



# Degradation behaviour of PLA-based polyesterurethanes under abiotic and biotic environments



Pavel Kucharczyk<sup>\*</sup>, Alena Pavelková, Petr Stloukal, Vladimír Sedlarík

Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, tr. Tomase Bati 5678, 760 01 Zlin, Czech Republic

## ARTICLE INFO

### Article history:

Received 18 February 2016

Received in revised form

15 April 2016

Accepted 28 April 2016

Available online 29 April 2016

### Keywords:

Poly lactide

Polyurethanes

Hydrolysis

Thermal decomposition

Biodegradation

## ABSTRACT

Study was conducted on the degradation of polyurethanes based on Poly(lactic acid)/Poly(ethylene glycol), containing three differing concentrations of di-isocyanate compound, under three conditions (hydrolytic, thermal and composting). In the hydrolysis study, the effect of temperature and time were studied by techniques including weighting and GPC. Thermal decomposition was examined by thermogravimetry and mass spectroscopy. Composting was performed under standardized conditions and the amount of CO<sub>2</sub> was measured. It was found that hydrolysis of the material started almost immediately after exposure to a water environment at both investigated temperatures (37 °C and 55 °C), whereas weight loss exhibited a certain delay. Thermal decomposition of the studied materials started below 230 °C and lactide was identified as the main product. A biodegradation experiment showed that all the investigated samples successfully (>80%) mineralized within 90 days under composting conditions.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Poly(lactic acid) (PLA) is a biodegradable thermoplastic polymer that possesses good mechanical and processing properties, which can be obtained from 100% natural sources as well as from petrochemical resources [1]. PLA does have a number of disadvantages, especially low elongation, poor hydrophilicity, complicated processes for preparing high-molecular-weight polymer and high price, the latter caused by exhaustive monomer purification [2–5]. Many approaches have been developed to overcome these limitations, including copolymerization, blending and plasticizing to improve the mechanical properties [6,7]. Another pertains to plasma treatment in order to change hydrophilic/hydrophobic properties [8]. Other synthesizing methods also exist like solid state polycondensation or chain linking, which facilitate preparation of high-molecular-weight polymer at low cost [9,10].

Chain linking is of especial interest, representing a highly interesting approach to PLA production. This comprises a two-step process: initially, functionalized low  $M_w$  prepolymer is prepared, which is then chain linked through reactive chain ends by a suitable chain-linking agent (e.g. di-isocyanates) [11,12]. A benefit of this

approach is that the process is relatively fast, although the resultant product is not neat PLA and usually shows a broad polydispersity index. As a prepolymer must have reactive end groups (hydroxylic, carboxylic), low-molecular-weight PLA is firstly functionalized with a suitable compound (typically 1,4-butanediol), which reacts with the chain linker in the second step. Consequently, the product contains at least three different compounds in its structure [12–14].

In a previous work [15], the authors successfully prepared PLA containing a PEG segment through chain-linking reactions with a diisocyanate compound (HMDI or MDI). Utilizing PEG (instead of commonly used butanediol) as the OH terminating agent significantly improved hydrophilicity. The same work investigated structure and physico-chemical properties, and it was shown that the material could be successfully utilized to form nanoparticles and pertain to applications for encapsulation.

Numerous papers have dealt with chain extending PLA to form high-molecular-weight poly(ester-urethane) (PEU), some of which are reviewed in the References [15]. However, few of these have analysed PEU based on PLA, PEG and a diisocyanate chain linker, or comprise degradation studies (biotic and abiotic) [16–24]. Table 1 summarizes research papers that have looked at the synthesis, degradation and stability of PEU based on PLA. The most extensive study on hydrolytic degradation was presented by authors [25,26], although the materials therein did not contain PEG segments. In most other works that apply PEG as the hydrophilic OH terminating

<sup>\*</sup> Corresponding author.

E-mail address: [kucharczyk@cps.utb.cz](mailto:kucharczyk@cps.utb.cz) (P. Kucharczyk).

**Table 1**  
Summary of previous works on the synthesis and degradation of PLA/PEG chain-linked polyurethanes.

Material composition	Notes on chemical structure	Hydrolytic degradation (in vitro)					Thermal degradation		Composting	Sample form	Notes on degradation experiments	Ref.
		Effects investigated		Variables observed			Method studied					
		pH	T (°C)	Weight change	MW change	SEM or TEM	TGA	Other				
PLA/PCL/PGA/PEG-HMDI	Polyesters in forms of triols	7.4	37	yes	no	yes	no	no	no	10–20 mg in vitro; 10 × 2 mm in vivo	tested also in presence of enzymes	[16]
PLA/PEG - TDI	Short PLA segments	7.4	37	yes	no	no	yes	no	no	5 × 5 × 2 mm	–	[17]
PLA/PEG - LDI	PLA/PEG/PLA segmented, BDO as chain extender	7.4, 6, 5		yes	no	yes	no	no	no	15 × 15 × 0.1 mm	tested also in presence of enzymes	[18]
PEG/PLA/PEG-HMDI	Photo-crosslinkable material	7.4	37	yes	no	no	no	no	no	10 × 10 × 2.5 mm		[19]
PLA/PEG - HMDI	Both alternating and random blocks investigated	7.4	37	yes	yes	yes	no	no	no	50 mg – 5 × 2mm	Degradation observed by NMR; GPC at end of experiment	[20]
PLA/PEG/PLA-HMDI	Crosslinked	7.4	37	yes	no	no	no	no	no	40 × 40 × 1mm		[21]
PLA/PEG/PLA-LDI	Containing BDO and phosphorylcholine end-capped	7.4	37	yes	yes	yes	no	no	no	15 × 15 × 0.1 and micelles 10–50 nm	tested also in presence of enzymes; GPC and NMR only on micelles	[22]
PLA/PEG/PLA-HMDI	DMPA inside structure	10.4; 11.3	25	no	no	no	no	no	no	Micelles 90–130 nm	Degradation studied by spectroscopy	[23]
PLA/PTMG – MDI or TDI	EG used for OH termination	7.4	25	no	yes	yes	yes	no	no	2 × 2 × 2 mm	tested also in presence of enzymes	[24]
PLA/BDO-HMDI	BDO as OH terminating agent	7.0	37 and 55	yes	yes	no	no	no	no	20 × 20 × 3 mm	During hydrolysis T <sub>g</sub> observed by DSC	[25]
PLA*/-HMDI	*3 chain extenders investigated PP, BDO, BDA	7.4	37	yes	no	yes	yes	no	no	Film 10 × 10 mm	pH monitored during hydrolysis	[26]
PLA - HMDI	High MW polymer chain linked with HMDI	8.0	25	yes	no	no	yes	no	no	0.5 × 0 × 5 × 0.01	Enzymatic hydrolysis	[27]
PLA/BDO – HMDI or BDI	High-molecular-weight polymer	no	no	no	no	no	no	no	yes	0.1–0.6 mm particles	Amines determined after composting	[28]
PLA/PEG - MDI	Racemic type of PLA	no	no	no	no	no	no	no	no	–	No degradation	[29]
PLA/PEG-HMDI	PEG = 1000 g mol <sup>-1</sup>	no	no	no	no	no	no	no	no	–	No degradation	[30]
PLA/PEG – EC-bp	Commercial PLA; block multifunctional isocyanate, PLA/PEG = 90/10	no	no	no	no	no	no	no	no	–	No degradation	[31]
PLA/PEG-MDI	Containing glycerol for crosslinking	no	no	no	no	no	no	no	no	–	No degradation	[32]
PLA/PEG-IPDI	PEG400-6000	no	no	no	no	no	no	no	no	–	No degradation	[33]
PLA/PEG/PEG-HMDI	High molecular weight	no	no	no	no	no	no	no	no	–	No degradation	[34]
PLA/PEG/PEG-HMDI	PEG 1000-10000	no	no	no	no	no	no	no	no	–	No degradation	[35]

HMDI – hexamethylene diisocyanate; MDI – methylene diphenyl diisocyanate; TDI – 2,4-Toluene diisocyanate; LDI – L-Lysine ethyl ester diisocyanate; IPDI – Isophorone diisocyanate; BDO – 1,4-butanediol; PP – piperazine; BDA – 1,4-butanediolamine; BDI – 1,4-butane diisocyanate; EC-bp – cellosolve-blocked polyisocyanate; DMPS – 2,2-dimethylolpropionic acid; PTMG – poly(tetramethylene ether) glycol; EG – ethylene glycol; NMR – nuclear magnetic resonance, T<sub>g</sub> – glass transition temperature; DSC – differential scanning calorimetry.

agent, hydrolysis was only studied through simple monitoring of mass change [16–21,27].

Since the PEUs have been intended also for thermoplastic processing, their thermal properties, including thermal degradation and assessment of their thermal degradation products, represents important part of their material characteristics. As for thermal degradation, merely a few papers are given over to the topic [17,24,26,27], wherein only thermogravimetric study is provided. An even worse circumstance affects composting behaviour, with just a single work found on the subject [28], which again utilizes BDO segments not PEG. As can be seen in Table 1, said papers on the synthesis of PLA/PEG-diisocyanate chain linking polymers did not

focus on degradation behaviour [23,29–35], hence the survey conducted demonstrates a significant lack of knowledge in this area.

The research presented herein focuses on the biotic and abiotic degradation (hydrolysis, biodegradation and thermal decomposition and characterisation of the degradation products) of PLA/PEG polyurethanes with differing concentrations of the di-isocyanate component (HMDI). Degradation was studied by methods of gel permeation chromatography (GPC), weight loss measurements, thermogravimetry (TGA), pyrolysis via mass spectroscopy (Pyr/MS) and the extent of mineralization during biodegradation.

## 2. Experimental

### 2.1. Materials

PLA-PEG chain-linked copolymers (properties summarized in Table 2), phosphate buffer (PB, 0.1 mol L<sup>-1</sup>, pH = 7, NaH<sub>2</sub>PO<sub>4</sub> adjusted with NaOH), and chloroform (HPLC-grade) were sourced from Chromspec, Brno, the Czech Republic.

### 2.2. Preparation of PLA-PEG chain-linked copolymer

This study utilized the same materials as prepared and described in the previous work by the authors [15]. In brief, preparation involved the following: PLA-PEG hydroxyl-terminated prepolymer, obtained through simple polycondensation of lactic acid with PEG (7.5% wt.), was subjected to a further chain-coupling reaction with hexamethylene diisocyanate (HMDI). The coupling reaction took place at 160 °C for 30 min. PEG with a degree of polymerization (DP) 400 was used.

### 2.3. Testing sample preparation

The material was moulded into a thin sheet (50 × 50 mm, thickness 1.5 mm) in a manual press at 140 °C for 4 min and cooled in a second cold press to ambient temperature. Specimens for tensile testing and the hydrolysis experiment were cut from these sheets.

## 3. Methods

### 3.1. Mechanical properties

Investigations into tensile property were carried out on a universal tensile testing machine, the M350-5 CT Materials Testing Machine (Testometric Company, Lancashire, UK), at a crosshead speed of 1 mm min<sup>-1</sup>. Rectangular specimens at dimensions of 50 × 7 × 1.5 mm (length, width, thickness) were cut from the compression moulded plates.

Statistical analysis was used to process the results of mechanical analysis. To eliminate outlying results, the authors used a Dean-Dixon test for homogeneity (Q-test; confidence level  $\alpha = 0.95$ ). After eliminating outliers, corresponding averages and standard deviations (SD) were calculated.

### 3.2. Thermogravimetric analyses (TGA)

The thermal stability of the PLA samples thus prepared was analysed on a thermogravimeter, the Setaram TG-GA 12 (Caluire,

France), in accordance with the given samples possessing masses of 8–10 mg. The heating rate was set at 10 °C min<sup>-1</sup> over a temperature range of 25 °C–500 °C; furthermore, an N<sub>2</sub> atmosphere (100 cm<sup>3</sup> min<sup>-1</sup>) was employed. Thermal stabilities were characterized by the temperatures at which 10% weight loss occurred (T<sub>10%</sub>), in addition to temperatures at which the highest degradation rates took place (T<sub>peak</sub>), as referenced from a derivative thermogravimetric curve (dTG).

### 3.3. Molecular-weight changes during hydrolysis by GPC

GPC analysis was conducted using the HT-GPC 220 chromatographic system (Agilent), equipped with an RI response detector. The samples were dissolved in CHCl<sub>3</sub> (~2 mg ml<sup>-1</sup>) overnight. Separation took place on a 2 × PL gel-mixed-D bed column (300 × 7.8 mm, 5 μm particles). Analyses were carried out at 30 °C in chloroform; the flow rate equalled 1.0 ml min<sup>-1</sup> and injection volume was 100 μL. The GPC system was calibrated with narrow polystyrene standards ranging 580 to 271,000 g mol<sup>-1</sup> (Polymer Laboratories Ltd., UK). The weight average molar mass M<sub>w</sub>, number average molar mass M<sub>n</sub> and molar-mass dispersity ( $\bar{D} = M_w/M_n$ ) of the tested samples were determined from peaks corresponding to the polymer fraction, these being expressed as “polystyrene-relative” molecular weights. All data processing was carried out using Cirrus software.

### 3.4. Pyrolysis-GC-MS measurements

GC/MS was carried out on a GCMS-QP 2010 MS (Shimadzu) gas chromatograph coupled with a pyrolysis system. In order to delineate pyrolysis components a capillary DB-5 column was used (30 m × 0.25 mm i.d. × 0.25 μm film thickness); the flow rate of inert gas (He) was set up at 1 ml min<sup>-1</sup> and the split ratio of 1/250 applied. Samples of approximately 1 mg were pyrolyzed at the temperatures 160 °C and 260 °C for 2 min (a fresh sample for each temperature). GC analysis occurred under the following conditions: T<sub>initial</sub> = 50 °C and holding temperature was T<sub>final</sub> = 370 °C for 30 min at the ramp rate 10 °C min<sup>-1</sup>. The mass spectrometer setting was 250 °C for an ion source, at the resolution 15 to 800 and scan speed 10,000. For the pyrolysis study, the sample 3.2HMDI was selected.

### 3.5. Hydrolysis test

The test was performed in liquid buffered medium (pH = 7) on round-shaped samples (diameter 3.4 mm and thickness 1.5 mm). The specimens were placed in 25 ml glass bottles fully immersed in hydrolysis medium and shaken. At each follow-up time, one

**Table 2**  
Summary of properties of the prepared PLA-PEG copolymers used in the experimental part.

Sample Label	LA/EO ratio <sup>a</sup>	NCO/OH ratio <sup>a</sup>	DP <sub>PEG</sub> <sup>***</sup>	DP <sub>PLA</sub> <sup>a</sup>	M <sub>w</sub> <sup>a</sup> [g/mol]	$\bar{D}$ <sup>a</sup>	T <sub>g</sub> <sup>b</sup> [°C]	T <sub>m</sub> <sup>b</sup> [°C]	AN <sup>c</sup> [mgKOH/g]	Water uptake <sup>d</sup> [%]	Water contact angle [°]	Density <sup>e</sup> [g/cm <sup>3</sup> ]	w <sub>c</sub> [%]
2.3HMDI	4.77	2.3	9	42	36,700	4.2	30	130	11.6	3.3	51.5	1.227	50.60
2.7HMDI		2.7			117,000	13.0	33	n.f.	7.4	3.3	52.9	1.229	50.06
3.2HMDI		3.2			300,000	9.2	34	n.f.	7.5	3.2	54.7	1.233	51.03

<sup>a</sup> measured by <sup>1</sup>H NMR.

<sup>\*\*</sup> calculation based on concentration of OH groups (from PEG) added to reaction feed.

<sup>\*\*\*</sup> degree of polymerization of PEG (based on calculation DP = 400/44).

n.f. – not found in the first heating scan.

<sup>a</sup> Values obtained from GPC (polystyrene relative calibration).

<sup>b</sup> Measured by DSC.

<sup>c</sup> Acidity number (determined by titration).

<sup>d</sup> After 140 h at 25 °C.

<sup>e</sup> Based on measuring weight in air and in water.

specimen was removed and analysed by GPC. Hydrolysis was studied under the temperatures 37 °C and 55 °C. Changes in weight during hydrolysis were monitored under the same conditions, except the diameter of the specimens measured 10 mm instead.

### 3.6. Biodegradation in compost

The method applied was similar to that described in the References [36,37]. 50 mg of dry material, 5 g of perlite and 2.5 g of dry-weight compost were weighed into each 500 ml biometric flask. The flasks were sealed with stoppers equipped with septa and incubated at 58 °C. Head-space gas was sampled at appropriate intervals through the septum with a gas-tight syringe and then injected manually into a GC instrument (GC-2010 Plus, Shimadzu), equipped with Porapak Q (1.829 m length, 80/100 MESH) and 5A-molecular-sieve (1.829 m length, 60/80 MESH) packed columns connected in series, as well as a thermal conductivity detector (carrier gas helium, flow 53 ml min<sup>-1</sup>, column temperature 60 °C). Concentrations of CO<sub>2</sub> and O<sub>2</sub> were derived from the calibration curve obtained using a calibration gas mixture of declared composition (Linde). Endogenous production of CO<sub>2</sub> by soil or compost in blank incubations was always subtracted to obtain values representing net sample mineralization. The blank sample was comprised of the 2.5 g compost matter without any polymer sample, so the production of CO<sub>2</sub> was related entirely to compost. From the concentration found, the percentage of mineralization with respect to the initial carbon content of the sample was calculated as follows:

$$M(\%) = \frac{m_{gc}}{m_s w_c} \quad (1)$$

where M is the percentage of mineralization,  $m_{gc}$  is the mass of carbon evolved as CO<sub>2</sub> and obtained from GC analysis,  $m_s$  is the weight of the polymer sample, and  $w_c$  is the percentage (w/w) of carbon in the polymer investigated. Values in  $w_c$  for the given materials were determined by a total organic carbon (TOC) analyser (TOC-L, Shimadzu), equipped with a solid sample module (SSM-5000A, Shimadzu); as summarized in Table 2. In parallel, oxygen concentration was also monitored to provide a control mechanism so as to ensure samples did not suffer from hypoxia. Three parallel flasks were run for each sample, along with four blanks.

## 4. Results and discussion

### 4.1. Tensile testing

Table 3 details the mechanical properties of the prepared samples. It is clear that tensile strength grows alongside an increased NCO/OH ratio, the highest value recorded being 21 MPa with 3.2HMDI. In the case of E-modulus, there was no clear trend observed for the NCO/OH ratio, all values ranging at 1000–1400 MPa. Strain at break appeared very poor for all samples (~1%), while only 3.2HMDI exhibited elongation beyond 3%, which is comparable with commercially available PLA [6]. Heightened tensile strength occurred in conjunction with increased molecular weight, while the low tensile strain discerned is probably

attributable to the amorphous nature of the products and the rigid molecule of di-isocyanate in the polymer chain. It is also probable that chain branching, or even partial crosslinking, which might potentially occur in such materials, as well as broad polydispersity, could contribute towards the poor elongation. Similar values for tensile properties were reported by Gu et al. [38], who used a similar concept for chain extension, although butanediol was applied by them instead of PEG. It should be noted that their product exhibited approximately similar  $M_w$  and polydispersity.

In contrast, Kylma et al. [11] reported findings, based upon HMDI for chain linking the PLA prepolymer, of nearly two-fold greater values for tensile strength and strain. However, in this case it was probably caused by a different molecular structure, e.g. low polydispersity (<3), and the presence of 1,4-butanediol in the main chain. Moreover, far fewer rigid HMDI segments were utilized, in addition to which synthesis was founded upon solution polymerization.

### 4.2. Thermogravimetry

The thermal stability of samples containing HMDI was examined by TGA (Fig. 1 and Table 4). Usually, increasing the thermal decomposition temperature brings about a more thermally stable product. In comparison with neat PLA (without any additives), which exhibits  $T_{10\%}$ –300 °C [39–42], the samples showed considerably lower values, ~230 °C. Similar figures were reported in the work by He et al. [17], who had prepared low-molecular-weight and low polydispersity PLA/PEG chain-linked polymer. The likelihood is that the relatively poor thermal stability of the materials prepared herein was affected by the presence of PEG segments, thereby increasing hydrophilicity and enhancing the hydrolysis of the ester bonds. Nevertheless, as seen in Fig. 1 and Table 4, no significant difference in thermal degradation behaviour was visible between the lowest and the highest amount of HMDI. Therefore, the conclusion was made that the thermal stability of these systems was not actually a function of HMDI concentration. The fact that only a one-step degradation process was observed suggests that all components degraded simultaneously. This contrasts with the study by Wang et al. [26], in which two-stage degradation was observed; however, important factors like  $M_w$ , polydispersity, the type of PEG and chain linker, and the preparation conditions all differed, too.

### 4.3. Pyrolysis-GC-MS

The averaged mass spectrum for pyrolysis products obtained at 160 °C is depicted in Fig. 2a. Therein, the spectrum contained a dominant series of signals with  $m/z = n.72$ –88 ( $n \geq 2$ ), which undoubtedly corresponds to MS fragments of cyclic oligomers ( $m/z = 56, 128, 200, 272, 344$ ). The ion  $m/z = 56$  is a fragment common to all oligomers, including lactide [43]. A series of fragments were also found with  $m/z = 73 + n.72$ , ( $m/z = 73, 145, 217$ ), which Ludeward [44] attributed to acyclic oligomers with free hydroxyl endgroups, but Kopinke [43] stated that these fragments belonged to a homologous series of acyclic oligomers of acrylic acid. The latter also suggested the ion  $m/z = 100$  pertained to pentanedione,

**Table 3**  
Mechanical properties of chain-linked products.

Sample	Tensile strength [MPa]	SD	Tensile modulus [MPa]	SD	Strain at break [%]	SD
2.3HMDI	5.7	1.1	1130	40	1.0	0.2
2.7HMDI	15.4	2.5	1350	140	2.0	0.2
3.2HMDI	21.0	1.1	1140	140	3.2	0.1

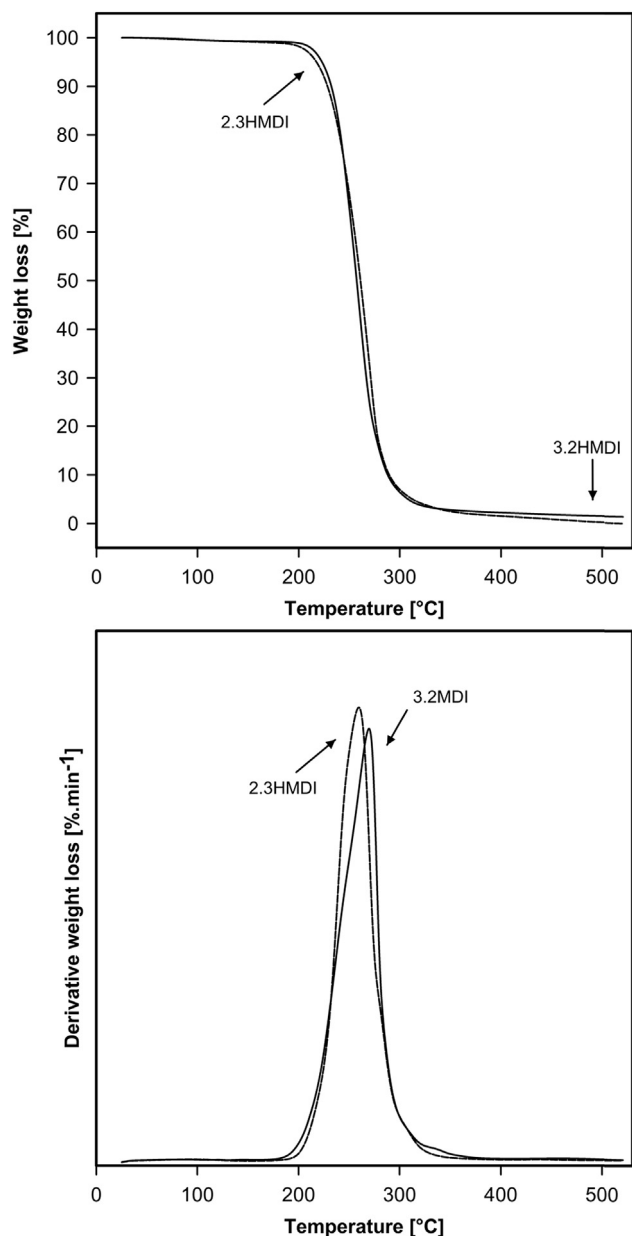


Fig. 1. TG and dTG curves for the prepared samples.

**Table 4**  
Summary of TGA results.

Sample	T <sub>10%</sub> [°C]	T <sub>peak</sub> [°C]	Residual weight [%]
2.3HMDI	228.9	269.2	0
2.7HMDI	231.8	268.3	0.2
3.2HMDI	232.0	264.9	0.5

whereas other authors refer to this signal as dimethyl propiolactone [44]. The other dominant ions corresponded to PEG hydroxyl terminated oligomers ( $m/z = 45, 89, 133$ ), in addition to which aldehyde-terminated PEG ( $m/z = 43, 87, 131$ ) was revealed as relatively significant. However, ethyl ether terminated PEG oligomers ( $m/z = 73, 117, 161$ ) exhibited a noticeably lower intensity. According to Lattimer [45], who studied the degradation products of PEG, the dominant degradation products at temperature 150 °C – hydroxyl and ethyl ether terminated PEG – are to be expected,

while aldehyde-terminated PEG should show significant abundance at elevated temperatures (250–300 °C). Hence, it was surprising that aldehyde terminated PEG oligomers were created at 160 °C, although it can be attributed to the presence of a highly complex matrix (PLA, isocyanates, water, catalyst). To conclude on thermal degradation behaviour at 160 °C, it may be stated that most degradation products were typical for the thermal decomposition of PLA (cyclic oligomers) and PEG (hydroxide, aldehyde and ethyl-ether terminated oligomers).

At the temperature 260 °C, mass loss was significant and a far more complicated degradation pattern was discerned (Fig. 2b). The same series of ions as observed at 160 °C were found at 260 °C, suggesting that the same degradation products also appeared at this elevated temperature. Furthermore, ions proving the presence of methylether end group PEG oligomers ( $m/z = 59, 103, 147$ ) were observed [45]. Through processing the chromatogram presented in Fig. 3b, other compounds typical for degrading PLA at temperatures above 250 °C were identified (CO<sub>2</sub> – 2.0 min and L-lactic acid – 10.2 min). Comparing the chromatographic signals between 12 and 17 min for both investigated temperatures (Figs. 4 and 6), a broad peak was seen at 260 °C and attributed to lactide. The other products identified in the spectrum were HMDI ( $m/z = 41, 56, 85, 99, 126$ ), which probably represented the non-reacted traces of chain linker, and tetraethylene glycol monoacetate ( $m/z = 45, 59, 87$ ), probably originating from the degradation of PEG oligomers. The remaining significant ions, especially those at  $m/z = 69, 170, 184$  and 312, were not identified; thus it was clear that other degradation products also evolved. The cause of this was a highly complicated matrix, as well as the fact that 260 °C is close to the temperature at which a radical degradation pathway might occur, hence more complicated products can be formed. Due to high volume loss at 260 °C determined by TGA, and on the basis of the chromatograms obtained, speculation centred on the likelihood of the dominant degradation product being lactide.

#### 4.4. Hydrolysis – GPC

The profile of molecular weight loss is depicted in Figs. 4 and 5. As can be seen, at 55 °C a sharp drop in  $M_n$  for all samples occurred, which was attributed to the sensitivity to elevated temperature by hydrolysis of the ester bonds. Similarly, significant decline in  $M_n$  was observed at 37 °C, although said decrease was more gradual than in the previous case; indeed, constant  $M_n$  was recorded after 25 days. The decrease in  $M_n$  was accompanied by narrowing  $D_M$ , caused by random cleavage of long molecular chains to shorter segments. A similar hydrolysis experiment (at 37 °C and 55 °C) was performed by Hiltunen [16], who reported a noticeably longer time to obtain the same constant molecular weight. In another work [9], the PLA/PEG-HMDI material was hydrolyzed under similar conditions and considerably slower hydrolysis was observed than is reported herein. The reason is that the former reported their investigated material as completely lacking PEG segments, hence it displayed higher hydrophobicity and  $T_g$ , whereas the latter used material with a considerably lower polydispersity index (<2), which was achieved by ring-opening polymerization instead of via direct polycondensation, as is the case herein.

The slowest rate of decrease in  $M_n$  was observed for samples with the highest NCO/OH ratio, which also corresponds to the highest molecular weight. This trend is more visible at 37 °C due to slightly slower hydrolysis.

#### 4.5. Hydrolysis – weight loss

The process for weight loss as dependent on time, temperature and the amount of HMDI is given in Figs. 6 and 7. What is



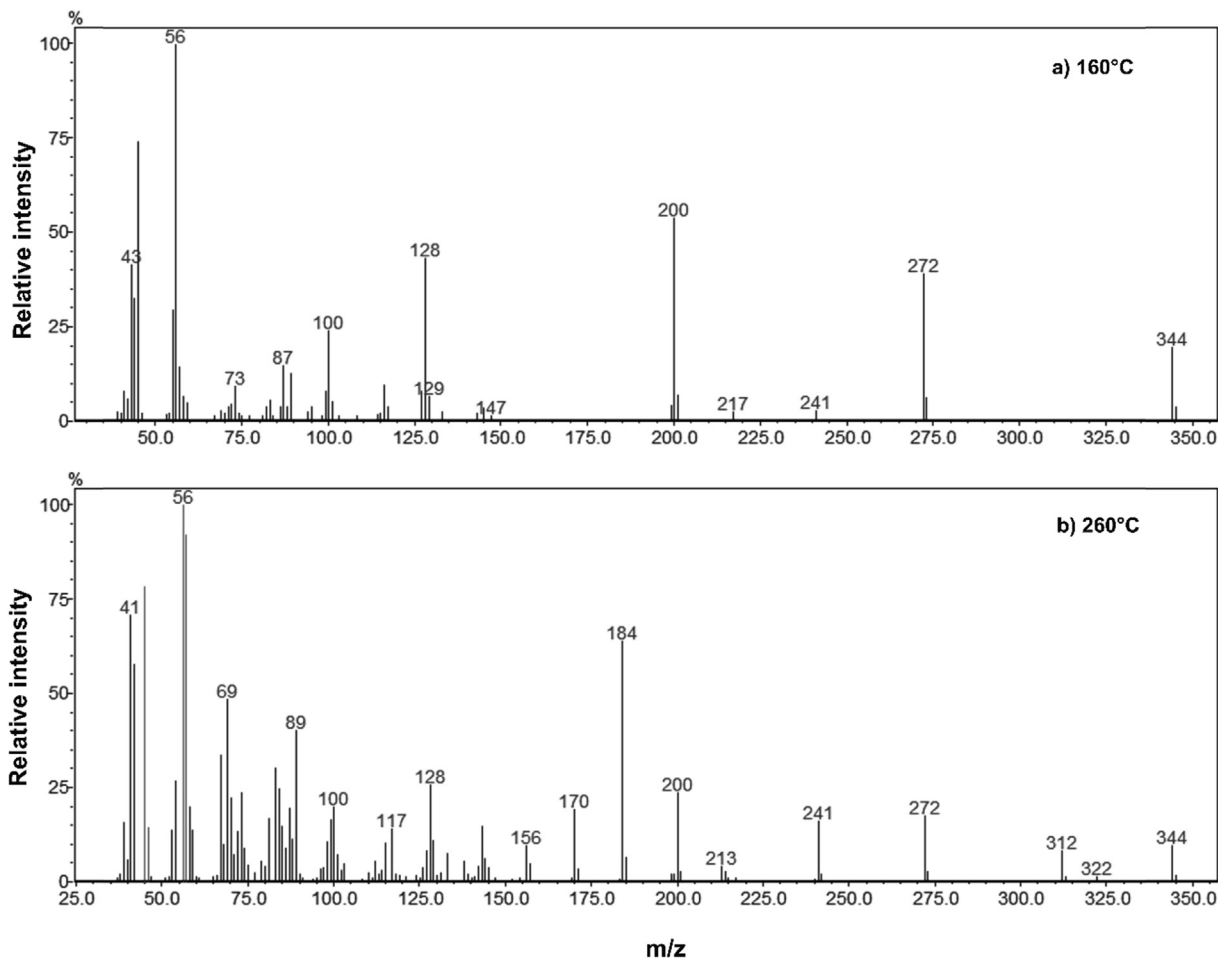


Fig. 2. Averaged mass spectrum for degradation products at 160 °C (a) and 260 °C (b) for the sample labelled 2.7HMDI.

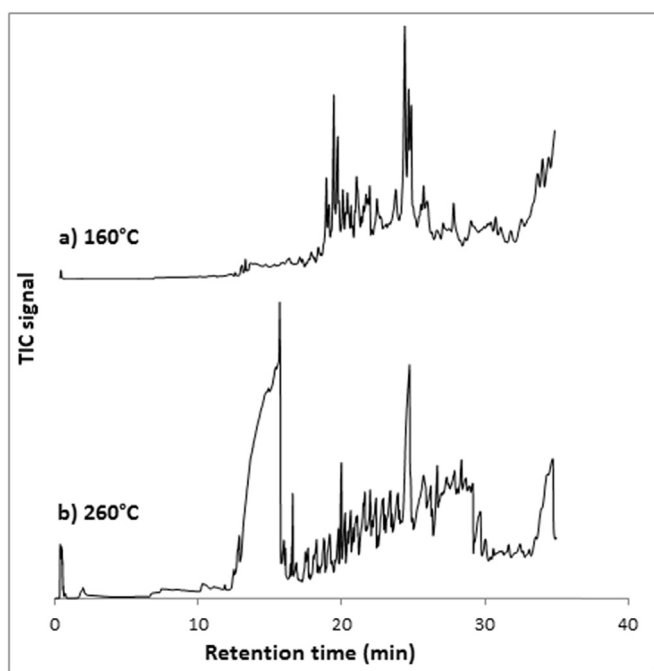


Fig. 3. Pyrolysis chromatogram obtained after decomposition at 160 °C (a) and 260 °C (b) for the sample labelled 2.7HMDI.

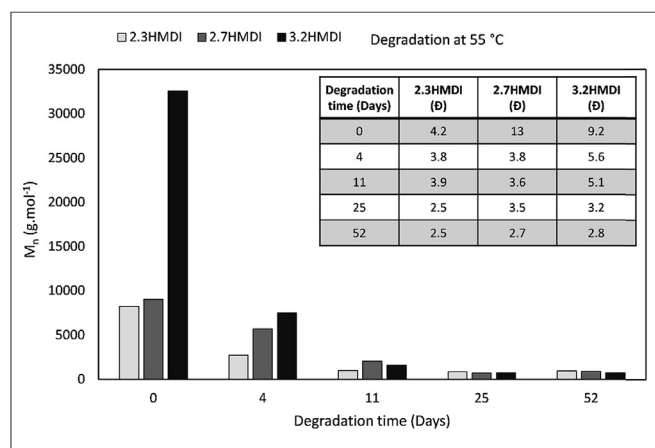


Fig. 4. Number average molecular weight loss for PLA-PEG copolymers as a function of hydrolysis time at 55 °C.

immediately apparent is the effect that temperature exerts. It is noticeable that, at 55 °C, the first recording of weight loss occurred as early as the 7th day of the experiment and continued over time. The 2.3HMDI sample disintegrated after the 14th day, whereas the other two samples disintegrated after 24 days. The rapid disintegration of the 2.3HMDI sample was likely due to its low molecular

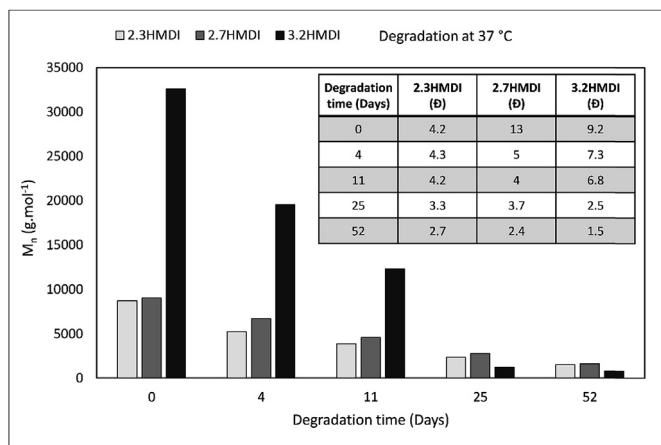


Fig. 5. Number average molecular weight loss for PLA-PEG copolymers as a function of duration of hydrolysis at 37 °C.

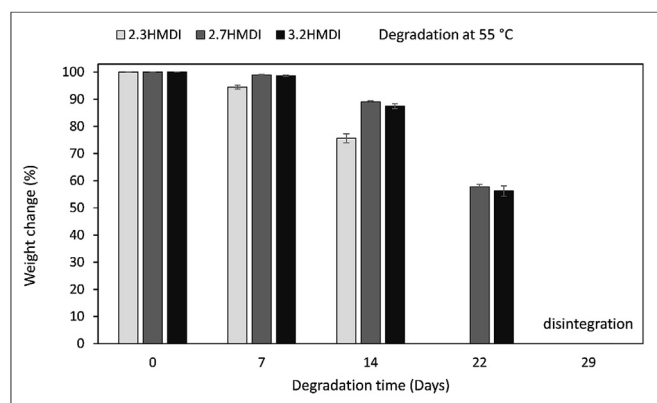


Fig. 6. Weight loss degradation profile for PLA-PEG copolymers as a function of time at 55 °C.

weight. On the contrary, weight loss at 37 °C was a considerable slower process than at 55 °C. The first changes in weight occurred on day 21 (2.3HMDI, 2.7HMDI) and day 37 (3.2HMDI), reflecting the molecular weight of the samples. At the end of the experiment (60 days), all samples exhibited a compact structure with weight loss of between 65 and 72%, in addition to which no disintegration was

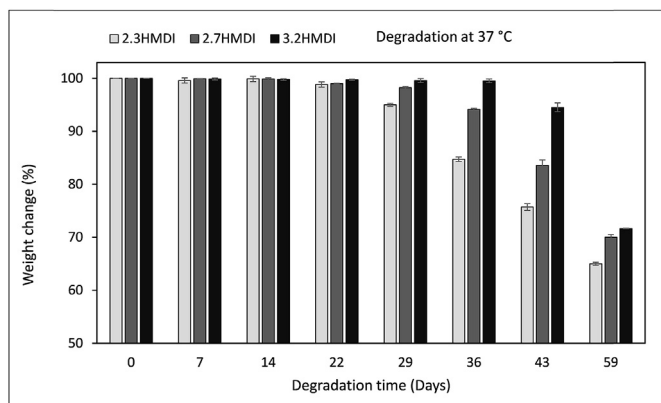


Fig. 7. Weight loss degradation profile for PLA-PEG copolymers as a function of time at 37 °C.

observed. This behaviour is typical for the bulk hydrolysis mechanism, during which samples can retain their compact structure till the last stage of hydrolysis [25]. Furthermore, no sign of mass change immediately after commencing the experiment indicates that no unreacted PEG was present in the samples, as this would have leached out in the very first stage; this finding is in agreement with References [16,20].

Observing  $M_n$  when the first recorded weight loss took place made it possible to determine the lowest  $M_n$  for fragments that was necessary for leaching out to occur. It is noticeable that this value equalled approximately  $3000 \text{ g mol}^{-1}$  for both temperatures. This finding resembles that of neat, low  $M_w$  PLA, where it is necessary to reach approximately  $3000 \text{ g mol}^{-1}$  prior to diffusion taking place [46]. This similarity shows that although PLA/PEG chain-linked polymer was more hydrophilic, the chemically more complicated fragments created during hydrolysis proved not to be more soluble than simple PLA oligomers.

#### 4.6. Biodegradation

The samples of the studied materials comprising different composition underwent biodegradation tests simulating the decomposition of materials under composting conditions at 58 °C. All the investigated samples reached about 80% of mineralization after 90 days of incubation, which indicates their easy biodegradability in a composting environment (Fig. 8). Despite substantial variety in composition of the sample materials and in molecular weight there is no significant difference in the rate of biodegradation among the samples. Interestingly, the sample with the highest molecular weight of nearly  $300,000 \text{ g mol}^{-1}$  (3.2 HMDI) also did not exhibit a lag phase or any kind of retardation at the beginning of process, which is typical for biodegradation of the high-molecular-weight form of neat PLA [47]. Some initial retardation or autocatalytic shape of the curves was also observed when biodegrading materials of similar composition, these comprising lactic acid and 1,4-butanediol monomers as well as 1,6-hexamethylene diisocyanate or 1,4-butane diisocyanate as the given chain linker under composting conditions [38]. The rapid onset of mineralization in

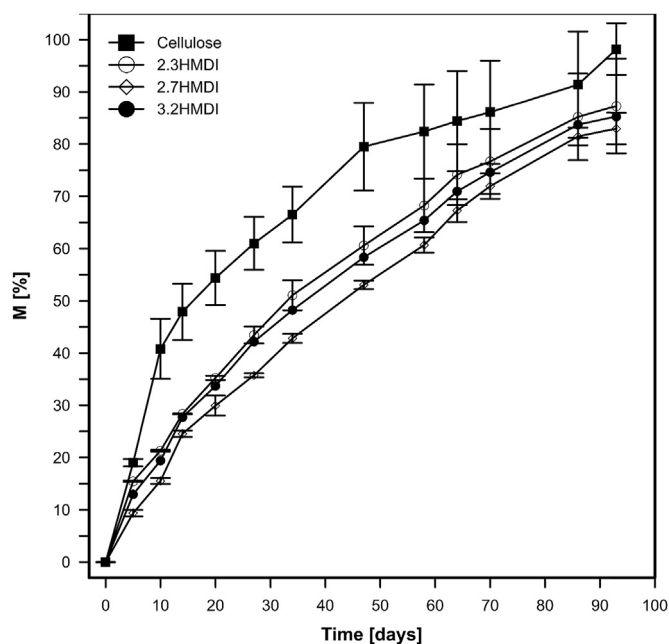


Fig. 8. Mineralization of materials under composting conditions at 58 °C.

the samples herein could be due to the broad polydispersity of the materials, as biodegradation started with low-molecular-weight fractions being mineralized by microorganisms. Faster decomposition could be also attributed to the presence of hydrophilic PEG, which effectively increased the amount of water uptake into the polymer matrix, triggering accelerated depolymerization of chains by the hydrolysis of ester bonds. Moreover, in comparison with the  $T_g$  of neat PLA (about 60 °C), the glass transition temperature for the samples lies considerably below the temperature of the experiment. It is well-known that polymer chains in the amorphous phase above the glass transition temperature  $T_g$  are highly mobile, thus easily degraded [48]. Finally, the diffusion rate of H<sub>2</sub>O, promoting hydrolytic depolymerization, is greater in the disorganised amorphous phase [49].

## 5. Conclusions

The degradation of PLA/PEG di-isocyanate chain-linked copolymers was investigated. It was found that newly prepared copolymers were accessible for relatively fast degradation in both liquid and composting environments. Molecular-weight decrease started immediately after exposure to the degradation environment, although weight loss occurred after a delay; therefore, it was concluded that a random bulk hydrolysis mechanism had taken place. The materials possessed relatively poor thermal stability, with decomposition starting below 230 °C, while, at 160 °C, degradation products typical for neat components were detected, namely lactide and PEG oligomers. At the temperature of 260 °C, far more numerous complex compounds evolved. All of the samples investigated reached about 80% of mineralization after 90 days of degradation under composting conditions, with no significant difference in mineralization behaviour becoming apparent among the samples.

## Acknowledgements

This work was financially supported by the Ministry of Education, Youth and Sports of the Czech Republic, under the NPU I programme (Grant no. LO1504).

## References

- [1] A.P. Gupta, V. Kumar, New emerging trends in synthetic biodegradable polymers – polylactide: a critique, *Eur. Polym. J.* 43 (10) (2007) 4053–4074, <http://dx.doi.org/10.1016/j.eurpolymj.2007.06.045>.
- [2] J. Lunt, Large-scale production, properties and commercial applications of polylactic acid polymers, *Polym. Degrad. Stab.* 1–3 (3) (1998) 145–152, [http://dx.doi.org/10.1016/S0141-3910\(97\)00148-1](http://dx.doi.org/10.1016/S0141-3910(97)00148-1).
- [3] R.M. Rasal, A.V. Janorkarc, D.E. Hirta, Poly(lactic acid) modifications, *Prog. Polym. Sci.* 35 (3) (2010) 338–356, <http://dx.doi.org/10.1016/j.progpolymsci.2009.12.003>.
- [4] R.E. Drumright, P.R. Gruber, D.E. Henton, Poly(lactic acid) technology, *Adv. Mater.* 12 (23) (2000) 1841–1846, [http://dx.doi.org/10.1002/1521-4095\(200012\)12:23<1841::AID-ADMA1841>3.0.CO;2-E](http://dx.doi.org/10.1002/1521-4095(200012)12:23<1841::AID-ADMA1841>3.0.CO;2-E).
- [5] L.T. Lima, R. Auras, M. Rubino, Processing technologies for poly(lactic acid), *Prog. Polym. Sci.* 33 (8) (2008) 820–852, <http://dx.doi.org/10.1016/j.progpolymsci.2008.05.004>.
- [6] P. Kucharczyk, V. Sedlarik, N. Miskolczi, H. Sakacs, T. Kitano, Property enhancement of partially biodegradable polyamide/polylactide blends through compatibilization with novel polyalkenyl-poly-maleic-anhydrideamide/imide-based additives, *J. Reinf. Plast. Compos.* 31 (3) (2012) 189–202, <http://dx.doi.org/10.1177/0731684411434150>.
- [7] O. Martin, L. Averous, Poly(lactic acid): plasticization and properties of biodegradable multiphase systems, *Polymer* 42 (14) (2001) 6209–6219, [http://dx.doi.org/10.1016/S0032-3861\(01\)00086-6](http://dx.doi.org/10.1016/S0032-3861(01)00086-6).
- [8] M. Zienkiewicz, J. Richert, P. Rytlewski, K. Moraczewski, Some effects of corona plasma treatment of polylactide/montmorillonite nanocomposite films, *Plasma Process. Polym.* 6 (2009) S387–S391, <http://dx.doi.org/10.1002/ppap.200930901>.
- [9] P. Kucharczyk, I. Poljansek, V. Sedlarik, The effect of various catalytic systems on solid-state polymerization of poly-(L-lactic acid), *J. Macromol. Sci. Pure Appl. Chem.* 49 (10) (2012) 795–805, <http://dx.doi.org/10.1080/10601325.2012.714312>.
- [10] N. Narayan, P.K. Roychoudhury, A.L. Srivastava, (+) lactic acid fermentation and its product polymerization, *Electron. J. Biotechnol.* 7 (2) (2004) 167–179.
- [11] J. Kylmä, J. Tuominen, A. Helminen, J. Seppälä, Chain extending of lactic acid oligomers. Effect of 2,2'-bis(2-oxazoline) on 1,6-hexamethylene diisocyanate linking reaction, *Polymer* 42 (8) (2001) 3333–3343, [http://dx.doi.org/10.1016/S0032-3861\(00\)00751-5](http://dx.doi.org/10.1016/S0032-3861(00)00751-5).
- [12] K. Hiltunen, J. Seppälä, M. Härkönen, Lactic acid based poly(ester-urethane)s: the effects of different polymerization conditions on the polymer structure and properties, *J. Appl. Polym. Sci.* 64 (5) (1997) 865–873, [http://dx.doi.org/10.1002/\(SICI\)1097-4628\(19970502\)64:5<865::AID-APP6>3.0.CO;2-N](http://dx.doi.org/10.1002/(SICI)1097-4628(19970502)64:5<865::AID-APP6>3.0.CO;2-N).
- [13] J. Tuominen, J. Kylmä, J. Seppälä, Chain extending of lactic acid oligomers. 2. Increase of molecular weight with 1,6-hexamethylene diisocyanate and 2,2'-bis(2-oxazoline), *Polymer* 43 (1) (2002) 3–10, [http://dx.doi.org/10.1016/S0032-3861\(01\)00606-1](http://dx.doi.org/10.1016/S0032-3861(01)00606-1).
- [14] J. Kylmä, J. Seppälä, Synthesis and characterization of a biodegradable thermoplastic poly(ester-urethane) elastomer, *Macromolecules* 30 (10) (1997) 28762882, <http://dx.doi.org/10.1021/ma961569g>.
- [15] A. Pavelkova, P. Kucharczyk, P. Stluka, M. Koutny, V. Sedlarik, Novel poly(l-lactic acid)-poly(ethylene oxide) chain-linked copolymer and its application in nano-encapsulation, *Polym. Adv. Technol.* 25 (6) (2014) 595–604, <http://dx.doi.org/10.1002/pat.3241>.
- [16] A.E. Hafeman, K.J. Zienkiewicz, A.L. Zachman, H.J. Sung, L.B. Nanney, J.M. Davidson, S.A. Guelcher, Characterization of the degradation mechanisms of lysine-derived aliphatic poly(ester urethane) scaffolds, *Biomaterials* 32 (2) (2011) 419–429, <http://dx.doi.org/10.1016/j.biomaterials.2010.08.108>.
- [17] X. He, C. Xiao, J. Xu, Synthesis and characterization of a novel poly(ester-urethane) containing short lactate sequences and PEG moieties, *J. Appl. Polym. Sci.* 128 (5) (2013) 3156–3162, <http://dx.doi.org/10.1002/app.38514>.
- [18] Z. Wang, L. Yu, M. Ding, H. Tan, J. Li, Q. Fu, Preparation and rapid degradation of nontoxic biodegradable polyurethanes based on poly(lactic acid)-poly(ethylene glycol)-poly(lactic acid) and L-lysine diisocyanate, *Polym. Chem.* 2 (3) (2011) 601–607, <http://dx.doi.org/10.1039/C0PY00235F>.
- [19] J.D. Clapper, J.M. Skeie, R.F. Mullins, C.A. Guymon, Development and characterization of photopolymerizable biodegradable materials from PEG-PLA-PEG block macromonomers, *Polymer* 48 (22) (2007) 6554–6564, <http://dx.doi.org/10.1016/j.polymer.2007.08.023>.
- [20] T. Mei, Y. Zhu, T. Ma, T. He, L. Li, C. Wei, K. Xu, Synthesis, characterization, and biocompatibility of alternating block polyurethanes based on PLA and PEG, *J. Biomed. Mater. Res. A* 102 (9) (2014) 3243–3254, <http://dx.doi.org/10.1002/jbm.a.35004>.
- [21] Z. Shen, D. Lu, Q. Li, Z. Zhang, Y. Zhu, Synthesis and characterization of biodegradable polyurethane for hypopharyngeal tissue engineering, *Biomed. Res. Int.* 2015 (2015) 1–11, <http://dx.doi.org/10.1155/2015/871202>.
- [22] Z. Wang, P. Wan, M. Ding, X. Yi, J. Li, O. Fu, H. Tan, Synthesis and micellization of new biodegradable phosphorylcholine-capped polyurethane, *J. Polym. Sci. A Polym. Chem.* 49 (9) (2011) 2033–2042, <http://dx.doi.org/10.1002/pola.24632>.
- [23] J. Zhang, M. Wu, J. Yang, O. Wu, Z. Jin, Anionic poly(lactic acid)-polyurethane micelles as potential biodegradable drug delivery carriers, *Colloids. Surf. A* 337 (1–3) (2009) 200–204, <http://dx.doi.org/10.1016/j.colsurfa.2008.12.025>.
- [24] S.H. Chen, C.T. Tsao, H.C. Chou, C.H. Chang, C.T. Hsu, C.N. Chuang, C.K. Wang, K.H. Hsieh, Synthesis of poly(lactic acid)-based polyurethanes, *Polym. Int.* 62 (8) (2013) 1159–1168, <http://dx.doi.org/10.1002/pi.4400>.
- [25] K. Hiltunen, J. Tuominen, J.V. Seppälä, Hydrolysis of lactic acid based poly(ester-urethane)s, *Polym. Int.* 47 (2) (1998) 186–192, [http://dx.doi.org/10.1002/\(SICI\)1097-0126\(199810\)47:2<186::AID-PI47>3.3.CO;2-5](http://dx.doi.org/10.1002/(SICI)1097-0126(199810)47:2<186::AID-PI47>3.3.CO;2-5).
- [26] Y. Wang, C. Ruan, J. Sun, M. Zhang, Y. Wu, K. Peng, Degradation studies on segmented polyurethanes prepared with poly(d, l-lactic acid) diol, hexamethylene diisocyanate and different chain extenders, *Polym. Degrad. Stab.* 96 (9) (2011) 1687–1694, <http://dx.doi.org/10.1016/j.polymerdegradstab.2011.06.015>.
- [27] B.H. Li, M.C. Yang, Improvement of thermal and mechanical properties of poly(L-lactic acid) with 4,4-methylene diphenyl diisocyanate, *Polym. Adv. Technol.* 17 (6) (2006) 439–443, <http://dx.doi.org/10.1002/pat.731>.
- [28] J. Tuominen, J. Kylmä, A. Kapanen, O. Venelampi, M. Itavaara, J. Seppälä, Biodegradation of lactic acid based polymers under controlled composting conditions and evaluation of the ecotoxicological impact, *Biomacromolecules* 3 (3) (2002) 445–455, <http://dx.doi.org/10.1021/bm0101522>.
- [29] J. Borda, I. Bodnár, S. Kéki, L. Sipos, M. Zsuga, Optimum conditions for the synthesis of linear polylactic acid-based urethanes, *J. Polym. Sci. Polym. Chem.* 38 (16) (2000) 2925–2933, [http://dx.doi.org/10.1002/1099-0518\(20000815\)38:16<2925::AID-POLA100>3.0.CO;2-E](http://dx.doi.org/10.1002/1099-0518(20000815)38:16<2925::AID-POLA100>3.0.CO;2-E).
- [30] J.M. Lee, S.H. Kim, H.Y. Jeong, N.R. Ahn, H.G. Roh, J.W. Cho, B.C. Chun, S.T. Oh, J.S. Park, Preparation and characterization of polyurethane foam using a PLA/PEG polyol mixture, *Fibers Polym.* 15 (7) (2014) 1349–1356, <http://dx.doi.org/10.1007/s12221-014-1349-7>.
- [31] T. Shen, M. Lu, D. Zhou, L. Liang, Effect of reactive blocked polyisocyanate on the properties of solvent cast blends from poly(lactic acid) and poly(ethylene glycol), *J. Appl. Polym. Sci.* 125 (3) (2012) 2071–2077, <http://dx.doi.org/10.1002/app.36276>.
- [32] Y.S. He, J.B. Zeng, G.C. Liu, Q.T. Li, Y.Z. Wang, Super-tough poly(l-lactide)/crosslinked polyurethane blends with tunable impact toughness, *RSC Adv.* 4 (25) (2014) 12857–12866, <http://dx.doi.org/10.1039/c4ra00718b>.
- [33] Z. Zhang, G.D. Fan, H.A. Yang, Study on chain extension and modification of



- poly(lactic acid) by isophorone diisocyanate/polyethylene glycol, *Adv. Mater. Res.* 476–478 (2012) 2067–2070, <http://dx.doi.org/10.4028/www.scientific.net/AMR.476-478.2067>.
- [34] M. Thieme, S. Agarwal, J.H. Wendorff, A. Greiner, Electrospinning and cutting of ultrafine bioerodible poly(lactide-co-ethylene oxide) tri- and multiblock copolymer fibers for inhalation applications, *Polym. Adv. Technol.* 22 (9) (2011) 1335–1344, <http://dx.doi.org/10.1002/pat.1617>.
- [35] D. Cohn, A. Hotohely-Salmon, Biodegradable multiblock PEO/PLA thermoplastic elastomers: molecular design and properties, *Polymer* 46 (7) (2005) 2068–2075, <http://dx.doi.org/10.1016/j.polymer.2005.01.012>.
- [36] P. Stloukal, A. Kalendova, H. Mattausch, S. Laske, C. Holzer, M. Koutny, The influence of a hydrolysis-inhibiting additive on the degradation and biodegradation of PLA and its nanocomposites, *Polym. Test.* 41 (2015) 124–132, <http://dx.doi.org/10.1016/j.polymertesting.2014.10.015>.
- [37] P. Stloukal, S. Pekarova, A. Kalendova, H. Mattausch, S. Laske, C. Holzer, L. Chitue, S. Bodnere, G. Maiere, M. Slouff, M. Koutny, Kinetics and mechanism of the biodegradation of PLA/clay nanocomposites during thermophilic phase of composting process, *Waste. Manag.* 42 (2015) 31–40, <http://dx.doi.org/10.1016/j.wasman.2015.04.006>.
- [38] S. Gu, M. Yang, T. Yu, T. Ren, J. Ren, Synthesis and characterization of biodegradable lactic acid-based polymers by chain extension, *Polym. Int.* 57 (8) (2008) 982–986, <http://dx.doi.org/10.1002/pi.2435>.
- [39] A. Nalbandi, Kinetics of thermal degradation of polylactic acid under N-2 atmosphere, *Iran Polym. J.* 10 (6) (2001) 371–376.
- [40] D. Rasselet, A. Ruellan, A. Guinault, G. Miquelard-Garnier, C. Sollogoub, B. Fayolle, Oxidative degradation of polylactide (PLA) and its effects on physical and mechanical properties, *Eur. Polym. J.* 50 (1) (2014) 109–116, <http://dx.doi.org/10.1016/j.eurpolymj.2013.10.011>.
- [41] M.G. Yang, Y.H. Lin, Measurement and simulation of thermal stability of poly lactic acid by thermogravimetric analysis, *J. Test. Eval.* 37 (4) (2009) 364–370.
- [42] A. Akbari, M. Jawaid, A. Hassan, H. Balakrishnan, Epoxidized natural rubber toughened polylactic acid/talc composites: mechanical, thermal, and morphological properties, *J. Compos. Mater.* 48 (7) (2014) 169–181, <http://dx.doi.org/10.1177/0021998313477461>.
- [43] F.D. Kopinke, M. Remmler, K. Mackenzie, M. Milder, O. Wachsen, Thermal decomposition of biodegradable polyesters. 2. Poly(lactic acid), *Polym. Degrad. Stab.* 53 (3) (1996) 329–342, [http://dx.doi.org/10.1016/0141-3910\(96\)00102-4](http://dx.doi.org/10.1016/0141-3910(96)00102-4).
- [44] I. Ltidewald, in: N. Grassie (Ed.), *Developments in Polymer Degradation-2*, Applied Science Publishers, London, 1979, p. 77.
- [45] R.P. Lattimer, Mass spectral analysis of low-temperature pyrolysis products from poly(ethylene glycol), *J. Anal. Appl. Pyrolysis* 56 (1) (2000) 61–78, [http://dx.doi.org/10.1016/S0165-2370\(00\)00074-7](http://dx.doi.org/10.1016/S0165-2370(00)00074-7).
- [46] P. Kucharczyk, E. Hnatkova, Z. Dvorak, V. Sedlarik, Novel aspects of the degradation process of PLA based bulky samples under conditions of high partial pressure of water vapour, *Polym. Degrad. Stab.* 98 (1) (2013) 150–157, <http://dx.doi.org/10.1016/j.polymdegradstab.2012.10.016>.
- [47] L. Husarova, S. Pekarova, P. Stloukal, P. Kucharczyk, V. Verney, V. Commereuc, A. Ramone, P. Koutny, Identification of important abiotic and biotic factors in the biodegradation of poly(L-lactic acid), *Int. J. Biol. Macromol.* 71 (SI) (2014) 155–162, <http://dx.doi.org/10.1016/j.ijbiomac.2014.04.050>.
- [48] K. Herzog, R.J. Muller, W.D. Deckwer, Mechanism and kinetics of the enzymatic hydrolysis of polyester nanoparticles by lipases, *Polym. Degrad. Stab.* 91 (10) (2006) 2486–2498, <http://dx.doi.org/10.1016/j.polymdegradstab.2006.03.005>.
- [49] N. Lucas, C. Bienaime, C. Belloy, M. Queneudec, F. Silvestre, J.E. Nava-Saudeco, Polymer biodegradation: mechanisms and estimation techniques, *Chemosphere* 73 (4) (2008) 429–442, <http://dx.doi.org/10.1016/j.chemosphere.2008.06.064>.