

## INFLUENCE OF TIME AND ROOM TEMPERATURE ON MECHANICAL AND THERMAL DEGRADATION OF POLY(LACTIC) ACID

by

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*Poly(lactic) acid (PLA), is a compostable thermoplastic which degrades fast under composting conditions of microorganisms, high humidity, and temperatures. However, PLA degrades slowly below its glass transition temperature and in low humidity, hence, when used as short-shelf life product containers and not disposed to composting systems, PLA may cause environmental pollution. Therefore, when not disposed to proper waste management systems, the effect of long incubation time at room temperature on mechanical and thermal properties of PLA is the main concern of this study. To determine the effect of room temperature on semi-crystalline PLA degradation at a low humidity percentage, PLA films (PLA2) were kept at room temperature for 5 years at 40±10% humidity. Some PLA films (PLA3) were pre-treated at 55 °C under dry conditions for one year and then kept at room temperature for four years. Influence of incubation time and temperature on PLA degradation was evaluated by mechanical, thermal analyses and by FTIR spectroscopy analysis and compared with the initial PLA samples (PLA1). Mainly mechanical properties of PLA were affected by incubation temperature and time since 68% tensile strength loss was observed in PLA3 samples which were pre-treated at 55 °C and 34% decrease in tensile strength was observed in PLA2 samples. Thermal behavior of PLA was also influenced by incubation time and temperature as degree of crystallinity decreased 5% and 3% in PLA2 and PLA3 samples, respectively. Deformation of CH bonds and amorphous phase degradation were revealed by FTIR analyses in PLA2 and PLA3 samples.*

Key words: *poly(lactic) acid, degradation, thermal properties, mechanical properties*

### Introduction

Conventional thermoplastics such as polyethylene (PE), polypropylene (PP), polystyrene (PS) have diverse applications mainly due to their strong mechanical properties [1-4]. However, these conventional thermoplastics are from non-renewable resources and when used as short-shelf life product containers such as food packagings, they cause environmental pollution problems since they are not biodegradable [3-5]. Therefore, these fossil fuel based plastics accumulate in the environment when they are disposed. Studies regarding environmental pollution problem have been conducted in the recent years [6-9]. The PLA is a compostable and

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biodegradable thermoplastic produced from renewable resources and has the potential to replace non-biodegradable plastics from non-renewable sources since PLA has strong mechanical properties comparable to non-degradable plastics [10, 11]. When composted, high molecular weight PLA degrades fast, in one-two months incubation time depending on the composition of PLA, influenced by high temperatures, 60 °C or higher; and high humidity (60%) of composting process and microorganisms present in compost [10, 12-17]. Temperatures near the glass transition,  $T_g$ , of PLA and high humidity cause hydrolysis of PLA chains and microorganisms in compost can decompose PLA [12, 15, 18-21]. Therefore, in the recent years PLA, is increasingly being used as an alternative to conventional plastics for short-shelf life product containers, packagings, *etc.* as it decomposes at elevated temperatures during composting. However, physical and chemical properties of PLA (molecular weight, optical purity, crystallinity,  $T_g$ , and melting temperature,  $T_m$ ) and also environmental conditions (temperature, incubation time, pH, humidity, microorganisms) affect environmental degradation rate of PLA at a great extent [12, 21-25]. When not entering composting system, PLA degradation is reported to be slow due to lack of high temperatures and humidity and lack of microorganisms [8, 12, 23, 26]. Since PLA is from renewable resources and it has the potential to replace non-biodegradable plastics from non-renewable sources due to its strong mechanical qualities comparable to fossil fuel based plastics, understanding its degradation behaviour when not entering proper waste management systems is important.

Therefore, this study aims to evaluate PLA degradation behavior under room temperature with low humidity (40 ±10%) in long term when PLA short-shelf life product containers are not disposed to composting systems.

## Materials and methods

### *Poly(lactic acid) source*

The PLA films were cut from PLA food containers produced from semi-crystalline PLA resins (Ingeo™ Biopolymer, Grade 2003D). The PLA resins were manufactured by NatureWorks LLC (USA) and distributed through VegWare, Edinburgh, UK, in the form of PLA food containers. Molecular weight of PLA films were determined as  $160000 \pm 5000$  g/mol, by gel permeation chromatography. According to the supplier, PLA resins contained 4% D-lactic acid isomer, had a density of  $1.24$  g/cm<sup>3</sup>, melting temperature of 160 °C, glass transition temperature of 60 °C, and crystallinity of 35%.

### *Preparation and incubation of PLA films*

The PLA food container lids were used to cut PLA films of  $7 \times 3 \times 0.02$  cm. The PLA films were surface sterilized with 70% (v/v) ethanol prior to incubation. Initial PLA samples, PLA1, was used in the beginning of the experiments. The PLA samples, PLA2, were then placed in a petri dish and kept at room conditions of  $20 \pm 2$  °C with 40 ±10% relative humidity [27] in dark for four years. The PLA3 samples were pre-treated by keeping them at 55 °C in a dry oven for a year. Then, PLA3 films were kept under the same conditions with PLA2 films for four years.

### *Thermal Analysis*

Thermal analysis of PLA films was used to determine the glass transition temperature,  $T_g$ , degree of crystallinity and melting temperature,  $T_m$ , of PLA films by using Perkin-Elmer DSC 8500 with programmed heating at 10 °C/min from 15 °C to 250 °C. Three replicates of 6 to 10 mg were tested for each PLA specimen. The degree of crystallinity,  $\chi_c$ , was determined

using eq. (1) where  $\Delta H_m$  is the enthalpy of melting and  $\Delta H_c$  is the crystallization enthalpy. Heat of fusion,  $\Delta H_f$ , is 93 J/g as the melting enthalpy of a PLA crystal that has infinite size [28].

$$\chi_c = 100 \frac{\Delta H_m - \Delta H_c}{\Delta H_f} \quad (1)$$

### Mechanical tests

Degradation of PLA films were evaluated by tensile tests according to ASTM D638 standard. The PLA Lloyd Instruments LF Plus Single Column Universal Materials Testing Machine with a crosshead speed of 10 mm/min at  $23 \pm 2^\circ\text{C}$  was used as previously described [29]. The PLA dumb-bell shapes of 3.8-4.2 mm width, 0.2-0.3 mm thickness, and 50 mm total length were cut from PLA films of  $7 \times 3 \times 0.02$  cm prior to mechanical tests using a manual press (Wallace Test Equipment, UK).

### Fourier-transformation infrared spectroscopy analysis

The PLA samples were analyzed using Perkin Elmer Spectrum 400 FTIR spectrometer. All PLA1, PLA2, and PLA3 films were taken in the  $4000\text{-}400\text{ cm}^{-1}$  range, with a resolution of  $2\text{ cm}^{-1}$  after 4 scans and transmittance mode was applied during the measurement.

## Results

### Physical changes of PLA films at room temperature

The PLA films kept at room temperature with  $40 \pm 10\%$  humidity were visually evaluated. Initial PLA films, PLA1 is shown in fig. 1(a). When PLA films were kept at room temperature for 5 years in dark, PLA2, films remained unchanged as they were still transparent compared to initial PLA films, fig. 2(b). The PLA films initially kept at  $55^\circ\text{C}$  for a year, PLA3, became cloudy at the end of a year and they were still more opaque after they were kept at room temperature for 4 years compared to PLA1 and PLA2 samples, fig. 1(c).

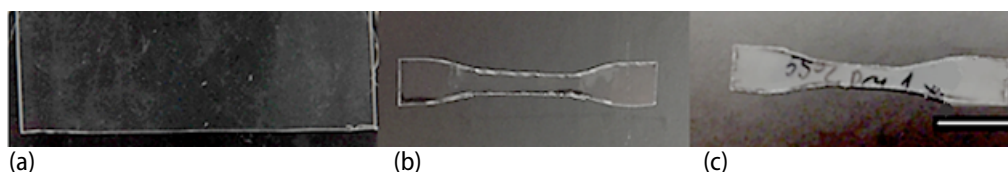


Figure 1. Physical changes in PLA films; (a) PLA1: initial films prior to mechanical tests, (b) PLA2 dumb-bell: PLA films kept at room temperature for five years, (c) PLA3 dumb-bell: PLA films pre-treated at  $55^\circ\text{C}$  for a year prior to four years of incubation at room temperature; Scale bar represents 1.5 cm

### Mechanical degradation assessment

Degradation of PLA1, PLA2, and PLA3 films were assessed by mechanical tests, tab. 1. Initial tensile strength of PLA, PLA1, was 64.93 MPa and after five years at room temperature tensile strength of PLA, PLA2, decreased to 42.88 MPa. Tensile strength of pre-treated PLA films, PLA3, decreased from 64.93 MPa to 20.814 MPa. Therefore 33.95% decrease in tensile strength when kept at room condition for five years and 68.00% decrease when pre-treated at  $55^\circ\text{C}$  were observed. In addition to this, Young's Modulus of PLA films were determined. Initial modulus was 1807.0 MPa and after five years at room temperature, modulus decreased to

**Table 1. Mechanical properties of PLA films throughout incubation time PLA1: initial films; PLA2: PLA films kept at room temperature for five years; PLA3: PLA films pre-treated at 55 °C for a year prior to four years of incubation at room temperature**

Samples	Tensile strength [MPa]	Percentage strain at break [%]	Young's modulus [MPa]
PLA1	64.93± 0.03	33.82 ± 0.04	1807.0±0.01
PLA2	42.88± 0.01	6.07± 0.01	1539.9±0.03
PLA3	20.814± 0.02	2.77± 0.03	1366± 0.01

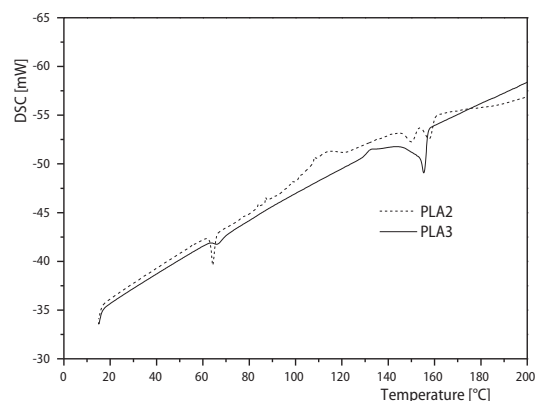
1539.9 MPa which is a 14.77% decrease. Modulus of PLA3, decreased to 1366 MPa after one year of incubation (24.40% decrease). Percentage strain at break also decreased significantly as in PLA2, it decreased from 33% to 6.07% and in PLA3 samples it decreased to 2.77%.

### Thermal behaviour assessment

The influence of room conditions on PLA films' the glass transition temperature,  $T_g$ , degree of crystallization and melting temperature,  $T_m$ , were assessed by differential scanning calorimetry (DSC) measurement. Enthalpy of melting,  $\Delta H_m$ , and the crystallization enthalpy  $\Delta H_c$  were also determined. Thermal properties of the same PLA2 and PLA3 samples are presented in tab. 2 and DSC heating curves of PLA2 and PLA3 are shown in fig. 2. Thermal properties of PLA1 samples were determined by the supplier as  $T_m$  of 160 °C,  $T_g$  of 60 °C, and degree of crystallinity of 35%. In the cooling portion of the thermogram, no cold crystallization exotherm was observed in PLA3 samples.  $T_m$  decreased from 160 °C to 157.57 °C and 155.39 °C in PLA2 and PLA3, respectively. Degree of crystallinity, eq. (1), slightly decreased in PLA2 and PLA3 samples, 5% and 3%, respectively, compared to PLA1 samples. The  $T_g$  of PLA2 and PLA3 increased to 64.15 °C and 66.21 °C, respectively, from 60 °C.

**Table 2. Thermal properties of PLA2: PLA films kept at room temperature for five years; PLA3: PLA films pre-treated at 55 °C for a year prior to four years of incubation at room temperature**

Samples	$T_c$ [°C]	$T_m$ [°C]	$T_g$ [°C]	$\Delta H_c$ [Jg <sup>-1</sup> ]	$\Delta H_m$ [Jg <sup>-1</sup> ]	$\chi_c$ [%]
PLA2	112.29	157.57	64.15	13.39	17.51	33.22
PLA3	–	155.39	66.21	–	31.52	33.89



**Figure 2. The DSC heating curves of PLA2 and PLA3 samples (10 °C/min heating from 15 °C to 250 °C). PLA2: PLA films kept at room temperature for five years; PLA3: PLA films pre-treated at 55 °C for a year prior to four years of incubation at room temperature**

### Infrared properties

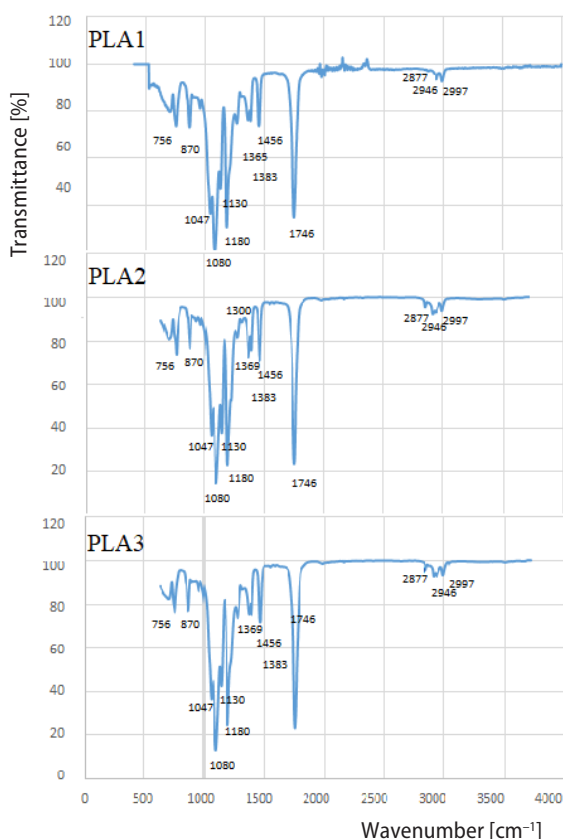
The FTIR spectra of PLA1, PLA2, PLA3 are presented in fig. 3. All PLA samples, PLA1, PLA2, PLA3, had similar FTIR peaks. The infrared (IR) bands detected at 2997, 2946, and 2877 cm<sup>-1</sup> were observed in all PLA samples corresponding to CH stretching region [30]. The PLA molecules' characteristic ester bond, C=O stretching, was detected as a strong peak at 1746 cm<sup>-1</sup> in all PLA samples [10]. A 1500-1300 cm<sup>-1</sup> region was assigned to CH<sub>3</sub> bands' deformation [30]. A peak observed at 1456 cm<sup>-1</sup> was assigned to anti-symmetric CH<sub>3</sub> bend of lactic acid units [30]. The CH deformation bend and asymmetric bands were detected at 1383 and 1365 cm<sup>-1</sup>, respectively [10]. These peaks had more amplitude in PLA2

and PLA3 samples. Peak appeared at  $1300\text{ cm}^{-1}$  was due to CH bending modes and this peak had more amplitude in PLA1 and PLA2 compared to PLA3 samples [10]. Two peaks detected at  $1130$  and  $1047\text{ cm}^{-1}$  were assigned to  $\text{CH}_3$  vibrations of lactic acid units and symmetrical C-O-C stretching was observed as a peak at  $1080\text{ cm}^{-1}$  and the peak at  $1180\text{ cm}^{-1}$  was due to antisymmetric stretching of C-O-C [30]. Specifically peaks at  $1180$ ,  $1130$ , and  $1080\text{ cm}^{-1}$  had more amplitude in PLA2 and PLA3 samples. Two peaks at  $871\text{ cm}^{-1}$  and  $756\text{ cm}^{-1}$  were assigned to amorphous and crystalline regions, respectively [10] and appeared in all PLA samples. However, peak at  $871\text{ cm}^{-1}$  corresponding to amorphous phase had more amplitude in PLA1 samples than PLA2 and PLA3 samples.

### Discussion

When PLA is used as short-shelf-life products containers, we investigated the effects of temperature and incubation time on PLA degradation when PLA products are kept at room temperature instead of being disposed to compost. Some PLA samples were pre-treated at  $55\text{ }^\circ\text{C}$  for a year prior to incubation at room temperature with  $40\pm 10\%$  humidity for four years. The PLA samples were kept in dark during incubation since UV light can influence PLA degradation [31]. Influence of room temperature on PLA degradation and PLA structural/thermal change were assessed by tensile, thermal and FTIR analyses.

The PLA degradation is reported to be slow at low temperatures and low humidity [8, 12, 23, 26]. It has also previously been shown that little or no degradation occurs at temperatures of  $25\text{ }^\circ\text{C}$  and  $37\text{ }^\circ\text{C}$  under dry conditions or even in composting systems at constant temperatures of  $25\text{ }^\circ\text{C}$  and  $37\text{ }^\circ\text{C}$  over a year of incubation time [15]. Temperature is a key factor on PLA degradation under humid conditions such as composting systems [10, 12-17]. Due to  $T_g$ , high molecular weight PLA degradation is reported to be fast near its  $T_g$  in the presence of water since PLA forms flexible chains at  $T_g$  enhancing water absorption therefore hydrolysis [10, 12, 15, 21]. In this study,  $T_g$  of semi-crystalline PLA1 was  $60\text{ }^\circ\text{C}$  and since  $55\text{ }^\circ\text{C}$  is near its  $T_g$ , when PLA was kept at  $55\text{ }^\circ\text{C}$  under dry conditions for a year, mechanical properties decreased the most as 68% of tensile strength loss was observed, whereas 34% tensile strength loss was observed in PLA2 samples. Moreover, approximately 24% of modulus decreased in PLA3 samples while 14% of modulus decrease was observed in PLA2 samples. Percentage strain at break



**Figure 3. The FTIR spectra of PLA samples; PLA1: initial films; PLA2: PLA films kept at room temperature for five years; PLA3: PLA films pre-treated at  $55\text{ }^\circ\text{C}$  for a year prior to four years of incubation at room temperature**

also decreased more in PLA3 samples (from 33% to 2.77%) compared to PLA2 which decreased to 6.07% indicating that PLA is more susceptible to more polymer cleavage when kept near its  $T_g$  even when no or little hydrolysis is occurring. The effect of elevated temperature pre-treatment near its  $T_g$  was also observed visually, fig. 1, since PLA3 turned partly opaque compared to PLA1 and PLA2. Previously, it was shown that transparent PLA films turn opaque and white when PLA is kept near its  $T_g$  and susceptible to mechanical disintegration [15].

Thermal behaviour of PLA was also affected by incubation time and pre-treatment of PLA near its  $T_g$ . The DSC revealed that  $T_m$  of PLA decreased from 160 °C to 157.57 °C and 155.39 °C in PLA2 and PLA3 samples, respectively, as an indication of PLA degradation. Moreover, degree of crystallinity decreased 5% and 3% in PLA2 and PLA3 samples, respectively. Crystallinity decrease was also shown by Young's Modulus decrease. Amorphous regions might have degraded initially in PLA samples since it has been reported that in semi-crystalline PLA degradation, initially ester linkages of amorphous regions are degraded [32, 33]. The PLA used in this study is also a semi-crystalline polymer that contain both crystalline and amorphous regions since the D-isomer is less than 6% [23, 34]. However, since pre-treatment was under dry conditions, decrease of  $T_m$  and  $T_g$  were not observed distinctly in thermal analyses, tab. 2. In the cooling portion of the thermogram, no cold crystallization exotherm was observed in PLA3 samples which was also observed in another study in literature as high molecular PLA did not crystallize during cooling [35]. The  $T_g$  decrease of PLA is associated with molecular weight reduction [12]. Interestingly,  $T_g$  of PLA2 and PLA3 increased to 64.15 °C and 66.21 °C from 60 °C in 5-year incubation time. Increase of  $T_g$  in this study might be due to amorphous regions degradation since PLA used in this study is a semi-crystalline. The FTIR spectra revealed that C-C stretch peak at 871  $\text{cm}^{-1}$  corresponding to amorphous phase and peak at 756  $\text{cm}^{-1}$  corresponding to crystalline phase had similar amplitudes in PLA1 samples, however, amplitude of peak at 871  $\text{cm}^{-1}$  decreased in both PLA2 and PLA3 samples revealing that initially amorphous phases were degraded in semi-crystalline PLA samples during this 5 year-incubation time. The change in this peak was previously reported to result from crystallization change [13] and aforementioned in thermal properties, PLA2 and PLA3 samples had less crystallization than PLA1 samples. Bond deformations were also observed by FTIR analysis. The CH deformation was observed in PLA2 and PLA3 samples since peaks related to CH deformation at 1456, 1383, and 1365  $\text{cm}^{-1}$  [10,13] had more amplitude in PLA2 and PLA3 samples than PLA1. Another peak related to CH deformation at 1300  $\text{cm}^{-1}$  appeared with more amplitude in only PLA3 samples. Peaks detected at 1180, 1130, 1047, and 1080  $\text{cm}^{-1}$  were mainly related to CO ester linkages [13, 30] and amplitude of these peaks were different in PLA2 and PLA3 samples than PLA1 samples. The CO ester linkage is assigned to be the site for hydrolysis [13]. Although PLA samples were kept under room conditions where humidity is lower than composting conditions, FTIR indicated signs of hydrolysis of ester linkages which is in accordance with the reports that in semi-crystalline PLA degradation, initially ester linkages of amorphous regions are degraded [32, 33].

## Conclusion

We comprehensively examined PLA degradation behaviour under room conditions in a 5-year incubation time and determined variation of mainly mechanical and thermal properties of PLA. Some PLA samples, PLA3, were incubated under dry conditions at 55 °C for a year prior to incubation under room temperature with 40±10% humidity for four years. The PLA2 samples were kept at room temperature for five years. The greatest variation was observed on mechanical properties of PLA since PLA3 samples and also PLA2 samples lost their mechanical properties to a great extent as PLA3 samples lost 68% of its tensile strength and PLA2 lost

34% of its tensile strength. Degradation was also observed in thermal properties of PLA since melting temperature of PLA decreased to 156 °C and 157 °C from 160 °C and the degree of crystallinity decreased in PLA2 and PLA3 samples, 5% and 3%, respectively, compared to PLA1 samples. Some of the bonds were also deformed due to degradation revealed by FTIR analysis. This study suggests that even when not disposed to composting systems, PLA can slowly degrade under room temperature.

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