

## Material behaviour

# Carbodiimide additive to control hydrolytic stability and biodegradability of PLA



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## ABSTRACT

Enhanced durability of bio-based polylactic acid (PLA) is one of the prerequisites to be considered as alternative to petroleum-based polymers in long time application. The effect of bis(2,6-diisopropylphenyl)carbodiimide (BDICDI) additive in various concentration on the extent of hydrolytic stabilization and subsequent degradation kinetics of PLA was studied in the process of abiotic hydrolysis and microbial decomposition under composting conditions. The study showed that BDICDI acts as an efficient stabilizer suppressing the hydrolytic scission of ester bonds of PLA in both degradation processes tested, especially at concentrations above 1.5% w/w. Within the stabilization period which strongly depends on concentrations of BDICDI, suppression of hydrolytic degradation also triggered preservation of thermal and mechanical properties. After the period of stabilization as the dose of stabilizer is depleted, probably via reaction with water molecules and carboxylic groups, the material was hydrolyzed at a comparable or even slightly higher rate than pure PLA. By applying the appropriate amount of BDICDI, the approximate duration of stabilization could be set to suit the desired requirements of the final product.

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## 1. Introduction

Poly lactid acid (PLA) has attracted considerable attention in recent years as a potential bio-base alternative to conventional petroleum-based polymers for industrial applications, e.g. the automotive and electronics industries, which in near future could be demanded by legislation or customers [1–4]. Nevertheless, in the case of PLA with poor mechanical and thermal properties as well as the propensity to hydrolytic degradation, the requirements for excellent mechanical properties and durability in such industrial areas could prove prohibitive [5–7]. For applications necessitating a long service life, it is resistance to hydrolytic decomposition during thermo-plastic processing and subsequently throughout the service life that has become a key requirement, one which has to be satisfactorily guaranteed [8].

During the lifetime of PLA products, the hydrolytic chain scission of ester bonds that randomly takes place in the polymer might be considered a primary cause of reduction in molecular weight

and the related deterioration of mechanical and physical properties of PLA [9]. In the natural environment, the abiotic hydrolysis of ester linkages also facilitates their subsequent assimilation and mineralization by microorganisms [6]. In particular, abiotic hydrolysis has been singled out as a potential, major depolymerization mechanism and as the rate-controlling step of PLA biodegradation during composting [10]. It is known that the hydrolysis process takes place via a diffusion-reaction mechanism. The aqueous medium penetrates the polymer matrix and simultaneously converts the long polymer chain to low-molecular-weight, water-soluble oligomers and the given monomer [11]. Moreover, ester bond hydrolysis can be autocatalyzed by any carboxyl end groups initially present or formed during the process [12]. It follows that an effective suppression of the degradation has to aim to retard the hydrolysis process, either prevent the water penetration or slow down the rate of hydrolytical reactions in conjunction with the autocatalysis phenomenon.

Recently, a number of authors have investigated improvement in PLA resistance to abiotic hydrolysis by incorporating suitable additives that suppress at least one step of the degradation mechanism [13,6]. The inhibition of diffusion kinetics can be achieved by intercalating nanofillers, such as cellulose nanowhiskers,

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which create the physical barrier in the polymer matrix hindering the penetration of water, thus delaying the onset of hydrolysis [14]. It is also well-known that the rate of water diffusion could be controlled to some extent through modifying the crystallinity of the material by adding nucleation agents [15,16]. The reaction kinetics of hydrolysis can be affected by appropriate agents that react preferably with water and/or carboxylic groups [17,18]. Recently, the use of compounds acting on the above-mentioned principle, e.g. polycarbodiimides [19], carbodiimide [27], tris(nonyl-phenyl) phosphite [20], have proven effective in stabilizing polyesters against thermal degradation during processing. In later phases of its life cycle, it is notable that carbodiimides are claimed to be an efficient stabilizer for polyesters susceptible to hydrolysis [21]. In the recent study [22], it was shown that the decomposition of PLA in abiotic and biotic degradation processes could be substantially retarded by a carbodiimide-based additive. However, the most of above-mentioned studies demonstrated only the positive effect of anti-hydrolysis additives during processing. There is a significant lack of information concerning the possibility to set the approximate duration of stabilization in a final material by applying the appropriate amount of the stabilizer. Therefore, further data concerning the stabilizing action of carbodiimides (CDI) in various concentrations, as well as its subsequent effect on the kinetics of abiotic hydrolysis and biodegradation, should be satisfactorily described.

Herein, the authors investigated the influence of bis(2,6-diisopropylphenyl)carbodiimide (BDICDI), incorporated as the anti-hydrolysis agent in a PLA polymer matrix in various concentrations, on the durability of the final material during its subsequent lifetime. According to the European chemicals agency the BDICDI additive, which is commonly applied for stabilization of polymers during processing, exhibits low acute toxicity if swallowed. On the other hand, positively, it is not classified as a hazardous to the environment and thus the application of such materials is possible e.g. in agriculture.

Testing and monitoring focused on the extent of stabilization and subsequent degradation kinetics of PLA as dependent on the concentration of the BDICDI, this by different experimental techniques in the process of abiotic hydrolysis and microbial decomposition under composting conditions. The experimental data from abiotic hydrolysis and aerobic composting were analysed by non-linear regression to fit first-order kinetic models and to calculate kinetic parameters.

## 2. Materials and methods

### 2.1. Materials

Poly(lactic acid) PLA2002D was purchased from NatureWorks® Ingeo™, USA. The antihydrolysis agent ZIKA-AH362 i.e. Bis(2,6-diisopropylphenyl)carbodiimide (BDICDI) was kindly supplied by Ziko Ltd. Seoul, Korea.

### 2.2. Procedure for processing the materials

#### 2.2.1. Preparation of PLA/BDICDI mixture

Prior to being compounded, PLA pellets were dried at 60 °C under reduced pressure for more than 24 h. A co-rotating, twin-screw micro-compounder (DSM Xplore, Geleen, the Netherlands), equipped with two stainless steel screws and a bypass allowing continuous recirculation of the materials, operated at 200 °C; the screw speed of 100 RPM was used for the compounding operations. Firstly, the master-batch of PLA with 20% w/w of BDICDI was prepared to allow more homogeneous dispersion of the additive. Secondly, the master-batch of PLA with BDICDI and neat PLA were

used to prepare mixtures with 0.125, 0.25, 0.5, 1.0, 1.25, 1.5, 1.75 and 2.0% w/w of BDICDI.

#### 2.2.2. Preparation of films

PLA films of 100 µm thickness were compression moulded. The material was brought up to the processing temperature of 200 °C for 1 min, then moulded for 2 min, and immediately cooled down under pressure after transferring the material to a second press kept at 20 °C.

### 2.3. Characterization

#### 2.3.1. Gel permeation chromatography

The weight average molecular weight ( $M_w$ ) and molecular weight distribution of samples and their changes during degradation tests were analysed by gel permeation chromatography (GPC) on an HT-GPC 220 system (Agilent), equipped with a dual detection system ("RI" refractive index and "VIS" viscosity detectors). Samples were dissolved in THF (~2 mg ml<sup>-1</sup>) overnight. Separation took place on a series of mixed bed columns (1xB, 1xD, 1xE) (300 × 7.8 mm, Polymer Laboratories). Analyses were carried out at 40 °C in THF as the mobile phase, at a 1.0 mL min<sup>-1</sup> flow rate and loading volume of 100 µL. The GPC system was calibrated with narrow polystyrene standards ranging from 580 to 3,000,000 g mol<sup>-1</sup> (Polymer Laboratories Ltd., UK). The molecular weight averages ( $M_w$ ,  $M_n$ ) and molecular weight dispersity index ( $MWD = M_w/M_n$ ) were calculated with the aid of a polystyrene-standards-based "universal" calibration curve. Values of intrinsic viscosity  $\eta$  were obtained directly from the viscosity detector. All data processing was carried out using Cirrus software.

#### 2.3.2. Thermal properties - differential scanning calorimetry

Thermal properties were investigated by differential scanning calorimetry (DSC) on a Mettler Toledo DSC1 STAR System. All measurements were carried out under a nitrogen atmosphere (50 cm<sup>3</sup> min<sup>-1</sup>). The temperature ramp was set from 0 °C to 200 °C (10 K min<sup>-1</sup>), followed by annealing at 200 °C for 5 min. Subsequently there was a cooling scan from 200 °C to 0 °C (20 K min<sup>-1</sup>), then an isothermal step at 0 °C for 5 min. Finally, a second heating scan was conducted from 0 °C to 200 °C (10 K min<sup>-1</sup>). Melting point temperature ( $T_m$ ) and the exothermic response relating to cold crystallization ( $T_c$ ) were obtained from the first heating cycle. The region of glass transition temperature ( $T_g$ ) was determined from the second heating scan. The degree of crystallinity  $\chi_c$  was calculated according to the following equation [23]:

$$\chi_c = \left( \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \right) \times 100 \quad (1)$$

where  $\Delta H_m$  is the heat of fusion,  $\Delta H_c$  cold crystallization enthalpy and  $\Delta H_m^0$  is the tabulated heat of fusion for theoretically 100% crystalline PLA homopolymer (93.1 J g<sup>-1</sup>) [23].

#### 2.3.3. Fourier transform infra-red spectroscopy

Fourier transform infra-red attenuated total reflectance (FTIR-ATR) spectra were recorded on a Nicolet iS10 instrument equipped with a Zinc/selenide crystal (Thermo Fisher Scientific, Waltham, MA). The collected spectra in the wavenumber range from 500 to 4000 cm<sup>-1</sup> represented the average of 64 scans at a spectral resolution of 4 cm<sup>-1</sup>. The spectra for film samples before and during the abiotic hydrolysis process were recorded.

#### 2.3.4. Mechanical properties

The tensile tests of samples before and during abiotic hydrolysis

were carried out according to the ČSN EN ISO 527-1-4 standard, using a tensile testing machine – the Testometric M350-5CT - at a crosshead speed of 5 mm min<sup>-1</sup>. The dimensions of dog-bone form specimens cut from the compression moulded plates were 60 × 4.0 × 0.1 mm. Prior to testing, the samples were dried at 60 °C for 4 h. A minimum of five specimens from each group were tested.

## 2.4. Degradation test

### 2.4.1. Abiotic hydrolysis

The extent and rate of PLA hydrolysis was followed for 90 days at 58 °C. PLA film samples (50 mg) were cut into 0.5 × 0.5 cm specimens and suspended in 50 mL of sodium phosphate buffer (0.1 mol L<sup>-1</sup>, pH 7) amended with a microbial growth-inhibiting substance (NaN<sub>3</sub>, 2% w/w). The experiment was carried out in three replications for each sample type. 1.5 mL aliquots of the medium were taken out at regular intervals, centrifuged (10,000g, 10 min), and the supernatants were analysed for dissolved organic carbon (TOC-L Analyser, Shimadzu). In parallel, at appropriate intervals, the materials were also analysed by GPC.

### 2.4.2. Biodegradation under composting conditions

Biodegradation tests were performed in 500 mL biometric flasks equipped with septa mounted on the stoppers. Three components were weighed into the flasks: polymer samples (50 mg), mature compost (5 g of dry weight) and perlite (5 g). The sample flasks were incubated at 58 °C. Head space gas was sampled at appropriate intervals through the septum with a gas-tight syringe (100 µL), and then injected manually into a GC instrument – an Agilent 7890 (Agilent technologies, USA), equipped with Porapak Q (1.829 m length, 80/100 MESH) and 5A molecular sieve (1.829 m length, 60/80 MESH) columns connected in series and a thermal conductivity detector (carrier gas helium, flow 53 mL min<sup>-1</sup>, column temperature 60 °C). From the CO<sub>2</sub> concentration found, the percentage of mineralization with respect to the carbon content of the initial samples was calculated. Endogenous production of CO<sub>2</sub> by the compost in blank incubations was always subtracted to obtain values representing net sample mineralization. Three parallel flasks were run for each sample, along with four blanks.

### 2.4.3. Degradation kinetics

The data obtained from the degradation experiment were investigated by applying the appropriate kinetic models. The parameters of all individual models were obtained in MS Excel. The fit of the individual models was compared using the coefficient of determination (R<sup>2</sup>).

**2.4.3.1. Biodegradation.** In order to evaluate the experimental data from the biodegradation test, the model expressing the degradation of organic carbon from a solid sample was adopted [24]. In the previous study by the authors [6] the resulting parameters of the solved model suggested that essentially PLA-materials exhibited only one type of carbon, so herein the hydrolysis component in the model was expressed by merely the hydrolysis rate constant for so called hydrolysable solid carbon.

The analytical solution to the proposed model is expressed by Equation (2) for  $t > c$  ( $C_{T,t} = 0$  for  $t \leq c$ ), where  $C_{T,t}$  represents the percentage of total cumulative CO<sub>2</sub> production at time  $t$  (days);  $C_{h,0}$ , are the initial content of hydrolysable solid carbon, respectively; and  $C_{aq,0}$  is the initial percentage of water-soluble carbon. The kinetic parameters  $k_{hr}$  (day<sup>-1</sup>) represent respective first-order hydrolysis rate constants for the hydrolysable solid carbon. Further,  $k_{aq}$  (day<sup>-1</sup>) represents the rate constant of mineralization (biodegradation) of water-soluble carbon to carbon dioxide. Finally, parameter  $c$  is the duration of the lag phase (days) during the initial

phase of biodegradation before the onset of CO<sub>2</sub> production.

$$C_{T,t} = \left\{ C_{aq,0} \left( 1 - e^{-k_{aq}(t-c)} \right) + \left[ C_{h,0} \left( 1 - \frac{k_{aq}}{k_{aq} - k_{hr}} e^{-k_{hr}(t-c)} + \frac{k_{hr}}{k_{aq} - k_{hr}} e^{-k_{aq}(t-c)} \right) \right] \right\} \quad (2)$$

The assumed mathematical constraints required to derive a valid model are as follows:

1.  $C_{c,0} = C_{aq,0} + C_{h,0}$
2.  $C_{c,final} = C_{aq,final} + C_{h,final}$
- 3 All parameters are positive
- 4  $C_{h,t}$ ;  $C_{aq,t}$  and  $C_{T,t} = 0$  for  $t \leq c$ , where  $C_{c,0}$  and  $C_{c,final}$  are the percentages of total and final initial carbon, respectively.

**2.4.3.2. Hydrolysis.** With the purpose of fitting the experimental data of dissolved organic carbon from the abiotic hydrolysis experiments, the mathematical model given above was modified to describe merely the first phase of the degradation process, namely the change of solid organic material into intermediate water-soluble organic carbon forms. Therefore, the rate constant  $k_{aq}$ , expressing the mineralization of water-soluble carbon into carbon dioxide, was excluded. The modified model is expressed by Equation (3):

$$C_{aq,t} = C_{aq,0} + C_{r,0} \cdot \left( 1 - e^{-k_{hr}(t-c)} \right) \quad (3)$$

## 3. Results and discussion

### 3.1. Material characterization

The degradation of PLA is critically affected by the properties of the input material, its composition and processing history. Therefore, investigation was carried out into the properties essential for interpreting data from the degradation experiments (Table 1).

It is well-known [25,26] that PLA easily undergoes degradation at increased temperatures during processing. Consequently, BDICDI anti-hydrolysis effects could also be expected during thermo-plastic processing. The GPC results listed in Table 1 show a slight decrease in molecular weight for non-stabilized PLA after processing in comparison with the original PLA. As expected, the drop in molecular weight was improved by increasing the concentration of BDICDI, and above 0.5% w/w there were no longer any significant changes indicating degradation during processing.

DSC analysis revealed that BDICDI had no significant effect on the Tm and Tg values in comparison with pure PLA film or with the initial PLA prior to processing. The crystallinity of the films was considerably low and quite resembled neat PLA, probably reflecting the relatively brief time available for crystallization during the preparation of films.

### 3.2. Abiotic hydrolysis

The sensitivity of PLA to abiotic hydrolysis, especially at elevated temperatures, is considered one of the limiting factors for application in products requiring a longer service life. In order to investigate the stabilization effect of BDICDI applied at various concentrations, the hydrolysis experiment was set up in the aqueous environment at 58 °C. The temperature selected was

**Table 1**  
Selected material properties of PLA-based films.

Sample	Content of BDICDI (% w/w)	$M_w^a$ [g mol <sup>-1</sup> ]	MWD <sup>b</sup>	$T_m^c$ [°C]	$T_g^d$ [°C]	$\chi_c^e$ [%]
PLA prior to processing	0	124,000	2.22	153.1	58.2	32.6
PLA	0	106,000	2.16	152.3	59.5	2.8
PLA + 0.125% BDICDI	0.125	116,000	2.16	152.8	59.5	1.9
PLA + 0.25% BDICDI	0.25	121,000	2.1	152.5	59.1	1.9
PLA + 0.5% BDICDI	0.5	129,000	2.08	152.3	59.6	0.9
PLA + 1% BDICDI	1	121,000	2.22	152.3	60.0	2.7
PLA + 1.25% BDICDI	1.25	137,000	2.19	152.0	59.0	9.1
PLA + 1.5% BDICDI	1.5	123,000	2.21	152.6	58.7	2.8
PLA + 1.75% BDICDI	1.75	122,000	2.26	151.3	58.8	7.3
PLA + 2% BDICDI	2	133,000	2.28	151.0	58.9	0.4

<sup>a</sup> Weight average molecular weight.

<sup>b</sup> Molecular weight dispersity.

<sup>c</sup> Melting temperature.

<sup>d</sup> Glass transition temperature.

<sup>e</sup> Crystallinity.

favourable for several reasons. Firstly, it was proven that degradation proceeds at a reasonable rate at this temperature [6], so technically the laboratory study was feasible, also stability at such temperature can be expected as a minimal requirement for e.g. in electrotechnic applications. Additionally, the temperature remained under the glass transition temperature ( $T_g$ ) of the material, consequently the results should be applicable to the temperate interval below  $T_g$ . Finally, 58 °C is the usual temperature used in laboratory composting tests, hence the results could provide some information on the eventual behaviour of the material during biodegradation under thermophilic conditions. Furthermore, the extent of stabilization and subsequent hydrolysis kinetics were studied by several techniques, including analysis of dissolved organic carbon (TOC), GPC, DSC, FTIR and tensile tests.

### 3.2.1. Release of water-soluble hydrolysis products

The accumulation of water-soluble, organic carbon products from PLA hydrolysis was observed (Fig. 1), and the data fitted with the kinetic model (Eq. (1)). The resulting parameters of the model with the coefficients of determination ( $R^2$ ) are shown in Table 2.

**Table 2**

Kinetic model parameters and coefficients of determination ( $R^2$ ) for abiotic hydrolysis of pure PLA and BDICDI-stabilized PLA films.

Sample	$C_{a,q,0}^a$ (%)	$C_{r,0}^b$ (%)	$k_{hr}^c$ (day <sup>-1</sup> )	$C^d$ (days)	$R^2$
PLA	0	100	0.0140	17.5	0.9989
PLA + 0.125% BDICDI	0	100	0.0128	17.4	0.9863
PLA + 0.25% BDICDI	0	100	0.0130	18.3	0.9879
PLA + 0.5% BDICDI	0	100	0.0127	20.6	0.9925
PLA + 1% BDICDI	0	100	0.0141	30.2	0.9850
PLA + 1.25% BDICDI	0	100	0.0142	38.5	0.9779
PLA + 1.5% BDICDI	0	100	0.0234	90.7	0.9770
PLA + 1.75% BDICDI	0	100	0.0266	109.1	0.9975
PLA + 2% BDICDI	0	100	0.0118	136.5	0.9633

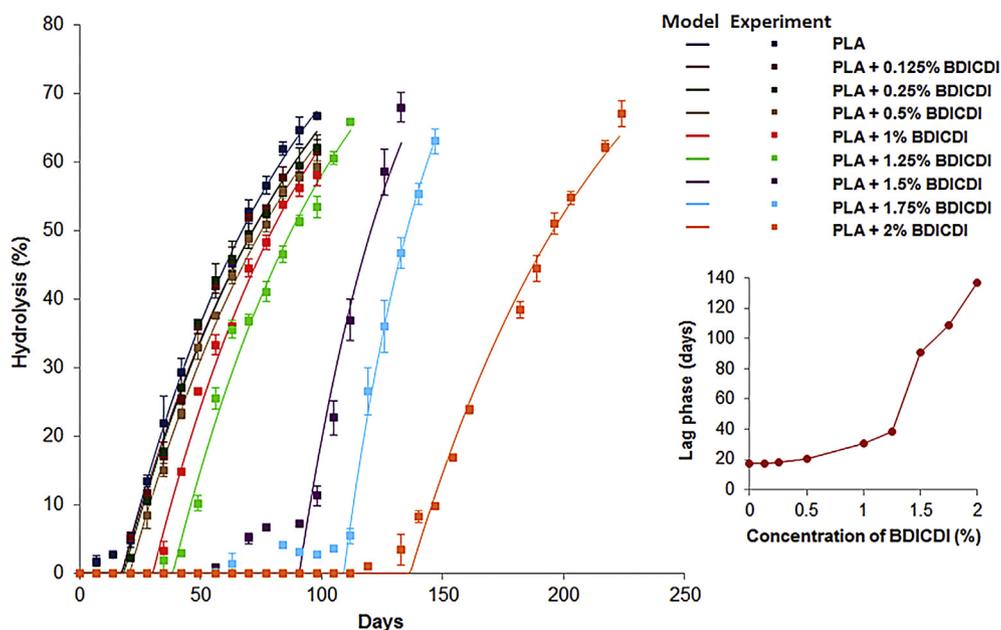
<sup>a</sup> Percentage of initial intermediate solid carbon.

<sup>b</sup> Percentages of initial hydrolysable solid carbon.

<sup>c</sup> First-order hydrolysis rate constants.

<sup>d</sup> Duration of lag phase during the initial phase of hydrolysis prior to water-soluble carbon production.

Coefficients of determination ( $R^2$ ) exceeding 0.96 were obtained for all data sets, indicating the excellent fit of the model.



**Fig. 1.** Abiotic hydrolysis of PLA film samples in 0.1M phosphate buffer (pH = 7) at 58 °C. Error bars correspond to twice standard deviation ( $n = 3$ ). The inner graph represents the dependence of lag phases of hydrolysis calculated from the kinetic model on the concentration of BDICDI.

The results revealed an insignificant stabilization effect of BDICDI at concentrations of up to 0.5% w/w, a moderate stabilization effect at concentrations of 1 and 1.25% w/w, and a very strong stabilization effect at the highest concentrations from 1.5% to 2% w/w, which counteracted the hydrolysis of PLA. This phenomenon was quantified by the resulting length of the lag phase  $c$  calculated from the kinetic model (inner graph in Fig. 1). While at the lower concentrations of BDICDI up to 1.25% w/w the length of lag phase was only slightly extended by increasing the amount of the anti-hydrolysis agent, at higher concentrations of BDICDI a steep rise in the length of lag phase was observed. It was discerned that the hydrolysis rate constants gradually rose with the increasing amount of BDICDI from  $0.0128 \text{ day}^{-1}$  pertained to BDICDI-stabilized PLA at the concentration of 0.125%, extending to  $0.0240 \text{ day}^{-1}$  for PLA + 1.75% BDICDI. Only PLA + 2% w/w BDICDI really stood out ( $0.0180 \text{ day}^{-1}$ ). The calculated rate constants suggest that PLA is protected against hydrolysis and the autocatalytic action of free carboxylic groups for a certain time, depending on the amount of BDICDI. After the dose of BDICDI is depleted, the material is hydrolyzed at a comparable or even slightly higher rate than pure PLA. The values of the rate constants are generally consistent with previous investigations by other authors [24].

In the work [14] authors demonstrated the stabilization effect of cellulose nanowhisker on the hydrolytic degradation behaviour of poly(D,L-lactide). No weight loss was observed for the composite of PLA with 5% nanowhisker, even after 12 weeks. In our case, no release of water-soluble products, which is equivalent to the weight loss, was observed during more than 100 days.

### 3.2.2. Changes in molecular weight distribution

In order to explain in more detail the time frame of the stabilization and the changes in the material at a molecular level, especially during the initial phase of the hydrolysis process, GPC measurements were carried out (Fig. 2) during the hydrolysis experiment.

The data obtained clearly confirmed previous findings that the chain scission during hydrolysis was significantly retarded by adding BDICDI in an amount above 1.5% w/w. The stabilization

effect of BDICDI is characterized by only slight reduction in  $M_w$  within a certain time (the “plateau period”), which increased alongside heightened concentration of the anti-hydrolysis agent. Afterwards, the rate of  $M_w$  decrease approximately equates to that of pure PLA.

The stabilization effect was quantified by the estimation of the time necessary to bring about 20% reduction in  $M_w$  in comparison with materials before hydrolysis (see the inner graph in Fig. 2). Such a drop in  $M_w$  roughly corresponded with the “plateau period” for highly stabilized samples. The drop in  $M_w$  even exceeding 20% after around 2 days of incubation signified the immediate onset of the hydrolytic scission of ester bonds for BDICDI at concentrations below 0.5% w/w. For higher concentrations, the stabilization effect gradually increased alongside heightened BDICDI concentration. The 20% decrease in  $M_w$  from the original value was delayed by 8, 23, 69, 87 and 95 days for BDICDI-stabilized PLA at concentrations of 1, 1.25, 1.5, 1.75 and 2% w/w, respectively. A significantly better stabilization effect was also achieved in comparison with the study [13], where the deceleration of PLA hydrolysis by addition of talc was demonstrated.

The insignificant stabilization effect of BDICDI at its low concentrations might be due to depletion of the same taking place as early as during thermal processing in the reaction of BDICDI with the moisture and carboxylic groups. It suggests that a certain amount of BDICDI above a minimal concentration limit should be necessary, depending on the time and conditions of thermal processing, so as to ensure the effective stabilization of PLA against hydrolysis during the expected lifetime of a product. In accordance with the amount of BDICDI applied above this minimal concentration, the duration of stabilization can be effectively tuned.

In order to evaluate the hydrolysis behaviour of pure BDICDI and that containing PLA at a molecular level, the changes in molecular weight distribution (MWD) for pure PLA and PLA with 2% w/w of BDICDI were observed during the hydrolysis experiment and compared (Fig. 3). Prior to hydrolysis, both materials - either non-stabilized or stabilized, possessed a narrow, unimodal and moderately symmetrical distribution with a polydispersity (PDI) index of about 2. In the course of the hydrolysis experiment, the MWD of

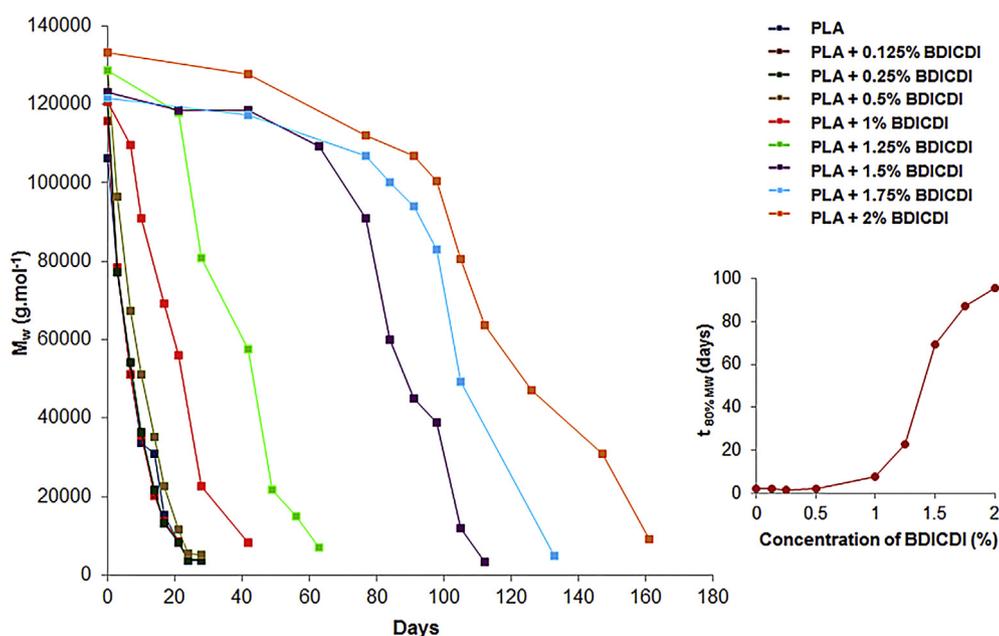


Fig. 2. Molecular weight evolution of PLA with a differing content of BDICDI. The inner graph represents the dependence of the time necessary for 20% reduction in  $M_w$  on the concentration of BDICDI.

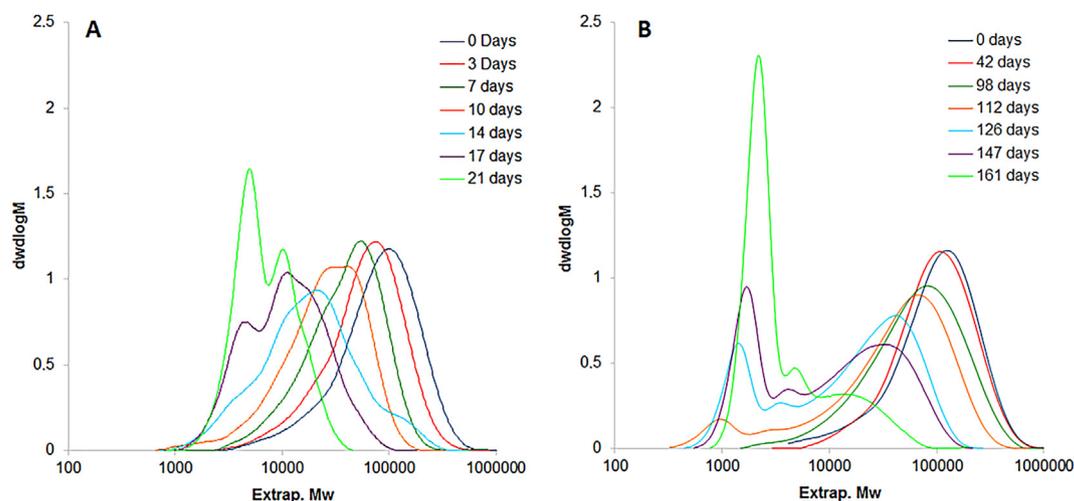


Fig. 3. Molecular weight distribution curves for pure PLA (A) and PLA with 2% of BDICDI (B) during abiotic hydrolysis.

non-stabilized PLA gradually broadened out (PDI = 2.94 after 14 days, and 1.36 after 28 days), and later the overall unimodal shape of the distribution changed to bimodal, with a distinct peak in substances with a  $M_w$  of several thousand, which was probably just over the water solubility limit for PLA oligomers [6].

A different situation arose in the case of PLA with BDICDI content. Firstly, for almost 100 days, the molecular weight distribution broadened out only slightly (the PDI changed from 2.28 to 2.77). After this period, rather rapid MWD changes could be observed, characterized by an overall shift in the distribution to a lower  $M_w$ , and building up a peak of low  $M_w$  substances. At the close of the hydrolysis experiment, the higher molecular weight fraction gradually disappeared and the PDI decreased to about 2.18. The described trends were detected for all stabilized samples with an intensity that depended on their BDICDI concentrations.

It is known that bimodal distribution is connected with hydrolysis of semi-crystalline PLA, herein exhibiting a different degradation rate for crystalline and amorphous regions within the samples [12,5]. Although the crystallinity of all the tested samples was initially considerably low, it increased during the hydrolysis experiment probably due to reorganization of loose polymer chains (see capture 3.1.3 and Table 3). This behaviour was significantly more intense in BDICDI stabilized materials, most likely as a consequence of the prolonged time available for recrystallization.

### 3.2.3. Thermal properties of the materials

The changes in thermal properties of the selected samples were observed with DSC in order to enable better interpretation of the stabilization effect of BDICDI and subsequent hydrolysis mechanisms (Table 3). A slight decline in  $T_m$  and  $T_g$  was revealed for pure

PLA and weakly stabilized PLA with 0.5% w/w BDICDI even after as little as three weeks of hydrolysis. The reduction in melting temperature indicated formation of a low-molecular-weight fragment, caused by chain scission of ester bonds entrapped in the polymer matrix. Consequently, the plasticizing effect of newly formed oligomers with sufficient mobility also decreased the glass transition temperature, potentially resulting in further acceleration of the hydrolysis processes. The obvious delay in reducing thermal properties alongside increase in concentration underlines the stabilizing effect of BDICDI in PLA.

The significant increment in the crystalline phase in all initially highly amorphous samples might also be caused by low-molecular-weight products of hydrolysis, which partially release the polymer chains and thus enhance mobility of the same [12]. Consequently, recrystallization of the polymer chains to produce a crystalline lattice is promoted. The effect is more obvious for rapidly hydrolyzing samples, with the degree of crystallization reaching 34% within 21 days.

### 3.2.4. Infrared spectroscopy

In order to support evidence for the stabilizing effect of BDICDI, which occurs through scavenging free carboxylic groups and water molecules, recordings were made of the FTIR-ATR spectra of the sample with 2% BDICDI prior to and during the hydrolysis experiment; these are presented as an example (Fig. 4). The reaction of aromatic BDICDI with carboxylic acids leads predominantly to N-acyl urea (Fig. 5A), witnessed by the secondary (C=O stretch at about  $1640\text{ cm}^{-1}$  and N–H bend at about  $1550\text{ cm}^{-1}$ ) and tertiary amide bands (C=O stretch at about  $1640\text{ cm}^{-1}$  and C–N bend at about  $1320\text{ cm}^{-1}$ ), as well as with water leading to urea derivatives

Table 3  
Thermal properties of selected materials prior to and during the hydrolysis process.

Sample	Initial			21 days			42 days			98 days			140 days		
	$T_m^a$ [°C]	$T_g^b$ [°C]	$\chi_c^c$ [%]	$T_m^a$ [°C]	$T_g^b$ [°C]	$\chi_c^c$ [%]	$T_m^a$ [°C]	$T_g^b$ [°C]	$\chi_c^c$ [%]	$T_m^a$ [°C]	$T_g^b$ [°C]	$\chi_c^c$ [%]	$T_m^a$ [°C]	$T_g^b$ [°C]	$\chi_c^c$ [%]
PLA	152.3	59.5	2.8	148.8	49.9	32.0	–	–	–	–	–	–	–	–	–
PLA + 0.5% BDICDI	152.3	59.6	0.9	149.2	49.1	34.0	–	–	–	–	–	–	–	–	–
PLA + 1% BDICDI	152.3	60.0	2.7	154.1	56.8	34.0	144.3	49.2	33.9	–	–	–	–	–	–
PLA + 1.5% BDICDI	152.6	58.7	2.8	152.5	59.2	24.4	153.3	59.0	26.6	154.7	54.2	33.5	–	–	–
PLA + 12% BDICDI	151.0	58.9	0.4	151.2	58.3	23.3	151.0	58.5	25.9	150.4	57.0	29.1	156.6	53.0	29.5

<sup>a</sup> Melting temperature.

<sup>b</sup> Glass transition temperature.

<sup>c</sup> Crystallinity.

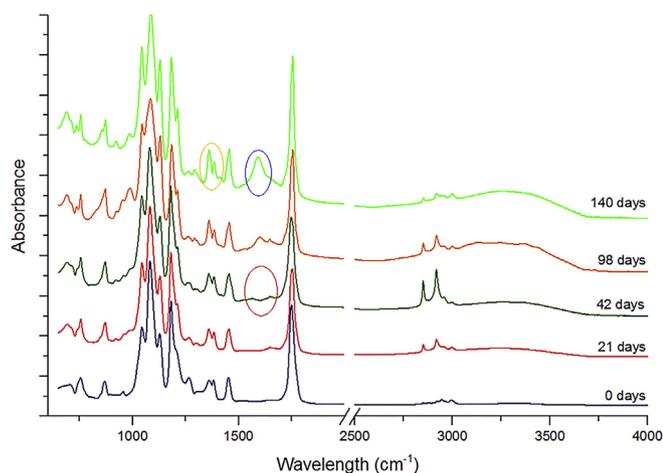


Fig. 4. FTIR-ATR spectra of PLA film stabilized with 2% of BDICDI during abiotic hydrolysis.

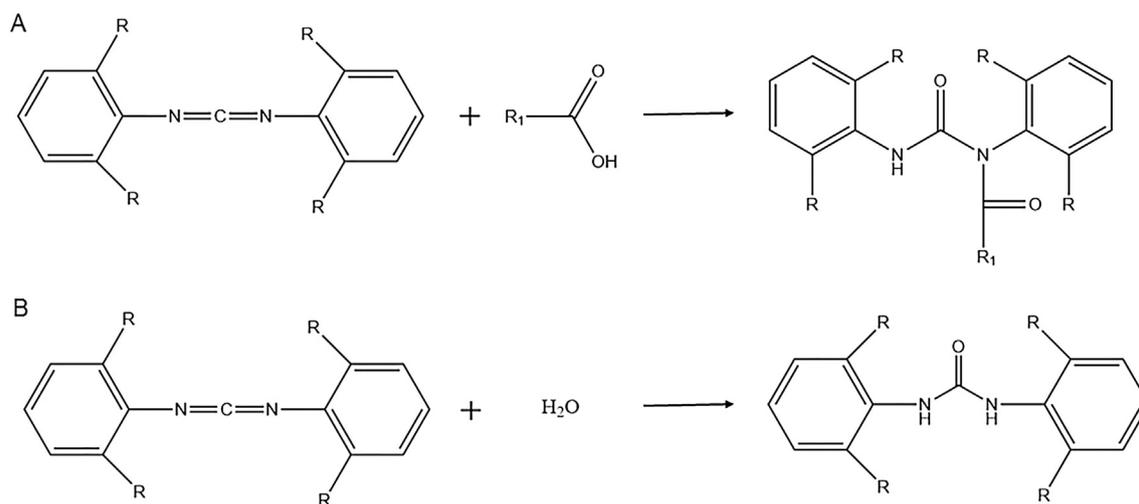


Fig. 5. Reaction of aromatic carbodiimide with carboxylic group (A) and water (B).

(Fig. 5B) characterized by a secondary amide band. The presence of these reaction products was visible from infrared peaks at about 1560 and 1640  $\text{cm}^{-1}$  (the red circle) as soon as after 42 days of hydrolysis (Fig. 4). After 98 days, which roughly corresponded to the duration of the stabilizing effect in PLA with 2% of BDICDI, and by which time the majority of the anti-hydrolysis agent should have transformed into reaction products, the appearance of newly formed peaks became obvious. Finally, the amides peak represented by the N–H bend continued to grow and become dominant, with a small peak (C=O stretch band) appearing as its shoulder (the blue circle). The tertiary amide peak at 1320  $\text{cm}^{-1}$  also proved distinctive and grew significantly (the yellow circle). Comparable peaks were recorded for all stabilized samples, their intensity depending on the given BDICDI concentrations.

Showing a relatively intensive secondary amide peak, it follows that the majority of BDICDI product was formed in reaction with water, although the product resulting from a reaction with the carboxylic groups represented by the tertiary peak was also clearly present. Thus, both of the stabilization mechanisms considered herein have been taken into account so as to explain the stabilization mechanism of BDICDI in PLA.

### 3.3. Mechanical properties

Mechanical properties were tested in order to verify the effect of BDICDI at higher concentrations on maintaining the long-term performance of PLA. The samples were examined before and after exposure to abiotic hydrolysis at appropriate time, that was adjusted for each individual samples. The time of sampling was logically chosen on the basis of evolution of molecular-weight analysis (Table 4). Insignificantly stabilized samples with concentrations of BDICDI of up to 1% w/w were subjected to testing after a short period of hydrolysis, despite an already considerable drop in  $M_w$ . By contrast, the times of sampling the materials stabilized with higher BDICDI concentrations approximately corresponded to the end of the individual plateau phases in Fig. 2, characterized by only a slight reduction in  $M_w$ .

The resultant tensile strengths, elongations at break and tensile modulus of the samples prior to and after hydrolysis are depicted in Figs. 6–8. Before hydrolysis the pure and BDICDI-stabilized PLA materials exhibited similar tensile strengths of approximately

57 MPa, elongation at break of about 5.5%, and tensile modulus from 2 GPa to 2.5 GPa, the latter slightly rising with increasing concentration of BDICDI. After hydrolysis a dramatic decline in tensile strength and elongation at break was detected for pure PLA and PLA with low concentrations of BDICDI (PLA with 0, 0.5 and 1% w/w, after 7, 10 and 21 days of exposure, respectively) (Table 4). An almost total drop in tensile strength exceeding 70% and similar trends in elongation at break indicated significant deterioration in the materials during the particular observation periods. For the record, the tensile modulus of materials remained almost unchanged.

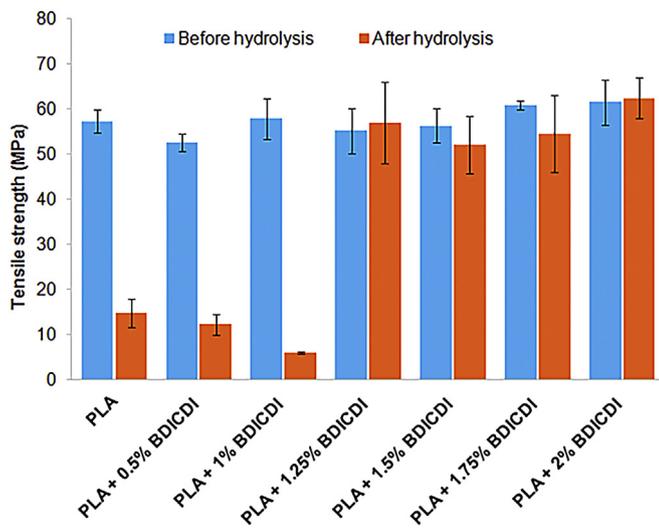
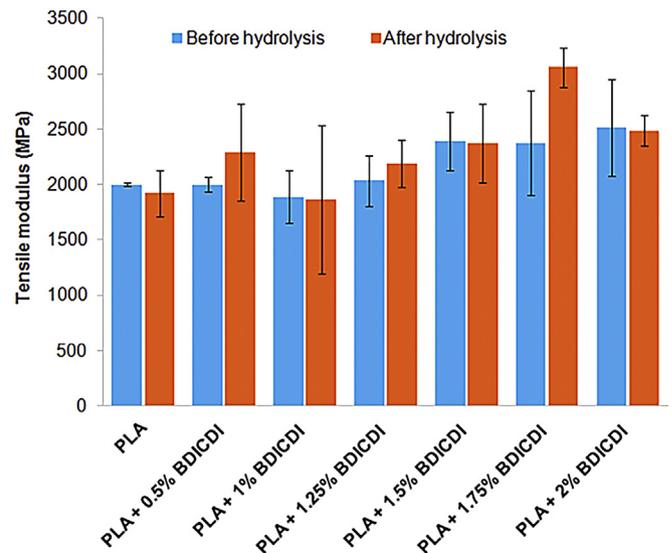
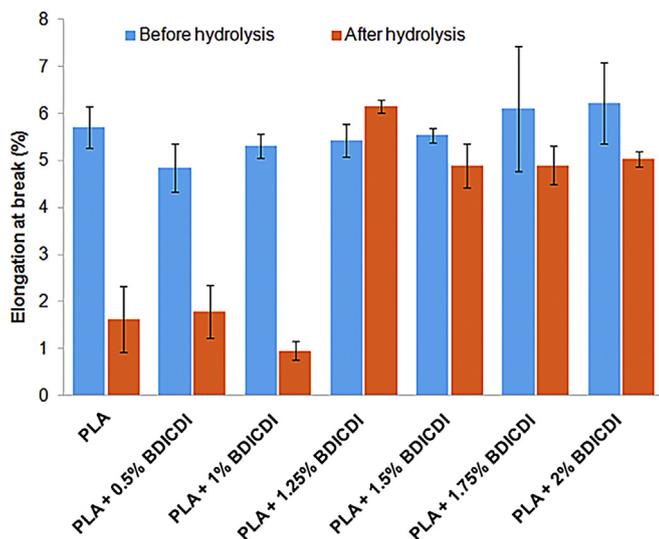
On the contrary, preservation of mechanical properties became evident for PLA with higher concentrations of BDICDI. The percentage differences in tensile strength and elongation at break for the materials between the initial and later stages of the stabilization period clearly documented substantial stability in mechanical properties (Table 4).

The above finding is in accordance with the evolution of molecular weights during hydrolysis as derived by GPC analysis. For PLA stabilized with up to 1% w/w of BDICDI, inclusive-rapid-chain scission resulted in loss of mechanical properties even during short periods of hydrolysis, whereas at higher BDICDI

**Table 4**

Changes in the mechanical properties of materials after exposure to abiotic hydrolysis at the time of sampling.

	Time <sup>a</sup> (days)	M <sub>w</sub> <sup>b</sup> (g mol <sup>-1</sup> )	Δ tensile strength <sup>c</sup> (%)	Δ elongation at break <sup>d</sup> (%)	Δ young modulus <sup>e</sup> (%)
PLA	7	51,000	-74.3	-71.5	-3.8
PLA N + 0.5% BDICDI	10	51,000	-76.8	-63.1	14.6
PL + 1% BDICDI	21	56,000	-89.8	-82.0	-1.2
PLA + 1.25% BDICDI	28	81,000	3.1	13.3	7.5
PLA + 1.5% BDICDI	63	110,000	-7.5	-11.6	-0.6
PLA + 1.75% BDICDI	77	107,000	-10.5	-19.6	28.9
PLA + 2% BDICDI	98	100,000	1.5	-19.2	-1.2

<sup>a</sup> Time of sampling of material.<sup>b</sup> Weight-average molecular weight of material at the time of sampling.<sup>c</sup> Percentage change in tensile strength before and after hydrolysis.<sup>d</sup> Percentage change in elongation at break before and after hydrolysis.<sup>e</sup> Percentage change in Young modulus before and after hydrolysis.**Fig. 6.** Tensile strength of samples before and after exposure to abiotic hydrolysis at 7, 10, 21, 28, 63, 77 and 98 days with respect to PLA containing 0, 0.5, 1, 1.25, 1.5, 1.75 and 2% w/w of BDICDI, respectively.**Fig. 8.** Tensile modulus of samples before and after exposure to abiotic hydrolysis at 7, 10, 21, 28, 63, 77 and 98 days for PLA containing 0, 0.5, 1, 1.25, 1.5, 1.75 and 2% w/w of BDICDI, respectively.**Fig. 7.** Elongation at break of samples before and after exposure to abiotic hydrolysis at 7, 10, 21, 28, 63, 77 and 98 days for PLA containing 0, 0.5, 1, 1.25, 1.5, 1.75 and 2% w/w of BDICDI, respectively.

preservation of performance by the materials over time, clearly depending on the relevant BDICDI concentration.

### 3.4. Biodegradation

The materials investigated were also subjected to an aerobic biodegradation test simulating decomposition under composting conditions, which represents the potential process for eventual disposal at the end of their service life (Fig. 9). The data describing PLA biodegradation were evaluated by applying Equation (2), which represents a model for the biodegradation of organic carbon. The parameters of the equation, along with the correlation coefficient *R*, are listed in Table 5. The model is generally in accordance with the plotted experimental data, and the resultant coefficients of determination proved significant at confidence levels less than 0.01.

The results obtained showed similar trends as revealed in abiotic hydrolysis experiments; these being either a non-existent or negligible stabilization effect at concentrations of 0.5 and 1% w/w BDICDI and strong effects at 1.5% and 2% w/w BDICDI, which increased in conjunction with the concentration of the anti-hydrolysis agent. The stabilization effect could be quantified by the length of lag phase *c* calculated from the kinetics model, which expressed the initial phase of biodegradation prior to the onset of CO<sub>2</sub> production. While the least delay in the onset of carbon

concentrations suppression of hydrolytic degradation led to

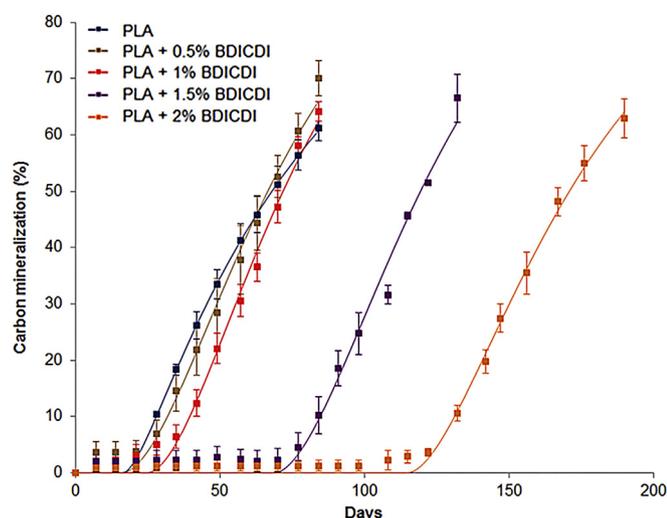


Fig. 9. Biodegradation experiment under composting conditions for pure PLA and BDICDI-stabilized PLA films; error bars correspond to twice standard deviation ( $n = 3$ ).

Table 5

Kinetic model parameters and coefficients of determination ( $R^2$ ) for the biodegradation of pure PLA and BDICDI-stabilized PLA films.

Sample	$C_{aq,0}^a$ (%)	$C_{h,0}^b$ (%)	$k_{aq}^c$ ( $\text{day}^{-1}$ )	$k_h^d$ ( $\text{day}^{-1}$ )	$C^e$ (days)	$R^2$
PLA	0	100	0.1866	0.0150	16.0	0.9999
PLA + 0.5% BDICDI	0	100	0.0330	0.0330	15.7	0.9961
PLA + 1% BDICDI	0	100	0.0358	0.0352	24.5	0.9953
PLA + 1.5% BDICDI	0	100	0.0320	0.0318	69.2	0.9922
PLA + 2% BDICDI	0	100	0.0589	0.0183	100	0.9977

<sup>a</sup> Percentage of initial intermediate solid carbon.

<sup>b</sup> Percentages of initial hydrolysable solid carbon.

<sup>c</sup> Rate constant for mineralizing water-soluble carbon into carbon dioxide.

<sup>d</sup> First-order hydrolysis rate constants.

<sup>e</sup> Duration of lag phase during the initial phase of biodegradation before the onset of  $\text{CO}_2$  production.

mineralization was almost identical for pure PLA and PLA +0.5% BDICDI (16 and 15.6 days respectively), for PLA with 1% of BDICDI it increased to 24.5 days. For PLA stabilized with 1.5 and 2% w/w BDICDI, the onset of decomposition was delayed to almost 70 and 100 days, respectively.

Previous works [10] have suggested that abiotic hydrolysis could represent the rate-limiting step of PLA biodegradation under composting conditions. In order for this assumption to be correct the lengths of lag phase  $c$  determined from both experiments - abiotic hydrolysis and biodegradation - should be relatively comparable for individual samples. However, after comparing the corresponding parameters, it became evident that while pure PLA with almost identical lengths of lag phase complied with this hypothesis, the stabilized samples - especially those with higher BDICDI concentrations - exhibited earlier onset of  $\text{CO}_2$  in comparison with the corresponding curve for abiotic hydrolysis (see Fig. 1).

This indicates a certain level of acceleration for depolymerization processes above the level set by abiotic hydrolysis during incubation under biotic composting conditions. In highly stabilized samples, which are well protected against abiotic hydrolysis, the cleavage of ester bonds by extracellular enzymes of microorganisms might have become manifest concurrently with abiotic hydrolysis. This assumption is also supported by the slightly higher hydrolysis rate constants for BDICDI-stabilized samples in comparison with pure PLA. Another explanation could be the low stability of the BDICDI additive in such a biotic environment.

#### 4. Conclusion

Investigation was made on the stabilization effects of various concentrations of the anti-hydrolysis agent (BDICDI) in PLA films, prepared by melt blending, and these were compared with the initial pure polymer during an abiotic hydrolysis experiment and aerobic composting.

Bis(2,6-diisopropylphenyl)carbodiimide (BDICDI) was shown to be an efficient stabilizer of PLA-suppressing chain scissions of ester bonds during abiotic hydrolysis, especially at concentrations above 1.5% w/w. Beyond this concentration limit the stabilization effect furthered in conjunction with greater concentrations of BDICDI. The period of stabilization can be characterized by only a slight reduction in  $M_w$ , not more than 20% from the original values at around 69, 87, and 96 days, in PLA film stabilized with 1.5, 1.75 and 2% w/w of BDICDI at 58 °C. After the dose of stabilizer is depleted, probably via reaction with water molecules and carboxylic groups, the material is hydrolyzed at a comparable or even slightly higher rate than pure PLA. At low BDICDI concentrations (of up to 1% w/w), the stabilization effect was insignificant, potentially caused by

depletion of BDICDI as early on as during melt processing at relatively high temperatures. Suppression of hydrolytic degradation within the suggested period also triggered preservation of thermal and mechanical properties, thereby meeting requirements for products intended for long-term performance. In the composting environment, the stabilization effect of BDICDI was comparable, albeit with a slightly faster onset of mineralization for samples stabilized with higher concentrations of BDICDI. The reasons for such modest acceleration in depolymerization processes might due to extracellular enzymes produced by microorganisms or more rapid degradation of the additive under biotic conditions. It can be concluded that a certain amount of BDICDI above the minimal concentration limit, dependent on the duration and conditions of thermal processing, shall be necessary for effectively stabilizing PLA against hydrolysis during the lifetime of a product. By applying the appropriate amount of BDICDI, the approximate duration of stabilization could be set to suit the desired requirements of the final product. This principle demonstrates the potential that exists to design a material with time-programmable properties. The strong stabilization effect shown at relatively low BDICDI concentrations, and the subsequent rapid onset of hydrolysis after BDICDI depletion, strongly support the hypothesis for autocatalytic mechanisms relating to hydrolytic degradation.

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