

Biocomposites Based on Lignin and Plasticized Poly(L-lactic acid)

Mohammed Arifur Rahman,^{1,2} Diego De Santis,¹ Gloria Spagnoli,¹ Giorgio Ramorino,¹ Maurizio Penco,¹ Vu Thanh Phuong,² Andrea Lazzeri²

¹Department of Mechanical and Industrial Engineering, University of Brescia, Brescia, Italy 25121

²Department of Chemical Engineering, Industrial Chemistry and Materials Science, University of Pisa, Pisa, Italy 56126

Correspondence to: A. Lazzeri (E-mail: a.lazzeri@ing.unipi.it)

ABSTRACT: In this research work, biocomposites based on a ternary system containing softwood Kraft lignin (Indulin AT), poly-L-lactic acid (PLLA) and polyethylene glycol (PEG) have been developed. Two binary systems based on PLLA/PEG and PLLA/lignin have also been studied to understand the role of plasticizer (i.e., PEG) and filler (i.e., lignin) on the overall physicomechanical behavior of PLLA. All samples have been prepared by melt-blending. A novel approach has also been introduced to improve the compatibility between PLLA and PEG by using a transesterification catalyst under reactive-mixing conditions. In PEG plasticized PLLA flexibility increases with increasing content of PEG and no significant effect of the molecular weight of PEG on the flexibility of PLLA has been observed. Differential scanning calorimetry and size-exclusion chromatography along with FTIR analysis show the formation of PLLA-*b*-PEG copolymer for high temperature processed PLLA/PEG systems. On the other hand, binary systems containing lignin show higher stiffness than PLLA/PEG system and good adhesion between the particles and the matrix has been observed by scanning electron microscopy. However, a concomitant good balance in stiffness introduced by the lignin particles and flexibility introduced by PEG has been observed in the ternary systems. This study also showed that high temperature reactive melt-blending of PLLA/PEG leads to the formation of a segmented PLLA-*b*-PEG block copolymer. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 202–214, 2013

KEYWORDS: Composites; biopolymers and renewable polymers; polyesters; polymer blends; mechanical properties

Received 9 February 2012; accepted 7 October 2012; published online 6 November 2012

DOI: 10.1002/app.38705

INTRODUCTION

Poly-L-lactic acid is a promising biodegradable polymer based on natural resources which is receiving increasing attention both in the scientific literature and in industrial applications. Compared to conventional oil-based plastics its cost is still relatively high. Together with its higher density, in relation to polyolefins, this limits possible large scale applications. One of the possible options to limit its cost is to blend PLLA with some filler.

Among possible fillers, lignin is particularly interesting because it is a byproduct of important process like paper or biodiesel production. Lignin is a natural polymer found in wood and in the secondary cell walls of plants and some algae. It results from oxidative coupling of primarily 4-hydroxyphenylpropanoids (coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol), therefore is the second most abundant biopolymer on Earth.¹ Because of its poly-disperse polyphenolic structure, with no extended sequences of regularly repeating units and variable degree of polymerization, there may be no two identical lignin macromolecules with the same primary sequence of phenyl units. Therefore, most often

these biopolymers are referred to in the plural as “lignins.” Because of its polyphenolic structure lignin shows antimicrobial¹ and antioxidant^{2,3} properties which along with the excellent mechanical properties of PLLA^{4,5} can be very useful for applications like packaging with improved shelf-life.

Lignin and its derivatives have been used in making composites and coatings because of its particle size, hydrophobicity, and ability to form stable mixtures. The most common application is the use of lignin as a filler material in thermoplastics^{6–9} and thermosetting^{10,11} polymers and rubbers¹² with limited positive to negative effects on mechanical properties. However, the heterogeneity in its molecular size, bond energies, and functional group distribution are significant complicating factors for lignin.²

Commercially available lignins resulting from industrial delignification processes, also known as technical lignins, can be divided into two categories. The first category includes the sulfur-free lignins, which are the technical lignins that resemble more closely to the original structure of native lignins. Sulfur-free lignins are mainly obtained from three sources: biomass conversion technologies mainly focused on biofuel production; organosolve pulping

This article is dedicated to Professor Maurizio Penco, originally the corresponding author, who passed away during the final stages of the preparation of the manuscript.

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processes; and soda pulping based on alternative resources like agricultural residues and nonwood fibers.¹³

The second category consists on the sulfur containing lignins, which result essentially from Kraft (Kraft lignins) and sulfite pulping processes (lignosulfonates, or sulfonated lignins). This category comprises almost the totality of the market of commercially available lignins.

Kraft lignins have number average molecular weight (M_n) in the range of 2000–3000, polydispersities between 2 and 3 and a sulfur content of 1–1.5% while lignosulfonates are characterized by a molecular polydispersity much higher than Kraft lignins, and their M_n is normally in the interval of 20,000 to 50,000 with a sulfur content of 4–8%.¹⁴ Kraft lignins exhibit maximum solubility in solvents having a Hildebrand's solubility parameter, δ , of 20.5–22.5 (MPa)^{1/2}.

In this work a commercial softwood Kraft lignin—Indulin AT—was chosen because it has been well characterized in the scientific literature and for its availability in large quantities.

On the other hand, poly-L-lactic acid (PLLA) —[CH(CH₃)COO]_n— is a biodegradable and semicrystalline polymer, depending on the molding conditions, that can be produced from renewable resources, such as corn.^{3,4} Its glass transition temperature is about 60°C with a melting point of 160°C. Unmodified PLLA is characterized by a high stiffness and its main limitations consist in high brittleness, a low heat distortion temperature, and slow crystallization rates.^{3,4} To increase the processability and flexibility of PLLA different types of plasticizers have been used.^{15,16} Polyethylene glycol is one of the most widely studied plasticizers for PLLA.^{17–20} Usually, the plasticization effect is enhanced by higher PEG content, however, systems of PLLA with PEG undergo phase separation at a certain PEG content, depending on PEG molecular weight.²⁰ One of the reasons of instability of PLLA/PEG systems is crystallization of PEG that depletes the amorphous phase of the plasticizer.¹⁹ On the other hand, several articles report the development of flexible composites based on blends of PLLA with flexible polymers such as poly(ϵ -caprolactone) (PCL), poly(butylene succinate) (PBS), and poly(butylene succinate adipate) (PBSA) to achieve a higher elongation and flexibility.^{21–23} The use of natural fillers such as cellulose, kenaf fiber, bamboo-flour, wood flour with a plasticized polymer matrix has also been investigated in several research works.^{24–28} Although the difference in chemical structure of PLLA and lignin might suggest little or no solubility between the two polymers, leading to phase separation during mixing, the presence of hydroxyl groups in lignin and of ester groups in PLLA can give rise to specific interactions that can lead to a good adhesion between the two phases. On the other hand PLLA is a very stiff and brittle polymer so the addition of fillers will make it even more brittle. For this reason it needs to be plasticized to compensate for the effect of the fillers and find a balance between cost and overall mechanical properties.

However, flexible biocomposites based on plasticized PLLA and lignin found very scant attention by the researchers.

In this work, PEG with different molecular weights and contents have been used to plasticize PLLA and its lignin filled composites. It is important to mention here that even if an important benefit

can be achieved in the flexibility of the composites, PEG can still be leached away if it comes in contact with aqueous media. The dissolution of the plasticizing agent in water can be strongly reduced if interexchange reactions between starting PLLA and PEG are promoted to obtain some amount of PLLA-PEG block copolymers. In particular, reactive blending could be a simple method for obtaining such result. Until now, very few papers²⁹ have been reported on lignin filled PLLA composites.

This research work deals with the development of biocomposites based on plasticized PLLA filled with lignin. Two different binary systems of PLLA/PEG and PLLA/lignin have been studied to better understand the role of plasticization in ternary system of PLLA/PEG/lignin. Both reactive and nonreactive melt-mixing conditions have been used to prepare all the samples. A novel approach has also been introduced to improve the compatibility between PLLA and PEG by using a transesterification catalyst under reactive-mixing conditions and the effects of this addition on the thermal and mechanical behavior of the composites have been investigated.

The effect of processing temperatures on the overall thermal and mechanical behavior of the composites has also been studied. The thermal and thermo-mechanical behaviors of the composites have been determined by DSC and DMTA, respectively. The flexibility of the composites has been evaluated by mechanical testing and a morphological characterization of has been carried out by scanning electron microscopy to examine the specimens after they had been cryogenically fractured to reveal their internal structure. A water leaching test has also been carried out to observe the dissolution of PEG from the samples and its effect on the degradation behavior of the composites.

EXPERIMENTAL

Materials

Indulin AT, a commercially available purified powder form of pine kraft lignin produced by acid precipitation of black liquor, was purchased from MeadWestvaco Corporation, Charleston Heights, SC. Indulin AT is derived by further acid hydrolysis of kraft lignin, which removes both the sodium and the hemicelluloses. However, it still contains the covalently bound sulfur originating from the kraft process resulting in a ash content of 1.59%.³⁰ This type of softwood Kraft lignin has a number average molecular weight $M_n = 1580$ Da, a weight average molecular weight $M_w = 6060$ Da ($M_w/M_n = 3.83$) and a $T_g = 171$ °C.³¹ Indulin AT has a specific density of 1.238 g·cm⁻³ and an average particle size of 8 μ m.

Poly-L-lactic acid was purchased from NatureWorks LLC having a nominal average molecular weight $M_w = 199,590$ Da (NatureWorks® Ingeo™ 2002D Extrusion Grade). Polyethylene glycol (PEG) with three different average molecular weight of 4000, 6000, and 8000 Da were purchased from Sigma–Aldrich. Tetra-butyl ammonium tetraphenylborate (TBATPB), a transesterification catalyst, was supplied by Sigma–Aldrich. Methanol and chloroform were purchased from Sigma–Aldrich.

Solubility Test and Viscosity Measurements of Lignin

To test the solubility of lignin, some organic solvents such as *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), chloroform (CHCl₃), dimethyl sulfoxide (DMSO), acetonitrile

(ACN), and toluene were used. For each solvent, the same concentration of solution was prepared for each solvent (10 mg·mL⁻¹). The test was performed at 25°C under magnetic stirring for 48 h to 1 week.

Intrinsic viscosity measurements were carried out on lignin solutions in DMF using a capillary Ubbelohde viscometer at 30°C. For each samples three solutions at different concentration were prepared by adding 1–2 g of lignin in 10 mL of solvent. Intrinsic viscosities were obtained using the following equation:

$$\text{Intrinsic viscosity, } [M_i] = 1/c \sqrt{2} (M_{\text{spe}} - \ln M_{\text{rel}})$$

where M_{spe} is the specific viscosity = $(T_1 - T_0)/T_0$, M_{rel} is the relative viscosity = T_1/T_0

Here, T_0 is the traveling time of solvent (DMF) and T_1 is the traveling time of lignin solution.

Preparation of Blends and Composite Materials

Poly-L-lactic acid and lignin were dried at 80°C under vacuum (1 mmHg) for 2 days before the use. Also the samples of PEG were dried for 3 days at room temperature in vacuum dessicator containing P₂O₅. A discontinuous mixing machine (Brabender Plastograph, Germany), having a mixing chamber with a total volume of 50 cm³. was used screw speed of 30–80 rpm and two different mixing temperatures of 160 and 200°C were used to prepare the binary systems. Ternary systems containing lignin were prepared at the same screw speed profile but mixed at 160°C. All samples were recovered from the mixing chamber and were kept in a vacuum at 80°C for 48 h before preparing sheets using a laboratory compression molding machine (Collin, P200E). Small pieces of blend materials were sandwiched between aluminum sheets with programmed temperature, pressure and residual time condition. Two different temperatures (180 °C and 200 °C) were used to prepare the sheets in the compression molding machine. The samples were then cooled at 25°C for 7 min. All samples were dried 72 h under vacuum before preparing specimens for tests.

Size-Exclusion Chromatography

Molecular weight distributions (MWD) were determined by size exclusion chromatography (SEC); an Erma instrument equipped with Shodex KF columns and Knauer RI detector, with tetrahydrofuran (THF) as eluent (1 mL·min⁻¹), was used. The values of M_w and M_n were calculated relative to polystyrene standards (Polymer Laboratories, Shropshire, UK).

Fractionation Test of PLLA/PEG System

PLLA/PEG system was fractionated using chloroform as solvent and methanol as nonsolvent. Dissolution and precipitation steps were performed using solvent/nonsolvent mixtures giving three fractions. At first, PLLA/PEG blend (3 g) was dissolved in 1 : 3 CHCl₃/MeOH mixtures (12 g). After complete dissolution, additional MeOH (4 g) was added. A white insoluble product was formed which was separated by filtration and repeatedly washed with MeOH. This constitutes the first fraction. Then again MeOH (4 g) was added to the remaining filtered solution and subsequently the separated solid was isolated as described above. Thus a second fraction was obtained. The final fraction (i.e., third fraction) was obtained in the same way by adding more MeOH. All the fractions

were dried in a vacuum dessicator. Fractionation was repeated three times for each sample. Each fraction obtained was analyzed subsequently with a Jasco FT/IR-300E infrared spectrometer. Samples of the blends for the FTIR investigation were dissolved in chloroform. Drop casting of the fractionated solution was used to analyze the FTIR of different fractions. The FTIR of the samples was performed in the wave number range 400–4000 cm⁻¹ and the spectrum was taken in transmittance mode. Moreover, ATR-FTIR was used to analyze chemical structure of blend films. The spectra of the blend films were recorded at a range of 650–4000 cm⁻¹ with 256 scan at a resolution of 2 cm⁻¹.

Dynamic Mechanical Thermal Analysis (DMTA)

All specimens were conditioned at 80°C for 24 h in a vacuum oven prior to testing. DMTA was conducted using a Rheometrics Scientific MkII DMTA apparatus (Reichelsheim, Germany) in three-point-bending on samples of 30 × 8 × 2 mm³ in size. The samples were scanned from -100°C to +100°C at 2°C min⁻¹ with oscillation frequency of 10 Hz.

Differential scanning calorimetry (DSC)

Thermal analysis was performed in nitrogen atmosphere (50 mL min⁻¹) with a TA Instrument differential scanning calorimeter (mod. Q100, USA) on a sample of 7.5 ± 0.3 mg, employing a constant heating rate of 10°C min⁻¹. The T_g is taken as the inflection point of the change in heat capacity versus temperature on the second scan between 25 and 190°C.

Mechanical Properties

To perform the tensile test the samples were dried at 80°C in a vacuum oven for 24 h. Mechanical tests were performed by an Instron dynamometer (mod. 3366) at room temperature and at a crosshead rate of 10 mm min⁻¹ (nominal strain rate of 0.1 min⁻¹) on specimens of 100 mm length (distance between grips of about 60 mm) and 10 mm width. ASTM D638 was followed for the tensile test and five replicates were tested for each sample to obtain an average value.

Water Leaching Test

Specimens having a dimension of 40 × 10 × 2 mm³ were maintained in contact with 10 mL of distilled water having a pH of 7.1 at 25°C for 10 days. The PEG release behavior of each specimen was studied by evaluating their water absorption or weight loss profile over time. Total weight variation (W_v) was determined for each sample to better understand their absorption or leaching behavior, by using the following equation:

$$W_v\% = 100(W_t - W_o)/W_o$$

where W_o and W_t are respectively the initial dry weight and the residual weight at time t of the sample, after wiping the surface.³²

Because in the samples where PEG was leached to the water solution, the resulting weight loss is partially obliterated by the concomitant water uptake and, on the contrary, in the samples where a significant water absorption, giving rise to an increase in weight, could partially mask the possible accompanying PEG leaching, the total dry weight loss was also calculated. Therefore after the leaching test, all samples were dried at 80°C for 48 h under vacuum and weighted again to determine the total weight

Table I. Compositions of Binary and Ternary Systems Containing Lignin, PLLA, and PEG and their Processing Conditions

Compositions			Mixing conditions		
PLLA (wt%)	PEG (wt%)		M_n of PEG	Mixing temperatures (°C)	Catalyst (wt%)
a) Binary blends of PLLA/PEG					
100	-		-	-	-
85	15		4000	160	-
85	15		4000	160	0.15%
80	20		4000	160	-
80	20		4000	160	0.15%
85	15		4000	200	-
85	15		4000	200	0.15%
80	20		4000	200	-
80	20		4000	200	0.15%
70	30		4000	160	-
70	30		4000	160	0.15%
70	30		6000	160	-
70	30		6000	160	0.15%
70	30		8000	160	-
70	30		8000	160	0.15%
b) Binary blends of PLLA/lignin					
85	15		-	160	-
85	15		-	160	0.15%
85	15		-	200	-
85	15		-	200	0.15%
c) Ternary system of PLLA/PEG/lignin					
PLLA ^a (wt%)	PEG ^b (wt%)	Lignin ^c (wt%)			
59.5	25.5	15	4000	160	-
59.5	25.5	15	4000	160	0.15%
59.5	25.5	15	6000	160	-
59.5	25.5	15	6000	160	0.15%
59.5	25.5	15	8000	160	-
59.5	25.5	15	8000	160	0.15%

^{a,b}The weight ratio of PLLA/PEG was maintained 70/30 (w/w) in all compositions of ternary blends.

^cThe lignin content was selected as 15 wt% with respect to the total polymer content (i.e., 85 wt% (PLLA/PEG)).

loss respect to the initial specimen due to determine the amount of PEG dissolved into the water phase.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy was used to examine the phase structure of the systems using a LEO EVO 40 scanning electron microscope. The compression molded specimens were cryofractured in transverse direction of the specimen. Samples were mounted with carbon tape on aluminum stubs and then sputter coated with gold to make them conductive prior to SEM observation.

RESULTS AND DISCUSSION

The majority of the ternary systems containing fillers possess a multiphase morphology and mechanical and physical properties which are strongly correlated to the behavior of the interfacial

region between polymer and filler. The mechanical behavior of the lignin based ternary systems has been discussed in the following by making a comparison with the corresponding binary systems. The aim of the discussion here is to analyze the evolution of flexibility in lignin-based biocomposites by observing their thermal and mechanical properties in relation to the morphology of these systems.

PLLA/PEG Binary Systems

The binary systems of PLLA/PEG were prepared by melt mixing using three different average molecular weights of PEG at a composition range of 15–30 wt%. In Table I compositions and melt mixing conditions of all systems are summarized.

The first goal was to study the compatibility and the related plasticization effect of PEG on PLLA in relation to their thermal and mechanical properties obtained by differential scanning

Table II. Calorimetric Data for PLLA/PEG Blends

Compositions		M_n of PEG (Da)	TBATPB (wt%)	T_{mix} (°C)	T_m PEG phase (°C)	ΔH PEG phase (normalized) J·g ⁻¹	T_m PLLA phase (°C)	ΔH PLLA phase (normalized) J·g ⁻¹
PLLA (wt%)	PEG (wt%)							
100	-	-					151.5	41.87
-	100	4000			57.16; 61.40	175.9		
-	100	6000			62.68	171.6		
-	100	8000			61.46	184.3		
85	15	4000	0	160	-	-	153.24	33.95
85	15	4000	0.15	160	56.89	14.5	154.25	34.49
80	20	4000	0	160	51.42	38.04	152.66	35.91
80	20	4000	0.15	160	49.16	13.77	153.92	41.85
70	30	4000	0	160	52.25	61.67	153.86	39.46
70	30	4000	0.15	160	55.23	72.17	155.68	43.58
70	30	6000	0	160	-	-	153.67	43.33
70	30	6000	0.15	160	56.02	84.67	154.74	39.90
70	30	8000	0	160	51.00	43.13	153.32	42.58
70	30	8000	0.15	160	57.71	66.63	155.99	40.01
85	15	4000	0	200	-	-	152.96	37.99
85	15	4000	0.15	200	-	-	153.46	36.92
80	20	4000	0	200	-	-	152.31	40.51
80	20	4000	0.15	200	49.49	5.815	153.32	40.91

Note: All the data reported here have been taken from the second heating scan of DSC.

calorimetry (DSC) and tensile testing as reported in Tables II and III, respectively. In particular, the melting point and fusion enthalpy (ΔH) of PEG and PLLA are reported in Table II, in fact, these systems generally show two fusion peaks at about 55 and 155°C due to the crystalline phases of PEG and PLLA, respectively. However, the 15 wt% PEG containing systems do not show any significant melting peak for the PEG phase. The glass transition temperature of PEG could not be detected possibly due to its high degree of crystallinity. Moreover, there exists a complex transition phenomenon regarding the T_g and T_m in PLLA/PEG systems since the melting peak for PEG occurs over a temperature range which is close to the T_g of PLLA. This is why it is difficult to evaluate the compatibility of the systems on the basis of their shifting values of T_g .

However, the variations in melting point (T_m) of the PLLA phase can give some significant information about the compatibility in the systems. In any case, the concomitant presence of the two crystalline phases clearly shows that partial or complete immiscibility exist between PLLA and PEG for the range of molar masses considered. This is in agreement with the results obtained by a simple solubility prevision scheme based on the Flory–Huggins theory developed by Sonja Krause.³³ In particular the parameter $\chi_{AB} - (\chi_{AB})_{cr}$ is computed as follows:

$$\chi_{AB} = (\delta_A - \delta_B)^2 \frac{V_R}{RT} \quad (1)$$

where δ_A and δ_B are the Hildebrand parameters computed by using the group contribution table proposed by Hoy,³⁴ and:

$$(\chi_{AB})_{cr} = \frac{[1/\chi_A^{1/2} | 1/\chi_B^{1/2}]^2}{2} \quad (2)$$

with χ_A and χ_B the number average polymerization degrees for polymers A and B, respectively.

The trend of $(\chi_{AB} - (\chi_{AB})_{cr})$ parameter versus molar mass of PEG (for a PLLA with $M_n = 200,000$ Da and also a comparison made for PLLA with lower $M_n = 10,000$ Da) is shown in Figure 1. A negative value suggests that some miscibility can exist, but this occurs only for PEG with M_n lower than 1000 Da.

In contrast with these predictions, it has to be noted that in the literature it has been reported that macroscopic phase separation occurred at 20 wt% for PEG200 and 30 wt% for PEG400. The limited solubility of the PEGs with lower M_n has been attributed to a more remarkably enhanced crystallization of PLA in the presence of PEGs.²⁴

The effect of composition on the overall thermal properties of PLLA/PEG systems can also be seen in Table II. It is evident that varying amount of PEG as well as their molecular weight does not significantly affect the melting point (T_m) of the PLLA phase (Table II). In addition to this, the degree of crystallinity is affected by the presence of PEG as the ΔH_m for the PLLA phase varies in the range of 33–44 J·g⁻¹. On the other hand, a slight decrease in T_m of the PEG phase is observed for higher molecular weight PEG. For example, the T_m of PEG4000 and PEG8000 are 52.3 and 51.0°C, respectively. Moreover, the crystallinity of PEG phase shows a composition-dependent behavior since the enthalpy of fusion for PEG phase increases with increasing its content in the blends. On the other hand, no

Table III. Mechanical Properties of PLLA/PEG Blends

Compositions		TBATPB (wt%)	T_{mix} (°C)	Young's modulus (GPa)	Yield stress (MPa)	Tensile strength (MPa)	Elongation at break (%)
PLLA (wt%)	PEG (4000 Da) (wt%)						
100	-	-	-	2.34 ± 0.13	68.8 ± 3.5		4.1 ± 0.9
85	15	0.15	160	0.95 ± 0.15	26.5 ± 2.7		40 ± 3.8
85	15	-	160	1.05 ± 0.11	26.1 ± 4.1		25 ± 1.9
85	15	0.15	200	1.05 ± 0.07	24.8 ± 1.9		3 ± 1.5
85	15	-	200	1.02 ± 0.08	26.2 ± 2.2		3.5 ± 1.2
80	20	0.15	160	0.53 ± 0.09	16.3 ± 1.5		72.6 ± 4.2
80	20	-	160	0.52 ± 0.1	15.2 ± 1.1		130 ± 8.6
80	20	0.15	200	0.52 ± 0.13	17.1 ± 2.3		68.5 ± 7.2
80	20	-	200	0.56 ± 0.09	17 ± 1.65		62 ± 5.4
70	30	0.15	160	0.26 ± 0.07	7.3 ± 0.7	9.6 ± 0.8	45 ± 3.6
70	30	-	160	0.17 ± 0.08	6.9 ± 0.5	10.1 ± 1.2	100 ± 7.5
PLLA (wt%) PEG (6000 Da) (wt%)							
70	30	0.15	160	0.28 ± 0.1	7.2 ± 1.2	9.7 ± 0.7	75.5 ± 6.3
70	30	-	160	0.26 ± 0.09	6.8 ± 1.1	10.1 ± 1.3	60 ± 8.2
PLLA (wt%) PEG (8000 Da) (wt%)							
70	30	0.15	160	0.24 ± 0.05	7.1 ± 0.9	10 ± 0.8	73.5 ± 4.3
70	30	-	160	0.27 ± 0.08	6.6 ± 0.7	9.1 ± 0.6	65 ± 3.7

appreciable variations are observed in T_m and ΔH_m of the PLLA phase in the systems containing PEG4000. However, significant variations can be observed for the other phase parameters. Although no clear fusion peak can be observed for samples containing 15 wt% PEG, higher PEG containing samples show a considerable fusion peak of the PEG phase (Figure 2). This suggests that a macroscopic phase separation occurred between 15 and 20 wt% PEG4000. Table III shows the mechanical properties of PLLA/PEG systems. It can be noticed that even the sample with 15 wt% PEG produces a strong decrease in the Young's modulus of PLLA. In fact, the value of Young's modulus measured

for unmodified PLLA is 2.34 GPa, while the 15 wt% PEG containing PLLA shows a modulus of 1.05 GPa. It is obvious that the elastic modulus of PLLA decreases with increasing PEG content in the systems. The postyield behavior is also modified by the content of PEG. Pure PLLA and its blends with PEG up to a content of 20 wt% show plastic instability and a clear necking phenomenon (Figure 3). On the contrary, the samples containing 30 wt% do not show necking (uniform yielding) and continue to deform after yielding only by increasing the stress level (strain hardening). It has been observed that the transition from necking to uniform yielding depends on a balance between strain softening and strain hardening.³⁵ Thus, it appears that PEG has a larger effect on the strain softening rather than on

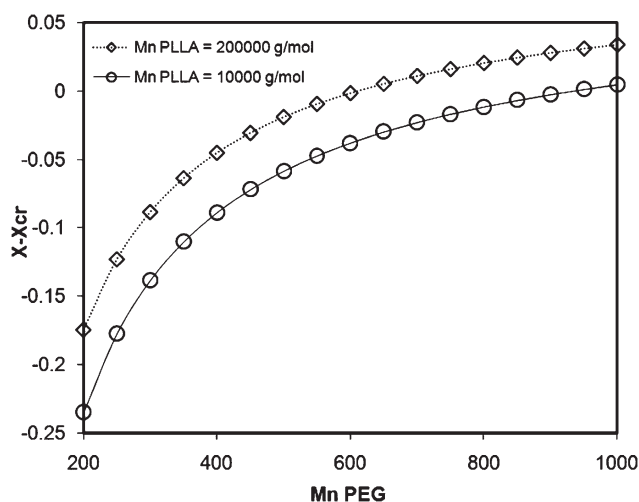


Figure 1. PLLA-PEG Compatibility curve using Hildebrand solubility parameter.

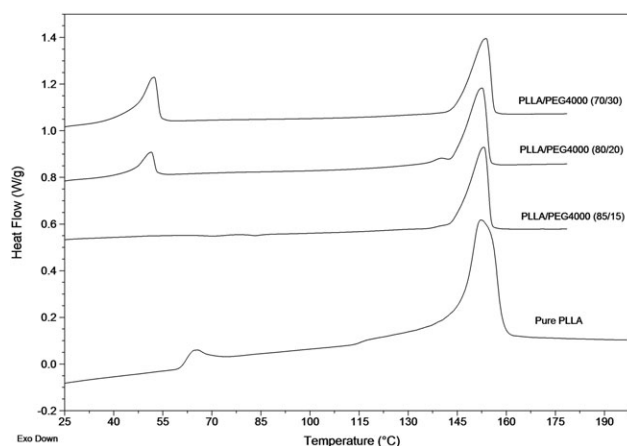


Figure 2. DSC Thermograms showing composition dependent phase structure of PLLA/PEG systems containing 15–30 wt% of PEG4000.

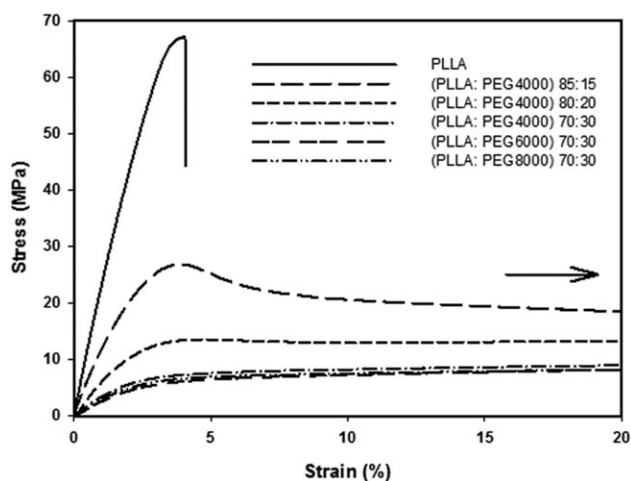


Figure 3. Transition from necking to uniform yielding behavior on increasing PEG content.

the strain hardening behavior. Moreover, the elongation at break increases with increasing PEG content. Thus, flexible PLLA was obtained by using oligomeric PEG. It is also important to note here that all systems appear to have good optical clarity even if the DSC data reveal the presence of two crystalline phases in the systems.

The morphology of the PLLA/PEG system was further analyzed by scanning electron microscopy. Figure 4(a,b) shows scanning electron micrographs of the systems containing 15 and 30 wt% of PEG, respectively. In case of lower PEG content (15 wt%) the surface appears rather uniform without clear evidence of secondary phases. However, a rougher surface morphology can be observed in the higher PEG containing samples, which could be associated to the presence of two separate phases as evidenced in the DSC study for the 30 wt% PEG containing systems. Although some miscibility has been observed for high temperature processed blends, incompatibility exists in the low temperature and nonreactive processed PLLA/PEG systems. Thus the high plasticizer content along with incompatible phase structure introduces ductility in the PLLA matrix while drastically diminishing either the mechanical properties like Young's modulus and yield stress of the blends.

Another important concern of this research was to avoid the loss of PEG in the ternary systems when exposed to aqueous media. The dissolution of this plasticizing agent can be strongly reduced if an interchange reaction can take place between PLLA and PEG or by obtaining some amount of PLLA/PEG segmented copolymer.

There are several articles that report the formation of segmented block copolymers during melt-blending of PLLA and PEG by a transesterification reaction.³⁶ In fact, this transesterification reaction occurs in definite ranges of mixing conditions. A specific catalyst which is active to promote interchange reactions can be used for promoting copolymer formation at lower temperatures.^{36,37} In any case, the hydrolytic degradation with decrement of the PLLA molar mass is always a competitive side reaction. The effect of the processing conditions on copolymer

formation and on the molar mass of the system components has been investigated with a fractionation method from polymeric solution coupled with infrared spectroscopy (FTIR), and size exclusion chromatography (SEC). Molar mass data for all materials studied (starting polymers and blends) are summarized in Table IV. The systems prepared at lower temperature (160°C) without catalyst do not reveal the presence of significant amounts of segmented copolymer and a limited decrease in the molar mass can be noticed. If the same amount of catalyst is added at the same mixing temperature (i.e., 160°C) only a hydrolytic reaction can occur which is also responsible for the decrease of molecular weight of the PLLA fraction. However, this situation is not observed for 15 and 30 wt% PEG4000 and also for 30 wt% PEG8000 containing systems where higher M_n could be measured in the presence of the catalyst. This suggests an increase in molar mass that can occur during mixing. These competitive reactions leading to either increasing molar mass or degradation are strongly controlled by the moisture content of polymers. In fact, it is not quite easy to control and maintain a similar water content in the starting PEGs. However, the

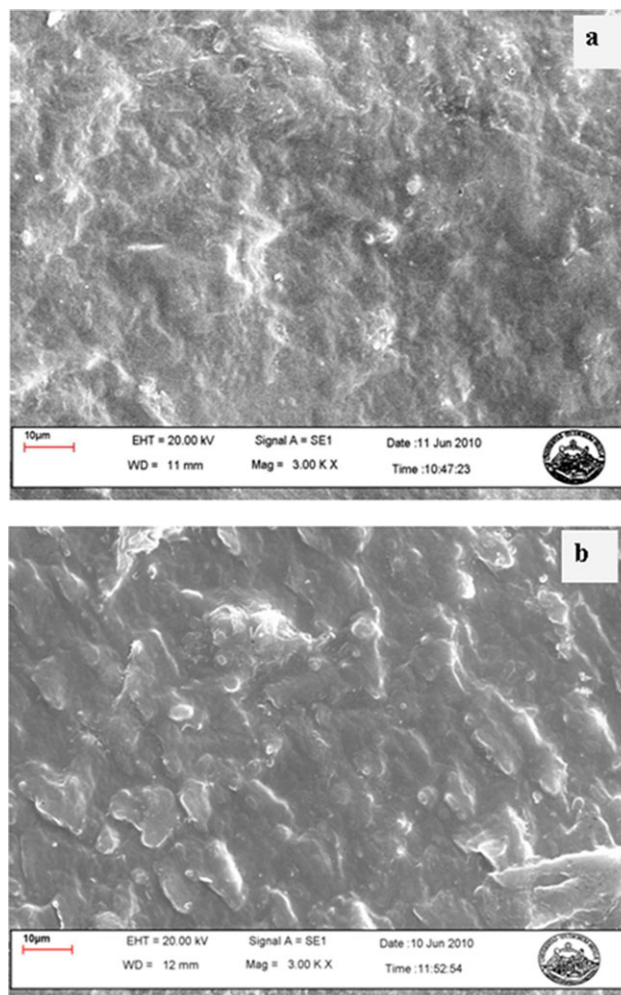


Figure 4. Scanning electron micrographs of 15 wt% (a) and 30 wt% PEG containing PLLA/PEG blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Molar Mass Distribution in PLLA/PEG Blends

Compositions		M_n of PEG (Da)	TBATPB (%)	T_{mix} (°C)	M_n (Da)	M_w (Da)	PDI
PLLA (wt%)	PEG (wt%)						
0	100	4000	-	-	5660	5890	1.04
0	100	6000	-	-	9380	9910	1.06
0	100	8000	-	-	12,400	12,890	1.04
100	0	-	-	-	162,940	199,590	1.2
85	15	4000	0	200	76,290	103,130	1.35
85	15	4000	0.15	200	114,900	143,180	1.25
85	15	4000	0	160	94,690	123,870	1.31
85	15	4000	0.15	160	88,330	116,460	1.32
80	20	4000	0	200	79,270	107,680	1.36
80	20	4000	0.15	200	66,990	91,300	1.36
80	20	4000	0	160	85,380	111,030	1.30
80	20	4000	0.15	160	65,870	88,810	1.35
70	30	4000	0	160	74,610	100,740	1.35
70	30	4000	0.15	160	55,920	73,790	1.32
70	30	6000	0	160	69,940	91,750	1.31
70	30	6000	0.15	160	72,670	94,160	1.30
70	30	8000	0	160	77,660	103,050	1.33
70	30	8000	0.15	160	105,370	125,400	1.19

decrease in molecular weight is the most usual scenario for all PLLA/PEG systems. The DSC and mechanical data (Tables II and III) are in agreement with this general observation. In fact, the higher T_m and ΔH_m of the PLLA phase can be explained with a lower molar mass which makes the polyester phase easier to crystallize. Mechanical data confirm the corresponding increase in the stiffness of the materials. On the contrary, the formation of the block copolymer is observed at higher processing temperature (200°C) with or without catalyst while a decrease in M_n can be also observed in this case. In the fractionation study by FTIR, relative intensities were calculated as the ratio of the intensity of the band at 1757.31 cm^{-1} (C=O stretching of ester) and that at 1130 cm^{-1} (ether stretching). The fractions containing samples prepared at 200°C show a significant intense band at 1130 cm^{-1} associated to the PEG ether band (relative intensity for pure PLLA is 1.6 and for samples prepared at 200°C is 2.0 in the first fraction). Because chloroform and methanol are both good solvents for PEG, the relative intensity of the high temperature processed system clearly confirm the presence of some amount of PEG linked with PLLA segments. This is why the samples prepared at high temperatures contain low molar mass PLLA segments along with some segmented PLLA-b-PEG copolymer, generally reducing the flexibility of the system (Table III).

PLLA/lignin Biocomposites

A binary system of PLLA/lignin was prepared by melt mixing at two different temperatures. It is important to note here that the starting lignin was characterized before preparing the composites on the basis of its molecular behavior. The measured value of the intrinsic viscosity for lignin (0.1 $\text{dL}\cdot\text{g}^{-1}$) indicates a low

molecular weight. Table V shows results of the solubility tests of lignin in different organic solvents together with literature value of Hildebrand solubility parameters of these solvents, as well as for pure PLLA, PEG, and lignin. It should be noticed that only DMF has a good solvent effect on lignin since the Hildebrand parameter is almost the same for each other. Moreover, the large difference in solubility parameter for PLLA and lignin indicates immiscibility between them.

The lignin particles lead to a significant increase in the melt viscosity when blended with PLLA. All these materials appear very brittle and highly stiff as is shown in Table VI. The elastic modulus of these systems slightly increases in comparison to pure PLLA because of the presence of lignin. On the other hand, the catalyst improve the elastic modulus of high temperature processed composites but catalyst has a negative impact (i.e., decrease in elastic modulus) on the elastic modulus at low temperature processing (Table VI). The effect of lignin filler on the T_g of PLLA was analyzed by dynamical mechanical thermal analysis (DMTA) (Figure 6). It should be noticed that the T_g shifts at higher temperatures for the systems prepared at 200°C. This effect is amplified if the catalyst is present. This observation is in agreement with the FTIR analysis of the composites (Figure 5) that indicates the interaction between lignin and PLLA when processed at high temperature (i.e., at 200°C).

The FTIR spectra of pure lignin, pure PLLA and PLLA/lignin system prepared at higher temperature are shown in Figure 5(a). It is evident in the spectra that the intensity of the band near 3400 cm^{-1} , corresponding to stretching of O-H groups present in lignin, decreases significantly in the PLLA/lignin binary system. Because these phenolic hydroxyl groups have

Table V. Solubility of Lignin in Different Organic Solvents

Organic solvents	Hildebrand solubility parameters ^{38,39} (MPa ^{1/2})	Concentration of solution (g·mL ⁻¹)	Solubility of lignin in organic solvents		
			(S)	(PS)	(NS)
<i>N,N</i> -Dimethylformamide (DMF) ³⁸	24.8	0.01	+		
Dimethyl sulfoxide (DMSO) ³⁸	29.7		+		
Tetrahydrofuran (THF) ³⁸	18.6			+	
Chloroform (CHCl ₃) ³⁸	19			+	
Poly(lactic acid) ³⁸	21.0	-			
Poly(ethylene glycol) ³⁸	17.7	-			
Lignin ³⁹	24.6				

S = completely soluble; PS = partially soluble; and NS = not soluble.

strong ability to form hydrogen bonds with the carbonyl groups (1757 cm⁻¹) of PLLA, the formation of hydrogen bonds would induce an obvious shift of the band to lower wave numbers, along with the increase in the intensity of C=O stretching band which is, in fact, evident in the FTIR spectra. In addition to this, the slight increased intensity of the band corresponding to C=O stretching for the PLLA/lignin system in Figure 6(b) (from 1757 to 1752 cm⁻¹) also indicates the presence of intermolecular hydrogen bonding between lignin and PLLA in these systems.

The morphology of the materials was studied by SEM analysis; a typical morphology is shown in Figure 7(a,b). The cryofractured surface of the material shows the features of a brittle material. A good dispersion of lignin particles was observed for all compositions. This is probably a consequence of a good adhesion between the lignin particles and PLLA matrix, related to the polyphenolic structure of lignin and the carboxyl group content of PLLA, as it has been observed for the FTIR analysis [Figure 5(b)]. However, the adhesion improved for the materials processed at higher temperatures [Figure 7(b)] as investigated by FTIR above.

PLLA/PEG/Lignin Biocomposites

Ternary systems containing lignin as a filler with plasticized PLLA have been prepared by melt-mixing. For the ternary systems, 30 wt% PEG has been used as plasticizer of PLLA to compensate for the brittleness introduced by incorporating lignin. Mixing at higher temperatures was not carried out for ternary

systems to avoid the degradation effects with higher amount of PEG that has been observed in the binary system PLLA/PEG.

Table VII shows the mechanical properties of the ternary system. It is noticeable that all the materials show some level of flexibility (7–13% of elongation) but comparing with PLLA/PEG binary blends containing the same amount of PEG, the flexibility of ternary systems is lower, as could be anticipated. Also the Young's modulus showed a marked increase in comparison with the 30 wt% PEG-containing PLLA/PEG binary systems. The thermo-mechanical analysis of the ternary systems shows a transition in the range of 60–62°C. On the other hand, it has been observed that the catalyst does not affect significantly the mechanical properties and transition temperatures of the ternary systems.

Figure 8(a,b) shows the surface features of the cryofractured samples of ternary systems containing PEG4000; with and without catalyst, respectively. It is also possible to observe that the lignin domains are rather inhomogeneously dispersed in the system. This inhomogeneity or low dispersion of lignin particles is probably due to the lower viscosity of the matrix resulting from the introduction of PEG during the mixing and to the higher difference of solubility parameter between PEG and lignin compared to PLLA and lignin. This result could be anticipated since the presence of PEG lowers the viscosity of the PLLA rich phase in the ternary system. Moreover, the volume fraction of lignin along with its inhomogeneous dispersion in the matrix induces some stiffness in the system and this is in agreement with the increase in Young's modulus of ternary

Table VI. Mechanical Properties of PLLA/Lignin Composites

Compositions			<i>T</i> _{mix} (°C)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PLLA (wt%)	Lignin (wt%)	TBATPB (wt%)				
100	-	-	-	2.34 ± 0.13	68.8 ± 3.5	4.10 ± 0.9
85	15	-	160	2.71 ± 0.25	44.5 ± 1.7	1.99 ± 0.25
85	15	0.15	160	2.07 ± 0.07	36.3 ± 1.8	2.15 ± 0.23
85	15	-	200	2.53 ± 0.09	17.8 ± 0.9	0.79 ± 0.12
85	15	0.15	200	2.62 ± 0.04	18.7 ± 0.7	1.35 ± 0.17

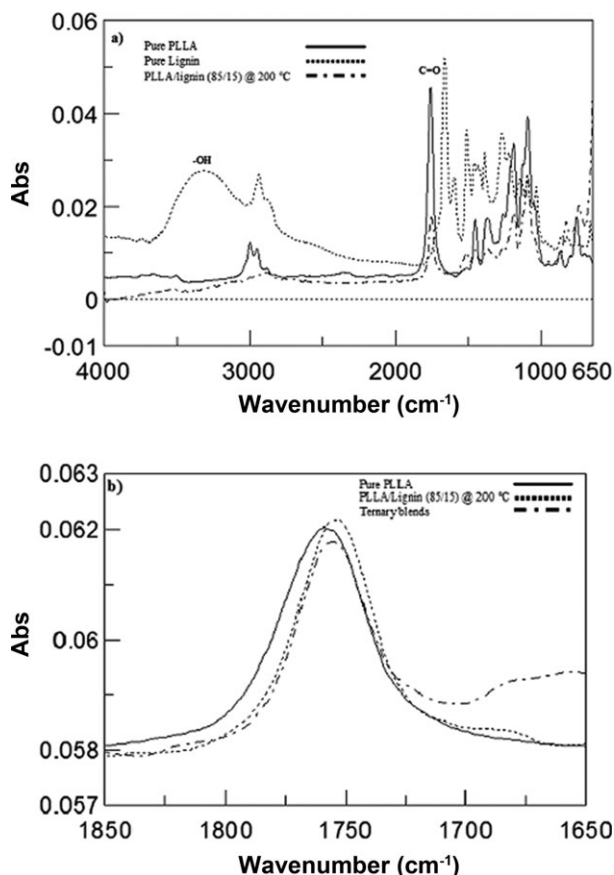


Figure 5. FTIR spectra of pure lignin, pure PLLA and PLLA/lignin blend (a); and variation in the intensity of C=O stretching of pure PLLA, PLLA/lignin blend, and ternary system (b).

systems in comparison with the modulus of the corresponding PLLA/PEG systems. No significant effect of the catalyst can be observed on the morphology of the ternary systems. However, the water absorption test on ternary systems and binary systems of PLLA/PEG can give valuable information about the effect of catalyst on the structural integrity of the both series of materials, in the presence of aqueous media.

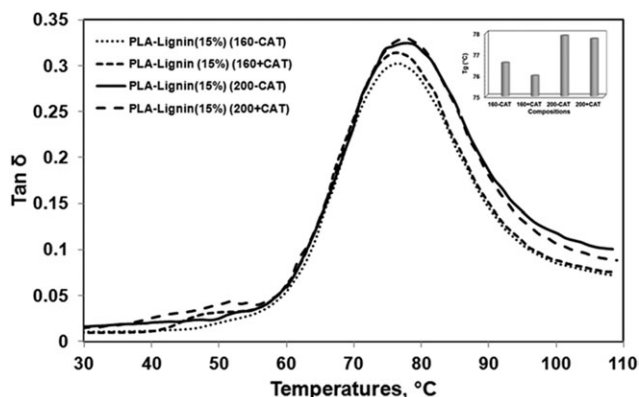


Figure 6. DMTA plot showing glass transition temperatures (T_g) of PLLA/lignin blends.

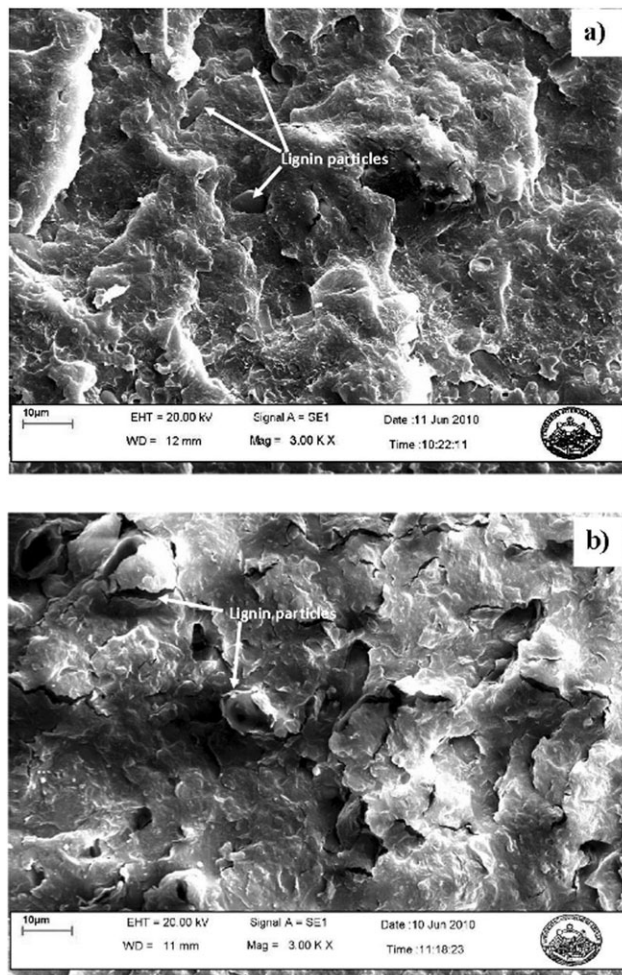


Figure 7. Scanning electron micrographs of PLLA/lignin biocomposites prepared at (a) 160 °C and (b) 200 °C.

Water Leaching Study

The release of PEG from PLLA/PEG binary systems and PLLA/PEG/lignin ternary systems when in contact with water is an important aspect concerning the biodegradability and environmental stability of the biocomposites. The release of PEG from the ternary system is a complex phenomenon since the dissolution can be influenced by the content of lignin, PLLA, PEG, and the type of catalyst used. Thus, the changing weight of the samples has been determined to investigate the degradation behavior of the specimens in an aqueous media.

Figure 9 shows the weight variation of two ternary systems containing 30 wt% PEG4000 (with and without catalyst) and three binary systems of PLLA/PEG, processed at two different temperatures (i.e., 160 and 200 °C) exposed to water. Binary systems processed at 160 °C and those containing 30 wt% PEG4000 show a weight loss of about 8%, although the sample containing the catalyst shows some water absorption up to 2% in the first 10 h. However, the binary systems containing 20 wt% PEG shows a slight increase in weight, probably to be associated to water absorption, while the systems containing 30 wt% PEG show a weight loss about 8% after 200 h of exposure. This can

Table VII. Mechanical Properties of PLLA/PEG/Lignin Ternary Systems

Compositions				TBATPB (wt%)	T_{mix} (°C)	Young's modulus (GPa)	Yield stress (MPa)	Elongation at break (%)
Lignin (wt%)	PLLA (wt%)	M_n of PEG	PEG (wt%)					
15	59.5	4000	25.5	–	160	1.14 ± 0.08	17.2 ± 0.9	9.5 ± 2
15	59.5	4000	25.5	0.15	160	0.85 ± 0.05	15.4 ± 1.1	12.7 ± 1.9
15	59.5	6000	25.5	–	160	1.15 ± 0.10	16.5 ± 1.2	6.5 ± 1.3
15	59.5	6000	25.5	0.15	160	1.12 ± 0.07	18 ± 0.8	7.2 ± 1.7
15	59.5	8000	25.5	–	160	1.2 ± 0.03	16.1 ± 0.5	7.3 ± 1.2
15	59.5	8000	25.5	0.15	160	1.26 ± 0.06	16.3 ± 0.8	7.1 ± 1.3

be explained considering the limited solubility of PEG in PLLA and in agreement with the GPC and FTIR analysis that showed the formation of a segmented PLLA-*b*-PEG copolymer at higher mixing temperature. However, the samples of ternary blends show increasing water absorption up to 13% in the first 48 h and after that period of time the level of water absorbed in the samples reaches a plateau. In addition to this, both ternary blends show a higher water absorption than the binary systems

of PLLA/PEG. It is noticeable that the ternary systems containing the catalyst show a slightly lower water absorption in comparison with the ternary systems containing no catalyst. However, the presence of lignin has compensated the loss of PEG in the ternary system.

It is evident that the sample containing 30 wt% PEG and no catalyst, shows progressive decrease in weight with time. The weight loss is probably due to the PEG not involved in copolymer formation and not soluble in PLLA. Thus, PLLA-*b*-PEG copolymer formation reduces the weight loss or degradation of the material in aqueous media. Interestingly, no weight loss was observed for ternary systems.

However, the total weight can give useful information about the real amount of PEG released which can be masked by the absorption of water. Figure 10 shows the total weight loss of all samples. The highest total weight loss was observed for the sample containing 30 wt% PEG in the binary systems and lower weight loss was encountered for the ternary blends. However, the high temperature processed binary systems of PLLA/PEG show the lowest weight loss which is an indication of the copolymer formation in the sample. Moreover, there are other factors

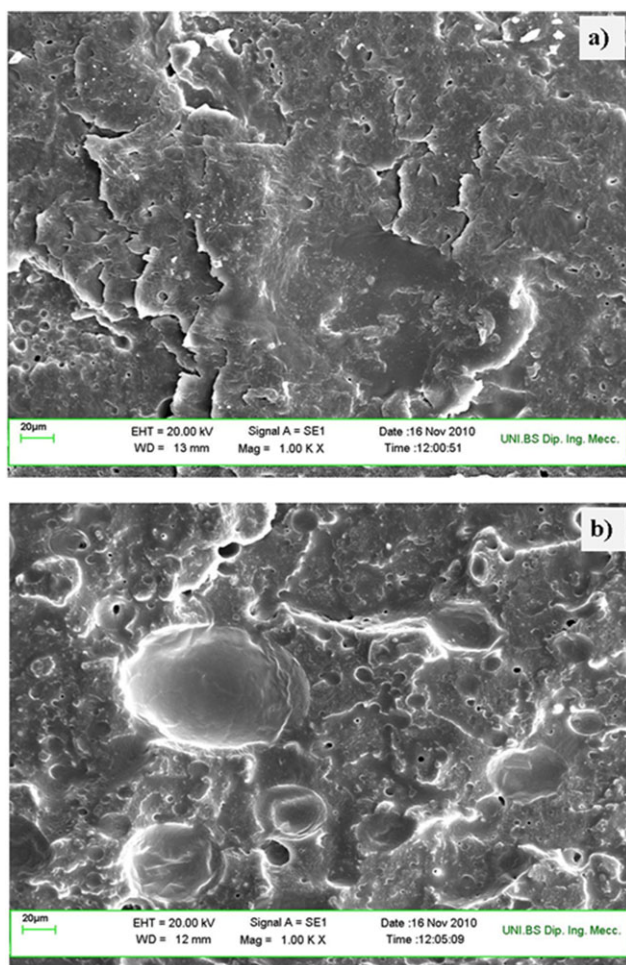


Figure 8. Scanning electron micrographs of PLLA/PEG/lignin biocomposites with (a) and without (b) catalyst. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

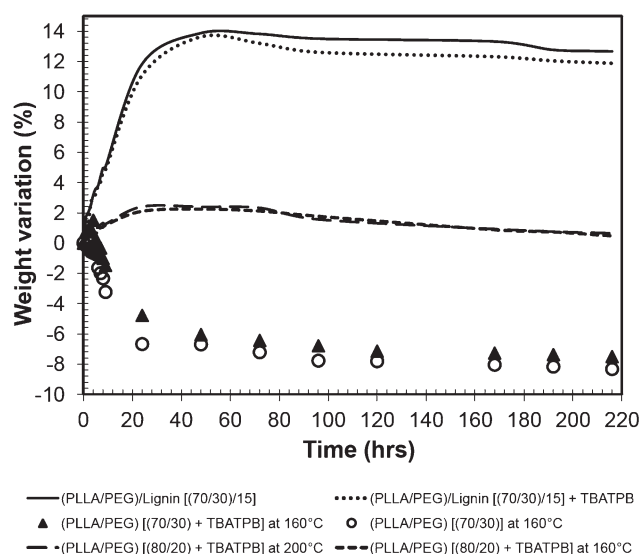


Figure 9. Water absorption profile of PLLA/PEG and PLLA/PEG/lignin systems.

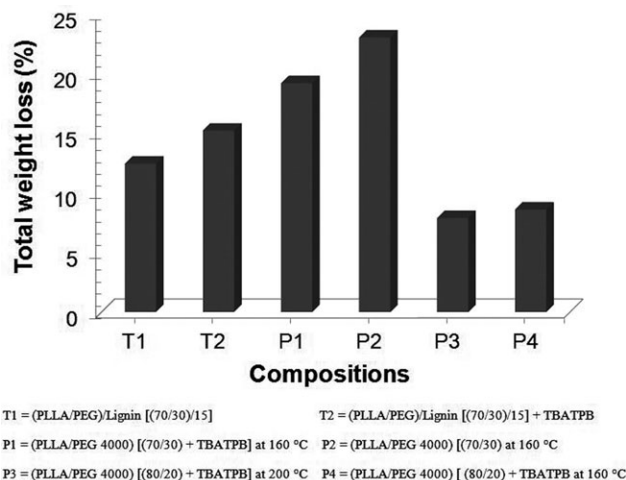


Figure 10. Total weight loss of PLLA/PEG and PLLA/PEG/lignin systems in aqueous media.

that can govern the weight loss of the samples such as the loss of low molecular weight fragmented PLLA, loosely attached lignin particles in the matrix, amount of porosity due to the inhomogeneous dispersion of lignin particles in the matrix and possible interaction among components.

CONCLUSIONS

The effect of the addition of lignin in the preparation of flexible biocomposites based on plasticized PLLA was studied. Two different binary systems based on PLLA/PEG and PLLA/lignin has been studied to understand the separate effects of plasticizer and lignin on the physicomaterial behavior of PLLA. PEG significantly improves the deformability of PLLA. The maximum elongation at break-100%-was obtained for the PLLA/PEG system containing 30 wt% PEG. As expected, the introduction of lignin in PLLA increased its brittleness of the resulting composite. However, the ternary systems where PLLA was plasticized with 30 wt% PEG and filled with lignin exhibited higher deformability in comparison with the unplasticized PLLA/lignin binary system. Thus, in the ternary systems with higher amount of PEG, a good balance between flexibility and stiffness has been achieved. It was also shown that high temperature reactive melt-blending of PLLA/PEG leads to the formation of a segmented block copolymer. This was also confirmed by the water absorption study which revealed that PEG release can be reduced in high temperature reactive melt-blending of PLLA/PEG since segmented block copolymer formation can reduce the PEG loss. In addition to this, PEG loss can be reduced by employing lignin with plasticized PLLA and thus improving the environmental stability of biocomposites.

ACKNOWLEDGMENTS

The authors acknowledge the support from FP7—KBBE project no. 212239 Forbioplast (Forest Resource Sustainability through Bio-Based Composite Development) to carry out this research. In particular Md. A. R. and T. V. P. both acknowledge a research sponsorship from project Forbioplast provided by the University of Pisa. Partial support from MIUR, PRIN-2008 is also acknowledged.

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