Egypt. J. Chem. Vol. 68, No. 1 pp. 247– 253(2025)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Biodegradability of Bio-based Polyurethane Films under The Action of Different Fungal Strains

Mona H. Abdel Rehim[a*], Nora N. Elgamal[b], Maysa E. Mohram[b]

[a] *Packaging Materials Department, Chemical Industries Research Institute, National Research Centre, Dokki-Giza, Egypt*
[b] *Microbial Chemistry Department, Biotechnology Research Institute, National Research Centre, 33 El Behooth St., Dokki Giza, Egypt*

Abstract
Polyurethanes (PUs) are characterized by different physicochemical and mechanical properties that enable their utilization in a wide range of applications. Recently, biobased polyurethanes have attracted great interest as an ecofriendly alternative to traditional polyurethanes. These biobased macromolecules display unique properties, such as renewability, low toxicity and abiotic or biotic degradability. This research investigated the biodegradation of biobased polyurethane films by different fungi, namely, *Aspergillus niger* (An), *Penicillium sp*. (Pen) and *Trichoderma hazardium* (Th). The biodegradation tests were performed under static conditions and in liquid media. The biodegraded polyurethane films were characterized using ATR-FTIR, thermal analysis and scanning electron microscopy (SEM). The chemical structure of the biodegraded samples demonstrated obvious evidence for degradation through the disappearance or shifting of absorption bands according to the fungal strain used. Thermal degradation investigations confirmed the effect of fungi on the hard segment of the urethane bonds in the polyurethans films, leading to their decomposition at lower temperatures than in the case of the untreated films. Additionally, surface imaging of the treated films revealed significant changes after exposure to metabolic reactions of the fungi used. The results confirmed that the presence of amino groups in the PU structure enhances polymer disintegration. Moreover, the effect of *Trichoderma hazardium* was more pronounced than that of the other strains.
Keywords: Biobased polyurethane; Biodegradation; Fungi.

1. Introduction

Polyurethanes (PUs) are widely used in contemporary life. They constitute a group of polymers that applied in industrial, automotive, and medical fields. Products including furniture, coatings, adhesives, construction materials, and bars are all made of polyurethane. (1) Polyurethanes have many advantages over other polymers as they have higher melting point and better mechanical properties making them of greater durability. (2) Moreover, they are excellent alternatives to plastics as they don't degrade when exposed to water, oils, or solvents. (3) Urthanes are esters of carbamic acid and polyurethane is a polymer composed of urethane groups as repeating units. (4) The polymer is produced through the reaction of a compound contains diisocyanate group and polyester or polyether polyol. The segments containing urethane moieties are considered hard segments while the parts of the polyol constitute the soft segments. PUs with properties ranging from linear to branched**,** and flexible to rigid, are created by varying the amount of substitutions as well as the distance between and within branch chains. (5) Concern over plastics has grown as a result of their inability to degrade, the elevated loss of natural resources, increased water and land issues. (6) Although more recycling used plastics is becoming more significant as raw materials (such as crude oil), it still comprises small ratio of **globally** produced plastics. (7) It is **predicted** that about 12000 MT of plastic wastes will be piled up. (8) Due to large annual production of PUs, its wastes continuously persist in the environment and transform into potentially toxic compounds because of their strong resistance to natural degradation, endangering both human health and the integrity of numerous ecosystems. Polymer degradation is a rational solution to PUs' wastes using either of the following methods: photo degradation, thermo-oxidative degradation, hydrolytic cleavage or biodegradation. (9) Nevertheless, PUs regularity makes it simple for the polymer chain to pack, which leads to the creation of crystalline areas and reduces the polymer chains' susceptibility to deterioration. (10) Degradability difficulties prompted researchers to look at modification of PU structures which resulted in chemically degradable or eco-friendly PUs. The possible modification of PU structure is utilization of bio-based building blocks to synthesize PU. (11) By employing a variety of novel structures as building blocks, such as bio-based polyesters (12) epoxy (13), amines (14), polyols (15,16) or furanes, (17) bio-based PU can be achieved. Additionally, there has recently been a lot of interest in the creation of mono- and polyisocyanates produced from biomass for the production of entirely bio-based PUs. (15, 18-20) However, presence of bio-based blocks in the PU structure facilities its biodegradation through microbial or fungal attack. This method is one of the most economical and environmentally responsible ways to manage bio-based wastes and numerous researches focuses solely on microbiological breakdown of PU. (21-25) Cangemi *et al*. investigated biodegradation of PU foam derived from castor oil. (26) Degradation of the polymer over 216 hours contact with microorganism cultures was tested. Microbial consortia from landfill were able to degrade PU within one week exposure. (27) Moreover, adipic acid butandiol were detected as degradation products in the supernatant of the consortia. Microbial **consortia** are very effective in PU biodegradation since it is a collection of microorganisms live and

*Corresponding author e-mail: monaabdelrehim23@gmail.com.; (Mona H. Abdel Rehim).
EJCHEM use only: Received date 14 March 2024; revised date 22 May 2024; accepted date 30 May 2024
DOI: 10.21608/ejchem.2024.276325.9455

interact together and they secrete several substances into their surroundings. (28) Nevertheless, fungi were found to have potential for PU-degradation and their effective substances were identified. (29) Matsumiya *et al*. reported a 27.5% weight reduction in ether-type PU after 10 weeks of incubation with the fungus *Alternaria* sp. The fungal strain was efficient to hydrolyze urethane and urea groups in PU to use the carbon from degradation products. (30) Khan et al. studied biodegradation of polyester polyurethane by *Aspergillus flavus* G10 extracted from the gut of a common cricket species (*Gryllus bimaculatus*). (31) The tested PU samples demonstrated physical and chemical changes confirming fungal hydrolysis of urethane groups with the polymer backbone. Moreover, the study showed that prior treatment of PU samples with UV or NaCl solution, enhanced biodegradation process. However, biodegradation of PU is still immature to fulfill the requirements of recycling. (32) Thus, there is a demand to investigate various active microbial strains capable of fulfilling this purpose. In this context, this research work focuses on biodegradation of biobased PU using *Aspergillus niger* (An), *Penicillium* sp. (Pen) and *Trichoderma hazardium* (Th). The chemical structures of biodegraded samples were characterized by FTIR and their morphology was examined by scanning electron microscope. Moreover, the thermal stability of the treated samples compared with the pristine polymer.

Experimental

- **Materials**

The biobased polyurethane films used for this study were prepared and fully characterized in our previous article. (16) The biodegradability of two films was studied. The first was a polyurethane (PU) film, while the second was modified through the incorporation of amino groups in its backbone (AmPU). The chemical structures of the films are shown in Figure 1A and B.

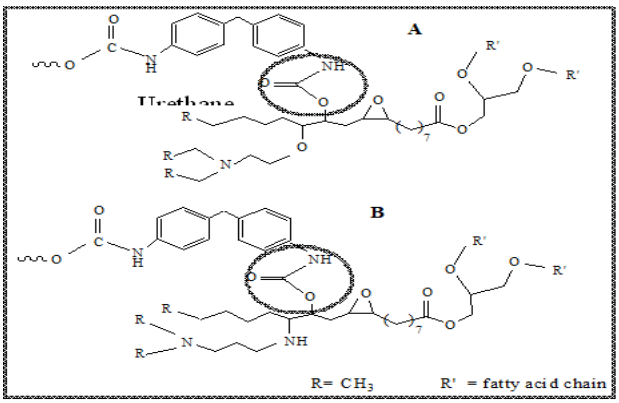

Figure 1: Chemical structures of polyurethane films examined for biodegradation; A) PU, and B) AmPU.

Instrumentation

Chemical structures of film samples were investigated by ATR-FTIR spectroscopic analysis on a JASCO instrument. The samples were scanned at a resolution of 4 cm^{-1} over a wavenumber range of 500−4000 cm^{-1}. Thermal gravimetric analysis (TGA) was performed using SDT Q600 instrument. The temperature was raised from room temperature to 600 °C at a heating rate of 10 °C min^{-1} under N2 atmosphere. Scanning electron microscope (SEM) was employed to examine surface morphology of the film samples. The instrument used is JEOL-SEM with acceleration voltage of 80 kV.

Biodegradation investigations

Microorganisms

The fungal strains used in this work are: *Aspergillus niger* NRRL 595 (An) which was obtained from Northern Regional Research Laboratory, United States, Department of Agriculture, Peoria, Illinois, *Penicillium sp.* (Pen) which isolated from orange peel, Microbial Chemistry Department, National Research Centre and *Trichoderma hazardium* (Th) was obtained from Agricultural Research Centre, Egypt.

Biodegradation under static conditions:

For this purpose, solid malt agar medium was prepared composed of (g/L): 30 g Malt, 0.5g $MgSO_4$ and 20 g Agar. After sterilization of the medium by autoclaving at 121°C for 20 min, it was poured in sterile petri dishes containing the films tested for biodegradation. These dishes were inoculated by 0.5 ml spore suspension of the tested fungal strains. The dishes were incubated for 15 day at 30 °C.

Biodegradation in liquid medium:

The tested fungi were added to Erlenmeyer flasks containing 200 ml of malt extract broth and 0.1 g of $MgSO_4$. After sterilization of the medium by autoclaving at 121 °C for 20 min, the flasks were inoculated with 2 ml of the fungal spore suspension. Then, after sterilization with UV radiation for 5 minutes, polyurethane was added to each flask, and the flasks were incubated at 30 °C under shaking growth (120 rpm) for 15 days. A control set without fungal cultures was prepared. (31)

Results and Discussion

1- Biodegradation of PU and AmPU films under static condition

Studying of biodegradation susceptibility of the biobased polyurethane film sample (PU) is carried out by exposing the sample to fungus *aspergillus sp*. (An) The visualization of transparent halos permits evaluation of the polymer biodegradation under the action of specific enzymes produced by the microorganisms. Figure 2A demonstrates the sample image after 10 days in the fungus medium, while images B, C and D show formation and development of the halo after 4, 6 and 10 days of immersing the film in the microorganism colonies. Investigation of the effect of three different fungi strains namely, *Aspergillus niger; An, and Penicillum sp.; Pen,* and *Trichoderma hazardium; Th,* on the other polyurethane sample AmPU was carried out using the same previously described procedure. The formation of halo zone could be noticed as revealed in the

images shown in figure 3. These images confirmed the biodegrading influence of the different strains in the solid media and the solubility of the polymer under the action of secreted enzymes.

1- *Biodegradation of PU films in liquid media*

Specimens of PU and AmPU films are subjected to fungal biodegradation under shaking liquid fermentation. As shown in figure 4 the used fungal strains succeeded to grow well through the experiment time acting on the PU and AmPU films. Fresh biomass ranged from 35.4 g with PU films exposed to *Aspergillus niger* to 50.6 g with the amPu films treated with *Aspergillus niger*. While dry weight ranged from 1.5 g with PU films treated with *Aspergillus niger* to 3.7 g with the AmPU films treated with *Pen* Sp

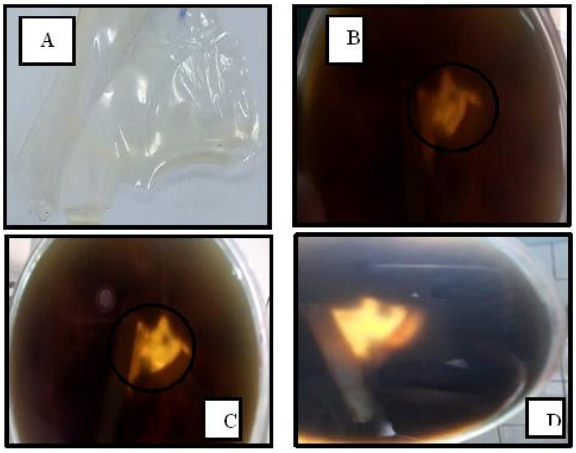

Figure 2: Development of halo zone using *aspergillus sp.* (An); A) Photo of tested sample PU, B) Photo of the formed halo after 4 days, C) Photo of the formed halo after 6 days, and D) after 10 days.

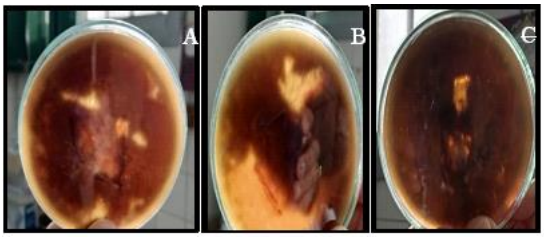

Figure 3: Solid biodegradation of AmPU using; A) Aspergillus niger; An, and B) Penicillum sp. ; Pen, and C) Trichoderma hazardium; Th.

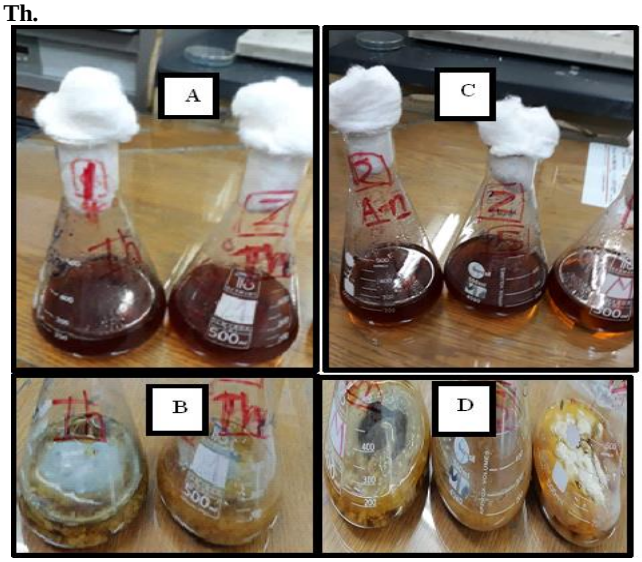

Figure 4: A) Control of specimens PU, B) Liquid medium after fermentation by *Trichoderma hazardium*; Th for two weeks. C) Control of specimen AmPU in liquid medium, and D) Liquid medium after two weeks of fermentation using *Aspergillus niger.*

Action of microorganism

It has lately been discussed that the extracellular enzymes secreted by fungi, which target carbon polymers based on organic matter in order to develop, are what cause the fungal biodegradation process. Hydrolytic enzymes like esterase, cutinase, lipase, protease, and urease, or oxidative fungal enzymes like peroxidase, laccase, and monooxygenase, are typically involved in the degradation of polymers (33). The breakdown of different polymers into pieces that can be absorbed and mineralized in the mycelial cells is frequently started by the oxidase and hydrolase enzymes released by fungal hyphae (34). Oxidative stress is typically formed in the presence of synthetic polymers and restricted carbon sources, resulting in the creation of reactive oxygen species (ROS), hydrogen peroxide, and oxidative enzymes. Polymer disintegration is caused by changes in the shape and content of the terminal groups of the enzymes. Laccase and peroxidase, in contrast to fungal hydrolases, function similarly against synthetic polymers by initiating redox processes that oxidize the polymer and produce radicals and parent polymer structures with terminal groups. Additionally, functional groups interact with oxidative enzymes to produce intermediate molecules, which are then hydrolysed into simple, absorbable carbon monomers. Extracellular fungal esterase, lipase, protease, catalase, cutinases, and other hydrolase enzymes are important hydrolytic enzymes that target and cleave specific ester and amide linkages in the polymer chain (35, 36) *A.niger* is one of the essential sources of functional biomolecules, including organic acids, vitamins, pesticides, valuable proteases, and therapeutic agents, which have potential applications in various fields. (37) *A. niger* is one of the excellent producers of valuable proteases, which have been widely used as detergents and food ingredients and additives, such as acetylesterase, amylase, fucosidase, glucose oxidase, glucosidase, mannanase, phospholipase, phytase, prolyl endopeptidase, triacylglycerol lipase and xylanase. *Trichoderma harzianum* is characterized by a group of lysing enzymes such as β-glucanase, cellulase, protease, and chitinase activities Examples of hydrolases of *Penicillium sp* include various cellulolytic enzymes and other polysaccharases, such as fJ-glucanases, hemicellulases, and pectic enzymes, together with a variety of lipases and proteolytic enzymes. Thus, these different groups of extracellular enzymes can explain the success of the used fungi in biodegradation of PU and AmPU films.

FTIR spectroscopy

The action of *An* or *Th* microorganisms on PU samples in liquid media was further investigated by FTIR spectroscopy. As the polyurethane is formed due to the reaction of polyol and isocyanates, the polymer's structure contains urethane identifying units and the used fungi secrete esterase enzyme which is mainly responsible for degrading urethane bonds. (38, 39) The main three spectral regions show changes are 3000–3500, 1500–1750, and 500–900 cm^{-1}. (40)

The characteristic bands of PU and that exposed to the action of fungi are shown in Figure 5. The results revealed a shift in the absorption band of OH group of PU from 3294 cm^{-1} to 3285 and 3277 $cm^{-1}$for samples PU-An and PU-Th respectively. There is no significant change in the region of C=O at 1706 cm^{-1}. However, the band at 1638 cm^{-1} in sample PU corresponding to C=O amide II disappeared in the biodegraded samples PU-Th and PU-An, which implies breaking the bond between C=O and NH of urethane groups and generation of new by-products such as polyether. (41) The main changes could be observed in the urethane groups region which is corresponding to the hard segment of polyurethane. However, no significant changes could be noticed at ether bond region of the soft segments since these segments are resistant to biodegradation as reported before. (42)

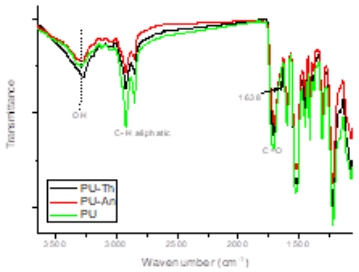

Figure 5: FTIR spectra of PU and biodegraded film samples

Table 1: FTIR band positions of different functional groups in AmPU after digestion by microorganisms

Group	AmPU	Pen	Th	An
OH	3293	3986	3273	3285
C-H aliphatic	2920, 2851	2925, 2854	2923, 2854	2925, 2854
C=O	1704	1704	1704	1704
C=O amide II	1649	1598	1598	1598
N-H amide 1	1599	1528	1528	1528

Characterization of biodegraded AmPU samples in liquid media

The changes in the functional groups present in the polymer structure due to biodegradation process have been investigated using FTIR (Figure 6). Increase in the bands intensities corresponding to OH groups for samples AmPU-Th and AmPU-An can be observed beside a shift in the band position by at least 10 cm^{-1} as revealed in table 1. As mentioned before, esterase is the main enzyme involved in the degradation of PU groups leading to formation of carboxylic acids and alcohols which explains the enhancement in the OH band in the biodegraded sample. (43) Consequently, an increase in the band

corresponding to C=O appears at 1704 cm^{-1} could be also observed. The changes in bands positions of ether groups are shown in table 1.

SEM

Surface morphology of PU, PU-An, and PU-Th samples has been investigated by SEM and the images are displayed in figure 7. Image related to PU sample shows more smooth surface compared to biodegraded samples PU-An, and PU-Th. The surface of sample PU-An showed formation of aggregates while surface of PU-Th depicted vein lines and swelling obviously due to the action of secreted enzymes.

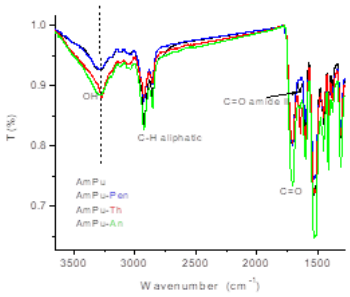

Figure 6: FTIR spectra of AmPU and biodegraded film samples.

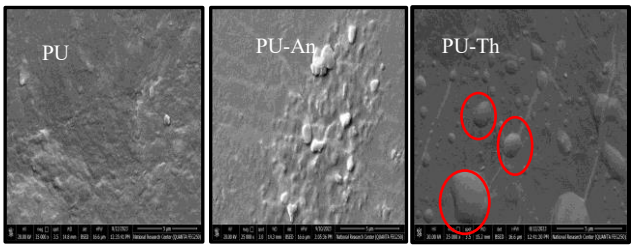

Figure 7: SEM micrographs of PU, PU-An, and PU-Th samples.

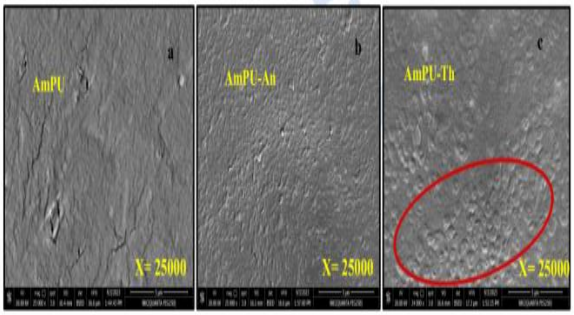

Figure 8: SEM micrographs of a) AmPU film. b) AmPU-An, and c) AmPU-Th are biodegraded samples.

The surface images of AmPU film sample compared with two films biodegraded by *An* and *Th* are depicted in figure 8. The surface images of biodegraded of AmPU appear different from those of the AmPU film. As surface of treated *An* film seems with small aggregations while the surface of the sample treated with *Th* appeared with larger bumps which reflects the apparent influence of *Th* compared to that of *An*.

Thermal stability

An investigation of the thermal stability of the biodegraded films was carried out, and the results are presented in Figure 9. For the PU, PU-An and PU-Th films, one main degradation step occurred at 237 °C for PU and 271 °C for both PU-An and PU-Th (figure 9-A). However, the samples showed a 10% weight loss at 278 °C for PU and 297 °C for the treated films. The total weight loss in the PU-An sample was 60% at 492 °C, the PU-Th-treated film, the total weight loss was 88% at 496 °C while for PU 75% at 493 °C. These results demonstrated that the used fungi digested the hard segments first at temperatures below 300 °C. The soft segments are mainly polyols that can bind to each other by intermolecular and intramolecular hydrogen bonding, leading to their decomposition at higher temperatures. (40) Studying the thermal stability of AmPU and its treated samples revealed that all the films were thermally stable until 100 °C, after which the AmPU-An biodegraded sample lost 5% of its original weight at 122 °C mostly moisture. (figure 9-B) Nevertheless, the three films showed a 10% weight loss at 277 °C for AmPU-Th and AmPU-An, and at 300 °C for the AmPU film. This result confirms the effect of fungi on the hard

segment of the urethane bonds in the polyurethans films, leading to their decomposition at lower temperatures than in the case of the untreated films. (43) Moreover, the AmPU-An sample showed 60% weight loss at 497 °C, which is lower than that found in the case of the AmPU and AmPU-Th films (≈ 30%), indicating that the *Th* fungal strain caused obvious thermal instability and a lower amount of remaining small organic compounds. Overall, the presence of amino groups in the Am-PU enhanced degradation process in comparison with unmodified PU, which is in accordance with results depicted previously. (16)

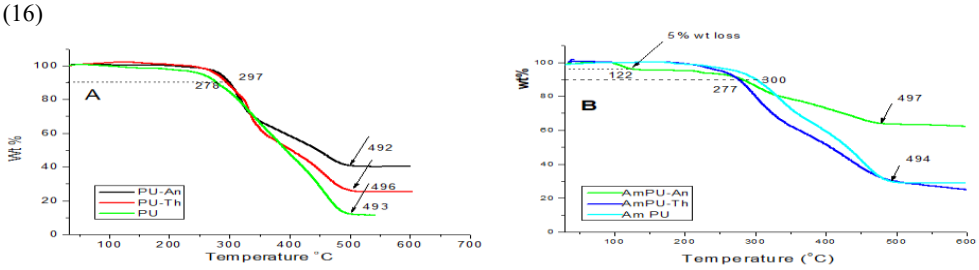

Figure 9: TGA thermograms of (A) PU and (B) AmPU before and after exposing to biodegradation.

Conclusion

The influence of different fungal strains on two biobased PU films was studied. Biodegradation testing was carried out under static and liquid conditions. The biodegradation process was followed by the formation of halo zones, and the obtained treated samples were characterized by FTIR, TGA and SEM. The analysis of chemical structure of the biodegraded samples using FTIR demonstrated disappearance or shifting of absorption bands according to the fungal strain used which confirms metabolic action of the microorganisms. Moreover, thermal degradation investigations confirmed the effect of fungi on the hard segment of the urethane bonds in the polyurethane films, leading to their decomposition at lower temperatures than in the case of the untreated films and *Trichoderma hazardium* (Th) is more effective at decomposing film compounds into small organic molecules. The results of this work confirmed that the fungal biodegradation of PU films is mainly linked to the secretion of several enzymes that cleave the urethane bond in the polymer either by hydrolysis or oxidation. Esterases and proteases are the two main families of enzymes involved in the biodegradation process, both of which are capable of hydrolysing the urethane bond. This study assured the ability of fungi to disembarrass biobased polyurethane in a short time.

Acknowledgment

The authors acknowledge National Research Centre for the financial support of this work through the in-house project number E120104.

Conflicts of interest

"There are no conflicts to declare".

References

[1] Gary T. Howard, Inter. Biodeterioration & Biodegradation **2002**, *49*, 245.
[2] Bayer, O., 1947. Polyurethanes. Modern Plastics 24, 149–152.
[3] J. H. Saunders, K. C. Frisch, Polyurethanes: Chemistry and Technology, Part II: Technology. Interscience Publishers, New York, **1964**.
[4] B. A. Dombrow, Polyurethanes. Reinhold Publishing Corporation, New York, **1957**.
[5] J. R. Fried, Polymer Science and Technology. Prentice-Hall, PTR, Englewood CliHs, NJ, **1995**.
[6] F. Kawai, Breakdown of plastics and polymers by microorganisms. Advances in Biochemical Engineering= Biotechnology **1995**, *52*, 151.
[7] W. Schnabel, Polymer degradation: Principles and Potential Applications. Macmillan Publishing Co., Inc., New York, **1981**, pp. 178.
[8] R. Geyer, J. R. Jambeck, K. L. Law, Sci. Adv. **2017**, *3(7)*, e1700782.
[9] A. L. Andrady, Mar. Pollut. Bull. **2011**, *62(8)*, 1596.
[10] W. Jiang, X. Yang, F. Gu, X. Li, S. Wang, Y. Luo, Q. Qi, Q. Liang . ACS Synth. Biol. **2022**, *11(2)*, 538.
[11] S. Wendels, L. Av´erous, Bioactive Mater. **2021**, *6*, 1083.
[12] T. Debuissy, E. Pollet, L. Averous, Chem. Sus. Chem. **2018**, *11 (22)* 3836.
[13] R. Auvergne, S. Caillol, G. David, B. Boutevin, J. P. Pascault, Chem. Rev. **2014**, *114 (2)* 1082.
[14] V. Froidevaux, C. Negrell, S. Caillol, J.P. Pascault, B. Boutevin, Chem. Rev. **2016**, *116 (22)* 14181.
[15] P. Furtwengler, L. Avérous, Polym. Chem. **2018**, *9 (32)* 4258.
[16] M. Naguib, M. A. Yassin, and M. Abdel Rehim. Macromol. Chem. Phys. **2023**, *224*, 2200231.
[17] M. Decostanzi, R. Auvergne, B. Boutevin, S. Caillol, Green Chem. **2019**, *21 (4)* 724.
[18] M. Charlon, B. Heinrich, Y. Matter, E. Couzign´e, B. Donnio, L. Av´erous, Eur. Polym. J. **2014**, *61*, 197.
[19] T. A. Phung Hai, L. J. S. De Backer, N. D. P. Cosford, M. D. Burkart, Org. Process Res. Dev. **2020**, *24*, 10, 2342.
[20] M. D. Zenner, Y. Xia, J. S. Chen, M. R. Kessler, Chem. Sus. Chem. **2013**, *6* (7)1182.
[21] S. Khan, S. Nadir, Z. U. Shah, A. A. Shah, S. Karunarathna, J. Xu, *et al.* Environ Pollu. **2017**, *225*, 473.
[22] G. T. Howard, W. N. Norton, T. Burks. Biodegradation. **2012**, *23*, 561.
[23] U. Zafar, A. Houlden, G. D. Robson. Appl. Environ. Microbiol. **2013**,79, 7313.
[24] U. Zafar, P. Nzeram, L.-F. A, A. Houlden, A. Heyworth, A. Saiani, *et al.* Bioresoure Technol. **2014**, *158*, 374.
[25] G. Mathur, R. Prasad. Appl. Biochem. Biotechnol. **2012**,*167*, 1595.

[26] J. M. Cangemi , A. M. dos Santos, S. C. Neto, G. O. Chierice, Polímeros: Ciência e Tecnologia **2008**, *18*, 201.
[27] T. Su, T. Zhang, P. Liu, J. Bian, Y. Zheng, Y. Yuan, Q. Li. Q. Liang, Q. Qi. Appl. Microbio. and Biotech. **2023**, *107*, 1983.
[28] J. Fuentes-Jaime, M. Vargas-Suarez, M. J. Cruz-Gomez, H. Loza-Tavera. Biodegradation **2022**, *33(4)*, 389.
[29] P. Bhavsar, M. Bhave, H. K. Webb. World J. Microbiol. and Biotech. **2023**, *39*, 122.
[30] Y. Matsumiya, N. Murata, E. Tanabe, K. Kubota, M. Kubo. J. Appl. Microbiol. 2010,108, 1946.
[31] S. Khan, S. Nadir, Y. Dong, D. A. Schaefer, et al. (**2020**) https://doi.org/10.1101/2020.06.25.170654
[32] J. Liu, J. He, R. Xue, B. Xu, X. Qian, F. Xin, L. M. Blank, J. Zhou, R. Wei, W. Dong, M. Jiang. Biotechnol. Adv. **2021**, *48*, 107730.
[33] M.Srikanth, T. Sandeep, K. Sucharitha, S. Godi. Bioprocess. **2022**, *9*, 1.
[34] A. K. Urbanek, A.M. Mirończuk, A. García-Martín, A. Saborido, I. de la Mata, M. Arroyo. Biochim. Et Biophys. Acta (BBA)-Proteins Proteom. **2020**, *1868* (2) , Article 140315
[35] Bano, K. M. Kuddus, M. R Zaheer, Q. Zia, M. F Khan, A. Gupta, G. Aliev. Curr. Pharm. Biotechnol. **2017**, *18 (5)*, 429.
[36] C. M aestri, L. Plancher, A. Duthoit, R. Hebert, and P. Martino. J. Fungi. **2023**, *9* (7), 760.
[37] R. Yu, J. Lui, Y. Wang, H. Wang, and H. Zhang, Frantiers in Chem. *2021*, 9, 1.
[38] R. Beran, L. Zarybnicka, D. Machova. J. Appl. Polym. Sci. 2020, 137(1): e49095.
[39] J. Fuentes-Jaime, M. Vargas-Suarez, M. J. Cruz-Gomez, H. Loza-Tavera. Biodegradation **2022**, *33*(4), 389.
[40] P. Zhu, S. Gong, M. Deng, B. Xia, *et al*. Front. Environ. Sci. Eng. **2023**, *17*(3), 38.
[41] E. Pellizzi, A. Lattuati-Derieux, B. Lavédrine, H. Cheradame. Polymer Degradation & Stability **2014**, 107, 255.
[42] Q. Li, J. Wang, L. Chen, H. Shi, J. Hao. Polymer Degradation & Stability, **2019**, *161*, 166.
[43] A. Magnin, E. Pollet, V. Phalip, L. Averous. Biotechnol. Adv. **2020**, *39*, 107457.