Influence of Plasticizers Over Some Physico-chemical Properties of PLA

MARIA RAPA[1], RALUCA NICOLETA DARIE NITA[2]*, CORNELIA VASILE

[1] ICPAO S.A., 8 Carpati St., 551022 Medias, Sibiu, Romania

[2] Petru Poni Institute of Macromolecular Chemistry, 41A Grigore Ghica Vodă Alley, 700487, Iasi, Romania

The use of polylactic acid (PLA) for food packaging is limited because it has poor mechanical and thermal properties, low ductility, and its oxygen barrier property is quite poor compared with polymers obtained from petrochemical resources. One main task of processors is to modify these properties in such a way that PLA to be able to compete with conventional polymers such as polyethylene, polypropylene or poly(vinylchloride). Our studies were conducted to test the effect of different types of plasticizers on the PLA melt processing and also on its mechanical and thermal performance.

Keywords: polylactic acid, plasticizer, melt processing, property

The main functions of food packaging are to maintain the quality and safety of food products during storage and transportation and to extend the shelf-life of food products by preventing unfavorable factors or conditions such as spoilage microorganisms, chemical contaminants, oxygen, moisture, light, external force, etc. [1, 2]. In order to perform such functions, the packaging materials shall provide physical protection and create proper physical-chemical conditions, such as mechanical, optical, and thermal properties (fig.1).
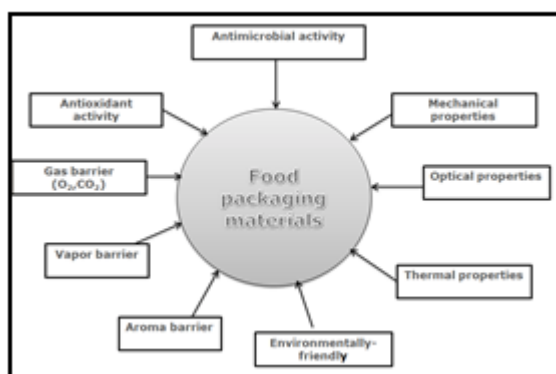

Fig. 1. General properties required for food packaging materials ([1])

The ideal packaging materials are obtained from renewable biological resources, usually called biopolymers, with excellent mechanical and barrier properties and being biodegradable at the end of their life. As a polymer derived from plants, poly(lactic acid) (PLA) is commercially available as thermoforming, injection and extrusion grades having good performance characteristics. For example, as packaging material, it is currently used for many short term applications, such as disposable cutlery (plates, cups, lids and drinking straws), bags and film packages [2]. PLA is recognized as safe for all food packaging applications [3].

The use of PLA for food packaging is limited because the PLA has poor mechanical and thermal properties, low ductility, and its oxygen barrier property is quite poor compared with equivalent petroleum based polymers [4, 5]. Similar to polystyrene, PLA is a brittle and stiff polymer with low elongation at break. One main task of processors is to modify these properties in such a way that PLA to be able to compete with other conventional polymers, such as polyethylene, polypropylene or poly(vinylchloride). There are some attempts to upgrade the PLA performance to compete with low-cost and flexible commodity polymers including: modification of PLA with plasticizers, blending with other polymers such as poly(butylene-adipate-co-terephtalate) PBAT [6, 7], poly([R,S]-3-hydroxy butyrate) [8] etc., copolymerization, and incorporation of fillers [9].

One interesting possibility to modify the properties of PLA consists on the introducing of biocompatible plasticizer systems into it. Candidates including poly(ethylene glycol) (PEG), citrate esters, glycerol triacetate, glucose monoesters, (partially) fatty acid esters, lactide monomer, lactic acid oligomers, epoxidized soybean oil, etc. have been widely studied to plasticize PLA [5, 10-15]. The main effect of plasticization is to increase the chain mobility. However, the drawback of using these low molecular weight additives is that they leach out of the PLA matrix, resulting in a brittle plastic over time [16]. The choice of plasticizers to be used as modifiers for PLA is limited by technical and legislative [European Directive 2002-72-CE] requirements for the application in food packaging [17].

Our present studies were conducted to test the effect of different types of plasticizers on the melt processing of PLA and also to its mechanical and thermal performance.

Experimental part

Materials

The poly(lactic acid) (PLA) used in this study was Ingeo Biopolymer 2002D type from, UK, 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). Bis[2-(2-butoxyethoxy)ethyl] adipate (DBEEA), batch no. 201312170002, Proviplast 01422, from Belgium, tributyl *orto*-acetyl citrate (ATBC), batch no. 201406120011 supplied by Belgium and tributyl citrate (TBC) ≥ 97.0 %, batch no. BCBM 9410V were used as bioplasticizers. According to our previous paper, the last two plasticizers improved the PHB properties [18].

Preparation of blends

Binary PLA/plasticizer blends of various compositions were prepared by melting in a Brabender Plastograph at 180 °C and rotor speed of 40 rpm for 10 min. The ratios between polymeric matrix and different plasticizers used were: 90/10 and 80/20 wt. % for PLA/DBEEA blends; 90/

* Phone: (+40) 740651480

10, 80/20 and 70/30 wt. % in the case of PLA/ATBC blends and respectively 90/10 and 80/20 wt. % for PLA/TBC blends. Because PLA can degrade by hydrolysis of the ester bond, drying of poly(lactic acid) pellets is commonly performed before processing. Thus, before mixing, the PLA was oven dried at 60 °C overnight. The melt mixed PLA/plasticizer blends were pressed into films using a hot laboratory press at 180 °C, pressing time of 2 min and 150 atm, while the sheets with thickness of 1 mm and 4 mm were obtained using the same press, at 175 °C, pressing time of 3 min and 125 atm. A neat PLA sample was prepared in the same conditions and was considered as a reference for further characterizations.

Investigation Methods
Melt processability

Melt processability (torque and melt viscosity) of the prepared blends was evaluated to constant values of 10 min at 40 rpm. Because the torque recorded on Brabender is an indirect indication of shear stress, while the rotor speed (rpm) is an indirect indication of shear rate, the melt viscosity ç can be estimated as the ratio of torque to rotor speed (1):

$$\eta = K(M/S) \qquad (1)$$

where K is a constant depends on temperature; M is torque (Nm) and S is rotor speed (rot/min).

ATR-FT-IR analysis

Structural changes in film blends were monitored by attenuated total reflectance infrared spectroscopy (ATR-FTIR) using an FTIR spectrometer FTLA 2000-104, equipped with an ATR device (ZnSe crystal). Twenty-two scans were recorded with a spectral resolution of 4 cm^{-1} in a 4000 to 750 cm^{-1} range, using air as background.

Differential scanning calorimetry (DSC) measurements

Thermal analysis of materials was carried out on a DSC analyzer (823^e Mettler Toledo). Small amounts (circa 3 mg) of sheets samples were placed into aluminium pans, sealed and heated between 30 and 200 °C at a scanning speed of 10 °C/min. An empty aluminium pan was used as reference. Calibration was performed using an indium ($T_m = 156.6$ ^0C; $\Delta H_m = 28.4$ J/g). From DSC curves the glass transition temperature, cold crystallization, and melting temperatures have been determined and corresponding crystallization and melting heats have been evaluated. The degree of crystallinity (X_c) of PLA was estimated using the ratio between the heat of fusion of the studied material and the heat of fusion of a perfect crystal of same material (equation 2) (93.1 J/g [19]) and the weight fraction of polymer matrix (w_{PLA}).

$$X_c = \frac{\Delta H_m}{\Delta H_{100\% \, PLA} \, x w_{PLA}} \, x100 \; \% \quad (2)$$

Tensile Properties

The tensile properties (tensile strength, elongation at break, the Young's modulus) were determined according to EN ISO 527-2. An Instron test machine operated at a crosshead speed of 10 mm min^{-1} was used for testing the specimens with thickness of about 1 mm taken from sheets. At least five samples were taken from sheets and tested for each composition, and the average value and error bars was reported.

VICAT softening temperature (VST) and Heat deflection (HDT) measurements

The VST and HDT tests were performed on a HDT/VICAT Softening Point Apparatus (CEAST Test Equipment). Determination of VICAT softening temperature was conducted at a heating rate 50°C h^{-1} with loading 10 N according to ISO 306, Method A50. Three test specimens with (20x10x4) mm dimensions taken from sheets were measured and the average value was reported.

HDT measurements were carried out by using specimens with (80x10x4) mm dimensions according to EN ISO 75, Method A. The test was conducted under a load of 1.8 MPa at a heating rate of 120°C h^{-1}. HDT was the temperature at which the specimen distortion increased to 0.32 mm during the heating process. Two test specimens were performed and the average value was reported.

IZOD impact strength

The unnotched IZOD impact strength was used to evaluate the brittleness or toughness of the plasticized PLA blends. Specimens with (80x10x4) mm dimensions were measured by means of an IZOD hammer of 2 J (CEAST, Italy) according to EN ISO 180. Ten specimens of each blend were tested to obtain the impact strength. IZOD impact strength (a_{IU}), expressed as kJ/m^2 is calculated by dividing impact energy in J by the area of specimen test, according to formula (3):

$$a_{IU} = \frac{E_c}{hxb} \, x10^{\,3} \quad kJ/m^2 \qquad (3)$$

where: E_c is energy used for breaking of specimen, J; h is thickness of specimen, mm and b is width of specimen, mm.

All measurements were performed at ambient conditions, i.e., a temperature of 23°C and a relative humidity of approximately 50 %.

Results and discussions
Torque-time curves of PLA/plasticizer blends

The torque-time curves and melt viscosity index of investigated PLA blends are plotted in figures 2 and 3.

From figure 2 it is observed that PLA shows the highest torque, emphasizing the hard melt processing and as consequence the high energy consumption required for
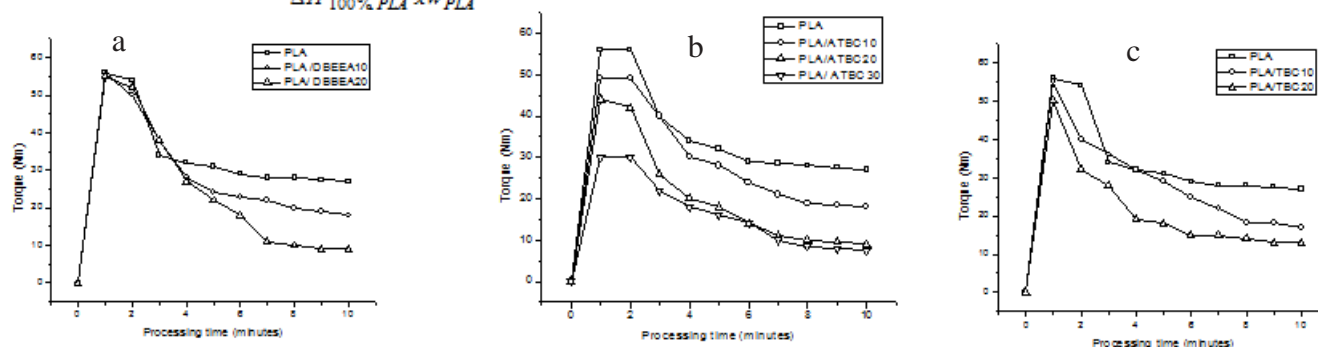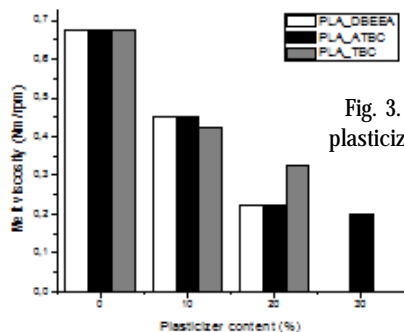

Fig. 2. Torque-time curve of the PLA/plasticizer blends at 180 °C and 40 rpm: (a) PLA/DBEEA blends; (b) PLA/ATBC blends; (c) PLA/TBC blends

Fig. 3. Melt viscosity of PLA/
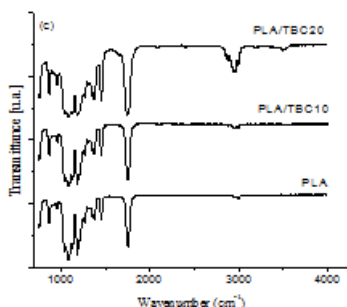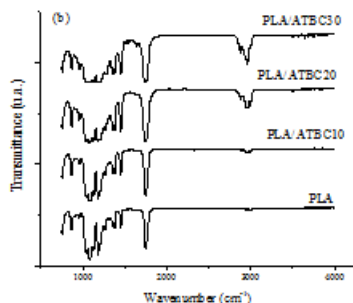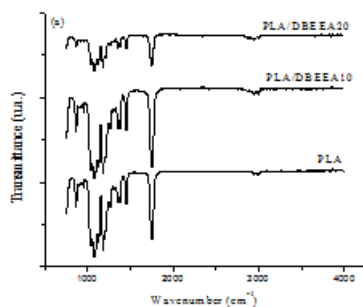plasticizer blends vs plasticizer
content

Fig. 4. Effect of plasticizer
type and concentration on
FTIR spectra of PLA/
plasticizer blend films
(a)Plasticized with DBEEA;
(b) Plasticized with ATBC;
(c) Plasticized with TBC

FTIR analysis

The effect of plasticizer on FTIR spectra of plasticized PLA in comparison with neat PLA is plotted in figure 4.

PLA exhibits the main absorption bands at following wavenumbers: 957 cm^{-1} (O-H vibration of carboxylic acid) [20], 1041 cm^{-1}, 1084 cm^{-1} (C-O stretching) [19], 1128 cm^{-1}, 1182 cm^{-1} (C-O stretching) [20, 21], 1360 cm^{-1} (C-H stretching of -CH$_3$; symmetric deformation) [22], 1454 cm^{-1} (C-H stretching of -CH$_3$; asymmetric deformation) [20, 22], 1749 cm^{-1} (C=O stretching) [19] and 2999 cm^{-1} (C-H stretching of -CH$_3$) [20]. The bands at 868 cm^{-1} and 754 cm^{-1} represent the amorphous and crystalline phases of PLA, respectively.

The main spectral bands of neat PLA were also found in plasticized PLA, with some small shifts of their wavenumbers. The interactions between PLA and plasticizer were recorded at 1749-1753 cm^{-1}, 1180-1176 cm^{-1}, 1128-1126 cm^{-1}, 1084-1080 cm^{-1}, 2995-2945 cm^{-1}. Together with increasing the plasticizer content in PLA blends is observed that characteristic bands were shifted at lower frequency. This indicates that physical interactions are present between components [21].

DSC analysis

DSC curves for the plasticized PLA are shown in figure 5. The glass transition (T_g), the melting temperature (T_m) and the degree of crystallinity (X_c) of PLA are summarized in table 1.
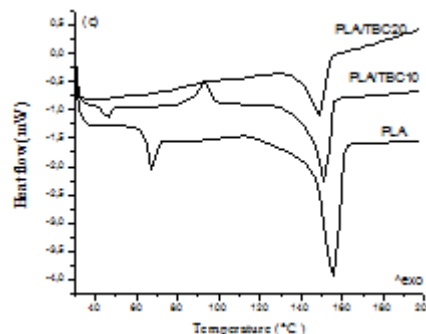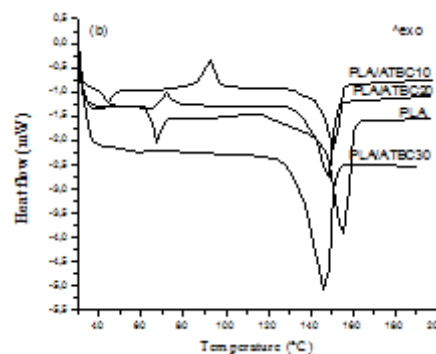

further manufacturing. The addition of plasticizer led to a low level of torque (fig. 2), especially after three minutes of mixing. It is observed that at 10 min the torque decreased as the plasticizer content increased. With increasing of plasticizer content, the viscosity decreased for all types of plasticizers compared with neat PLA matrix (fig. 3).

This decrease of viscosity indicates that the chains of PLA are easily deformed and their frictional resistance is diminished. PLA/TBC10 blend shows the lower melt viscosity in comparison with DBEEA and ATBC at the same concentration. This order is changed for 20 % loading of plasticizer, where DBEEA and ATBC exhibit lower values than TBC, due to the marked increase of chain mobility induced by the plasticization process. The addition of ATBC 30 wt. % into the PLA matrix led to a phase separation, the exudation of plasticizer was observed immediately after melt processing.

All used plasticizers were found very suitable to modify the processability of PLA. Among the used plasticizers, DBEEA and ATBC up to 20 wt. % in content are found the most effective plasticizers for significantly improvement of the melt processability of PLA.
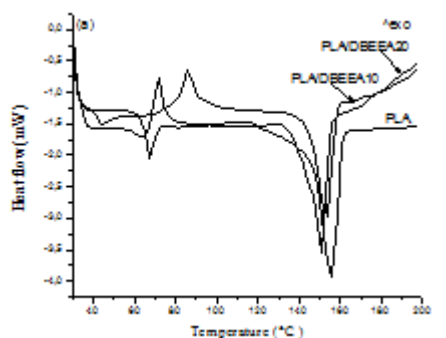
Fig. 5. DSC curves for plasticized PLA, as first scan
(a) Plasticized with DBEEA; (b) Plasticized with ATBC;
(c) Plasticized with TBC

Sample Code	T_g, °C	T_{cc}, °C	ΔH_{cc}, J g^{-1}	T_m, °C	ΔH_m, J g^{-1}	$X_{c,PLA}$, %
PLA	63.4	113.7	3.4	155.3	29.3	31.5
PLA/DBEEA10	41.9	85.8	12.5	153.3	30.2	36.0
PLA/DBEEA20	Not tested	71.1	5.2	151.1	33.2	44.6
PLA/ATBC10	45.8	92.4	9.1	151.7	27.5	32.7
PLA/ATBC20	Not tested	71.6	3.5	148.7	26.3	35.2
PLA/ATBC30	Not tested	-	-	147.1	24.2	37.1
PLA/TBC10	42.1	93.3	0.7	151.9	33.0	39.3
PLA/TBC20	Not tested	-	-	148.9	29.5	39.5

DSC curve of neat PLA recorded in the first heating run displays the glass transition temperature at 63.4°C as an evident endothermal peak due to the relaxed enthalpy, the cold crystallization process at 113.7°C and the melting endothermal peak at 155.3 °C. DSC curves for all modified PLA with 10 wt. % plasticizer reveal the glass transition at lower temperatures than that of neat PLA, thanks to the plasticizer action increasing the segmental mobility of PLA chains [12]. Due to the thermal profile of DSC measurement, the T_g for samples containing 20 wt. % and 30 wt. % plasticizer can not be evidenced. The melting behaviour of investigated blends emphasizes the decrease of T_m with loading of plasticizer in comparison with neat PLA (table 1). Other authors also observed a decrease of T_m of PLA blends with adding of plasticizer due to a higher number of lamellae but thinner lamellae during the cold-crystallization step [12].

From figure 5 is also observed that the cold crystallization temperature (T_{cc}) is shifter to low temperature when the amount of plasticizer was increased. Thus, for PLA/ATBC blends the T_{cc} decreased from 92.4 °C for 10 wt. % plasticizer

and to 71.6 °C when 20 wt. % plasticizer was added. Similar, the T_{cc} for PLA/DBEEA blends decreased from 85.8°C to 71.1°C with increasing of plasticizer at 20 wt. % content. This signifies that the plasticizer could promote the crystallization of PLA. Hassouna et al. [13] showed that the increase of PLA chain motion due to the amount of citrates (lower T_g) allows an easier rearrangement of the polyester chains in order to crystallize. According to table 1, melting enthalpy (ΔH_m) is independently of the plasticizer amount, it decreases from 29.3 J/g for neat PLA to 27.5 J/g for PLA/ATBC10, to 24.2 J/g for PLA/ATBC30 blend and to 29.5 J/g for PLA/TBC20 blend, while for others blends the ΔH_m increased (29.5-33.2 J/g). The ΔH_m is *directly related to* the content of polymer crystals. We found for pure PLA a degree of crystallinity of 31.5 %, while for PLA/plasticizer blends the degree of crystallinity increase compared with pure PLA (with 1-15 %) (table 1), this effect being amplified with increasing the amount of plasticizer in blends. The increase in the crystallinity degree has an decrease effect of impact strength. The order of the efficiency of plasticizer
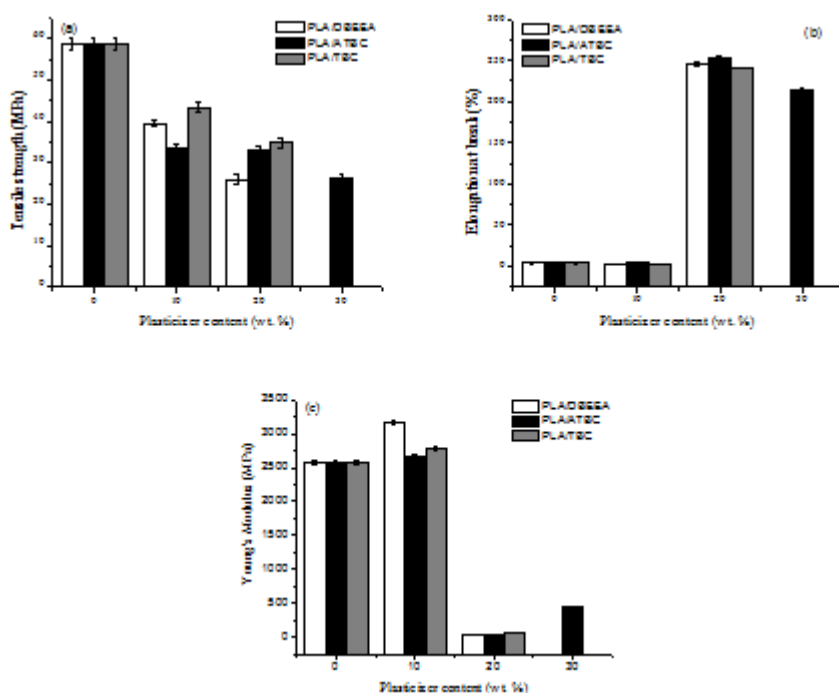

Fig. 6. Dependence of the tensile properties on the plasticizer type and content for the PLA blends in comparison with neat PLA
(a)Tensile strength; (b) Elongation at break; (c) Young's Modulus

evaluated from DSC analysis is: DBEEA > TBC > ATBC. **Tensile properties**

The influence of plasticizers over tensile strength, elongation at break and Young's modulus for PLA blends is presented in figure 6 (a), (b), (c). Error bars represent standard deviation.

Neat PLA has a Young's modulus of 2583.3 ± 25 MPa, which is considerably higher than that of polyethylene and polypropylene, showing that PLA is a brittle material. When 10 % of plasticizer is added to neat PLA, the Young's modulus increased. At 20% plasticizers the blends recorded the lowest Young's moduli with values between 23 and 45 MPa (fig. 6(c)). We think that the mobility of the plasticizer at 20 % content is restricted by its interaction with PLA, thus leads to dramatically decrease of modulus. Addition of plasticizer causes the decrease of tensile strength and Young's modulus because the plasticizer penetrates between the polymer chains and decreases the intermolecular forces which cause the lower polymer chain cohesion. The addition of 20 wt. % plasticizer to neat PLA raised the elongation at break up to 250%. Similar, Mekonnen et al. [9] reported that 20 % tributhyl citrate in PLA exhibits significant elongation at break of 350% and tensile stress at yield of 7.1 MPa since loading of 20% acetyl tributhyl citrate leads to elongation at break of 420 % and tensile stress at yield of 9.2 MPa.

Izod impact strength

Our results show that the addition of each type of investigated plasticizer significantly decrease the impact strength of PLA blends as observed in table 2.

Table 2
IZOD IMPACT STRENGTH

Code blend	Type of failure	
	C*	N*
PLA	33 kJ/m^2	
PLA/DBEEA10	22 kJ/m^2	
PLA/DBEEA20	15 kJ/m^2	
PLA/ATBC10	22 kJ/m^2	
PLA/ATBC20	-	(N)
PLA/ATBC30	-	(N)
PLA/TBC10	22 kJ/m^2	
PLA/TBC20	-	(N)

* where: C means complete break; N means non-break.

The Izod impact strength values are also reduced when plasticizer concentration increases. In the case of 20 wt. % and 30 wt. % ATBC and respectively 20 wt. % TBC, no values were registered because the samples were too flexible to be broken. When the content of the plasticizer was doubled, the resulted PLA plasticized materials became soft, this behavior being in accordance with the obtained tensile results – drastically decrease of Young's modulus for 20 wt. % incorporated plasticizer.
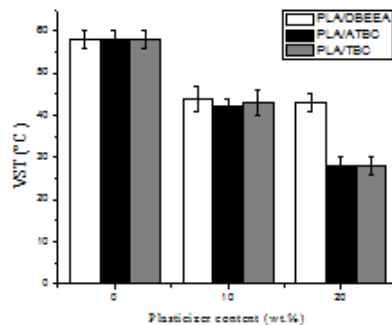

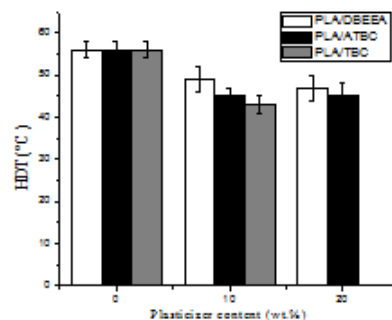Fig. 7. VST for plasticized PLA vs. plasticizer content

Fig. 8. HDT for plasticized PLA vs. plasticizer content

VST and HDT measurements

VST and HDT measurements were also carried out on the different plasticized PLA (fig. 7 and 8) to determine the influence of used plasticizers on these thermal properties of PLA.

The obtained data plotted in figure 7 show a decrease of temperature as the plasticizer content increased. DBEEA exhibits almost the same VST value at 20 wt. % in content compared with 10 wt. % incorporation in PLA, instead the lower VST was recorded in the cases of 20 wt. % ATBC and respectively TBC used. Also, HDT results show the same trend to decrease as VST values. The obtained results are in accordance with DSC recorded data for the plastified PLA systems, the low values of the HDT and VST measurements being related with the decrease of T_g. The molecular chain segments have a higher mobility at low temperature and less resistance to distorsion. However, the softening temperature and heat deflection of the resulting PLA/plasticizer blends require further improvement for practical applications.

Conclusions

The plastification influence of bis[2-(2-butoxyethoxy) ethyl] adipate (DBEEA), tributyl *orto*-acetyl citrate (ATBC) and tributyl citrate (TBC) on some physico-chemical properties of PLA was investigated.

The processability and properties of modified PLA were evaluated in terms of viscosity, FT-IR, DSC, tensile properties, IZOD impact strength, VST and HDT measurements. All plasticizers have been found adequate for PLA modification, among which DBEEA and ATBC up to 20 wt. % in content have been considered the best for significantly improvement the PLA processability and flexibility. Also, the plasticizing effect is confirmed by the modification of T_g which is significantly decreased by comparison to the neat PLA matrix, led to the low softening and heat deflection temperatures.

References

1. RHIM, J.W., PARK, H.M., HA, C.S., Progr. Polym. Sci. **38** (10-11), 2013, p.1629.

2. LOPEZ, O.V., CASTILLO, L.A., GARCIA, M.A., VILLAR, M.A., BARBOSA, S.E., Food Hydrocolloid. **43,** 2015, p.18.

3. ANSARI, S., FATMA, T., Int. J. Innovative Res. in Sci, Eng and Technol. **3** (2), 2014, p. 9494.

4. JAMSHIDIAN, M., TEHRANY, E.A., IMRAN, M., JACQUOT, M., DESOBRY, S., Food Sci. and Food Safety **9,** 2010, p. 552.

5. LEMMOUCHI, Y., MURARIU, M., DOS SANTOS, A.M., AMASS, A.J., SCHACHT, E., DUBOIS, P., Eur. Polym. J. **45,** 2009, p. 2839.

6. AL-ITRY, R., LAMNAWAR, K., MAAZOUZ, A., Eur. Polym. J. **58,** 2014, p. 90.

7. GU, S.Y., ZHANG, K., REN, J., ZHAN, H., Carbohydr. Polym. **74,** 2008, p. 79.

8. BARTCZAK, Z., GALESKI, A., KOWALCZUK, M., SOBOTA, M., MALINOWSKI, R., Eur. Polym. J. **49,** 2013, p. 3630.

9. MEKONNEN, T., MUSSONE, P., KHALIL, H., BRESSLER, D., J. Mater. Chem. **A 1**, 2013, p.13379.

10. CHOI, K.M., CHOI, M.C., HAN, D.H., PARK, T.S., HA, C.S., Eur. Polym. J. **49,** 2013, p. 2356.

11. TEE, Y.B., TALIB, R.A., ABDAN, K., CHIN, N.L., BASHA, R.K., MD YUNOS, K.F., Agric. Agric. Sci. Procedia **2,** 2014, p. 289.

12. HASSOUNA, F., RAQUEZ, J.M., ADDIEGO, F., DUBOIS, P, TONIAZZO, V., RUCH, D., Eur. Polym. J. **47,** 2011, p. 2134.

13. HASSOUNA, F., RAQUEZ, J.M., ADDIEGO, F., TONIAZZO, V., DUBOIS, P, RUCH, D., Eur. Polym. J. **48,** no 2, 2012, p. 404.

14. HERRERA, N., MATHEW, A.P., OKSMAN, K., Compos. Sci. Technol. **106,** 2015, p. 149.

15. DARIE-NITA, R.N., VASILE, C., IRIMIA, A., LIPSA, R., RAPA, M., J. Appl. Polym. Sci. **133** (13), 2016, p. 1. DOI: 10.1002/APP.43223.

16. ABDELWAHAB, M.A., FLYNN, A., CHIOU, B.S., IMAM, S., ORTS, W., CHIELLINI, E., Polym. Degrad. Stabil. **97** (9), 2012, p. 1822.

17. PILLIN, I., MONTRELAY, N., GROHENS, Y., Polymer **47,** 2006, p. 4676.

18. RAPA, M., DARIE NITA, R.N., GROSU, E., TANASE, E.E., TRIFOI, A.R., PAP, T., VASILE, C., J. Optoelecton Adv Mat **17,** 2015, p. 1778.

19. COCK, F., CUADRI, A.A., GARCÍA-MORALES, M., PARTAL, P., Polym. Test. **32,** 2013, p. 716.

20. GONZALEZ, A., ALVAREZ IGARZABAL, C.I, Food Hydrocolloid. **33,** 2013, p. 289.

21. WANG, N., ZHANG, X., MA, X., FANG, J., Polym. Degrad. Stabil. **93,** 2008, p. 1044.

22. ZEMBOUAI, I., KACI, M., BRUZAUD, S., BENHAMIDA, A., CORRE, Y.M., GROHENS, Y., Polym. Test. **32,** 2013, p. 842