



Compatible blends of biorelated polyesters through catalytic transesterification in the melt

Maria-Beatrice Coltelli^{a,b,*}, Claudio Toncelli^a, Francesco Ciardelli^{a,b}, Simona Bronco^c

^a Department of Chemistry and Industrial Chemistry, Via Risorgimento 35, 56126 Pisa, Italy

^b SPIN-PET s.r.l., Spin-Off company of the University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy

^c Istituto per i Processi Chimico-Fisici (IPCF-CNR), Area della Ricerca, Via G. Moruzzi 1, I-56124 Pisa, Italy

ARTICLE INFO

Article history:

Received 2 August 2010

Received in revised form

11 January 2011

Accepted 28 January 2011

Available online 21 March 2011

Keywords:

Biodegradable polyesters

Reactive blending

Transesterification

Poly(lactide)

Poly(butylene adipate-co-terephthalate)

ABSTRACT

The transesterification during the melt blending of polylactide (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) was investigated in presence of $Ti(OBu)_4$ as a catalyst. Both the effect of catalyst concentration and reaction duration was considered. The process was studied by analyzing the molecular weight of the polyesters by size exclusion chromatography (SEC). The rheological, thermal and morphological properties of the blends were investigated by melt flow rate, DSC and SEM analyses, respectively. Evidences about the formation of PBAT-PLA copolymers were obtained and discussed. The tensile properties of compression moulded films were also determined and correlated to the structure and phase morphology development of the blends. In particular, the use of $Ti(OBu)_4$ resulted in the improvement of compatibility. Moreover, the decrease in stiffness and the increase in elongation at break with the increase of mixing time was observed, in good agreement with the improved compatibility of the modified blend.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The general tendency of employing biodegradable materials coming from renewable resources in many large scale applications [1–3] focused the attention of many industries and research groups onto biopolymers, such as polysaccharides and proteins, or polymers industrially synthesized from natural monomer, such as poly(L-lactide) (PLA). In the latter case, the kind of polymerization and the optical properties of the monomer influence the mechanical, morphological, thermal properties of the material. Anyway the intrinsic stiffness and brittleness of PLA, due to its glass transition temperature, makes it suitable only for a restricted field of applications. The possible replacing of large-scale application actually employing polyolefins (e.g. packaging and agricultural applications) requires an improved versatility and properties modulation for PLA based materials. The blending of PLA with other biodegradable polymers such as starch [4–7] or natural fibers [8–10] keep as the main approach, even if the processing of the obtained composites appeared difficult to control. The blending of biosynthetic [10,11] or synthetic polyesters [11–14] can be carried out

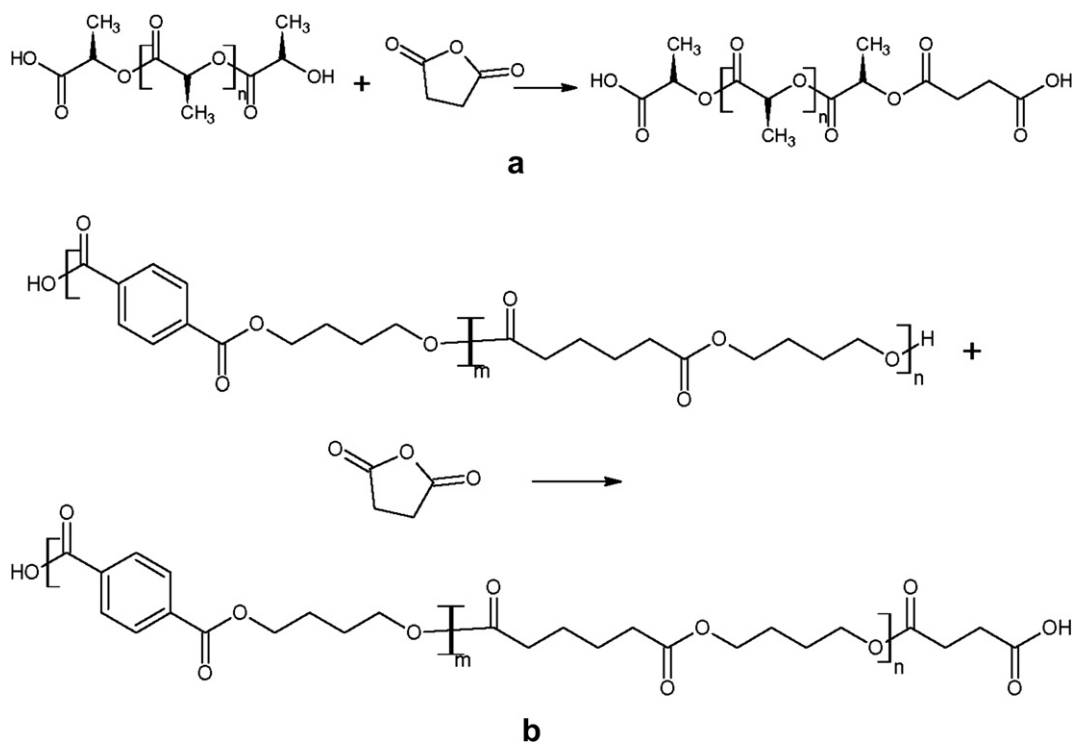
through the use of traditional processing devices, giving a partial modulation of the PLA stiffness. In particular the blending of poly(butylene adipate-co-terephthalate) (PBAT) allowed to obtain toughened PLA in proper conditions of composition and processing [15–18]. The possibility of further optimizing PLA/PBAT properties can require the use of proper compatibilizers [6,13,19] able to give an improvement of interfacial adhesion during the melt blending. In particular the use of transesterification catalysts in the blending could be promising to obtain formation of low amount of PLA-PBAT copolymer acting as compatibilizer in the interfacial region of the immiscible PLA/PBAT blend.

The use of transesterification catalysts in aliphatic polyester blends, despite of their interesting perspectives, were not much investigated, whereas poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) blends were the object of major interests. In particular the transesterification in melt of polyester functionalized polyethylene [19–23] or SEBS [23–25] and PET was studied as a function of catalysts and polymers structures and composition. These studies, made by comparing the yield in comb-like copolymers formation using Zn and Ti catalysts, showed that transesterification yield was improved when $Ti(OBu)_4$ or $Zn(OOCCH_3)_2$ were used, although the latter resulted in a more pronounced trend to PET degradation.

Gallardo et al [26], predicted the molecular weight of transesterified PLA with poly(ethylene glycol) (PEG) by building a model

* Corresponding author. Department of Chemistry and Industrial Chemistry, Via Risorgimento 35, 56126 Pisa, Italy. Tel.: +39 502219212; fax: +39 502219320.

E-mail address: beacolts@ns.dcci.unipi.it (M.-B. Coltelli).



Scheme 1. Derivatization of PLA (a) and PBAT (b) with succinic anhydride.

on the basis of data obtained from experiment in the melt or in solution. The transesterification of PLA with small molecules, such as ricinoleic acid [27–29] in bulk conditions or diacrylates [30] in solution, was also investigated, with the purpose of synthesizing proper copolymers in the former case or telechelic double bond terminated PLA oligomers in the latter one.

Transesterification reaction concerning PLA blends were investigated by many authors, in particular blends of PLA and poly(ϵ -caprolactone) (PCL) [31–33] or blends of PLA and poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) [34], with the objective of developing a new method for the synthesis of block or random copolymers. Stevels et al. [33] showed that the preparation of multiblock copolymers of PLA and PCL by controlled transesterification reactions cannot effectively be performed in an extruder, primarily due to the small processing window of PLA. However, di- and triblock copolymers are very effectively produced in high yield by coextrusion of L-lactide with hydroxyl terminated PCL and poly(ethylene glycol) with stannous octoate as a catalyst.

In the present paper the transesterification during melt blending of polylactide (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) was investigated in the presence of $\text{Ti}(\text{O}i\text{Bu})_4$ as transesterification catalyst by considering both the effect of its concentration and reaction time.

2. Experimental

2.1. Materials

PLA (PLA 2002D) and PBAT (Ecoflex FBX7011) were purchased from Dow Chem. and BASF Chem., respectively. This two polymers have been vacuum-dried at 60 °C for two hours before use.

THF ($T_b = 66.9$ °C) and triethylamine ($T_b = 89.3$ °C) purchased from J.T.Baker were distilled at atmospheric pressure

All the other reagents were purchased from commercial sources.

2.2. Preparation of blends and samples based on PLA and PBAT

The reactive blending process was carried out by a discontinuous mixer Brabender Plastograph OHG47055 having a mixing chamber of 50 cc, by introducing 41 g of polymeric material (PLA/PBAT 75/25 by weight). The samples were prepared at a temperature of 200 °C with a rotors speed of 50 rpm in flux of nitrogen to limit the thermo-oxidative degradation of polyesters [18]. The concentration of $\text{Ti}(\text{O}i\text{Bu})_4$ in the blend was 0.07% by weight. This concentration was established after a preliminary work about analysis of final torque, molecular weight and phase morphology as a function of $\text{Ti}(\text{O}i\text{Bu})_4$ content in blends prepared with a mixing time of 10 min (data not shown). This concentration resulted in the highest value of torque and molecular weight (RI detector).

2.3. Derivatization reaction of hydroxylic terminal groups of PLA and PBAT with succinic anhydride

In order to titrate and calculate the concentration of hydroxylic terminal groups of these polyesters, they were derivatized with succinic anhydride in anhydrous conditions [44]. (Scheme 1).

The reaction was carried out for 72 h at a temperature of 40 °C in the presence of triethylamine as a base catalyst; the product has been purified by double reprecipitation in absolute ethanol.

Table 1
Titration data about PLA and PBAT.

	[COOH] (meq/Kg)	$\sigma_{[\text{COOH}]}$ ^a	[OH] (meq/Kg)	$\sigma_{[\text{OH}]}$ ^a	$\overline{M}_{n\text{tit}}$ ^b ($\cdot 10^{-3}$)	$\overline{M}_{n\text{sec}}$ ^c ($\cdot 10^{-3}$)	DI_{sec} ^c
PLA	11.4	1.8	1.3	5	80 ± 20	102.0	1.9
PBAT	38.8	1.4	43.2	6	24 ± 3	28.5	2.5

^a Standard deviation calculated on the basis of three measurements.

^b Calculated from titrations.

^c Calculated from SEC measurements.

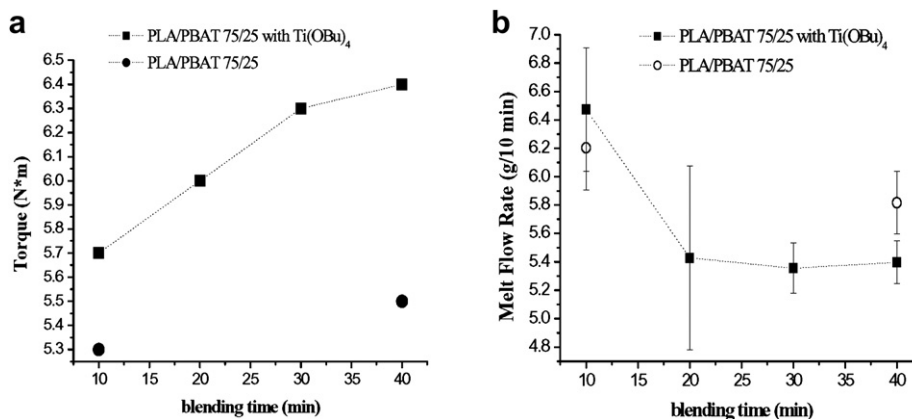


Fig. 1. Final Torque values (a) and Melt Flow Rate values (b) as a function of blending time.

2.4. Titration of PLA and PBAT

Carboxylic end groups were titrated at room temperature using KOH in MeOH, standardized daily with *p*-toluenesulfonic acid. A Mettler-Toledo pH-meter was employed to determine the equivalent point. Polymers were dissolved in 20/80 and 15/85 volume ratio dichloromethane/methanol solutions for not derivatized and derivatized sample respectively.

Pure PLA, PBAT and derivatized samples were purified in ethanol in order to remove possible contribution to titration given by very short oligomer chains.

2.5. Characterization of prepared blends and samples

The UV spectra have been registered in a wavelength range between 800 nm and 300 nm at room temperature, by using a Perkin–Elmer Lambda 650 spectrometer with linear polarizer Glan–Taylor interfaced with PC. The spectra were recorded in isotropic conditions by keeping the chloroform solution in quartz cells.

Size Exclusion Chromatography (SEC) analysis were carried out onto chloroform solutions by a JASCO chromatograph equipped with a PU-2089 pump, a CO-2065 oven with an HSS-2000 control system and PL Gel 5 μ m Mixed-D columns. The analysis were carried out by using an RI-2031 refractive index, and a UV-2077 UV detector set at 252 nm to selectively observe the signal of PBAT in PLA/PBAT blends. In fact value of the ratio between the molar extinction coefficient of PBAT and PLA was maximum (about 20), as revealed

by a UV analysis with a Perkin Elmer, Lambda 650 UV/Vis spectrometer. The SEC equipment was interfaced with software Borwin 1.5 (JMBS DEVELOPMENT). The eluent was chloroform at a flow of 1 ml/min.

SEM micrographs were recorded by a Jeol JSM mod.5600 LV instrument. Analyses were carried out on the sample surface, after metallization with gold.

Mel Flow Rate (MFR) and Melt Volume Rate (MVR) measurements were carried out by using a Modular Melt Flow Code 7026.000 commercialized by Ceast s.p.a interfaced with software CeastVIEW.

Tensile tests were performed at 1 mm/min onto compression moulded specimens obtained by using a Campana PM20/200 press at a 200 °C temperature and a 5 MPa pressure, for about 2 min. A Tinius Olsen H10KT dynamometer equipped with a QMat Pro software were employed.

DSC thermograms were recorded by using a Mettler Toledo Stare System, model DSC 822e differential scanning calorimeter equipped with a Star^c software.

Thermogravimetric analysis were carried out by using a Mettler Toledo TGA/SDTA 851 equipment with a software Star^c.

3. Results and discussion

3.1. Analysis of terminal groups through titration and SEC analysis

The titration of terminal groups of PLA and PBAT before and after the derivatization with succinic anhydride, allowed to

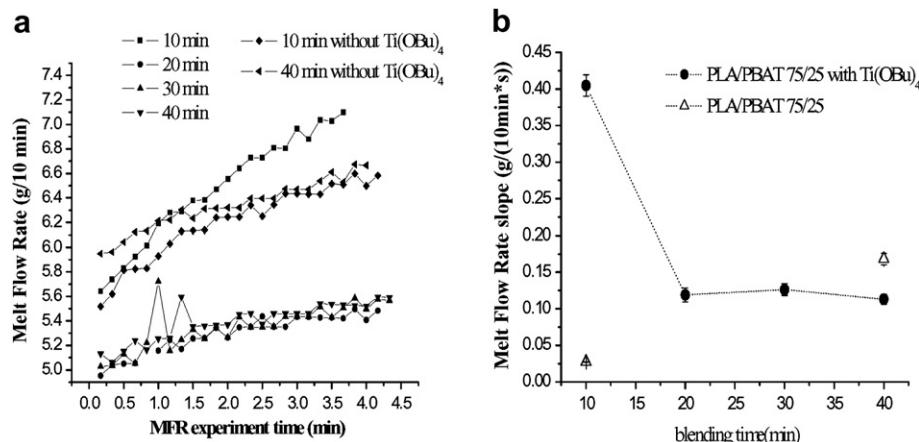


Fig. 2. Melt Flow Rate as a function of experiment time (a) and MFR slope as a function of mixing time.

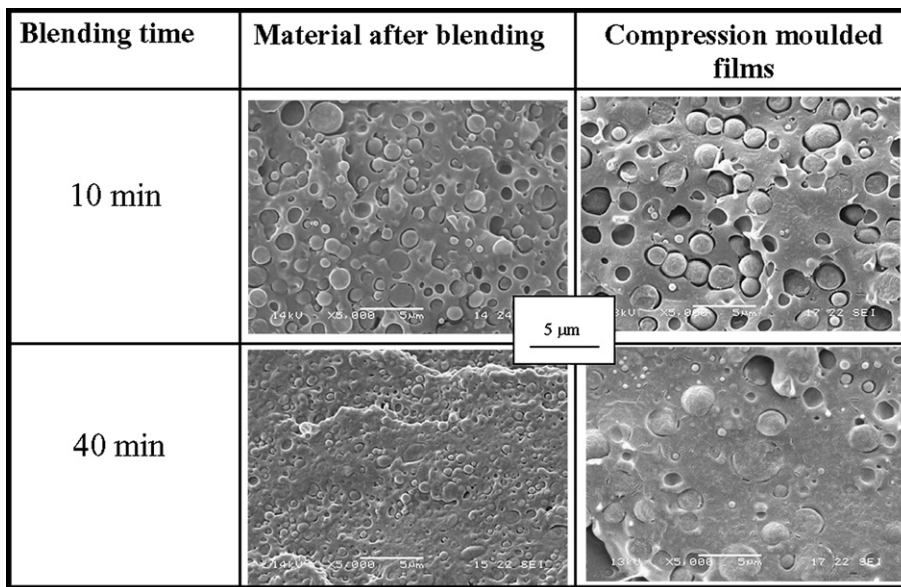


Fig. 3. SEM micrographs of PLA/PBAT 75/25 blends prepared without catalyst mixing times of 10 (top) or 40 (bottom) minutes, before (left) and after (right) the compression moulding for 2 min at 200 °C.

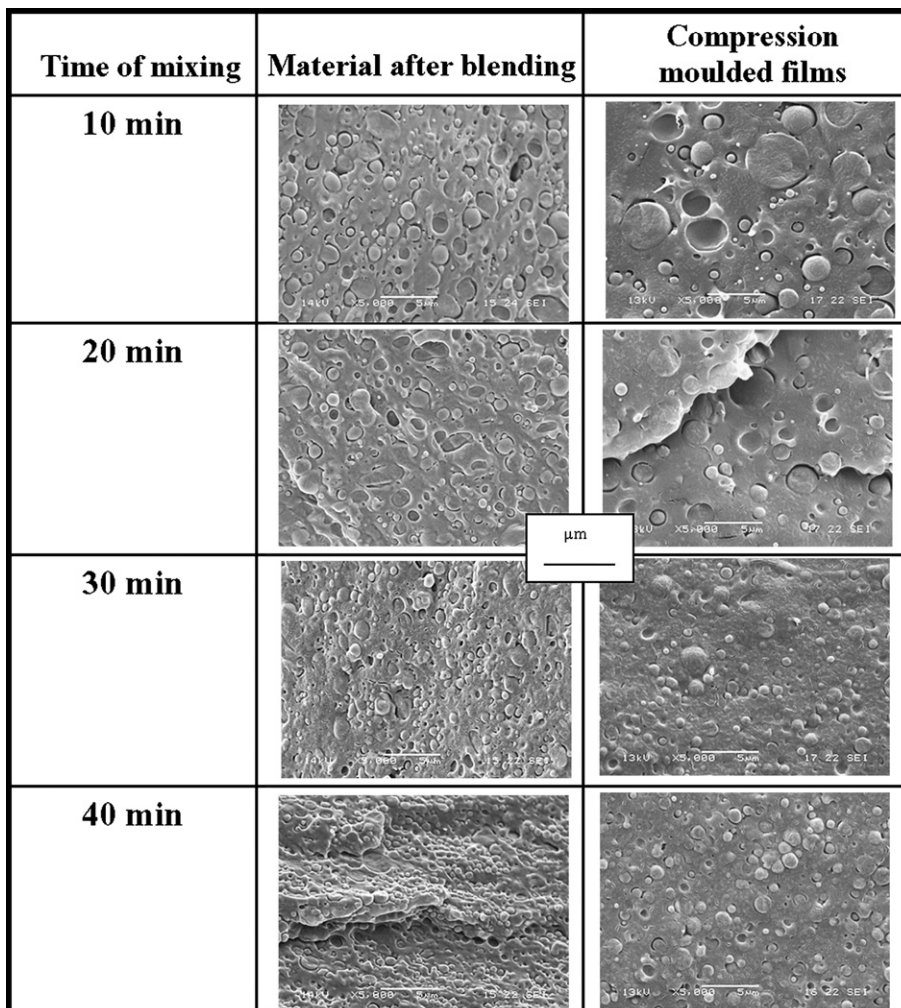


Fig. 4. SEM micrographs of PLA/PBAT 75/25 blends prepared with $Ti(OBu)_4$, before (left) and after (right) the compression moulding for 2 min at 200 °C.

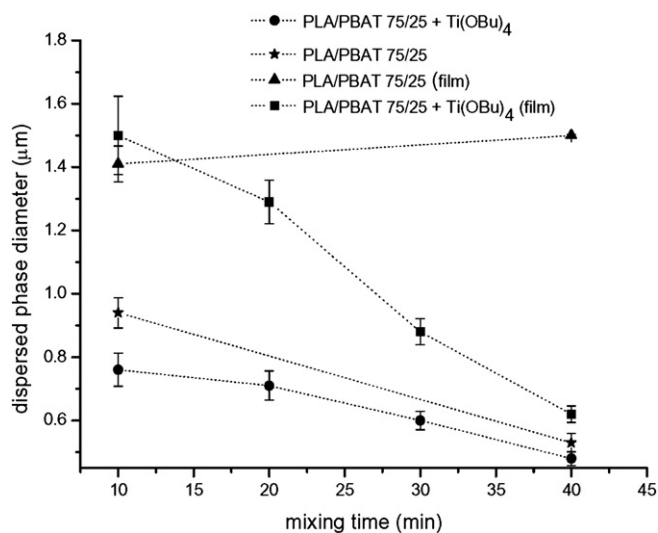


Fig. 5. Dispersed phase diameter as a function of mixing time for blends obtained with or without $\text{Ti}(\text{OBu})_4$ in blends or compression moulded films.

determine both concentration of hydroxyl and carboxyl terminal groups (Table 1). The results showed that the PLA terminals consisted in $-\text{COOH}$ groups, as the concentration of $-\text{OH}$ was lower than the standard deviation calculated on the basis of three replied titrations. The comparison with SEC data, showing \bar{M}_n of about 102 000, showed a discrepancy with titration results, obtained by considering two terminal carboxyl groups for each macromolecule. A better agreement was obtained assuming one $-\text{COOH}$ and one not reactive group per macromolecule. In this way, a \bar{M}_n of 80000 ± 20000 was obtained from titration data.

In the ring opening polymerization usually employed for PLA synthesis, metallic alcoholates, carboxylates or alcohols are used as catalysts and initiators. This kind of polymerization can thus result in terminal groups such as ester, alcoxyl or hydroxyl groups in dependence of the adopted procedure [35,36]. When the polymerization is carried out in bulk, some authors evidenced side transesterification or degradation reaction which can be controlled by balancing the ratio between the lactide and catalyst concentrations [37]. Anyway the authors did not show any effect onto the nature of terminal groups.

Similar concentration of $-\text{COOH}$ and $-\text{OH}$ were found for PBAT. Hence one $-\text{COOH}$ and one $-\text{OH}$ terminal for each macromolecule can be reasonably hypothesized [38], in good agreement with the

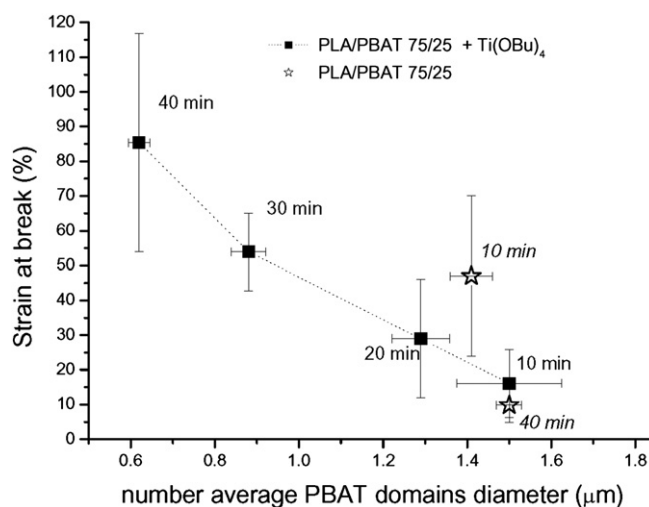


Fig. 7. Strain at break as a function of PBAT domains diameter.

results obtained by SEC measurements. Anyway, SEC data showed higher values than titration data for both PLA and PBAT, because the calibration was SEC calibration line was built by employing poly (styrene) standards, having a different hydrodynamic radius with respect to PLA and PBAT. It should be pointed out that SEC results, although more precise, are less accurate than titration results.

The comparative analysis of the results obtained from PLA and PBAT granules and the reprecipitated polymers afforded the concentration of $-\text{COOH}$ groups in the oligomers of 4.6 meq/Kg of $-\text{COOH}$ for PLA oligomers, corresponding to 28.7% of total carboxyl groups, and 18.1 meq/Kg for PBAT oligomers, corresponding to 31.8% of total carboxyl groups.

3.2. Properties and compatibility of PLA/PBAT blends

As evidenced in Fig. 1a, the values of final torque of the PLA/PBAT 75/25 blend treated with $\text{Ti}(\text{OBu})_4$ (B25Ti) was higher than the one of untreated blend B25 in the investigated range of time. The melt flow rate data as a function of mixing time (Fig. 1b) gave a result in good agreement with final torque data, because the fluidity in the melt decreased by increasing the blending time more rapidly in the presence of $\text{Ti}(\text{OBu})_4$ content.

During the melt flow rate test the recorded value was stable as a function of time for the samples prepared by using the

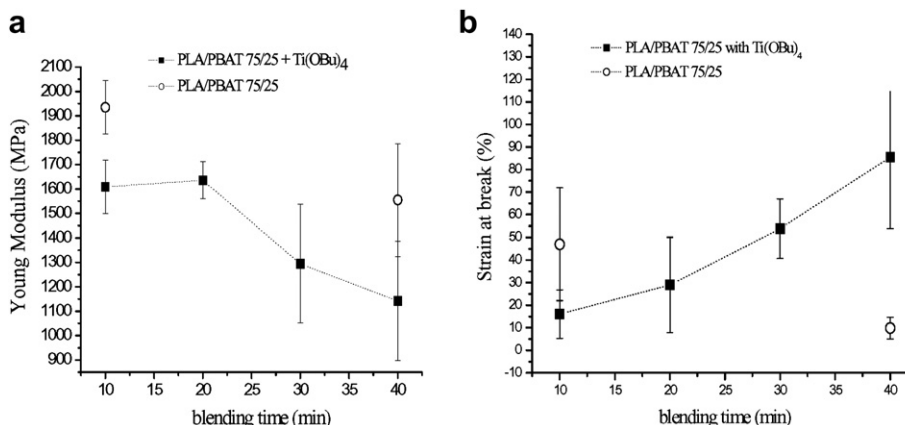


Fig. 6. Young Modulus and strain at break of compression moulded film obtained from PLA/PBAT 75/25 blends with or without $\text{Ti}(\text{OBu})_4$ as transesterification catalyst.

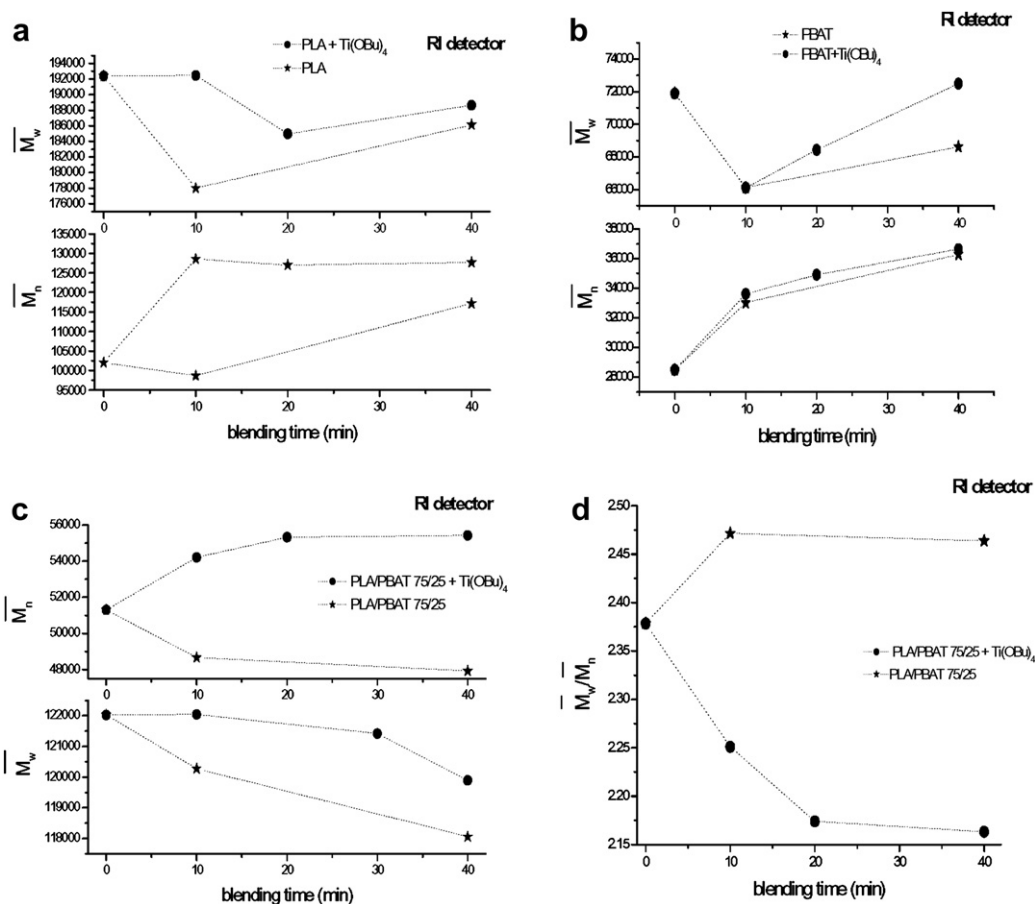


Fig. 8. \overline{M}_w and \overline{M}_n trends as a function of blending time of (a) PLA based samples, RI detector; (b) PBAT based samples, RI detector; (c) PLA/PBAT 75/25 blends, RI detector; (d) Dispersity index ($Id = \overline{M}_w / \overline{M}_n$) for PLA/PBAT 75/25 blends, RI detector.

transesterification catalyst and by a mixing time higher than 20 min (Fig. 2a), as confirmed by the value of the slope of MFR trends as a function of mixing time for the different samples (Fig. 2b). The rheological properties are affected by the presence of the catalyst and the mixing time. In particular the predominance of transesterification onto degradation can be hypothesized.

The morphological analysis carried out by SEM (Fig. 3) showed that the dispersed phase diameter was affected by the mixing time. In particular, the value decreased for longer blending time and the adhesion between matrix and dispersed phase increased. Anyway the phase morphology developed during the blending was not stable and evolved towards an increase of the diameter during compression moulding. When the $Ti(OBu)_4$ was added (Fig. 4) both phase morphology and its stability were improved for mixing time higher than 20 min.

The value of dispersed phase diameter as a function of mixing time followed the trend showed in Fig. 5 both in the presence (circles) and absence (stars) of $Ti(OBu)_4$. In compression moulded specimens (films) the situation was completely different. In the presence of $Ti(OBu)_4$ (squares) a decrease in dispersed phase diameter can be observed. The compression moulding process seemed to give reorganization of phase morphology resulting in the coalescence of different PBAT domains. On the contrary, in the presence of $Ti(OBu)_4$, when probably the interphase region was stabilized in term of surface energy thanks to a more consistent formation of PLA-PBAT copolymers, the coalescence between different PBAT domains was difficult and the phase morphology was more stable during compression moulding.

Table 2

Results of SEC analysis, Torque and melt Flow Rate data about PLA/PBAT 75/25 blends and pure polymers.

Samples	UV detector			RI detector			Torque (N*m)	MFR (g/10 min)
	\overline{M}_n	\overline{M}_w	Id	\overline{M}_n	\overline{M}_w	Id		
PLA ^a	nd ^b	nd	nd	102.0	192.4	1.88	nd	4.6
PLA10	nd	nd	nd	98.6	178.0	1.80	8.4	3.2
PLA40	nd	nd	nd	117.2	186.1	1.59	9.0	3.3
PLATI10	nd	nd	nd	128.5	192.5	1.50	9.4	3.5
PLATI20	nd	nd	nd	127.0	184.9	1.46	10.1	3.2
PLATI40	nd	nd	nd	127.7	188.6	1.48	9.4	3.3
PBAT	28.0	71.9	2.56	28.5	71.9	2.52		19.7
PBAT10	28.1	67.2	2.38	33.0	66.1	2.00	1.1	16.0
PBAT40	27.0	67.2	2.49	36.3	68.6	1.89	1.2	15.4
PBATTi10	26.8	66.8	2.49	33.6	66.1	1.97	1.1	16.0
PBATTi20	28.9	67.7	2.34	34.9	68.4	1.96	0.9	14.4
PBATTi40	32.5	72.1	2.22	36.6	72.4	1.98	1.0	11.1
B25 ^c	30.1	71.2	2.37	51.3	122.0	2.38	nd	nd
B2510	26.1	66.1	2.54	48.7	120.2	2.47	5.3	6.204
B2540	26.7	70.7	2.65	47.9	118.1	2.46	5.5	5.817
B25Ti10	28.2	65.4	2.32	54.2	122.0	2.25	5.7	6.47
B25Ti20	26.7	67.3	2.52	55.3	nd	2.17	6.0	5.43
B25Ti30	30.1	72.3	nd	nd	121.4	2.17	6.3	5.35
B25Ti40	29.5	76.5	2.59	55.4	119.9	2.16	6.4	5.40

^a In the samples name PLA, PBAT or B25 indicate PLA, PBAT or PLA/PBAT 75/25 blend respectively; Ti indicates the presence of $Ti(OBu)_4$; the number 10, 20, 30 or 40 indicate the blending time in minutes.

^b In the case of PLA only the data resulting from the RI detector were kept into account. nd = not determined.

^c B25 is the blend obtained in $CHCl_3$ solution.

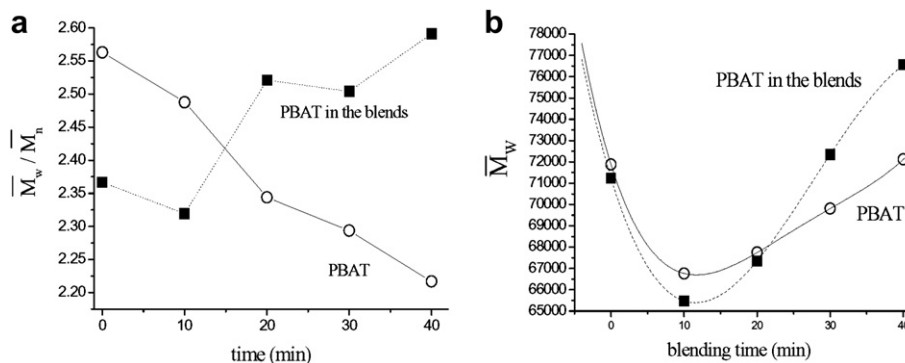


Fig. 9. Dispersity index $\overline{M}_w / \overline{M}_n$ (a) and \overline{M}_w (b) for pure PBAT and PBAT in the blends, both in the presence of Ti(OBu)₄.

The tensile measurements, carried out onto compression moulded films specimens, showed the slight decrease in Young Modulus as a function of mixing time (Fig. 6a). On the other hand the strain at break (Fig. 6b) as a function of mixing time increased only in blends containing Ti(OBu)₄. High dispersed phase diameter did not allow the yielding of the material, with domains behaving as defects in the materials. On the contrary, with smaller dispersed domains, the yielding of the material is possible, as the material is toughened thanks to the presence of a dispersed phase with rubber-like properties. For achieving a not fragile material a critical value of the dispersed phase was evidenced in synthetic condensation polymers (Polyamide and polyesters)/rubber blends [39–42], usually employed in toughened materials. In good agreement with these investigations, the correlation between strain at break and dispersed phase diameter (Fig. 7), showed that the decrease in the dispersed phase diameter gave an increase in elongation at break in blends obtained by using Ti(OBu)₄. On the other hand the blends obtained without the catalyst showed a reduced strain at break, independently on the time of blending.

On the whole the results showed that in the presence of Ti(OBu)₄ an improvement of compatibility can be achieved when the time of blending was higher than 20 min. The transesterification between PLA and PBAT probably give not negligible amount of copolymer able of improving and stabilizing the blend morphology.

3.3. Catalyzed transesterification of a PLA/PBAT blends

In order to understand the behaviour observed during the blending the study of the transesterification reaction in pure PLA and pure PBAT was performed. In the presence of Ti(OBu)₄ PLA \overline{M}_w and \overline{M}_n was higher than without it (Fig. 8a).

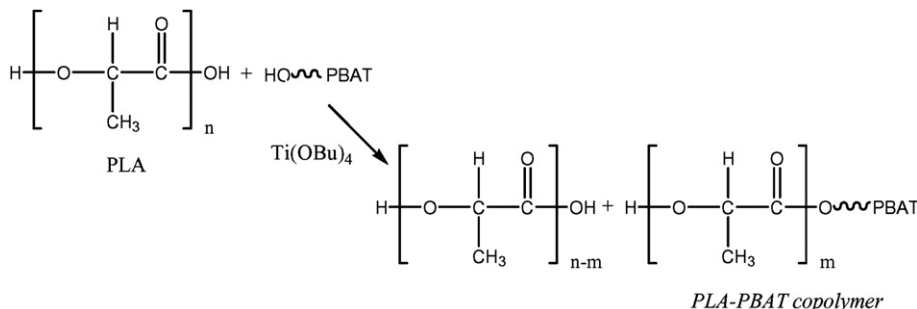
The processing of neat PLA gave in any case a decrease in \overline{M}_w independently on the presence of Ti(OBu)₄. Anyway, in the presence of transesterification catalyst the effect as much more evident. On the contrary the catalyst seemed to affect the \overline{M}_n by increasing

the value in the first 10 min of processing time, after that it remains almost constant.

During the processing PBAT gave a decrease in \overline{M}_w and an increase in \overline{M}_n which resulted independent on the presence of Ti(OBu)₄ (Fig. 8b). The discrepancy between the decrease of \overline{M}_w and the increase of \overline{M}_n , is probably linked to the redistribution of molar masses leading to a distribution more usual in polyesters with $\overline{M}_w / \overline{M}_n = 2$. With Ti(OBu)₄ the increase in \overline{M}_w was higher, especially at higher blending time. No influence were observed on the final torque but interestingly the trend of MFR as a function of blending time showed a progressive decrease as a function of blending time, more pronounced in the sample containing Ti(OBu)₄ (Table 2), showing an increase in the viscosity in the melt.

In PLA/PBAT 75/25 blend the role of Ti(OBu)₄ became much more evident. Under these conditions, \overline{M}_n increased as a function of blending time, whereas \overline{M}_w slightly decreased (Fig. 8c). Both \overline{M}_w and \overline{M}_n decreased by adding the catalyst in the mixture. As a consequence a decreasing trend as a function of blending time was observed for the dispersity index $\overline{M}_w / \overline{M}_n$ (Fig. 8d) in blends with Ti(OBu)₄, whereas a slightly increasing trend was observed for blends obtained without it. This result could be due to a not negligible extent of the transesterification reaction between lower molecular weight PBAT chains with higher molecular weight PLA chains with the consequent decrease in dispersity index.

Enlightening results came from the use of UV detector for the SEC analysis of the blends. In this way, the value of PBAT molecular weight of the PBAT segments in the blends obtained with Ti(OBu)₄ was determined and compared with those of pure PBAT processed with the catalyst. The dispersity index of the PBAT fraction in the blends increased, being in contrast with the decreasing trend of the Id observed with the RI detector (Fig. 8d). This result seems to support the hypothesis of reaction between PBAT and PLA, in full contrast with the trend recorded for pure PBAT (Fig. 9a). The trend of Mw was also compared with that of pure PBAT (Fig. 9b).



Scheme 2. Transesterification of PBAT with PLA.

From the comparative analysis of the \overline{M}_w of the PBAT segments, it is evident that in the presence of $\text{Ti}(\text{OBU})_4$ the \overline{M}_w of PBAT in the blends was higher than the \overline{M}_w of neat PBAT when the time of mixing was higher than 21.7 min. This value was obtained by fitting the trends through polynomial fit, and by calculating the intersection point. The difference of \overline{M}_w can be attributed to the transesterification reaction of PBAT with PLA, which resulted in the formation of copolymer having a higher molecular weight than neat PBAT. In an attempt to determine the yield of the transesterification reaction, a system consisting of PLA; PBAT and an interphase region was considered. The molecular weight data obtained for the blends from SEC analysis with the UV-detector gave a result dependent on the molecular weight of PBAT plus the PLA-PBAT copolymer. In an attempt to determine from these data the yield of copolymer formation (despite of the low accuracy of the data due to the use of polystyrene standards in the calibration of SEC), some further simplification assumptions were necessary:

- The \overline{M}_w of PLA and PBAT in the blends is the same as that of the neat polymers processed in the presence of $\text{Ti}(\text{OBU})_4$, hence the $\overline{M}_w_{\text{PLA}}(t)$ and the $\overline{M}_w_{\text{PBAT}}(t)$ function can be determined by fitting the experimental trends (Fig. 8)
- As reactive hydroxyl groups, on the basis of titration results, could be found only in the PBAT, the unique reaction occurring in the interphase region was the transesterification of hydroxyl groups of PBAT with ester or carboxylic groups of PLA (Scheme 2). This assumption is more correct when lower blending time were considered.
- As a consequence of the previous assumption, the average molecular weight of the copolymer is assumed to be as $[\overline{M}_w_{\text{PBAT}}(t) + \overline{M}_w_{\text{PLA}}(t)/2]$

For the $\text{Ti}(\text{OBU})_4$ treated systems, the SEC $\overline{M}_w_{\text{PBAT}}(t)$ obtained for pure PBAT from the UV detector, the $\overline{M}_w_{\text{PLA}}(t)$ for pure PLA from RI detector and the $\overline{M}_w_{\text{B}}(t)$ for PBAT in the blend from UV detector were obtained by fitting the experimental values with a polynomial function of fourth order.

By considering the definition of $\overline{M}_w_{\text{B}}(t)$, that is the average weight molecular weight of macromolecules revealed by UV detector (PBAT macromolecules and PBAT-PLA copolymers), as a function of time of blending t , the Eq. (1) can be written:

$$\overline{M}_w_{\text{B}}(t) = \frac{1000 \cdot M_{w\text{PBAT}}(t)^2 + N_{\text{COP}}(t) \cdot \left(M_{w\text{PBAT}}(t) + \frac{M_{w\text{PLA}}(t)}{2} \right)^2}{1000 \cdot M_{w\text{PBAT}}(t) + N_{\text{COP}}(t) \cdot \left(M_{w\text{PBAT}}(t) + \frac{M_{w\text{PLA}}(t)}{2} \right)} \quad (1)$$

where $N_{\text{COP}}(t)$ is the number of copolymer macromolecules per 1000 PBAT macromolecules. From experimental SEC data obtained for PLA, PBAT and PLA/PBAT 75/25 blends in the presence of $\text{Ti}(\text{OBU})_4$ it is possible the calculation of $N_{\text{COP}}(t)$ as a function of $M_{w\text{PBAT}}(t)$, $M_{w\text{PLA}}(t)$ and $M_{w\text{B}}(t)$ from the Eq. (2)

Table 3
Equations obtained through fitting of experimental SEC data.

Quantity	Fitting equations
Mw of PBAT in the PLA/PBAT blends with $\text{Ti}(\text{OBU})_4$	$\overline{M}_w_{\text{B}}(t) = 13234 - 1125.05t + 63.76t^2 - 0.914t^3 + 0.00266t^4$
Mw of PBAT in PBAT samples with $\text{Ti}(\text{OBU})_4$	$\overline{M}_w_{\text{PBAT}}(t) = 71881 - 1088.25t + 74.77t^2 - 1.883t^3 + 0.01744t^4$
Mw of PLA in PLAsamples with $\text{Ti}(\text{OBU})_4$	$\overline{M}_w_{\text{PLA}}(t) = 197237 + 1505.71t - 224.84t^2 + 8.48t^3 - 0.0965t^4$
Number of PLA-PBAT copolymer per 1000 PBAT macromolecules	$N_{\text{COP}}(t) = 17.45 - 79.24 \cdot e^{-\frac{t}{150}}$

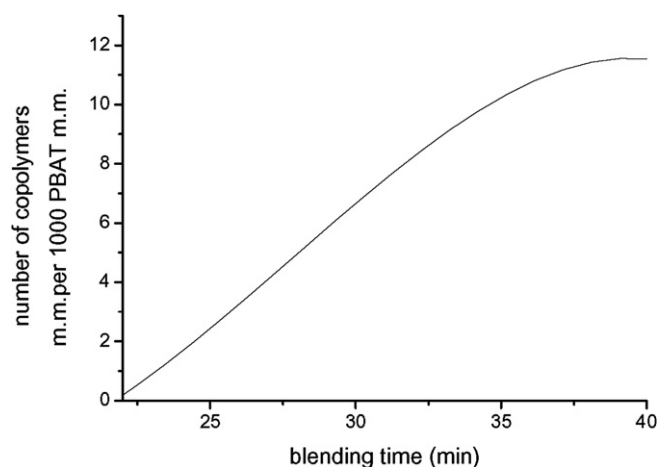


Fig. 10. Fitting equation providing the number of copolymers per 1000 PBAT macromolecules as a function of blending time.

$$N_{\text{COP}}(t) = \frac{1000 \cdot \overline{M}_w_{\text{PBAT}}(t) \cdot (\overline{M}_w_{\text{B}}(t) - \overline{M}_w_{\text{PBAT}}(t))}{\left(\overline{M}_w_{\text{PBAT}}(t) + \frac{\overline{M}_w_{\text{PLA}}(t)}{2} \right) \cdot \left[\left(\overline{M}_w_{\text{PBAT}}(t) + \frac{\overline{M}_w_{\text{PLA}}(t)}{2} \right) - \overline{M}_w_{\text{B}}(t) \right]} \quad (2)$$

Through a fitting of calculated point with a third order exponential decay function, resulting the most adequate for fitting experimental data, the function $N_{\text{COP}}(t)$ was obtained (Table 3, Fig. 10) and could be used to roughly evaluate the amount of copolymer formed during the blending. By using this equation the amount of PLA-PBAT copolymer formed after 40 min of blending was estimated to be about 0.65% by weight of the blend. However this amount was enough to give a not negligible improvement of morphological and mechanical properties, as evidenced in the previous part of this paper, in good agreement with Koning et al. [43].

4. Conclusions

In the present work the transesterification reaction occurring between PLA and PBAT during the melt blending was investigated in the presence of $\text{Ti}(\text{OBU})_4$ as transesterification catalyst by considering the effect of reaction duration. The process was studied by analyzing the molecular weight of the polyesters by SEC and the rheological, thermal and morphological properties of the blends by melt flow rate, DSC and SEM analysis. The tensile properties of compression moulded films were also determined and correlated to the structure and phase morphology development. In particular, the use of $\text{Ti}(\text{OBU})_4$ resulted in the improvement of compatibility as shown by the effective reduction of the PBAT dispersed phase diameter. Moreover, the decrease in the stiffness and the increase in elongation at break with the increase in blending time was observed, in good agreement with the evidences about the improved compatibility. On the basis of the experimental results, the investigated process resulted in an improvement of morphological and tensile properties as a function of mixing time. On the basis of SEC-UV detector analysis the results were attributed to the formation of a PLA-PBAT copolymer in low amount.

Acknowledgements

Toscana PC – RIPLAS (CIPE, 2008–2010) and RiGePlast (Tuscany Region – POR CREO FESR 2007–2013) projects are thanked for financial support.

References

- [1] Auras R, Harte B, Selke S. An overview of polylactides as packaging materials. *Macromolecular Bioscience* 2004;4(9):835–64.
- [2] Sorrentino A, Gorrasi G, Vittoria V. Potential perspectives of bio-nanocomposites for food packaging applications. *Trends in Food Science & Technology* 2007;18(2):84–95.
- [3] Ray SS, Bousmina M. Biodegradable polymers and their layered silicate nanocomposites: in greening the 21st century materials world. *Progress in Materials Science* 2005;50(8):962–1079.
- [4] Wang H, Sun X, Seib P. Strengthening blends of poly(lactic acid) and starch with methylenediphenyl diisocyanate. *Journal of Applied Polymer Science* 2001;82(7):1761–7.
- [5] Zhang J-F, Sun X. Mechanical properties of Poly(lactic acid)/starch composites compatibilized by maleic anhydride. *Biomacromolecules* 2004;5(4):1446–51.
- [6] Wu C-S. Improving polylactide/starch biocomposites by grafting polylactide with acrylic acid - characterization and biodegradability assessment. *Macromolecular Bioscience* 2005;5(4):352–61.
- [7] Sarazin P, Li G, Orts WJ, Favis BD. Binary and ternary blends of polylactide, polycaprolactone and thermoplastic starch. *Polymer* 2008;49(2):599–609.
- [8] Masirek R, Kulinski Z, Chionna D, Piorkowska E, Pracella M. Composites of poly(L-lactide) with hemp fibers: morphology and thermal and mechanical properties. *Journal of Applied Polymer Science* 2007;105(1):255–68.
- [9] Oksman K, Mathew AP, Bondeson D, Kvien I. Manufacturing process of cellulose whiskers/polylactide acid nanocomposites. *Composites Science and Technology* 2006;66(15):2776–84.
- [10] Serizawa S, Inoue K, Iji M. Kenaf-fiber-reinforced poly(lactic acid) used for electronic products. *Journal of Applied Polymer Science* 2006;100(1):618–24.
- [11] Furukawa T, Sato H, Murakami R, Zhang J, Duan Y-X, Noda I, et al. Structure, dispersibility, and crystallinity of Poly(hydroxybutyrate)/Poly(L-lactide) blends studied by FT-IR microspectroscopy and differential scanning calorimetry. *Macromolecules* 2005;38(15):6445–54.
- [12] Kikkawa Y, Suzuki T, Tsuge T, Kanesato M, Doi Y, Abe H. Phase structure and enzymatic degradation of Poly(L-lactide)/Atactic poly(3-hydroxybutyrate) blends: an atomic force microscopy study. *Biomacromolecules* 2006;7(6):1921–8.
- [13] Na Y-H, He Y, Shuai X, Kikkawa Y, Doi Y, Inoue Y. Compatibilization effect of poly(epsilon-caprolactone)-b-poly(ethylene glycol) block copolymers and phase morphology analysis in immiscible poly(lactide)/poly(epsilon-caprolactone) blends. *Biomacromolecules* 2002;3(6):1179–86.
- [14] Shibata M, Inoue Y, Miyoshi M. Mechanical properties, morphology, and crystallization behavior of blends of poly(L-lactide) with poly(butylene succinate-co-L-lactate) and poly(butylene succinate). *Polymer* 2006;47(10):3557–64.
- [15] Liu T-Y, Lin W-C, Yang M-C, Chen S-Y. Miscibility, thermal characterization and crystallization of poly(L-lactide) and poly(tetramethylene adipate-co-terephthalate) blend membranes. *Polymer* 2005;46(26):12586–94.
- [16] Jiang L, Wolcott MP, Zhang J. Study of biodegradable polylactide/poly(butylene adipate-co-terephthalate) blends. *Biomacromolecules* 2006;7(1):199–207.
- [17] Coltelli M-B, Della Maggiore I, Bertoldo M, Signori F, Bronco S, Ciardelli F. Poly(lactic acid) properties as a consequence of poly(butylene adipate-co-terephthalate) blending and acetyl tributyl citrate plasticization. *Journal of Applied Polymer Science* 2008;110(2):1250–62.
- [18] Signori F, Coltelli M-B, Bronco S. Thermal degradation of poly(lactic acid) (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) and their blends upon melt processing. *Polymer Degradation and Stability* 2009;94(1):74–82.
- [19] Wang L, Ma W, Gross RA, McCarthy SP. Reactive compatibilization of biodegradable blends of poly(lactic acid) and poly(epsilon-caprolactone). *Polymer Degradation and Stability* 1998;59(1–3):161–8.
- [20] Coltelli M-B, Aglietto M, Ciardelli F. Influence of the transesterification catalyst structure on the reactive compatibilization and properties of poly(ethylene terephthalate) (PET)/dibutyl succinate functionalized poly(ethylene) blends. *European Polymer Journal* 2008;44(5):1512–24.
- [21] Coltelli M-B, Bianchi S, Aglietto M. Poly(ethylene terephthalate) (PET) degradation during the Zn catalyzed transesterification with dibutyl maleate functionalized polyolefins. *Polymer* 2007;48(5):1276–86.
- [22] Coltelli M-B, Bianchi S, Savi S, Liuzzo V, Aglietto M. Metal catalysis to improve compatibility at PO/PET blends interfaces. *Macromolecular Symposia* 2003;204:227–36.
- [23] Coltelli M-B, Savi S, Della Maggiore I, Liuzzo V, Aglietto M, Ciardelli F. A model study of Ti(OBu)₄ catalyzed reactions during reactive blending of polyethylene (PE) and poly(ethylene terephthalate) (PET). *Macromolecular Materials and Engineering* 2004;289(5):400–12.
- [24] Coltelli M-B, Della Maggiore I, Savi S, Aglietto M, Ciardelli F. Modified styrene-butadiene-styrene block copolymer as compatibilizer precursor in poly(ethylene)/poly(ethylene terephthalate) blends. *Polymer Degradation and Stability* 2005;90(2):211–23.
- [25] Coltelli M-B, Harrats C, Aglietto M, Groeninckx G. Influence of compatibilizer precursor structure on the phase distribution of low density poly(ethylene) in a poly(ethylene terephthalate) matrix. *Polymer Engineering and Science* 2008;48(7):1424–33.
- [26] Gallardo A, San Roman J, Dijkstra PJ, Feijen J. Random polyester transesterification: prediction of molecular weight and MW distribution. *Macromolecules* 1998;31(21):7187–94.
- [27] Slivniak R, Domb AJ. Lactic acid and ricinoleic acid based copolyesters. *Macromolecules* 2005;38(13):5545–53.
- [28] Slivniak R, Ezra A, Domb AJ. Hydrolytic degradation and drug release of ricinoleic acid-lactic acid copolyesters. *Pharmaceutical Research* 2006;23(6):1306–12.
- [29] Slivniak R, Langer R, Domb AJ. Lactic and ricinoleic acid based copolyesters stereocomplexation. *Macromolecules* 2005;38(13):5634–9.
- [30] Coullerez G, Lowe C, Pechy P, Kausch HH, Hilborn J. Synthesis of acrylate functional telechelic poly(lactic acid) oligomer by transesterification. *Journal of Materials Science: Materials in Medicine* 2000;11(8):505–10.
- [31] Harada M, Iida K, Okamoto K, Hayashi H, Hirano K. Reactive compatibilization of biodegradable poly(lactic acid)/poly(epsilon-caprolactone) blends with reactive processing agents. *Polymer Engineering and Science* 2008;48(7):1359–68.
- [32] Shieh Y-T, Lin Y-T. Transesterification and polymerization reactions of aliphatic polyesters in supercritical CO₂ fluids without the presence of a catalyst. *European Polymer Journal* 2007;43(5):1847–56.
- [33] Stevels WM, Ankone MJK, Dijkstra PJ, Feijen J. Well-defined block copolymers of epsilon-caprolactone and L-lactide using Y5(micro-O)(OiPr)₁₃ as an initiator. *Macromolecular Chemistry and Physics* 1995;196(4):1153–61.
- [34] Schreck KM, Hillmyer MA. Block copolymers and melt blends of polylactide with Nodax microbial polyesters: preparation and mechanical properties. *Journal of Biotechnology* 2007;132(3):287–95.
- [35] Albertsson A-C, Varma IK. Recent developments in ring opening polymerization of lactones for biomedical applications. *Biomacromolecules* 2003;4(6):1466–86.
- [36] Dechy-Cabaret O, Martin-Vaca B, Bourissou D. Controlled ring-opening polymerization of lactide and glycolide. *Chemical Reviews* 2004;104(12):6147–76.
- [37] Degee P, Dubois P, Jacobsen S, Fritz HG, Jerome R. Beneficial effect of triphenylphosphine on the bulk polymerization of L, L-lactide promoted by 2-ethylhexanoic acid tin(II) salt. *Journal of Polymer Science, Part A: Polymer Chemistry* 1999;37(14):2413–20.
- [38] Flory PJ. Random reorganization of molecular-weight distribution in linear condensation polymers. *Journal of the American Chemical Society* 1942;64:2205–12.
- [39] Loyens W, Groeninckx G. Deformation mechanisms in rubber toughened semicrystalline polyethylene terephthalate. *Polymer* 2003;44(17):4929–41.
- [40] Wu S. Impact fracture mechanisms in polymer blends: rubber-toughened nylon. *Journal of Polymer Science, Polymer Physics Edition* 1983;21(5):699–716.
- [41] Wu S. Phase structure and adhesion in polymer blends: a criterion for rubber toughening. *Polymer* 1985;26(12):1855–63.
- [42] Wu S. A generalized criterion for rubber toughening: the critical matrix ligament thickness. *Journal of Applied Polymer Science* 1988;35(2):549–61.
- [43] Koning C, Van Duin M, Pagnoulle C, Jerome R. Strategies for compatibilization of polymer blends. *Progress in Polymer Science* 1998;23(4):707–57.
- [44] de Jong SJ, Arias ER, Rijkers DTS, van Nostrum CF, Kettenes-van den Bosch JJ, Hennink WE. New insights into the hydrolytic degradation of poly(lactic acid): participation of the alcohol terminus. *Polymer* 2001;42:2795–802.