Thermal Properties of Plasticized Poly (Lactic Acid) (PLA) Containing Nucleating Agent

Seyedmohammadkazem Fehri, Patrizia Cinelli, Maria-Beatrice Coltelli, Irene Anguillesi, and Andrea Lazzeri

Abstract—**The present research reports the investigation of the role of an oligomeric polyadipate plasticizer (206 3NL), and a nucleating agent aromatic sulfonate derivative (LAK301) on thermal behaviours of poly-lactic acid (PLA) evaluated through differential scanning calorimetry (DSC) measurements in order to investigate the separated effect due to the addition of plasticizer and nucleating agent on the thermal behavior of PLA respectively. Binary and ternary systems containing PLA/206 3NL/LAK301 have been developed. All samples have been prepared by melt-blending. The results of the present study show that LAK301 acts as a very efficient nucleating agent by increasing crystallinity percentage from 5.6% in pure PLA to 12% in PLA/LAK301 5%wt/206 3NL, and that (206 3NL) is a compatible plasticizer for PLA as the glass temperature drops down from 59.4 ℃ in pure PLA to 38.9 ℃ in blends of PLA-NL 15 wt%. Also the approach of investigating the compatibility in ternary system where the plasticizer and nucleating agent have a synergic effect on thermal properties as well on crystallinity and glass transition temperature of PLA were addressed. In fact in ternary blends of PLA/LAK301/206 3NL with 5 wt% of LAK301 the glass transition temperature was reduced to 30.3 ℃ and PLA crystallinity increased to 39 wt%.**

Index Terms—**Crystallinity, nucleating AGENT, POLY LACTIC ACID (PLA), thermal properties.**

I. INTRODUCTION

Polylactic acid (PLA) as compostable, thermoplastic and aliphatic polyester which can be produced from annually renewable resources, is currently considered an alternative choice for synthetic plastic materials in the food packaging market due to its relatively low cost and good processability. This polymer is expected to reduce the impact on the environment due to the production and use of petrochemical polymers [1].

In recent years, investigation on the crystallization behavior of PLA attracts much attention because the degree of crystallinity (X_c) determines most of the performance of PLA. Poly (lactic acid) has a slow-crystallization rate, affecting its processing and limiting its use in plastic or film

applications.

The main drawback in application of semi crystalline PLA based materials is due to PLA brittle behavior and the low thermal resistance, due to glass transition temperature (Tg) of about 60 ℃ [2].

In principle, PLA based materials that are able to maintain their mechanical properties at a temperature above Tg and below the melting temperature can be obtained by a crystallization process.

The most efficient way is improving the chain mobility of Poly (lactic acid) to form better crystalline structure.

Another way to improve the crystallization behavior is applying nucleating agent to decrease the nucleating activation energy and promote heterogeneous nucleation effect to achieve higher crystallinity inside Poly (lactic acid) or either by physical mixing with a second polymer component, immiscible with the PLA [3], [4].

Plasticizers such as poly (ethylene glycol) PEG, Oligomeric lactic acid, Citrate Ester and different nucleating agents such as calcium carbonate, Talc, Boron Nitride were proposed to improve thermal properties of PLA while PLA modifications are carried out more rarely [4]-[8].

According to author knowledge, few studies have been done to investigate the combined effect of both plasticizer and nucleating agent on crystallization rate of PLA.

Huneault [5] investigated the effect of heterogeneous nucleating agent by adding both talc and PEG in PLA matrix. The results showed that talc can be an effective nucleating agent and PEG was an efficient plasticizer inducing an increasing in crystallization even at fast cooling rates [6], [7]. B. Suksut *et al.* [8] also studied the effect of both plasticizer and nucleating agent on mechanical and thermal properties of PLA. Their results showed that the presence of nucleating agents (Cyclodextrin (CD)), Calcium carbonate (CaCO3) and Talc in neat PLA increases the degree of crystallinity. Muller J. *et al.* [9], studied isothermal cold crystallization of PLA/PBAT (poly butylene adipate-*co*-terephthalate) blends with and without the addition of ATBC (acetyl tributyl citrate) and the results showed a synergic effect on the increase in the overall crystallization rate of the PLA when both ATBC and PBAT were present in the blends.

Recently, GLYPLAST®206 3NL was introduced as a low viscosity saturated polyester and is suggested to be an excellent plasticizer for PLA. According to the supplier's data sheet, GLYPLAST®206 3NL is an alternative for monomeric plasticizer, limiting plasticizer losses due to volatility, migration or extraction and it is, in particular, resistant to extraction.

As a nucleating agent with molecular formula

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(C10H9KO7S) and platelet shape, LAK301 can be used as a nucleating agent in the PLA matrix system. In particular in this work binary PLA/LAK301 compounds and ternary PLA/LAK301/206 3NL compounds were prepared with the aim of LAK301 as nucleating agent and 206 3NL as novel plasticizer to improve thermal properties moulding also tensile properties of PLA. The crystallization behavior of the plasticized PLA (with and without nucleating agent) was also studied by differential scanning calorimetry (DSC).

II. EXPERIMENTAL PROCEDURE

A. Material

Poly (lactic acid) 2003D was provided by Nature Works LLC., USA (average molecular weight 200,000 g/mol, melting point temperature 210 ˚C, glass temperature T_g=55-58 ˚C); LAK301 (Dimethyl 5-sulfoisophthalate, potassium salt) having a density of 1.00 g/cm^3 and a platelet shape (Fig. 1), was purchased from Takemoto oil and fat Co. Ltd.
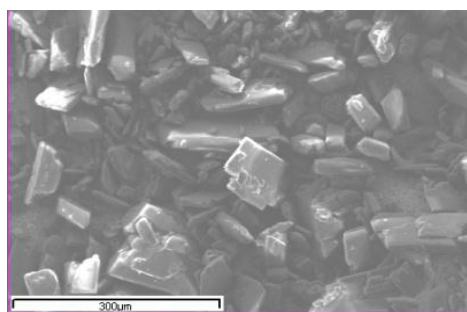

Fig. 1. SEM micrograph of the LAK301 (M 300).

GLYPLAST®206 3NL (polyester of adipic acid with 1,3-butanediol, 1,2-propanediol and 2-ethyl-1-hexanol) a saturated polyester with the density of 1,07 (g/cm^3 at 25 ℃) andwas kindly provided by Condensia Quimica S.A (Spain).

TABLE I: COMPOSITION OF PLA BASED SAMPLES

PLA	LAK301	206 3NL
100	0	0
99	1	0
97	3	0
95	5	0
85	0	15
84.2	1	14.9
82.5	3	14.6
80.8	5	14.3

B. Preparation of Blends and Composite Materials

PLA and LAK301 were dried at 65 ℃ under vacuum (1 mm Hg), two days before the use. Binary and ternary systems, reported in Table I were prepared by processing in a COMAC "HIGH-VOLUME" EXTRUDER (D/d ratio ≈ 1.65, Screw number of lobes: 2, Numbers of Heating zone: 11, Output: 20 kg/h, mod. COMAC EBC – Italy) with

rotating speed of 220 rpm. The blends were extruded through a multi holes die (3mm), and then converted to granules, dried at 65 ℃ overnight before further processing on ALLROUNDER 920 S injection molding machine. Specimens of the ASTM D638 V dog-bone were produced, and samples from them used for thermal characterizations. In the injection condition the set temperature from feed zone to nozzle 190/180/160 ℃-155/150/130 ℃ were used as injection conditions. Molding temperature and cooling time were 120 ℃ and 240 s, respectively.

The materials produced were immediately packed in plastic bags for vacuum sealing to prevent water absorption.

III. CHARACTERIZATION

Thermal analysis was performed in nitrogen atmosphere with a TA differential scanning calorimeter (mod. Q200, USA) on 7±0.3 mg of sample. The samples were heated from -100 to 200 ℃ at a rate of 10 ℃/min (first heating) and held for 2 minutes at 200 ℃ in order to erase the thermal history. Subsequently, the samples were cooled down to -100 ℃ at a rate of 20 ℃/min and heated again to 200 ℃ through a constant heating rate of 10 ℃/min. T_g was measured at the inflection point in heat flow versus temperature trend on the first and second heating scans between 25 and 200 ℃.

The degree of crystallinity X_c (%) of PLA was calculated using the following (1):

$$X_c(\%) = \frac{\Delta H_m}{\Delta H_m^{\circ}} \tag{1}$$

where ΔH_m is the melting enthalpy (J/g) of the sample, ΔH_m° is the melting enthalpy of the 100% crystalline PLA (93.7 J/g) [9].

IV. RESULTS AND DISCUSSIONS

DSC data are reported in Table II referred to second heating, they include glass transition temperature (T_g), crystallization peak temperature (T_c), melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity percentage (%C). Non-detected values are due to very slow crystallization rate versus the DSC scan rate, 10 ℃/min.

TABLE II: THERMAL CHARACTERIZATION OF PLA AND LAK301/206 3NL COMPOSITES (SECOND HEATING)

	ΔH_m (J/g)	Cryst (%)	T_c (℃)	T_g (℃)	T_{m1} (℃)	T_{m2} (℃)
PLA	5.22	5.6	108.8	59.4	148	154
PLA-1%LAK	10.1	10.8	104.6	56.7	145	154
PLA-3%LAK	8.29	8.8	106.5	59.9	148	153
PLA-5%LAK	11.2	12	104.5	60.0	149	153
PLA-NL	8.54	9.12	85.04	38.9	138	152
PLA-NL-1%LAK	36.1	38.6	nd	40.1	149	153
PLA-NL-3%LAK	34.4	36.8	nd	34.1	146	152
PLA-NL-5%LAK	36.5	39.0	nd	30.2	147	153

*nd: non-detected

Results from Table II indicate that the plasticizer is partially miscible in the PLA matrix. In fact all plasticized samples show decreased value in T_g. As an example, the value of T_g in pure PLA shifted from 59.4 ℃ to 30.2 ℃ in PLA/206 3NL with 5 wt% LAK301 as shown in Fig. 2.
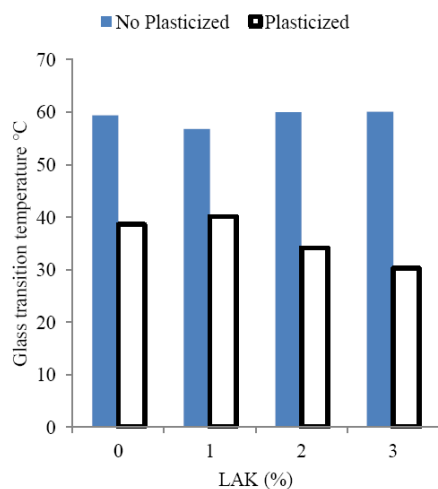

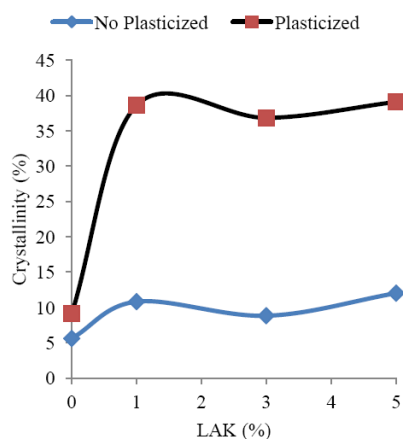Fig. 2. Dependence of glass transition temperature on LAK301 content.

Fig. 3. Dependence of crystallinity on LAK301 content.

The decreased T_g indicates that 206 3NL plays the role of a plasticizer on the PLA by facilitating the segmental mobility of the PLA chains.

There are not significant changes in glass transition temperature in binary blends of PLA/LAK301 with increasing amount of LAK301, thus LAK301 has not a relevant action as plasticizer or filler.

As reported previously, PLA crystallization can be increased by adding nucleating agent, alone or in presence of plasticizers. According to the values reported in Table II and Fig. 3, the addition of a nucleating agent such as LAK301 increased the crystallinity percentage. It also induced a more significant effect in composition with both plasticizer and LAK301, thus the maximum value for crystallinity (39.0%) was observed in PLA/206 3NL/LAK301 5wt%.

Moreover, the value of the melting enthalpy (ΔH_m) in ternary systems increased. In fact the melting enthalpy in pure PLA increased from 5.22 (J/g) to 36.55 (J/g) in ternary PLA/206 3NL/LAK301 5%wt system in corresponding with degree of crystallinity.

It should be pointed out that reduction in T_g enabled crystallization to start at lower temperature upon heating.

The DSC results from first round (not presented here) confirmed this matter. In good accordance also the cold-crystallization of PLA in the second heating was at 108 ℃ in pure and 85 ℃ in PLA/206 3NL. Besides, the presence of the nucleating agent which is already formed during the cooling process caused heterogeneous nucleation to overcome the free energy barrier; and thus inducing higher and faster nucleation [10], [11]. Therefore, all of these components promote crystallinity while they provide a lower cold crystallization temperature. The cold crystallization temperature in ternary system could not be detected probably due to the high degree of crystallinity [12], [13]. Nevertheless, in binary systems the effect of nucleating agent on cold crystallization was not prominent.

The DSC curves in second heating round of pure PLA and the PLA/206 3NL/LAK301 composites are shown in Fig. 4. Upon the second scanning, the melting peaks of all the compositions show two endothermic peaks attributed to the two types of crystalline phases in PLA compositions (α, and α') [9], [11] which became more pronounced when the plasticizer is added.
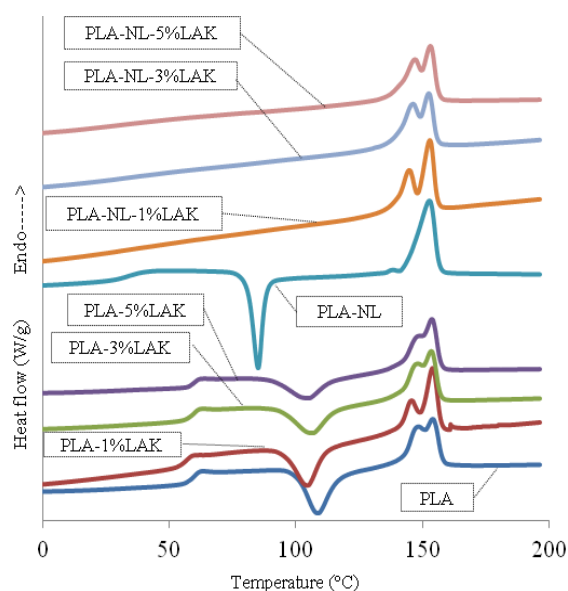

Fig. 4. DSC analyses of samples in heating.

The first peak corresponds to the melting of thinner crystals and the second peak is attributed to the melting of more stable crystals.

V. CONCLUSION

The authors within the current research, produced PLA with different contents of nucleating agent (LAK301) and plasticizer (206 3NL), and further investigated the thermal behavior of PLA in the presence of mentioned additives. The results of the study revealed that LAK301 acts as nucleating agent in PLA matrix and leads to increased crystallinity. Moreover, plasticizer (206 3NL) significantly favours the crystallization of PLA while in blend with LAK301 finds synergic effect to increase crystallinity and decreases glass transition temperature in PLA matrix.

Therefore this study can be useful for moulding process-ability and thermo-mechanical properties in several application, especially in injection moulding.

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