

DOI: 10.34658/9788366741751.55

ACCELERATED HYDROLYSIS OF PLA FIBERS AT LOW TEMPERATURE

Anita Tarbuk^{1(*)}, Ivana Čorak¹, Dragan Đorđević², Zbigniew Draczyński³¹ University of Zagreb Faculty of Textile Technology, Prilaz baruna Filipovića 28a, Zagreb, Croatia² University of Niš, Faculty of Technology, Bulevar oslobođenja 124, 16000 Leskovac, Serbia³ Lodz University of Technology, Stefana Żeromskiego 116, 90-924 Łódź, Poland

(*) Email: anita.tarbuk@ttf.unizg.hr

ABSTRACT

The polylactide (PLA) is the most common biodegradable material. However, its biodegradation requires hydrolysis of PLA to oligomers or monomers before microbes can act. Hydrolytic degradation of PLA depends on temperature, time and relative humidity. It takes months and years until complete biodegradation. If a catalyst is introduced, i.e. alkali or alcohol, it can be done in weeks. In this article, the alkaline hydrolysis was performed at low temperatures 40–60°C without and with the addition of cationic compound as an accelerator for the purpose of saving energy and time for complete PLA degradation. It has been shown that complete degradation can be achieved in only 10 min at 40°C.

KEYWORDS

PLA, alkaline hydrolysis, cationic surfactant, low temperature.

INTRODUCTION

The polylactide (PLA) or poly(lactic acid) is produced from renewable sources (vegetables, corn, sugar) and is the most commonly used biodegradable material. It is the most frequently used biodegradable polyester, due to its good strength, biocompatibility, and biodegradability. However, its biodegradation requires hydrolysis of PLA to oligomers or monomers before microbes can act in a certain medium. These monomers are crucial for reducing the necessity of raw materials as well as the environmental impact related to PLA production and disposal [1–9]. Its degradation depends on the chemical, physical and biological agents that are used, the molecular and supramolecular structure of the polymer, i.e. the crystalline form, pH, the rate of hydrolytic degradation, the content of the D-lactide isomer, temperature, the content of nanomaterials. When chemical/physical processes have been done, hydrolysis is random, whilst when enzymes are applied hydrolysis occurs at the end of polymer chains. The hydrolysis occurs in amorphous regions, which results in an increment in crystallinity [6–9].

During hydrolysis the ester linkages on PLA backbone chains are cleaved and the polymer is converted into soluble oligomers and monomers. The cleavage of ester linkage results in carboxylic and hydroxyl end-groups on polymer chains (Figure 1).

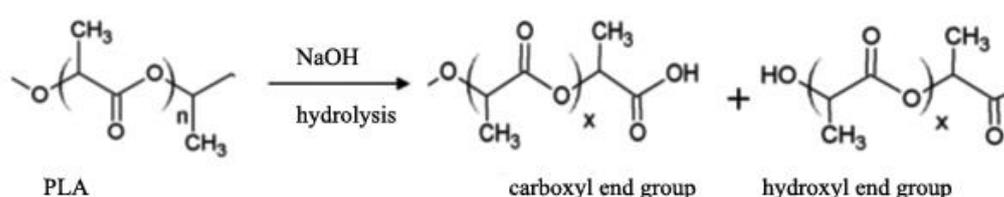


Figure 1. The alkaline hydrolysis of ester bond in PLA.

At neutral or alkaline medium, the hydrolytic degradation occurs through backbone of PLA polymer, while hydrolytic degradation of D, L-lactic acid oligomers in alkaline media show random ester cleavage. Hydrolysis can take place not only in water and alkali, but also in alcohol and alcoholic solutions, or acetonitrile solutions [6]. However, in the absence of any catalyst, the hydrolysis of PLA consumes plenty of energy and time.

According to literature, hydrolytic degradation of polymer structures takes a few weeks and it should be conducted at the temperature near to the glass transition of the polymer. The time required for PLA hydrolysis highly depends on the temperature and relative humidity. Testing of PLA in real conditions lead to the degradation in several months depending on the conditions and the initial material. PLA degradations carried out in laboratory conditions are artificial weathering, composting, and thermal degradation. These PLA degradation processes require months and years until complete biodegradation, i.e. at 4°C needs 2-5 years, at 25°C 1 year, at 60°C 15-30 days [3]. Some researchers [1,3] hydrolyzed PLA at the temperature of 90°C in distilled water what took 21 days. For quicker degradation, high temperature is necessary; i.e. more than 95 % of PLA can be hydrolyzed within 120 min at 160–180°C [4]. Chen *et al.* [9] studied alkaline hydrolysis at temperature range 40–60°C, and found that for at 60°C 120 h is necessary for 50% degradation.

It is well known that some cationic surfactants and polymers accelerate the process of polyester hydrolysis [10,11]. Therefore, in this article, the alkaline hydrolysis was performed at low temperatures 40-60°C without and with the addition of cationic compound as an accelerator for the purpose of saving energy and time for complete PLA degradation.

MATERIALS AND METHODS

The PLA fibers were spun as multifilament in the laboratory at Lodz University of Technology, Łódź, Poland from Ingeo™ Biopolymer 6201D (Nature Works LLC, Minnetonka, USA). Fibers were cut to 5 cm. These staple fibers were needle-punch into the non-woven fabric on Asselin machine (Elbeuf, France).

The non-woven fabrics were hydrolysed in the Linitest, Original Hanau with LR 1:50 owf. 0.5 g of fabric was hydrolysed in 1.5 mol/L sodium hydroxide (NaOH) without or with addition of 1 g/l HDTMAC (hexadecyltrimethylammonium chloride, 25 % aqueous solution, Fluka), cationic surfactant (Figure 2).

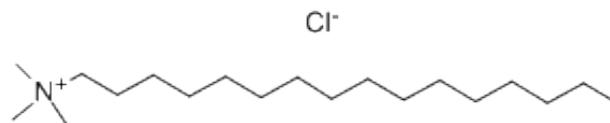


Figure 2. HDTMAC (hexadecyltrimethylammonium chloride).

Fabrics were treated at 40 and 60°C for 5, 10, 15, 20, 30, 45, and 60 min. After hydrolysis, the fabric was rinsed in hot, warm, and cold distilled water and neutralized in acetic acid then rinsed in cold distilled water and dried overnight at 102°C and cooled in a desiccator.

Weight loss was determined by measuring the PLA nonwoven fabric before and after degradation using KERN ALJ 220-5DNM digital scale with a precision of 0.1 µg. The weight loss (Δm) was calculated according to the following equation:

$$\Delta m = \frac{m_0 - m_h}{m_0} \cdot 100 [\%] \quad [1]$$

where, m_0 is the weight of the PLA before hydrolysis and m_h is the weight of the PLA after hydrolysis.

RESULTS AND DISCUSSION

For the purpose of studying PLA degradation with catalyst and accelerator at low temperature, the alkaline hydrolysis was performed at 40 and 60°C. NaOH was used as catalyst and cationic surfactant, hexadecyltrimethylammonium chloride (HDTMAC) as an accelerator, which was proven to accelerate alkaline hydrolysis of poly(ethylene terephthalate) at low temperatures [11].

The results of weight loss are calculated and expressed as a function of the time, considering the temperature of process. The results are shown in Figures 3 and 4.

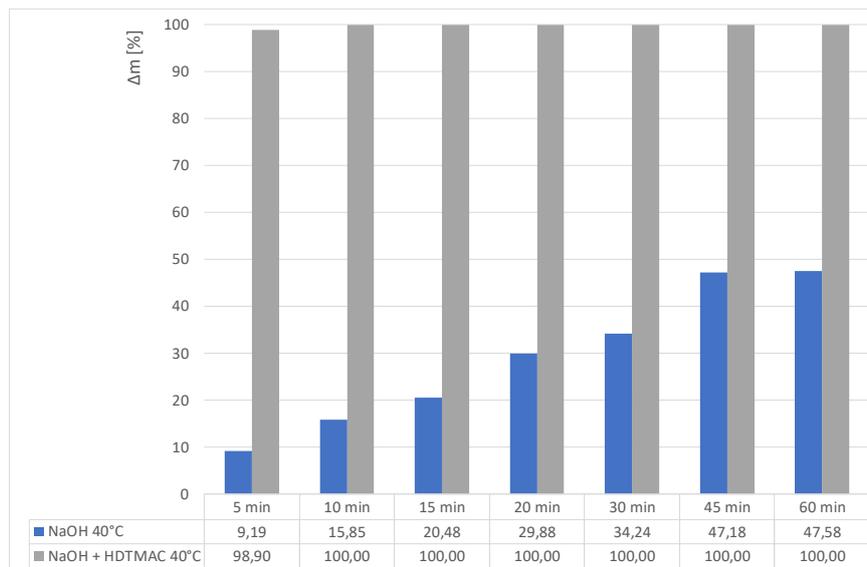


Figure 3. The weight loss of PLA non-woven fabric in alkaline hydrolysis with 1.5 mol/L NaOH without and with addition of cationic surfactant HDTMAC at 40°C.

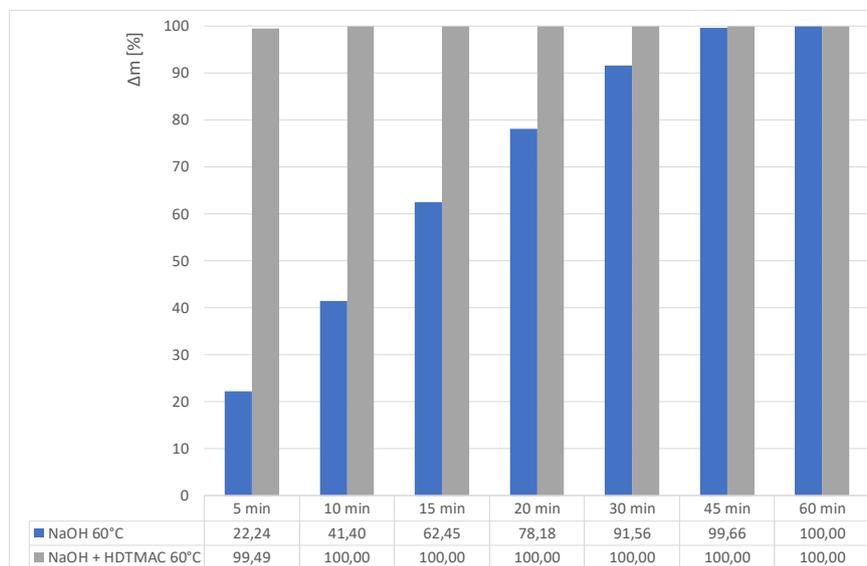


Figure 4. The weight loss of PLA non-woven fabric in alkaline hydrolysis with 1.5 mol/L NaOH without and with addition of cationic surfactant HDTMAC at 60°C.

Alkaline hydrolysis carried out for 60 min at 60°C, results in complete degradation of PLA. Reducing the time, degradation is low, i.e. weight loss of 22.24 % is achieved after 5 min. Introducing accelerator to alkaline hydrolysis, HDTMAC, led to complete degradation after only 10 min, while after 5 min the weight loss was 99.49%.

Lowering temperature led to lower degradation if only NaOH was used. Weight loss after 60 min was 47.58 %, and after 5 min only 9.19%. However, when HDTMAC was used as accelerator, similar degradation was observed as at 60°C. After 5 min weight loss was 98.9% and in 10 min it was complete.

CONCLUSION

In this research 1.5 mol/L NaOH was used as catalyst and hexadecyltrimethylammonium chloride (HDTMAC) as accelerator of PLA hydrolysis. Both catalyst and accelerator significantly help PLA degradation. When only alkali is used, PLA can be completely degraded in 60 min at 60°C. If HDTMAC is used as accelerator of alkaline hydrolysis, it takes only 5 min to degrade 99% of PLA, and in 10 min PLA degradation is complete. It can be concluded that this process saves energy and time, what makes it more sustainable.

ACKNOWLEDGMENT

This work is a result of Croatia-Serbia cooperation in science and technology, 2019-2022 entitled “Bio-innovative polyesters”. The work has been supported by Croatian Science Foundation under the project UIP-2017-05-8780 HPROTEX.

REFERENCES

- [1] Giełdowska M., Puchalski M., Szparaga G., Krucinska I., *Investigation of the Influence of PLA Molecular and Supramolecular Structure on the Kinetics of Thermal-Supported Hydrolytic Degradation of Wet Spinning Fibres*, Materials 2020, vol. 13(2), no 2111.
- [2] Puchalski M., Kwolek S., Szparaga G., Chrzanowski M., Krucinska I., *Investigation of the Influence of PLA Molecular Structure on the Crystalline Forms (α' and α) and Mechanical Properties of Wet Spinning Fibres*, Polymers 2017, vol. 9(1), no 18.
- [3] Way C., *Fundamental Understanding of Polylactic Acid – Lignocellulose Composites*, unpublished Thesis submitted to Swinburne University of Technology in fulfillment of the degree of Doctor of Philosophy, Faculty of Science, Engineering and Technology, Swinburne University of Technology, Swinburne 2014.
- [4] Piemonte V., Gironi F., *Kinetics of Hydrolytic Degradation of PLA*, J. Polym. Environ. 2013, vol. 21, pp. 313-318.
- [5] Elsayy M.A., Kim K.-H., Park J.-W., Deep A., *Hydrolytic degradation of polylactic acid (PLA) and its composites*, Renewable and Sustainable Energy Reviews 2017, vol. 79, pp. 1346-1352.
- [6] Teixeira S., Eblagon K.M., Miranda F., R. Pereira M.F., Figueiredo J.L., *Towards Controlled Degradation of Poly(lactic) Acid in Technical Applications*, C 2021, vol. 7, no 42.
- [7] Zaaba N.F., Jaafar M., *A review on degradation mechanisms of polylactic acid: Hydrolytic, photodegradative, microbial, and enzymatic degradation*, Polym. Eng. Sci. 2020, vol. 60, pp. 2061–2075.
- [8] Tham C.Y., Abdul Hamid Z.A., Ahmad Z., Ismail H., *Surface Modification of Poly (lactic acid) (PLA) via Alkaline Hydrolysis Degradation*, Advanced Materials Research 2014, vol. 970, pp. 324- 327.
- [9] Chen H.M., Shen Y., Yang J.H., Huang T., Zhang N., Wang Y., Zhou Z.W., *Molecular ordering and α' -form formation of poly(l-lactide) during the hydrolytic degradation*, Polymer 2013, vol. 54, pp. 6644–6653.
- [10] Gawish S.M., Bourgeois M., Ambroise G., *Effect of Cationic Surfactants on the Alkaline Hydrolysis of Polyester Fabrics*, Am. Dyest. Report 1986, vol. 75, pp. 19–24.
- [11] Ćorak I., Tarbuk A., Đorđević D., Višić K., Botteri L., *Sustainable Alkaline Hydrolysis of Polyester Fabric at Low Temperature*, Materials 2022, vol. 15, no 1530.