packaging. The thermal differences induced by the presence of USE into PLA matrix could be observed from Figure 2 and Table IV.

The decrease of glass transition temperature (T_g) from 60.7°C in neat PLA to 57.4°C for PLA/USE, together with the slight increase of melting temperature were recorded in DSC curves.
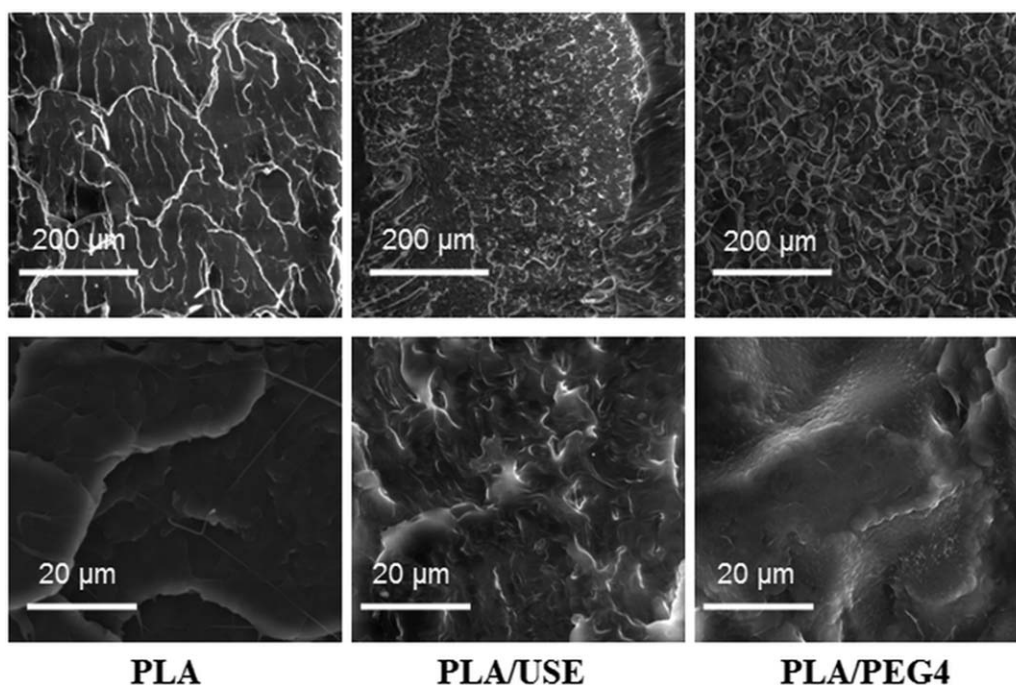

Figure 3. SEM micrographs of PLA and its blends with two plasticizers USE and PEG 4000 at two different magnifications indicated on images.
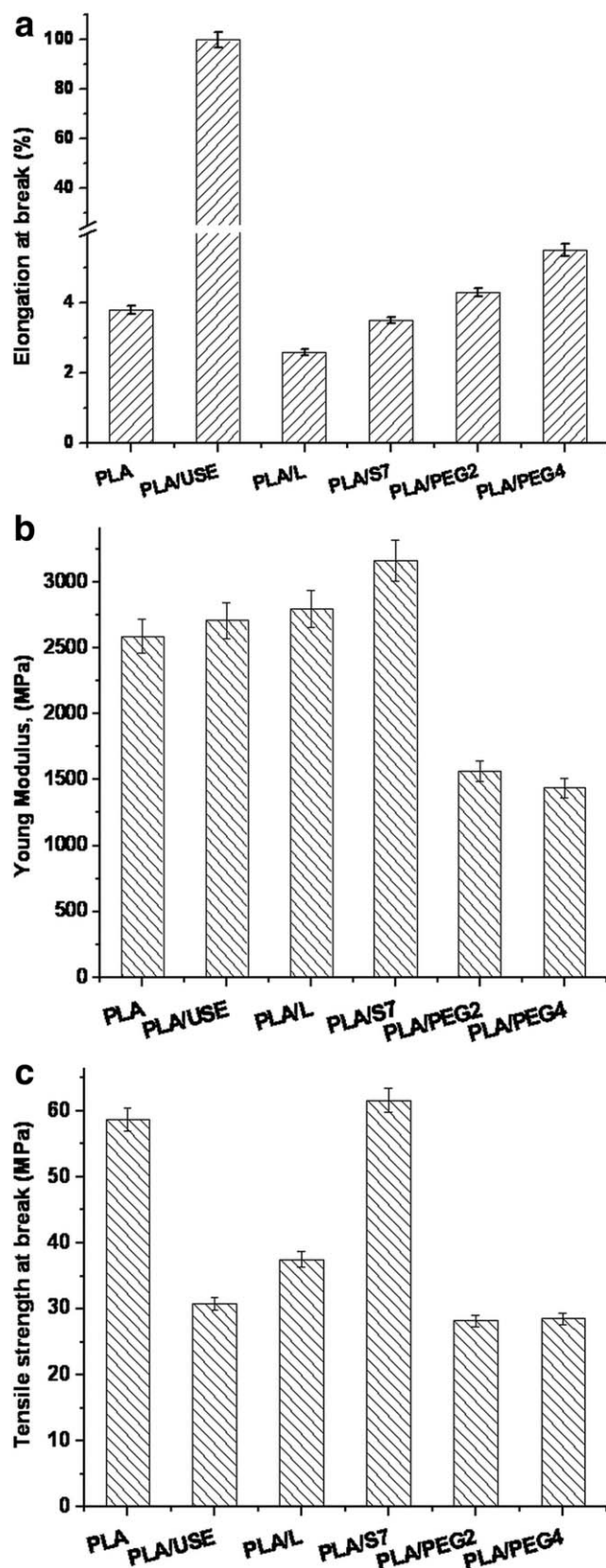
Figure 4. Mechanical properties (a) elongation at break, (b) Young modulus, (c) tensile strength at break for neat PLA and PLA/plasticizers blends.

The most obvious variation was reflected in the cold crystallization temperature as well as in a sharpening of the cold crystallization peak, this value decreasing with more than 10°C, from 125.9°C for PLA to 103.7°C for PLA/USE.

DSC data (Table IV) evidenced that PLA shows a small crystallinity degree, while PLA/USE blend presents an increase in crystallinity degree value. The same changes are found for the PLA/PEG blend in accordance with those given in literature. This behavior is not uncommon in plasticized thermoplastics, where plasticizers may promote crystallinity due to enhanced chain mobility, according to the results obtained by other authors.[26]

The plasticization effect is enhanced by the decrease of the molecular weight and stronger interaction between components.[27] The plasticizers enhanced the segmental mobility of PLA chains, increasing the mobility of the amorphous to the plastic deformation. Therefore, the decreased Tg is also assumed to decrease the tensile strength and increase the elongation at break, which will be discussed in the mechanical properties section.

SEM Results
SEM micrographs examination—Figure 3—reveals a good compatibility of components without distinct phase separation and morphological units are smaller in case of the plasticized PLA.

The results are in accordance with those found by Wang et al.[28] for PLA plasticized with *N*-octyl lactate. There are no significant differences between the cross-sectional microstructures of PLA films plasticized with various plasticizers used in this study. A uniform phase with well-distributed plasticizers in the PLA matrix is easily remarked, indicating a good compatibility and more compact morphology. The homogeneity seems to be better for PLA/PEG4 blend. The morphology determines the mechanical properties variation.

Tensile Properties
Material flexibility is a very important property for use in food packaging applications. As an indicator of change caused by plasticization, the evaluation of tensile properties is most frequently used. The effect of used plasticizers on the elongation at break, tensile strength at break, and Young modulus of PLA are plotted in Figure 4. As observed from Figure 4(a), among the values for the elongation at break registered for the studied blends, the highest has been obtained for PLA/USE. The addition of 15 wt % epoxidized soybean oil plasticizer to neat PLA raised the elongation at break to 99% and PEG 4 two times. Thus, their presence in PLA enhances the mobility of PLA polymer chains, causing an increase in flexibility and extensibility of the PLA. The other used plasticizers, L-lactide, S7 oligomer, PEG of various molecular weights led to materials having elongation at break and thus flexibility close with that of neat PLA. However and increase of elongation at break with molecular weight of plasticizers of various nature (compare L and S7 and also PEG2 and PEG4) can be remarked. This improvement of tensile properties depends on their ability to form different hydrogen bonds.[29]

A significant improvement of elongation at break for PLA/USE was achieved at the expense of tensile strength. The obtained materials show a general decrease for strength at break values
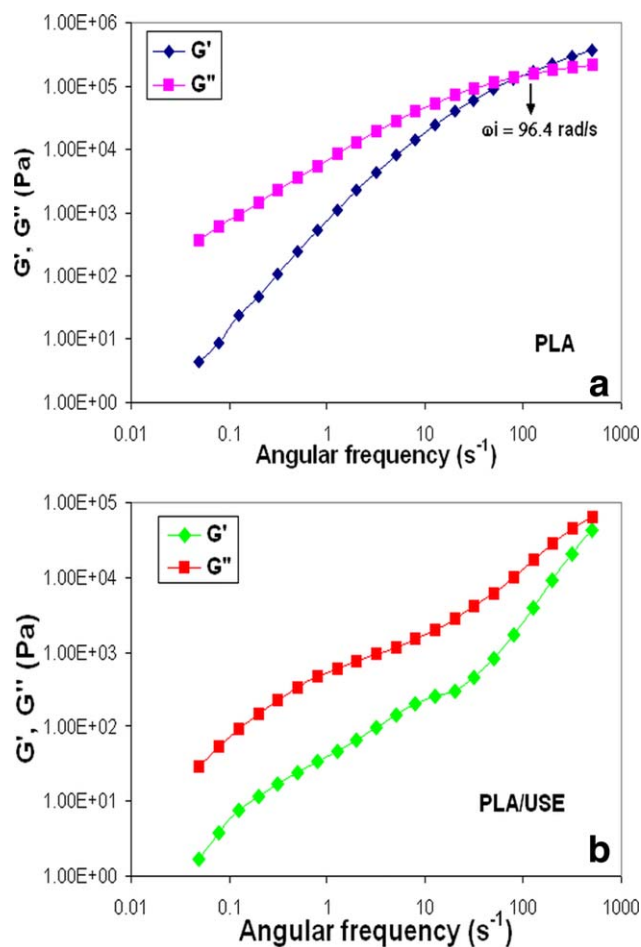
Figure 5. Dynamic moduli vs angular frequency for a) neat PLA and b) plasticized PLA (PLA/USE). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with almost 50% compared with the neat PLA, while the Young modulus values remain similar for PLA/USE and PLA/L. The presence of S7 oligomer resulted in an improvement with approximately 22% of Young modulus and ~5% of strength at break of the new materials when compared with unmodified PLA.

It is known that the addition of plasticizer causes the decrease of tensile strength because the plasticizer penetrates between the polymer chains and decreases the intermolecular forces which cause the lower polymer chain cohesion.

Dynamic Rheology

Rheological measurements started with the strain sweep mode, in view of finding the suitable strain value as the experiments to be conducted in the linear viscoelastic region. The determined value of 10% was further used in all frequency sweep modes so that all samples were tested in the linear viscoelastic region (LVE). Frequency dependencies of complex viscosity and dynamic moduli—Figures 5 and 6—were recorded in the linear viscoelastic region. Measurements were performed from high to low frequencies (500 down to 0.05 s^{-1}), starting when the temperature had stabilized after loading the sample between the rheometer plates (fix gap of 1 mm).

The viscoelastic properties of the neat PLA and their studied blends, namely storage modulus (G'), loss modulus (G'') and dynamic viscosity ($\eta^\star$), at 175°C are shown in Figure 6. The slopes of $G'(\omega)$ and $G''(\omega)$ for all PLA blends melts were considerably lower than neat PLA melt, especially at low oscillation frequencies.
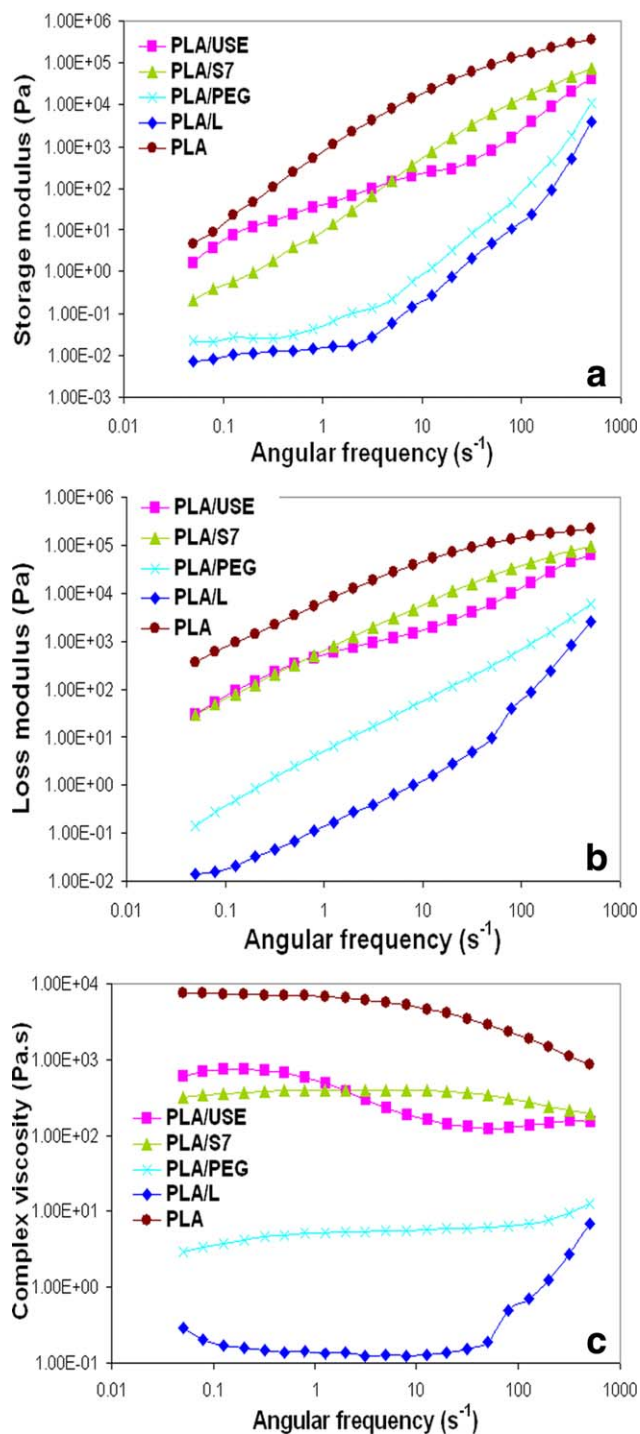

Figure 6. Variation of a) storage moduli, b) loss moduli, and c) complex viscosity function of angular frequency for neat PLA and plasticized blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
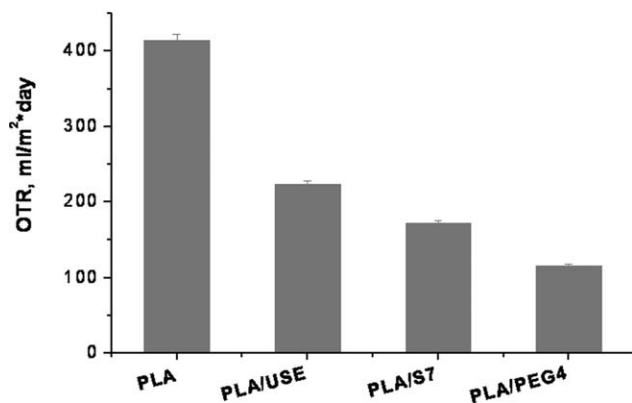
Figure 7. OTR vs. sample composition.

Table V. Thermogravimetric Data for Neat PLA and Plasticized Materials

Sample	T_i (°C)	T_{max} (°C)	T_f (°C)	ΔW (%)	W_r (%)
PLA	253	330	415	70.4	27.04
PLA/USE	258	353	487	82.8	14.07
PLA/S7	254	350	426	76.7	5.56
PLA/L	157	310; 347	410	80.3	8.15
PLA/PEG2000	200	336	489	79.6	8.89
PLA/PEG4000	212	338	502	80.7	9.44

T_i, onset temperature; T_{max}, temperature corresponding to maximum mass loss rate; T_f, final temperature; ΔW, mass loss; W_r, residual mass at 650°C.

It is known that the PLA exhibits a Newtonian plateau at low frequency and shear-thinning at high frequency.[30,31] Ahmed et al.[32] showed that in the 184 to 196°C temperature range PLA predominantly behaves as solid-like ($G' > G''$) and the complex viscosity (η^*) decreased systematically as the temperature increased. At 175°C, which is the testing temperature in this study, the melting behavior for the PLA is typical, the viscous nature is dominant at low frequencies (i.e. $G'' > G'$), the elastic characteristic being dominant at high frequencies (i.e. $G' > G''$)—Figure 5(a). One can observe that the incorporation of plasticizers changes the melt behavior of the plasticized PLA within the tested frequency sweep range—Figures 5(b) and 6.

Sears and Darby mentioned that plasticization on the molecular level is the weakening or rupturing of selective secondary bonds between molecules, increasing intermolecular space (free volume), while leaving others strong, allowing thus the shaping, flexing, or molding of the material.[33] The dependency of dynamic moduli function of angular frequency plotted in Figure 5(b) for PLA/USE show that the incorporation of the plasticizer led to appearance of "rubbery" zone in the 10 to 40 s^{-1} frequency region, where G' is constant, independent of frequency.

Rheological properties are improved through the addition of a plasticizer as observed from the decrease of complex viscosity plotted in Figure 6(c). Similar results have been obtained by
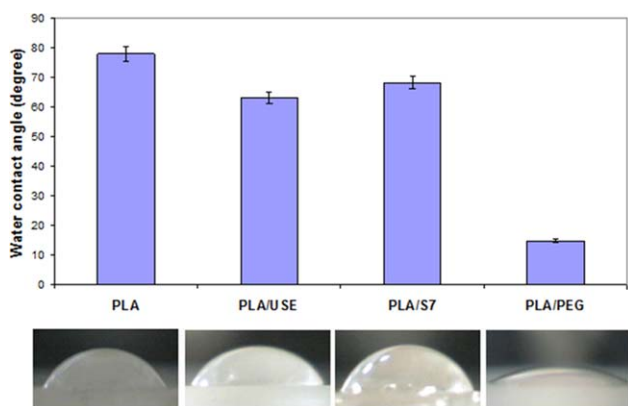

Figure 8. Water contact angle values for neat PLA and plasticized materials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Sungsanit et al. studying PLA plasticized with PEG 1000 at various concentrations.[30] The toughness was increased by plasticizing up to 15% PEG and then at high concentration decreases because of phase separation.

PLA/USE shows a Newtonian behavior in the frequency region up to 1 s^{-1} and $\omega > 45$ s^{-1}, where the complex viscosity remains constant, a shear-thinning effect appearing at frequencies between 1 and 45 s^{-1}. In case of PLA/USE system, a "full rheological flow curve" was registered. The plateau at higher oscillation frequencies could be possible explained based on the intermolecular interactions in the melt during elongation and orientation of macromolecular chains that stabilize and resist to deformation.[34] The Newtonian plateau is larger for other plasticizers especially PEG, S7, and L-lactide. The constant values of complex viscosity function of angular frequencies were recorded in some regions also for the mentioned systems as observed in Figure 6(c). The low values of complex viscosity for PLA/L system could be justified by the low molecular mass of lactide oligomer that improves PLA melt flow. Increasing the oscillation frequencies and thus deformation, a thickening effect appears leading to an increase of viscosity.

Data plotted in Figure 6(a–c) show that the decrease of storage modulus, loss modulus and dynamic viscosity follows the order: PLA > PLA/USE $\approx$ PLA/S7 > PLA/PEG > PLA/L. This decrease can be explained by the possibility of plasticizers to penetrate into PLA chains acting as internal plasticizers, increasing fluidity and decreasing melt strength.

Oxygen Permeability
Variation of the oxygen permeability values with blend composition shown in Figure 7 is in good accordance with SEM results as a compact morphology determines a decrease of this property, making the system more suitable for application such as a material for food packaging. The PLA/S7 and PLA/PEG4 samples have the lowest oxygen transmission rate (OTR).

The results are in accordance with those obtained by other authors using PEG as plasticizers,[35] while for other plasticizers Martino et al.[36] reported that the oxygen transmission rate tended to increase with the content of adipate, a commercial PLA plasticizer.

Water Contact Angle
The addition of plasticizers into PLA matrix has influenced the wettability of the obtained materials. In order to improve PLA

biocompatibility, which presents a strongly hydrophobic surface, various surface and bulk modifications have been shown to enhance hydrophilicity.[37] Bulk modification of PLA by incorporating hydrophilic plasticizers led to the decreased water contact angles especially for PLA/PEG system and to a good miscibility with PLA chains—Figure 8. The most hydrophilic obtained materials are those containing PEG and lactide, for the last one water rapidly spread on the surface.

Increase the hydrophilicity will favors the action of microorganisms on materials. Behaviour of some of these blends during inoculation with mycelium of the fungus *Trichoderma viride* will be presented in a future article.

Thermogravimetry Results

TG measurements were performed in order to determine the influence of plasticizers over thermal stability of PLA. The thermogravimetric data given in Table II show that thermal degradation of neat PLA and PLA-based blends takes place in a single weight loss step. The onset temperatures of the PLA/USE and PLA/S7 blends are not significantly changed in respect with that of neat PLA, while temperature corresponding to the maximum weight loss rate (T_{max}) is increased. This could be a proof for an increased thermal stability of these blends. An increase of the maximum and final degradation temperature, as well as weight loss percentage was also observed for the plasticized systems related to neat PLA. Similar results have been presented in literature for different plasticizers.[38]

Contrary the other three blends show a decreased thermal stability, onset temperatures being inferior to that of PLA while T_{max} show values close to that of PLA (Table V).

CONCLUSIONS

In this paper, the influence of five nontoxic plasticizers/lubricants, namely PLA oligomer (S7), L-lactide, poly(ethylene glycol) 2000 and 4000 (PEG2 and PEG4) and epoxidized soybean oil (USE) on some physicochemical properties of plasticized PLA was investigated. All plasticizers improved the PLA processability. It was clearly demonstrated in this study that the use of different plasticizers affected the thermal properties, mechanical properties, and water contact angle of PLA-based films prepared by melt processing. The PLA blend films maintained the transparency of the PLA matrix upon visual inspection (Table II, last column).

Epoxidized soybean oil significantly increased the elongation at break, reduced the glass transition temperature, the PLA chain mobility being increased. PLA/USE and PLA/S7 blends show an improvement in thermal stability.

The oxygen transmission rate was significantly reduced by PLA plasticization.

PLA plasticized with PEG is the most hydrophilic and less oxygen permeable material. The change in properties is explained by interaction between components of the blends evidenced by FT-IR study.

The results concerning the plasticizers evaluation indicate that the PLA/USE blend is recommended as flexible material while the PLA/PEG4 blend as hydrophilic, low permeability material. Therefore the PLA plasticization with about 15% nontoxic selected plasticizers could yield flexible films (PLA/USE) with appropriate optical and barrier properties (PLA/PEG) being recommended for applications in the food-packaging.

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