

THE EFFECTS OF CHEMICAL AND ENVIRONMENTAL CONDITIONS ON THE DEGRADATION OF POLY LACTIC ACIDS

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ABSTRACT:

This paper describes a detailed study concerning the effects of chemicals like sodium hydroxide and environmental conditions such as temperature and time on the degradation of Poly lactic acid (PLA) as compared to Polyethylene terephthalate (PET). The aim is to study the effects of chemical and environmental conditions on the degradation of Poly lactic acids. In view of this, samples of PLA flat filament yarns and partially oriented PET yarns were hydrolysed with two different pH media i.e. neutral pH 7, and alkali pH 12.0-13.5 to study the physical changes that occurred in the yarn structure. Both the hydrolysed and non-hydrolysed yarns subjected to tensile test, DSC scans and FTIR analysis and the changes and the effects that took place before and after hydrolytic degradation at varied temperatures and times were analysed. The study showed that, at 60°C and 90°C hydrolysis yielded significant change in the physical appearance of the sample yarns as well as the structure. It could therefore be concluded that degradation highly occurred in the alkali medium than in the neutral medium when the time and temperatures were increased. This was also testified by the fact that elevated time and temperature aided in degrading the PLA flat filament yarns significantly than that of the partially oriented PET yarns.

Key words: Chemical, Environmental, Degradation, Poly lactic acid, Polyethylene terephthalate

1. INTRODUCTION

Recently, there has been a considerable interest in the study of degradable polymers due to their increasingly attractive environmental, biomedical and agricultural applications. One of the most promising classes of materials is the aliphatic polyesters. Currently, they are used for packaging application, and mulch films to solve the problems relating to plastic waste accumulation Albertsson (2002). Aliphatic polyesters are among the mostly used biodegradable polymers especially in medical applications and have been extensively investigated in the past. The ester linkages are frequently encountered in nature and hence it is expected that synthetic polymers containing such linkages and an appropriate structure would be environmentally degradable Pistner et al (1993). The degradation of aliphatic polyesters can be achieved by several mechanisms which include chemical hydrolysis, microbial, enzymatic and thermal degradation.

According to Albertsson (2002), aliphatic polyester degradation proceeds either at the surface

or within the bulk and this can be controlled by a wide variety of compositional and property variables such as matrix morphology, chain orientation, chemical composition, molecular weight and distribution, the presence of residual monomers, oligomers and other low molecular weight products, size and shape of the specimen and the degradation environment. The degradation environment depends on conditions such as the presence of moisture, oxygen, microorganisms, enzymes, pH, and temperature. These chemical and environmental conditions do have measurable effect on aliphatic polyesters such as poly lactic acids (PLA). Poly lactic acid (PLA) polymer derived from annually renewable resources such as corn is fully compostable and biodegradable compared to conventional poly ethylene terephthalate (PET). It has the advantage of being recycled quickly than PET and therefore they are now widely used for food packaging.

PLA can be described as linear aliphatic polyester produced by poly-condensation of naturally produced lactic acid or by the catalytic ring opening of the lactide group. Lactic acid is produced (via starch fermentation) as a co-product of corn wet

milling. The ester linkages in PLA are sensitive to both chemical hydrolysis and enzymatic chain cleavage. PLA is often blended with starch to increase biodegradability and reduce costs. According to Blackburn (2005), PLA is biodegradable, compostable and recyclable

PLA can be biodegraded in the soil in 20 – 30 months Perepelkin (2002), and in 45 – 60 days in compost conditions Tokiwa et al (2006), (typically 50 – 60°C and 90 -95% humidity). Its rate of biodegradability is subject to the size and shape of the article and the environment to which it is exposed. PLA degrades essentially by hydrolysis in the field and compost sites, even in the absence of microorganisms Hok et al (1999).

The degree of PLA hydrolysis is dependent on time, temperature and pH. PLA can degrade by hydrolysis degradation under combined aqueous high temperature and alkaline conditions. PLA is very sensitive to alkali and high temperatures therefore degrade in alkali solution and in water at higher temperatures by simple hydrolysis. This problem is more severe in aliphatic polyesters than in the aromatic polyesters such as poly (ethylene terephthalate) (PET). This is partly so because PLA has lower melting and softening temperatures than PET.

1.1 Problem Statement

The disposal of synthetic materials that are neither degradable nor renewable is clearly a major environmental problem. The uses of synthetic fibres for many applications such as food packaging are associated with recycling problems due to their non-degradable properties as compared to renewable biodegradable fibres like PLA. The volume of waste disposal and landfills of these non-renewable synthetic fibres is very high and these affect the environment in so many ways.

1.2 Aim and Objectives

The aim of this paper is to study the various hydrolytic effects and the changes that occur in the degradation of Poly lactic acid and Polyethylene terephthalate.

The specific objectives of the study are:

- To identify the effect of chemical and environmental conditions on the degradation of PLA as compared with PET
- To identify the changes that occur on the PLA after the hydrolysis
- To establish the time and temperature related degraded effects on PLA as compared with PET.

2. RESEARCH METHODS

The materials used in the study were Flat filament PLA yarn and partially oriented PET yarn. The PLA flat filament yarns were provided by Nature Works LLC, USA. The specifications of the yarns used in the study are shown below:

PLA Flat filament yarn: 153 denier (16 tex); 34 filaments,

PET Partially Oriented Filament Yarn: 298 denier (31 tex); 27 filaments.

- Hydrolysis with neutral and alkali solutions

Samples of both PLA and PET yarns were immersed separately in 100mls of distilled water, 0.5% and 1.0% sodium hydroxide solution at temperatures of 40°C, 60°C and 90°C respectively, and for duration of 5mins, 15mins, 30mins and 60mins tested. The sodium hydroxide solution is a liquor ratio of 10:1. The procedure was carried out in a 100mls volumetric flask placed in heated water bath. Temperature was controlled by thermometer to make it constant. The pH was 7.0 for the neural solution and 12.0 – 13.5 for the alkali solution.

- Tensile Tests

All tensile tests measurements were carried out in accordance with British Standard EN ISO 2062:1995, using and Instron Model 4411 tensile tester, under standard laboratory conditions (20 ± 2°C; 65 ± 2 % r.h.), with gauge-length of 50mm and at an applied strain rate of 1 min⁻¹. Five replicates of PLA and PET were tested for each nominally-equivalent sample.

- FTIR – ATR Tests

Appreciable lengths of yarn from both PLA and PET yarns (non-hydrolysed and hydrolysed) samples were placed between the Perspex slide and the ATR crystal in the instrument. The total internal

reflectance energy arises along the ATR crystal (Zinc Selenide (ZnSe) ATR) – yarn interface. Entrance beam from the source of the energy goes into the ATR crystal and beam is reflected within the crystal. Depth of penetration with a ZnSe crystal is 1.5 microns. The non – hydrolysed and hydrolysed PLA and PET yarns were individually mounted on the sample holder to detect changes that occur on the surface of the fibres before and after hydrolysis. The FTIR – ATR measurement was conducted in ATR (Attenuated Total Reflection) mode. The FTIR – ATR measurements were done using Nicolet Nic-Plan™ FTIR Microscope with ATR accessory – ZnSe crystal (~1.5 microns). The sample yarns were analysed at 5cm resolution and 150 scans per measurement.

- DSC Tests

The DSC results were obtained using a TA Instruments Model Q100 Modulated DSC (MDSC®) with refrigerated cooling system (RCS). 4 – 6mg of sample size of PLA and PET were scanned in the temperature range of 0 - 200°C for PLA and 0 - 300°C for PET at a heating rate of 20°C min⁻¹. The samples were heated to 200°C and 300°C respectively in the first scan under the same conditions. T_m (the major peak melting point) and ΔH_f were determined from the first scan, while T_g (inflection point of the glass transition step) was determined from the third scan. There are three cycles i.e. cycle 1 heating of the samples, cycle 2 represents the cooling of the sample at a cooling rate of 10°C and cycle 3 represents the heating of the sample again. The glass transition temperature (T_g), crystallinity temperature (T_c) and melting temperature (T_m) were taken and analysed.

3. RESULTS AND DISCUSSION

- Assessment of Hydrolysed Samples

The hydrolysed PLA and the PET yarns at 40°C for 5mins and 15mins with water did not show any change in the structure. As the time was increased to 30mins and 60mins, they exhibited a slight change. At 60°C, hydrolysis for 5mins and 15mins, the yarns exhibited steady degradation in the structure but as the time was increased to 30 and 60mins, there was some weight loss and the yarns became slightly weak. At 90°C, for 5 and 15mins, there was a slight change due to the elevated temperature. The yarns became very weak at 30 and 60mins. The hydrolysed PLA and PET yarn at 40°C

for 5 and 15mins with 0.5% and 1.0% sodium hydroxide solution exhibited a slight degradation of the structure. For 30 and 60mins, there was a significant change since both PLA and PET were sensitive to alkali. At 60°C, hydrolysis for 5 and 15mins, the yarns were weak, but weaker at 30 and 60mins. At 90°C for 5 and 15mins, the yarns became very weak indicating how highly the yarns have been degraded. For 30 and 60mins, both yarns degraded and became very weak that it was difficult to retrieve an appreciable length of yarn for FTIR and tensile test.

- Characterization Studies

Data relating to the as-received yarns is represented in Figs. 1 – 10 and Tables 1 – 6

PLA Flat filament yarn vs. PET Partially Oriented Filament Yarn

Fig. 1 – 3 presents tensile stress – strain curves obtained from both non-hydrolysed and hydrolysed PLA and PET yarns at 30mins with water, 30mins with 0.5% sodium hydroxide solution and 15mins at 1.0% sodium hydroxide solution respectively.

Fig. 4 – 10 presents data on the FTIR and DSC tests conducted on both non-hydrolysed and hydrolysed yarns. Tables 1 – 6 represent the glass transition, crystallinity and melting temperatures both the non-hydrolysed and hydrolysed PLA and PET 40, 60 and 90 degrees.

The observed tensile properties of the non-hydrolysed and hydrolysed PLA and PET yarns are clearly different. In particular, both tenacity and initial modulus for the PLA yarns were higher than that for the PET yarns both for the non-hydrolysed and hydrolysed at varied temperatures.

TENSILE STRESS – STRAIN CURVES

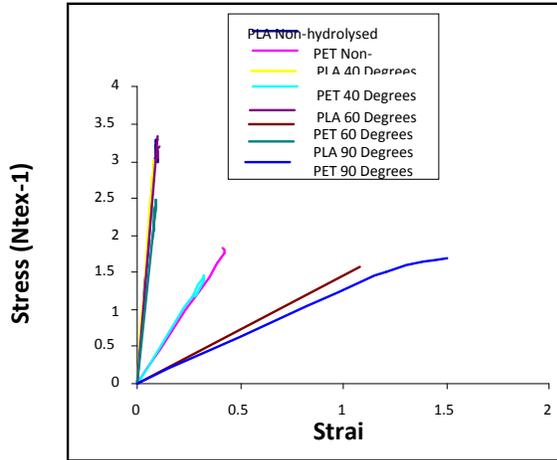


Fig. 1 Tensile Stress-Strain Curves for Hydrolysis with Water for 30minutes

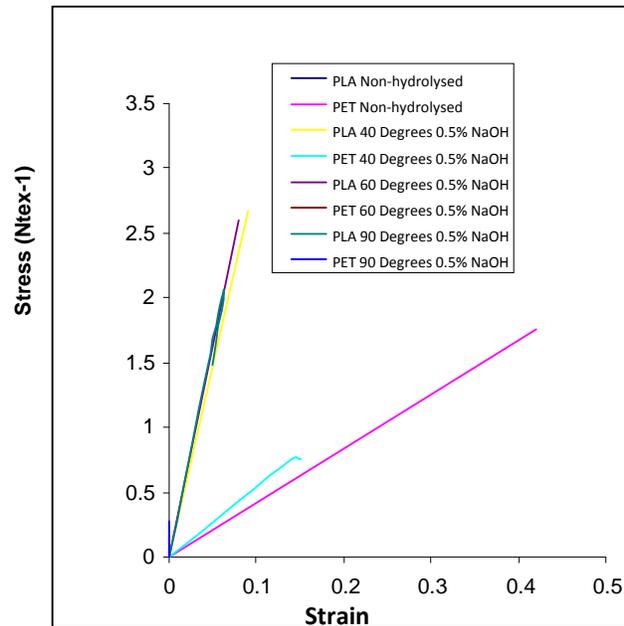


Fig. 2 Tensile Stress-Strain Curves for Hydrolysis with 0.5% NaOH for 30minutes

At 40 °C, the maximum steady specific stress needed to break the hydrolysed PLA and PET yarns is almost the same for the controlled yarns (non-hydrolysed). At 60 °C and 90 °C, the tenacity reduced as the yarns became slightly weak for 30mins and 60mins. The hydrolysed PET yarns

became more elastic therefore needed higher percentage strain due to the fact that the amorphous regions increased after the hydrolysis due to the partially oriented filament compared with the PLA yarns which was fully oriented. Both hydrolysed PLA and PET yarns hydrolysed with the alkali solution degraded appreciably with increased in the time and the concentration of the alkali. The alkali highly attacked the amorphous regions of the PET and degraded most of the fibres and made it very weak compared to PLA which became slightly weak.

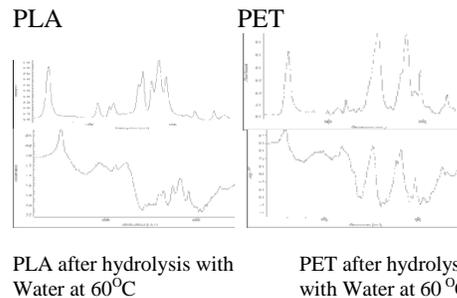
Changes in Morphology of PLA and PET

According to Kisteret *al* (1998), the very strong absorption band at about 1760cm⁻¹ can be assigned to the C=O stretching mode. They assigned those at 1452 and 1388⁻¹ to the CH₃ asymmetric bending and symmetric bending, respectively. The bands at 1300cm⁻¹ belong to C-H bending. The absorption around 1270cm⁻¹ represents a combination of C-H bending and C-O-C stretching.

Table 1 Comparisons between the crystallinity temperatures of non-hydrolysed and hydrolysed yarns symmetric C-O-C stretching mode appears near 1100cm⁻¹. The C-CH₃ stretching appears at 1045cm⁻¹. The medium intensity band at about 875cm⁻¹ belongs to C-COO stretching Agarwa et al (1998).

Non-hydrolysed and hydrolysed PLA and PET yarns with water and sodium hydroxide solution were evaluated with FTIR measurements to check the uniformity of the degraded yarns compared with the virgin yarns. Measurements for FTIR absorbance of both PLA and PET yarns before and after hydrolysis exhibited some decrease in differences. This could be expected because the hydrolysis with both water and sodium hydroxide imparted some degradation to the yarns during the reaction.

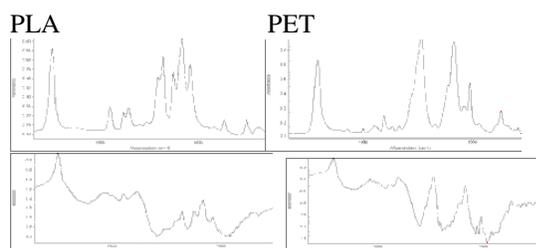
The FTIR measurements of the hydrolysed yarns with sodium hydroxide expected to be less because both yarns are highly sensitive to strong alkali solution under high temperatures.



PLA after hydrolysis with Water at 60°C

PET after hydrolysis with Water at 60°C

Fig. 3 ATR spectra of PLA and PET after hydrolysis for 30minutes



PLA after hydrolysis with 0.5% NaOH at 60°C

PET after hydrolysis with 0.5% NaOH at 60°C

Fig. 4 ATR spectra of PLA and PET after hydrolysis 15minutes

The FTIR results indicate that there was a no difference when the sample yarns were hydrolysed at 40 °C with water instead there was significant change in both PLA and PET yarns when hydrolysed with water at 60 °C and 90 °C. The results also showed a drastic change when the yarns were hydrolysed with sodium hydroxide at 40 °C, 60 °C and 90 °C. The – C – O – ester linkages under hydrolytic conditions were found to be different from the non-hydrolysed. This signified that there was some amount of degradation when temperatures were increased under neutral and alkali conditions.

The tables 1- 5 below shows the DSC technique that was used to monitor the changes that occur in the glass transition temperatures, crystallinity temperatures and melting temperatures before and after hydrolysis.

Sample Yarns	Crystallinity Temperature(T _c)				
	Start °C	Onset °C	Maximum °C	Stop °C	Area J/g
Hydrolysis with Water for 30mins					
PLA Non-hydrolysed	114.71	110.68	99.26	78.59	25.66
PET Non-hydrolysed	97.37	101.80	117.28	146.46	15.83
PLA Hydrolysed @ 40°C	95.35	104.29	123.98	148.36	17.93
PET Hydrolysed @ 40°C	89.51	99.51	117.78	137.11	14.25
PLA Hydrolysed @ 60°C	93.92	103.90	122.63	145.87	17.30
PET Hydrolysed @ 60°C	100.71	104.72	119.30	159.98	15.36
PLA Hydrolysed @ 90°C	92.15	103.96	122.67	149.07	18.45
PET Hydrolysed @ 90°C	96.45	104.74	119.05	144.61	13.80

Table 1 Comparisons between the crystallinity temperatures of non-hydrolysed and hydrolysed yarns

Sample Yarns	Melting Temperature (T _m)				
	Start °C	Onset °C	Maximum °C	Stop °C	Area J/g
Hydrolysis with Water for 30mins					
PLA Non-hydrolysed	140.41	156.05	166.88	182.09	53.36
PET Non-hydrolysed	179.34	241.93	253.60	264.55	47.20
PLA Hydrolysed @ 40°C	137.69	155.46	167.35	181.45	46.11
PET Hydrolysed @ 40°C	202.44	241.07	253.04	270.11	46.75
PLA Hydrolysed @ 60°C	139.82	155.6	166.53	177.90	42.03
PET Hydrolysed @ 60°C	195.44	242.31	254.66	269.17	49.35
PLA Hydrolysed @ 90°C	143.38	163.74	167.39	189.28	49.20
PET Hydrolysed @ 90°C	235.83	221.65	212.18	187.21	33.12

Table 2 Comparisons between the melting temperatures of non-hydrolysed and hydrolysed yarns

It can be seen that before hydrolysis, PLA exhibited an endothermic peak T_m at 167 °C with T_c and T_g at 124 °C and 65 °C and respectively. PET showed exhibited 254, 117 and 80 for T_m, T_c, and T_g respectively. After hydrolysing both PLA and PET yarns with water at 40 and 60°C, the DSC results exhibited no significant change in the T_g, T_c and the T_m. At 90 °C, the T_m for PET dropped significantly than PLA proving that there was higher degradation in PET than PLA and therefore the PET yarn appeared weaker than PLA. The crystallinity temperature values for PLA were taken from the second cycle because there were more amorphous regions and therefore did not indicate any T_c in the

first cycle. PET on the other hand indicated its T_c in the first cycle because it has fair crystalline regions.

Sample Yarns	Glass Transition (T_g)			
	Onset	Midpoint	End	Height
Hydrolysis with 1.0% NaOH for 30mins	°C	°C	°C	W/g
PLA Non-hydrolysed	57.89	62.02	64.36	0.120
PET Non-hydrolysed	79.28	80.86	81.22	0.180
PLA Hydrolysed @ 40°C	56.86	61.54	65.86	0.096
PET Hydrolysed @ 40°C	79.18	80.98	80.79	0.133
PLA Hydrolysed @ 60°C	57.01	61.94	66.36	0.104
PET Hydrolysed @ 60°C	77.70	81.19	81.40	0.170
PLA Hydrolysed @ 90°C	60.65	62.22	64.82	0.046
PET Hydrolysed @ 90°C	129.26	128.85	132.96	0.056

Table 3 Comparisons between the glass transitions of non-hydrolysed and hydrolysed yarns

Sample Yarns	Crystallinity Temperature(T_c)				
	Start	Onset	Maximum	Stop	Area
Hydrolysis with 1.0% NaOH for 30mins	°C	°C	°C	°C	J/g
PLA Non-hydrolysed	114.71	110.68	99.26	78.59	25.66
PET Non-hydrolysed	97.37	101.80	117.28	146.46	15.83
PLA Hydrolysed @ 40°C	117.76	111.36	101.63	76.85	27.80
PET Hydrolysed @ 40°C	99.78	104.11	117.73	155.31	16.77
PLA Hydrolysed @ 60°C	121.68	111.4	102.10	79.69	28.81
PET Hydrolysed @ 60°C	94.18	101.08	115.43	147.38	19.29
PLA Hydrolysed @ 90°C	121.68	111.76	102.82	82.89	30.32
PET Hydrolysed @ 90°C	106.63	114.85	126.26	141.83	3.022

Table 4 Comparisons between the Crystallinity temperatures of non-hydrolysed and hydrolysed yarns

Sample Yarns	Melting Temperature (T_m)				
	Start	Onset	Maximum	Stop	Area
Hydrolysis with 1.0% NaOH for 30mins	°C	°C	°C	°C	J/g
PLA Non-hydrolysed	140.41	156.05	166.88	182.09	53.36
PET Non-hydrolysed	179.34	241.93	253.60	264.55	47.20
PLA Hydrolysed @ 40°C	142.31	155.85	166.63	185.72	45.14
PET Hydrolysed @ 40°C	187.04	241.49	253.60	271.04	50.38
PLA Hydrolysed @ 60°C	135.91	156.47	166.78	188.93	46.66
PET Hydrolysed @ 60°C	192.64	238.63	252.55	274.77	47.15
PLA Hydrolysed @ 90°C	142.67	157.53	162.27	183.94	45.66
PET Hydrolysed @ 90°C	229.35	221.08	210.92	181.19	48.41

Table 5 Comparisons between the melting temperatures of non-hydrolysed and hydrolysed yarns

DSC results exhibited significant change in the melting temperature (T_m), crystallinity temperature (T_c) and the glass transition temperature (T_g). The T_m for PLA and PET after hydrolysis with sodium hydroxide solution at 40 °C, 60 °C and 90 °C indicated a significant reduction. T_c rather increased at 60 °C showing that both PLA and PET became more crystalline and therefore less temperature was required to melt. There were no T_g and T_c in the first cycle for PLA because the fibres after hydrolysing with NaOH solution become very weak and more amorphous. With PET, although the fibres were weak, there were some amounts of crystalline regions since the initial yarn before hydrolysis was partially oriented.

4. CONCLUSIONS

PLA and PET yarns were hydrolysed and the effects of chemicals and environmental conditions under which these fibres degrade were studied. The hydrolysis of the yarns under neutral pH7.0 conditions did not show any significant change at 40°C at various the times that the yarns tested. There was a slight change when the temperature was set at 60°C and 90°C respectively under the same conditions. Under alkali conditions with pH of 12.0-13.5, there was slight change at 40°C but a very significant change (degradation) at 60°C and 90°C. The yarns became very weak and were difficult to retrieve an appreciable strand for FTIR, and Tensile test 90°C when the time was increased to 30minutes and 60minutes respectively. The partially oriented PET yarn became more amorphous and hydrolysed at a faster rate making the yarns very weak whereas the PLA flat filament yarn became highly crystalline and hydrolysed at a slower rate. Hydrolysis induced physical weight loss and showed significant degradation treatment conditions increased.

- There was no significant change in tensile properties under neutral conditions at 40°C. Tensile strength and modulus of PLA

decreased whereas that of PET increased because it was partially oriented. Elongation at break significantly reduced when temperatures were increased under alkali conditions.

- The degradation effect was quantitatively evaluated by FTIR-ATR analysis and the results reveal no significant differences after 40°C hydrolysis rather there was a reduction in the strong absorption regions. This confirmed that the yarns were degraded at elevated temperatures as the absorption peaks reduced.

- DSC showed that PLA became more amorphous after degradation and therefore did show crystallinity temperatures in the first cycles. The PET showed the reverse by indicating a higher crystallinity peaks. There was a gradual reduction in the melting peaks as the fibres were degraded.

5. RECOMMENDATIONS

It is being recommended that further investigations of other alkali and higher temperatures could be done to know the extent of degradation of other aliphatic polyesters.

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