

THERMAL AND MECHANICAL CHARACTERIZATION OF PLASTICIZED POLY (*L*-LACTIDE-CO-*D,L*-LACTIDE) FILMS FOR FOOD PACKAGING

Veronica P. Martino^{1*}, Roxana A. Ruseckaite² and A. Jiménez¹

¹University of Alicante, Analytical Chemistry, Nutrition and Food Science Department, P.O. Box 99, 03080 Alicante, Spain

²INTEMA – University of Mar del Plata, Juan B. Justo 4302, 7600 Mar del Plata, Argentina

In this work amorphous poly(*L*-lactide-co-*D,L*-lactide) (PLLA/PDLLA) was blended with four different commercial adipates to obtain films with enhanced mechanical and thermal properties. Efficiency of plasticizers was evaluated by studying their compatibility with the polymer and their effect on its glass transition temperature. All plasticizers were compatible with the matrix up to a critical composition depending on its molar mass. The addition of plasticizers caused a decrease in elastic modulus and tensile stress, meanwhile elongation at break had a maximum increase for polyadipates with the lower molar mass. Monomeric adipate showed some migration at concentration higher than 10 mass%, while the addition of the higher molar mass plasticizer lead to eventual phase separation. Polyadipates with low molar mass showed a promising behaviour to overcome the brittleness in PLLA/PDLLA films.

Keywords: additives, mechanical properties, plasticizer, polyester, poly(*L*-lactide-co-*D,L*-lactide)

Introduction

Petrochemical based plastics have been increasingly used as packaging materials, because of their availability in large quantities at low cost, light mass, favorable functionality and good barrier properties. Unfortunately and in spite of the above mentioned advantages, many of these polymers are traditionally designed to resist microbial attack and to become recalcitrant to the environment [1]. This drawback gives rise to the search for more environmentally friendly packaging formulations based on biodegradable polymers [2, 3]. Among them, aliphatic polyesters, and in particular polylactides, are considered as potential candidates to produce films and laminates which combine similar properties to those of commodity polymers with the additional advantage of being biodegradable [4].

Lactic acid exists as two enantiomeric forms, the *D*(+) configuration and the naturally occurring *L*(-) configuration. They produce the corresponding enantiomeric polymers by conservation of the chiral center. Commercial PLAs are also copolymers of *L*-lactide and *D*-lactide and their optical purity strongly affects their properties. Optically pure PLA is isotactic and highly crystalline. Decreasing the optical purity reduces the degree of stereoregularity and crystallinity. Poly(*L*-lactide) with more than 15 mol% *D*-lactide is mostly amorphous [2].

One of the potential application fields of PLA polymers and copolymers is as film or as a component of film laminates [4]. However, amorphous PLA films are rigid and brittle below their glass transition temperature (50–60°C) with low plastic deformation [5, 6]. One strategy to overcome these limitations is by using plasticizers which are commonly applied in polymer industry to improve extensibility, workability and general handling properties. However, for environmentally friendly polymers, the choice of plasticizers is limited by the requirements of complete biodegradability, being non-toxic, low migration rates and good miscibility with the matrix by creating a homogeneous blend [6, 7]. In addition, if the films are intended to be applied for food packaging, the plasticizers have to meet the regulations governing the use of additives in food-contact applications [8].

PLA plasticization can be achieved by blending PLA with commercial or synthesized plasticizers. In this field, Martin and Avérous [5] analyzed the plasticization of PLA by using common plasticizers including glycerol, citrate ester, polyethyleneglycol (PEG), different types of starch and oligomeric lactic acid (OLA). Glycerol was found to be the least efficient plasticizer, meanwhile OLA and the lower molar mass PEG gave the best results. Kulinski and Piorowska [6] reported the effect of plasticization on semicrystalline and amorphous PLA with PEG. Semicrystalline PLA increased the elongation at break up to 20% for plasticizer content of 10 mass%, keeping

* Author for correspondence: vp.martino@ua.es

the melting temperature in the range of 150–160°C. Ljungberg and Wesslén [7, 9, 10] reported the plasticization of PLA with different monomeric and oligomeric home-made plasticizers. Monomeric tributyl citrate and triacetine showed good plasticizing efficiency, but these compounds had the tendency to migrate upon aging conditions [7]. Oligomeric plasticizers based on tributylcitrate [9] and diethyl-bis-hydroxymethylmalonate (DBM) [9, 10] showed good compatibility and plasticizing effect for low concentrations. For amounts of plasticizer higher than 20 mass%, the trimer displayed phase separation upon aging with the concomitant exudation to the films surface, meanwhile the heptamer showed phase segregation even at concentrations as low as 15 mass%. As a consequence, the migration of low molar mass plasticizers eventually occurred. The introduction of a polar amide group in the oligomeric esters increased the compatibility and morphological stability of the plasticized films. Unfortunately, these plasticizers are not commercially available, and the synthesis of such compounds may impact unfavorably on the final cost of the films.

The present work is focused on plasticizing amorphous poly(*L*-lactide-co-*D,L*-lactide) (PLLA/PDLLA) with four different commercially available adipates with the aim to obtain stable films with enhanced mechanical and thermal properties, able to be applied in packaging formulations. Monomeric and polymeric adipates were used in order to establish the effect of molar mass on PLLA/PDLLA/plasticizer compatibility. The efficiency was evaluated from their effect on thermal and mechanical properties. The obtained results were related with polymer-plasticizer miscibility and the morphologies were observed by Scanning Electronic Microscopy (SEM).

Experimental

Materials

Poly(*L*-lactide-co-*D,L*-lactide) (PLLA/PDLA) was purchased from Boehringer Ingelheim (Ingelheim, Germany), with 67:33 to 73:27 *L*-lactide:*D,L*-lactide molar ratio. Monomeric and polymeric commercial plasticizers were selected according to their intended use in food packaging, i.e. low migration and non-toxic for foodstuff. They were di-2-ethylhexyl-adipate (DOA) and three polymeric adipates with different molar masses, which will be identified in the present work as G206/3 ($M_n=2000$), G206/5 ($M_n=2700$) and G206/7 ($M_n=3400$), provided from Condensia Química S.A. (Barcelona, Spain). Chloroform of chromatographic degree was used for casting.

Preparation of the films

0.9 g of PLLA/PDLLA were dissolved in 40 mL of chloroform at room temperature and then, different amounts of plasticizers (5–20 mass%) were added to the dissolution. The obtained homogeneous solutions were cast into Petri dishes (15 cm diameter) and solvent evaporation was accomplished at room temperature until constant mass was reached. Residual chloroform (as it was determined by thermogravimetry) was eliminated by further treatment at 80°C for 10 min. After this treatment, residual chloroform was not detected (within the error of the technique). The obtained films were completely transparent.

Methods

Thermogravimetric analysis (TG) was performed in a TGA/SDTA 851 Mettler Toledo thermal analyzer (Schwarzenbach, Switzerland). Temperature was raised from room temperature up to 700°C at 10°C min⁻¹ and under nitrogen atmosphere (200 cm³ min⁻¹) in order to prevent thermo-oxidative reactions.

Differential Scanning Calorimetry (DSC) was conducted on a TA Instruments DSC Q-100 (New Castle, DE, USA) under nitrogen atmosphere. The materials were exposed to the following thermal cycle in order to erase the previous thermal history [11]: 1) heating from -30 to 180°C, 2) cooling from 180 to -30°C, and 3) heating from -30 to 300°C. The glass transition temperature (T_g) was determined from the second scan and was taken at the mid-point of heat capacity changes. The DSC traces of the pure plasticizers were also recorded from -90 to 80°C in order to determine their glass transition temperature. All runs were performed at 10°C min⁻¹.

Tensile and tear strength tests were carried out on a Universal Electronic Dinamometer from LLOYD Instruments, model LR30K (Fareham Hants, UK). Film thickness was measured using a Starrett Micrometer Caliber (L.S. Starrett Co. Ltd.) to ±0.001 mm. The average thickness of the films was 0.05±0.005 mm. Tensile tests were performed on rectangular probes (dimensions: 100·10·0.05 mm³) at a crosshead speed of 10 mm min⁻¹. Initial grip separation was 6 cm and a load gripping force of 50N was applied. Average tensile strength (TS) (4 measurements), elongation at break (EB%) and elastic modulus were calculated from the resulting stress-strain curves according to the standard procedure (ASTM D882-91).

Tear strength experiments were carried out according to ASTM 1938 standard, using the trouser tear method. The sample size was 100 mm long and 40 mm wide with a cut of 50 mm at the center of one

end. The experiments were conducted at 180 mm min⁻¹ extension rate.

Surface and cross sections of the obtained films were analyzed by Scanning Electronic Microscopy (SEM) on a JEOL JSM-840.

Results and discussion

Plasticizer selection is normally based on the compatibility with the polymer, its permanence in the obtained film and its efficiency in terms of the plasticizing effect [12]. Efficiency depends on the chemical structure, molar mass and concentration of the plasticizer. In general, plasticizers act by reducing the polymer chain-to-chain interactions by distributing itself homogeneously within the polymer, increasing the free volume [13]. One way to determine the polymer-plasticizer compatibility is by estimating their solubility parameters (δ) [14]. The global solubility parameters of PLLA/PDLLA and plasticizers were calculated by group contribution according to the Hoy's cohesive energy contributions [15] by using the following equation:

$$\delta = \frac{\rho \Sigma G}{M} \quad (1)$$

where δ is the solubility parameter, ρ is the density, M is the molar mass and G is the group molar cohesive energy. The calculated solubility parameters, for PLLA/PDLLA and the four selected plasticizers are summarized in Table 1. The δ_{PLA} value is higher than that of DOA ($\delta=16.7 \text{ (J cm}^{-3})^{1/2}$) and lower than those of the polymeric adipates. The slight differences in δ values between the polymeric plasticizers analyzed are mainly ascribed to the small difference in their molar masses and densities. As shown in Table 1, the four plasticizers had predicted solubility parameters close to that of PLLA/PDLLA, thus one can assume that they should be miscible, at least for a given PLLA/PDLLA-plasticizer composition.

The efficiency of plasticizers can be evaluated from their effect on the glass transition temperature (T_g) of the matrix. Effective plasticization induces the depression in T_g as shown in Table 2. The obtained re-

Table 1 Boiling point, global solubility parameters and glass transition temperature of the individual components

Material	Boiling point/ °C	δ / (J cm ⁻³) ^{1/2}	T_g / °C
PLA/PDLLA	–	20.1	56.6
DOA	216	16.7	-79.0
G206/3	250–270	20.6	-75.6
G206/5	250–270	22.4	-58.2
G206/7	290–310	23.0	-54.0

Table 2 Glass transition temperature (T_g) and maximum degradation rate (T_{max}) for different content for the four plasticizing agents

Plasticizer	Content/ mass%	T_g / °C	T_{max}^a / °C
PLA/PDLLA	–	55.1	364.0
	5	43.2	365.4
	10	40.9	363.9
PLLA/PDLLA+DOA	15	39.2	364.2
	20	38.9	363.6
	5	45.4	365.8
	10	34.2	365.5
PLLA/PDLLA+G206/3	15	33.2	363.9
	20	28.3	366.1
	5	46.3	357.3
PLLA/PDLLA+G206/5	10	41.0	364.1
	15	35.1	363.7
	20	26.9	364.8
PLLA/PDLLA+G206/7	5	46.2	361.9
	10	36.8	364.6
	15	31.4	362.3
	20	28.0	364.2

^aDetermined from the maximum of DTG curves (Fig. 2)

sults indicate that all plasticizers seem to be compatible with the matrix up to a critical composition which depends on the molar mass of the plasticizer. Low molar mass compounds are reported to be more efficient plasticizers [7, 9, 10]. However, small molecules have also the higher diffusivity, thus extraction during casting process is highly probable. In the case of DOA, concentrations higher than 10 mass% do not induce significant variation in T_g values. The morphologies of all samples are shown in Fig. 1. Those developed for 20 mass% DOA (Fig. 1b) suggest that low molar adipate is less compatible than the polymeric plasticizers for similar mass content. As it was above mentioned, for concentrations higher than 10 mass%, DOA may be easily exuded out of the matrix, leaving only a fraction of the initial amount dispersed in the matrix which creates irregularities in its structure (Fig. 1b) and slightly influences T_g (Table 2). For the polymeric adipates, T_g decreases gradually with the increment in plasticizer content, which is an evidence that G206/3 and G206/5 are miscible at least for compositions ranged from 5–20 mass%. This result is supported by the homogeneous morphologies observed by SEM (Figs 1c and d). In contrast, 20 mass% G206/7 seems to have the lower compatibility among polyadipates, as can be concluded from the higher average

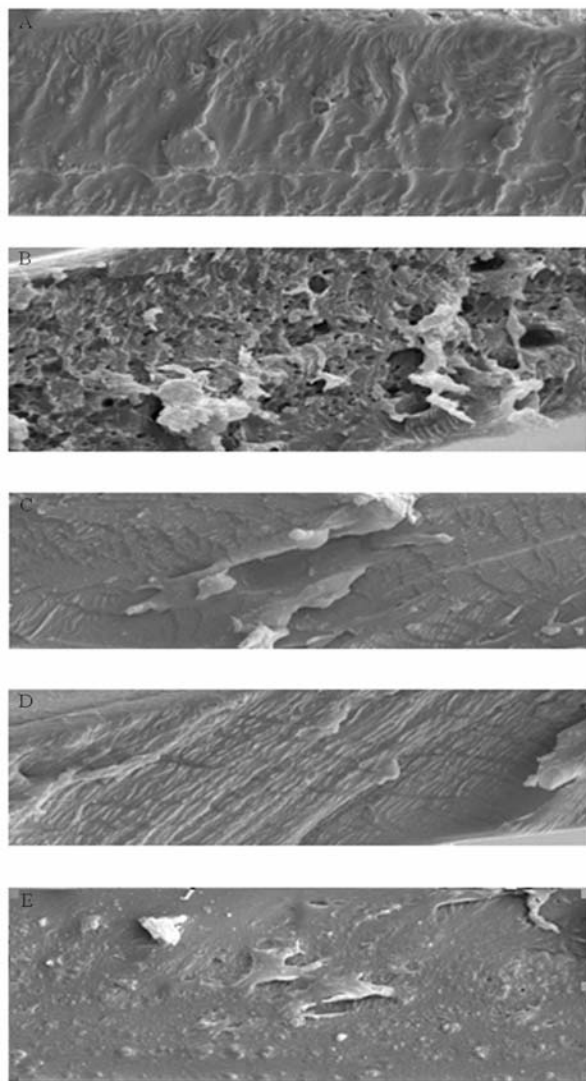


Fig. 1 SEM micrographs ($\times 1000$) of PLLA/PDLLA and mixtures with 20 mass% of commercial adipates. A – neat PLLA/PDLLA; B – 20 mass% DOA; C – 20 mass% G206/3; D – 20 mass% G206/5, E – 20 mass% G206/7

domain size observed by SEM (Fig. 1e), in accordance with its higher solubility parameter.

The effect of plasticizer on the thermal stability of PLLA/PDLLA was also analyzed. Figure 2 shows the TG/DTG curves obtained at $10^\circ\text{C min}^{-1}$ under nitrogen atmosphere for neat PLLA/PDLLA and plasticized with 20 mass% of the selected commercial adipates. Neat PLLA/PDLLA decomposes in a single step process with a maximum degradation rate (T_{max}) centered at 360°C , in accordance to the results previously reported [16, 17]. Plasticized PLLA/PDLLA thermal degradation seems to follow a one-step process with temperatures of maximum mass loss similar to those of the neat polymer. However, DTG curves evidence that there are two other thermal events at lower temperatures: one of them is observed below 120°C and may be related to the loss of low molar mass compounds,

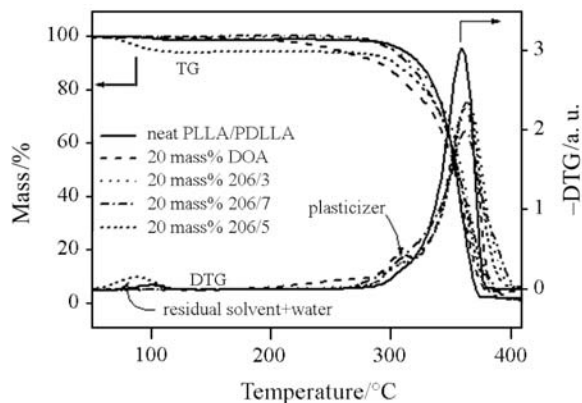


Fig. 2 TG/DTG curves obtained at $10^\circ\text{C min}^{-1}$ and under nitrogen atmosphere for neat PLLA/PDLLA and plasticized with 20 mass% of the four selected adipates

such as residual chloroform and absorbed water; the second one is partially overlapped to that of PLLA/PDLLA decomposition and may be associated to the evaporation of plasticizer components with low molar mass, which have boiling temperatures within this temperature range (Table 1). TG studies evidenced that the addition of plasticizers had no significant influence on the thermal stability of PLLA/PDLLA whatever the amount considered, as can be concluded from the values of T_{max} reported in Table 2. As a consequence, PLLA/PDLLA plasticized with adipates could be processed by usual thermoplastic technologies (extrusion, compression molding) in similar conditions to those already reported for PLA [6, 9, 10] without risking thermal degradation.

The results of tensile properties of PLLA/PDLLA plasticized with different contents of the four adipates are collected in Figs 3–5. Amorphous PLLA/PDLLA behaves as a brittle material with an elongation at break 5%, high modulus ($E=2.3$ GPa) and tensile stress 32 MPa. As expected, the addition of plasticizers (10 mass%) causes a decrease in elastic modulus and tensile stress values, meanwhile elongation at break increases up to 150% for plasticizers G206/3 and G206/5. The increment of plasticizers content to 20 mass% further decreases the elastic modulus, being the higher reduction of about 70% for G206/5. In addition, the elongation at break exceeds 200% for the same plasticizers. These results reveal that polyadipates G206/3 and G206/5 behave as the more efficient plasticizers for PLLA/PDLLA.

It is interesting to analyze the behavior of PLLA/PDLLA films plasticized with the lowest (DOA) and highest (G206/7) molecular mass plasticizers. Films plasticized with DOA show the higher decrease in the elastic modulus for contents lower than 10 mass%. Further additions conduct to an increase in the elastic modulus (Fig. 3). As it was discussed before, DOA may migrate easily from the bulk

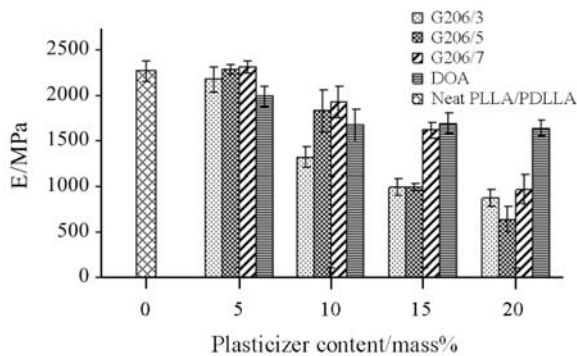


Fig. 3 Elastic modulus (E) for neat PLLA/PDLLA and plasticized with increasing amounts of plasticizers

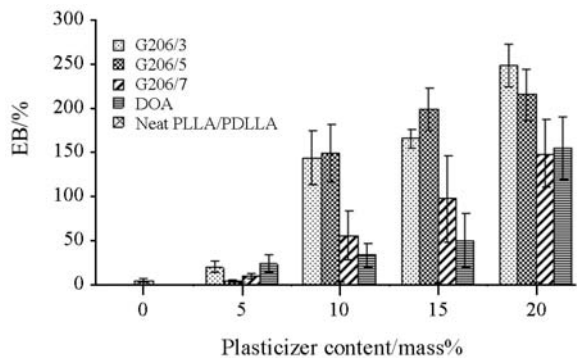


Fig. 4 Elongation at break (EB%) for neat PLLA/PDLLA and increasing amounts of the four adipates

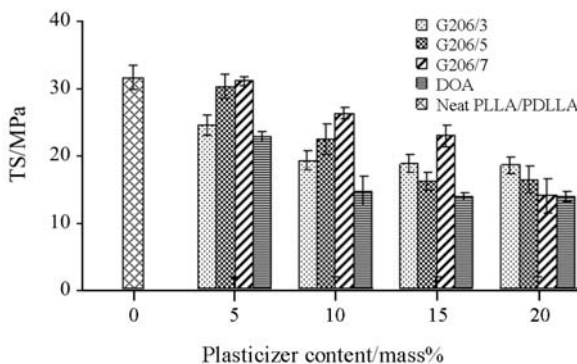


Fig. 5 Tensile strength (TS) for neat PLLA/PDLLA and increasing amounts of the four adipates

to the film surface due to its low molar mass, regaining part of the inherent brittleness. Similar results were reported by Ljungberg and Wesslén for PLA plasticized with tributyl citrate and DBM [9]. The authors observed cold crystallization for plasticized PLA films showing T_g values close to room temperature. The increase in crystalline phase induces the segregation of the low molar mass plasticizer, and the material becomes more brittle. In the present work, no evidence of cold crystallization was found during calorimetric experiments even at low heating rates (2°C min^{-1}) because the experiments were performed

immediately after residual solvent was eliminated. In this condition, no aging was evidenced. Thus, we can assume that DOA was just diffused out of the PLLA/PDLLA matrix because of the low compatibility between both components which conducts to the plasticizer segregation for a critical composition (higher than 10 mass%).

On the other side, the addition of G206/7 (the highest molar mass plasticizer) influences tensile properties in a lower degree, as can be concluded from Figs 3–5. Even though larger molecules generally provide greater interaction with the matrix, high molar mass plasticizers are less efficient than low molar mass ones, when compared on molar basis (mole of plasticizer/mole of polymer) within the window of polymer-plasticizer miscibility. By comparing tensile properties obtained for PLLA/PDLLA-10 mass% DOA and PLLA/PDLLA-10 mass% G206/7, it is noteworthy that the low molar mass plasticizer produces higher plasticization than the high molar mass one, which can be attributed to its greater molar content. Higher amounts of DOA conduct to plasticizer segregation, meanwhile for G206/7 the average size of the dispersed domains increases up to reach a critical size (corresponding to a critical plasticizer content) and phase separation becomes inevitable.

Besides high flexibility at room temperature, films for packaging require tearing resistance during package manufacturing [7]. Tear resistance for PLLA/PDLLA films is reported in Fig. 6. Tear resistance increases with plasticizer content, being more important for polyadipates. This is an important fact for the intended application of these films in food packaging.

Looking at the ultimate mechanical properties of plasticized PLLA/PDLLA films (Figs 3–6), PLLA/PDLLA-20 mass% G206/3 exhibits the best mechanical characteristics which make this material suitable for packaging formulations: a high elongation at break (increases up to 250%) combined to an ultimate stress of about 18 MPa (reduction of 56%), low elastic modulus (reduction of about 62%) and an increment in tear resistance of 235%. In addition, G206/3 seems to be compatible with amorphous PLA

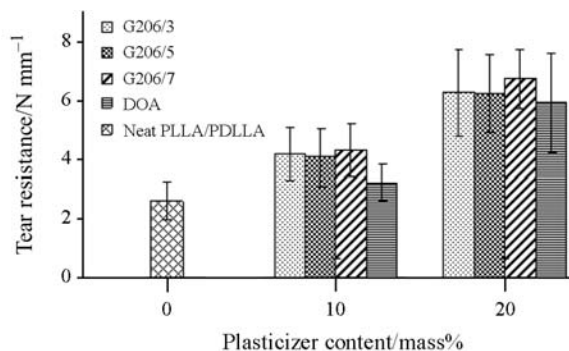


Fig. 6 Tear resistance for neat and plasticized PLLA/PDLLA

within the whole composition range analyzed (5–20 mass%), as can be concluded from SEM observations (Fig. 1).

Conclusions

The use of commercially available adipates as plasticizing agents of PLLA/PDLLA was explored. The efficiency of monomeric and polyadipates was evaluated through their effect on the glass transition temperatures and mechanical properties of plasticized samples. Results revealed that DOA (the lowest molar mass compound) and G206/7 (the highest molar mass compound) were the less efficient plasticizers. The former may diffuse out of the films for compositions higher than 10 mass%, and the materials regain a brittle behavior with no improvement in flexibility after further additions of plasticizer. On the other hand, the higher molar mass of G206/7 conducted to higher domains within the matrix and eventually, phase separation is expected.

The best results were found for G206/3. The glass transition temperature decreased from 56.6 to 28°C for 20 mass%. The elastic modulus decreased about 62%, meanwhile the elongation at break increased 250% combined with a reduction in the ultimate stress of 56% and an increment in tear resistance of 235%.

However, since it is well reported that long-term aging can induce cold crystallization in plasticized PLLA/PDLLA films with T_g values near room temperature [6, 9, 10], further work must be undertaken in order to ensure the stability of the proposed formulation under aging at room temperature.

Acknowledgements

The authors would like to express their gratitude to Condensia Química S.A. (Barcelona, Spain) for kindly supply the plasticizers and to Prof. José M. Kenny from the Department of Civil and Environmental Engineering, University of Perugia in Terni, for his assistance with tensile experiments. R. Ruseckaite wants to thank to the National Research Council (CONICET) of Argentina (PIP 2903) and ANPCYT (PICT 12-15074) for their financial support

References

- 1 A. Corti, G. Vallini, A. Perea, F. Cioni, R. Solaro and E. Chielini, Composting Microbial Eco-systems for Testing the Biodegradability of starch-filled polyethylene films, in *Biodegradable Polymers and Plastics*, M. Vert, J. Feijen, A. Albertsson, G. Scott, E. Chiellini (Eds.), RSC, Redwood Press Ltd., Melksham, Wiltshire (1992).
- 2 R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, 4 (2004) 835.
- 3 R. Tharanathan, *Trends in Food Science & Technology*, 14 (2003) 71.
- 4 J. M. Fang, P. A. Fowler, C. Escrig, R. González, J. A. Costa and L. Chamudis, *Carbohydr. Polym.*, 60 (2005) 39.
- 5 O. Martin and L. Avérous, *Polymer*, 42 (2001) 6209.
- 6 Z. Kulinski and E. Piorkowska, *Polymer*, 45 (2005) 10290.
- 7 N. Ljungberg and B. Wesslén, *Polymer*, 44 (2003) 7679.
- 8 D. Balafas, K. J. Shaw and F. B. Whitfield, *Food Chem.*, 65 (1999) 279.
- 9 N. Ljungberg and B. Wesslén, *Biomacromolecules*, 6 (2005) 1789.
- 10 N. Ljungberg and B. Wesslén, *J. Appl. Polym. Sci.*, 86 (2002) 1227.
- 11 Y. Wang and J. F. Mano, *J. Therm. Anal. Cal.*, 80 (2005) 171.
- 12 R. Sothornvit and J. M. Kotcha, *J. Food Eng.*, 50 (2001) 149.
- 13 S. Rosen, *Fundamental Principles of Polymeric Materials*, Wiley, USA, 1982.
- 14 V. Krevelen, *Properties of polymers*, 3rd edn, Elsevier, The Netherlands, 1990.
- 15 A. F. M. Barton, *Handbook of Solubility Parameters and other cohesive Parameters*, CRC Press, Boca Raton, FL, 1985, p. 142.
- 16 T. Malmgren, J. Mays and M. Pyda, *J. Therm. Anal. Cal.*, 83 (2006) 35.
- 17 W. S. Drumond, C. G. Mothé and S. H. Wang, *J. Therm. Anal. Cal.*, 85 (2006) 173.

PAT 2005

OnlineFirst: October 20, 2006

DOI: 10.1007/s10973-006-7897-3