UNIWERSYTET
WARMIŃSKO-MAZURSKI
W OLSZTYNIE

WYDZIAŁ GEOINŻYNIERII

mgr inż. Magdalena Zaborowska

Recykling organiczny wybranych biodegradowalnych materiałów polimerowych

Rozprawa doktorska wykonana
w Katedrze Biotechnologii w Ochronie Środowiska
pod kierunkiem dr hab. inż. Katarzyny Bernat, prof. UWM

Olsztyn 2023

UNIVERSITY
OF WARMIA AND MAZURY
IN OLSZTYN

FACULTY OF GEOENGINEERING

MSc Eng. Magdalena Zaborowska

Organic recycling of selected biodegradable bioplastics

Doctorate thesis carried out
in the Department of Environmental Biotechnology
under the supervision of Dr Habil. Eng. Katarzyna Bernat, prof. UWM

Olsztyn 2023

Składam serdeczne podziękowania
Pani dr hab. inż. Katarzynie Bernat, prof. UWM
za opiekę promotorską,
cenne uwagi i wskazówki merytoryczne,
poświęcony czas oraz za nieocenioną pomoc,
dzięki której możliwe było przygotowanie rozprawy doktorskiej.

Pani prof. Irenie Wojnowskiej-Baryle oraz
Pani dr hab. inż. Dorocie Kulikowskiej, prof. UWM
za merytoryczne wsparcie i konsultację naukową
w trakcie przygotowywania rozprawy doktorskiej.

Dziękuję Rodzicom oraz Bartoszowi za motywację i wiarę w moje możliwości.

Wykaz spójnych tematycznie publikacji stanowiących rozprawę doktorską

W skład rozprawy doktorskiej wchodzi pięć recenzowanych publikacji naukowych opublikowanych w czasopismach znajdujących się w wykazie czasopism naukowych zamieszczonym w komunikacie Ministra Edukacji i Nauki z dnia 21 grudnia 2021 r.:

P1. Zaborowska Magdalena, Bernat Katarzyna, 2022. The development of recycling methods for bio-based materials - A challenge in the implementation of a circular economy: A review. *Waste Management Research*, 41(1), 68-80. https://doi.org/10.1177/0734242X221105432 (Punktacja MNiSW 70, IF 4.432)

P2. Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Anaerobic degradability of commercially available bio-based and oxo-degradable packaging materials in the context of their end of life in the waste management strategy. *Sustainability*, 13(12), 6818. https://doi.org/10.3390/su13126818 (Punktacja MNiSW 100, IF 3.889)

P3. Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Challenges in sustainable degradability of bio-based and oxo-degradable packaging materials during anaerobic thermophilic treatment. *Energies*, 14(16), 4775. https://doi.org/10.3390/en14164775 (Punktacja MNiSW 140, IF 3.252)

P4. Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Cydzik-Kwiatkowska Agnieszka, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Multi-faceted analysis of thermophilic anaerobic biodegradation of poly (lactic acid)-based material. *Waste Management*, 155, 40-52. https://doi.org/10.1016/j.wasman.2022.10.031 (Punktacja MNiSW 200, IF 8.816)

P5. Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Assessment of biodegradability of cellulose and poly(butylene succinate)-based bioplastics under mesophilic and thermophilic anaerobic digestion with a view towards biorecycling. *Waste Management*, 168, 413-422. https://doi.org/10.1016/j.wasman.2023.06.022. (Punktacja MNiSW 200, IF 8.816)

Łączna liczba punktów publikacji stanowiących spójny tematyczny zbiór będący rozprawą doktorską wynosi 710, sumaryczny współczynnik wpływu Impact Factor (IF) – 29,205.

Wyniki badań przedstawione w publikacjach P2-P5 składających się na rozprawę doktorską były realizowane w ramach badań statutowych (29.610.024-110).

Część wyników przedstawionych w publikacjach P4 i P5 uzyskano na podstawie badań przeprowadzonych w ramach realizowanego projektu badawczego nr rej.: 2021/41/N/NZ9/01750 pt. „Recykling organiczny materiałów biobazowych i bioodpadów – możliwości i ograniczenia" uzyskanego przez mgr inż. Magdalenę Zaborowską w konkursie Preludium 20, organizowanym przez Narodowe Centrum Nauki.

Koszt Open Access oraz korekty lingwistycznej publikacji P3 i P4 finansowano z programu "Regionalna Inicjatywa Doskonałości" w latach 2019-2023 organizowanym przez Ministra Edukacji i Nauki, nr projektu 010/RID/2018/19, kwota finansowania 12.000.000 złotych.

Spis treści

Załączniki – publikacje stanowiące rozprawę doktorską:

Załącznik 1.

P1. Zaborowska Magdalena, Bernat Katarzyna, 2022. The development of recycling methods for bio-based materials - A challenge in the implementation of a circular economy: A review. *Waste Management Research*, 41(1), 68-80.

Załącznik 2.

P2. Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Anaerobic degradability of commercially available bio-based and oxo-degradable packaging materials in the context of their end of life in the waste management strategy. *Sustainability*, 13(12), 6818.

Załącznik 3.

P3. Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Challenges in sustainable degradability of bio-based and oxo-degradable packaging materials during anaerobic thermophilic treatment. *Energies*, 14(16), 4775.

Załącznik 4.

P4. Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Cydzik-Kwiatkowska Agnieszka, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Multi-faceted analysis of thermophilic anaerobic biodegradation of poly (lactic acid)-based material. *Waste Management*, 155, 40-52.

Załącznik 5.

P5. Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Assessment of biodegradability of cellulose and poly(butylene succinate)-based bioplastics under mesophilic and thermophilic anaerobic digestion with a view towards biorecycling. *Waste Management*, 168, 413-422.

Streszczenie

Biotworzywa pochodzenia biologicznego i/lub biodegradowalne są alternatywą tworzyw sztucznych wytwarzanych z surowców nieodnawialnych, jak ropa naftowa czy gaz ziemny. Biorąc pod uwagę, że są uznawane za biodegradowalne oraz priorytety hierarchii postępowania z odpadami komunalnymi, odpady biotworzyw powinny być zbierane selektywnie wraz z bioodpadami i przetwarzane w procesach recyklingu organicznego (kompostowanie lub fermentacja metanowa). Obecnie, powszechnie zakłada się beztlenowy recykling organiczny bioodpadów w wyniku fermentacji metanowej. W dostępnej literaturze brakuje holistycznej oceny efektywności beztlenowej biodegradacji biotworzyw, pozwalającej na określenie wpływu biotworzyw na biodegradację bioodpadów w warunkach beztlenowych. W dysertacji zastosowano wieloaspektową analizę do określenia wpływu temperatury i wstępnej obróbki biotworzyw na ich beztlenową biodegradację. Analiza obejmowała i) określenie wydajności biogazu lub metanu, stałych kinetycznych produkcji biogazu (PB) lub metanu (PM), oraz przydatności biotworzyw do produkcji biogazu i kofermentacji z bioodpadami, ii) zmiany powierzchni (makro- i mikroskopowe lub topografię) oraz właściwości mechanicznych (wytrzymałość na rozciąganie, wydłużenie materiału przy zerwaniu) i termicznych (skaningowa kalorymetria różnicowa), iii) identyfikację grup funkcyjnych na podstawie spektroskopii fourierowskiej w podczerwieni (FTIR), iv) określenie stopnia biodegradacji biotworzyw (na podstawie teoretycznej produkcji metanu (TPM)).

Testowano pięć rodzajów komercyjnie dostępnych biotworzyw, tj. folie (F) na bazie skrobi (F_S), celulozy (F_Cel), polilaktydu (F_PLA) i poli(bursztynianu butylenu) (F_PBS) oraz sztywne (S) jednorazowe kubeczki do napojów na bazie PLA (S_PLA). Biodegradację prowadzono w beztlenowych warunkach mezofilnych (M) i/lub termofilnych (T) oraz po wstępnej obróbce biotworzyw (chemicznej (0,1 M KOH, 2 h, temperatura pokojowa) lub hydrotermicznej (H_2O, 2 h, 90°C)).

Wykazano, że warunki temperaturowe wpływają na biodegradowalność biotworzyw. Na podstawie wydajności biogazu lub metanu w warunkach mezofilnych uszeregowano biotworzywa od najbardziej biodegradowalnego:

F_Cel$_M$ >> F_PBS$_M$ > F_S$_M$ ≥ F_PLA$_M$.

Przydatność biotworzyw do produkcji biogazu lub metanu, z wyjątkiem F_Cel$_M$, była technologicznie niezasadna ze względu na czas beztlenowej biodegradacji powyżej 30 dni.

W warunkach termofilnych nastąpił wzrost szybkości produkcji i wydajności metanu z F_PBS, a szereg biodegradowalności na podstawie wydajności metanu różnił się od szeregu biodegradowalności w temperaturze mezofilnej:
S_PLA$_T$ > F_Cel$_T$ > F_PBS$_T$ > F_PLA$_T$ ≥ F_S$_T$.

Podobnie jak w warunkach mezofilnych, ze względu na długi czas beztlenowej biodegradacji, przydatność biotworzyw do produkcji metanu była technologicznie niezasadna, z wyjątkiem F_Cel$_T$ i F_PBS$_T$. Biotworzywa (S_PLA$_T$, F_PLA$_T$, F_S$_T$) nie powinny być poddawane termofilnej fermentacji metanowej czy np. kofermentacji z bioodpadami.

Wykazano zależność pomiędzy biologicznymi i fizycznymi wskaźnikami biodegradowalności. Wydajność biogazu lub metanu w warunkach mezofilnych i termofilnych zależała od wartości wydłużenia przy zerwaniu biotworzyw. Wydajność biogazu lub metanu z biotworzyw charakteryzujących się wysokimi wartościami wydłużenia (F_S, F_PLA) była kilkakrotnie niższa niż z biotworzyw o niskich wartościach wydłużenia (F_Cel, F_PBS). Dodatki stosowane do polepszenia właściwości użytkowych folii, w tym ich elastyczności (wysokie wartości współczynnika wydłużenia), obniżają biodegradowalność i wydajności biogazu lub metanu.

Warunki termofilne przyspieszały fragmentację biotworzyw. Jednak fragmenty biotworzyw (z wyjątkiem F_Cel$_M$, F_Cel$_T$, F_PBS$_T$) pozostawały widoczne w inokulum do 66 dnia beztlenowej biodegradacji i dłużej. Oznacza to, że przy HRT ok. 20-30 dni, stosowanym przy fermentacji bioodpadów, fragmenty biotworzyw stanowiłyby zanieczyszczenie pofermentu, tzw. *mikrobioplastik*.

Wstępna obróbka biotworzyw przed beztlenową mezofilną lub termofilną biodegradacją nie wpłynęła na biodegradowalność ocenianą na podstawie wskaźników biologicznych, natomiast wpływała na zmiany powierzchni oraz właściwości mechaniczne biotworzyw. Po wstępnej obróbce biotworzywa szybciej traciły właściwości mechaniczne. Niezależnie od zastosowania wstępnej obróbki, czas biodegradacji biotworzyw był kilkukrotnie dłuższy niż bioodpadów, co wskazuje na brak możliwości wspólnej kofermentacji z bioodpadami.

Niezależnie od warunków temperaturowych oraz zastosowania obróbki wstępnej, wyniki analizy spektrofotometrycznej FTIR wykazały wzrost intensywności pików odpowiadających grupom funkcyjnym, co wskazywało na postępującą biodegradację biotworzyw, natomiast nie obserwowano powstawania nowych grup funkcyjnych.

W dysertacji wykazano celowość zastosowania wieloaspektowej oceny efektywności beztlenowej biodegradacji biotworzyw na podstawie wskaźników biodegradowalności. Wyniki badań dotyczących beztlenowej biodegradacji testowanych biotworzyw stanowią podstawę przygotowania wytycznych, wskazują kierunki recyklingu organicznego biotworzyw, co jest niezbędne do planowania gospodarki bioodpadami z udziałem biotworzyw.

Słowa kluczowe: biotworzywa, fermentacja metanowa, beztlenowa biodegradacja, wydajność metanu, biodegradowalność, polilaktyd, skrobia, celuloza, poli(bursztynian butylenu)

Abstract

Bioplastics that are of biological origin and/or biodegradable are an alternative to plastics produced from non-renewable raw materials, such as petroleum or natural gas. As bioplastics are labelled biodegradable, the priorities of the municipal waste management hierarchy indicated that bioplastic waste should be selectively collected with biowaste and processed via organic recycling processes (composting or methane fermentation). Currently, anaerobic organic recycling of biowaste by methane fermentation is widely employed. However, the literature lacks a holistic assessment of the effectiveness of anaerobic biodegradation of bioplastics, which would allow determination of the effect of bioplastics on the biodegradation of biowaste under anaerobic conditions. Therefore, in this dissertation, a multi-faceted analysis was used to determine the effect of temperature and pre-treatment of bioplastics on their anaerobic biodegradation. The analysis included i) determination of the yield of biogas and methane, the kinetics of biogas (BP) and methane (MP) production, and the suitability of bioplastics for biogas production and co-digestion with biowaste, ii) surface changes on bioplastics (macro- and microscopic or topographic) and their mechanical (tensile strength, elongation at break) and thermal (differential scanning calorimetry) properties, iii) identification of functional groups using Fourier infrared spectroscopy (FTIR), and iv) assessment of the degree of bioplastic biodegradation (based on theoretical methane production (TMP)).

Five types of commercially available bioplastics were tested: foils (F), based on starch (F_S), cellulose (F_Cel), polylactide (F_PLA) and polybutylene succinate (F_PBS), as well as rigid (S) disposable PLA-based beverage cups (S_PLA). Biodegradation was carried out under anaerobic mesophilic (M) and/or thermophilic (T) conditions and after pre-treatment of the bioplastics via chemical (0.1 M KOH, 2 h, room temperature) or hydrothermal methods (H_2O, 2 h, 90°C).

The temperature conditions affected the biodegradability of the bioplastics. Based on the biogas or methane yield under mesophilic conditions, the bioplastics were ranked from the most to the least biodegradable: $F\_Cel_M >> F\_PBS_M > F\_S_M \geq F\_PLA_M$.

Under mesophilic conditions, the time of anaerobic biodegradation exceeded 30 days for all the bioplastics except F_Cel_M. This indicates that all of them (except F_Cel_M) are unsuitable for anaerobic co-digestion with biowaste under the conditions commonly applied at technical scale.

The yield and rate of MP from F_PBS were higher under thermophilic than under mesophilic conditions. The biodegradability of the bioplastics was different under thermophilic than under mesophilic conditions and decreased in the following order: S_PLA$_T$ > F_Cel$_T$ > F_PBS$_T$ > F_PLA$_T$ ≥ F_S$_T$.

As under mesophilic conditions, the bioplastics, except for F_Cel$_T$ and F_PBS$_T$, were unsuitable for methane production under thermophilic conditions at technical scale due to the long time necessary for anaerobic biodegradation. S_PLA$_T$, F_PLA$_T$, and F_S$_T$ should not be subjected to thermophilic methane fermentation or co-digestion with biowaste.

A relationship between the biological and physical indicators of biodegradability was found. The yield of biogas or methane under mesophilic and thermophilic conditions was associated with the elongation at break of the bioplastics: biogas or methane yield from bioplastics with high values of elongation at break (F_S, F_PLA) was several times lower than the yield from those with low values (F_Cel, F_PBS). The additives used to improve the properties foils, including its flexibility (high value of elongation at break), may reduce biodegradability and biogas or methane yield.

Thermophilic conditions enhanced the fragmentation of the bioplastics. However, the fragments of the bioplastics (except for F_Cel$_M$, F_Cel$_T$, and F_PBS$_T$) remained visible in the inoculum up to the 66th day of anaerobic degradation or longer. This means that with an HRT of about 20-30 days, as commonly used in the digestion of biowaste, fragments of bioplastics (*microbioplastics)* would contaminate digestate.

Pre-treatment of bioplastics prior to anaerobic, mesophilic, or thermophilic biodegradation did not affect biodegradability as assessed by biological indicators, but it did affect the changes in surface and mechanical properties. After pre-treatment, bioplastics lost their mechanical properties in a shorter time. Regardless of the use of pre-treatment, the time of biodegradation of bioplastics was several times longer than that of biowaste, indicating not effective co-digestion with biowaste. Regardless of the temperature conditions and the use of a pre-treatment, the results of the FTIR spectrophotometric analysis showed an increase in the intensity of the peaks corresponding to the functional groups that indicated progressive biodegradation of bioplastics, while the formation of new functional groups was not observed.

This dissertation has demonstrated the utility of a multi-faceted assessment of the effectiveness of anaerobic biodegradation of bioplastics based on indicators of biodegradability. The results on the anaerobic biodegradation of the tested bioplastics can

be used to design guidelines and instructions for the organic recycling of bioplastics, which are needed to plan management of biowaste with bioplastics.

Keywords: bioplastics, methane fermentation, anaerobic biodegradation, methane yield, biodegradability, polylactide, starch, cellulose, polybutylene succinate

1. Wprowadzenie do tematyki badań

Dynamiczny wzrost produkcji oraz zwiększająca się skala zastosowań tworzyw sztucznych prowadzi w ostatnich dekadach do zwiększenia ilości powstających odpadów, co stanowi wyzwanie w związku z ich zagospodarowaniem, zarówno na poziomie lokalnym, jak i globalnym. Odpady z tworzyw sztucznych w zależności od regionu stanowią od 8 do 18% całkowitej ilości odpadów komunalnych (Liang i in., 2021). Tworzywa sztuczne są wytwarzane z surowców nieodnawialnych, takich jak ropa naftowa, gaz ziemny, a większość odpadów tworzyw sztucznych jest trudno biodegradowalna, co prowadzi do długotrwałego zanieczyszczenia środowiska (Tejaswini i in., 2022). By zminimalizować negatywny wpływ odpadów z tworzyw sztucznych na środowisko oraz zdrowie człowieka (Prata i in., 2020) wdrażane są strategie obejmujące zakaz m.in. stosowania jednorazowych produktów z tworzyw sztucznych, tzw. *single use plastic*, (Dyrektywa EU 2019/904) oraz dodatku mikrogranulek do kosmetyków (Miraj i in., 2021). W związku z powyższym poszukuje się alternatywy dla tworzyw sztucznych – biotworzyw (bioplastików), czyli tworzyw pochodzenia biologicznego i/lub biodegradowalnych (Atiwesh i in., 2021). Termin biotworzywo jest używany w odniesieniu do polimerów ulegających biodegradacji, w tym i tych produkowanych z nieodnawialnych surowców, co może prowadzić do dezorientacji konsumentów (Walker i Rothman, 2020). Biotworzywa są jednak przede wszystkim biodegradowalnymi polimerami pochodzenia biologicznego. W 2023 r. światowa produkcja biotworzyw osiągnęła 5,2 milionów ton, z czego 4,1 miliona ton to tworzywa bio-bazowe i biodegradowalne (Ali i in., 2022). Wyróżnia się pięć metod otrzymywania biotworzyw w zależności od pochodzenia surowców oraz zastosowanej technologii produkcji polimerów: (1) bezpośrednią ekstrakcję z biomasy, (2) syntezę z monomerów pochodzenia biologicznego, (3) wytwarzanie przez mikroorganizmy, (4) syntezę z produktów petrochemicznych, (5) kombinację metod 1–4 (Jogi i Bhat, 2020).

W procesie bezpośredniej ekstrakcji wykorzystuje się biomasę pierwszej, drugiej i trzeciej generacji (Rosenboom i in., 2022, Zanchetta i in., 2021). Biomasę pierwszej generacji pozyskuje się z roślin uprawnych, takich jak np. ziemniaki (Arikan i Bilgen, 2019), trzcina cukrowa (Pohare i in., 2017), kukurydza (Marichelvam i in., 2019) czy chlebowiec różnolistny (Krishnamurthy i in., 2019); natomiast biomasę drugiej generacji z np. odpadów rolno-spożywczych (Otoni i in., 2021; Tsang i in., 2019), organicznej frakcji odpadów komunalnych, osadów ściekowych (Astolfi i in., 2020). Do surowców trzeciej generacji zalicza się glony, których wykorzystanie jest w początkowej fazie badań

(Dang i in., 2022; Nanda i Bharadvaja, 2022). Glony są perspektywicznym surowcem do produkcji biotworzyw, mogą być stosowane bezpośrednio lub pośrednio, poprzez ekstrakcję polimerów z komórek mikroorganizmów (Rahman i Miller, 2017).

Do najpopularniejszych polimerów ekstrahowanych bezpośrednio z biomasy należą polisacharydy, tj. skrobia, celuloza, chityna oraz białka, np. gluten. Skrobia, ze względu na dostępność oraz niskie koszty produkcji, jest jednym z najpowszechniej stosowanych polimerów do wytwarzania biotworzyw, a ok. 50% komercyjnie wytwarzanych biotworzyw zawiera w swoim składzie skrobię (Marichelvam i in., 2019). Do produkcji skrobi wykorzystuje się głównie ziemniaki (Ismail i in., 2016), kukurydzę (de Azevedo i in., 2020), maniok (Zoungranan i in., 2020) i skórki z bananów (Sultan i in., 2017). Natywna skrobia, w pierwszym etapie zostaje przekształcona do skrobi termoplastycznej (TPS). Proces polega na destrukturyzacji granulek polimeru w obecności plastyfikatora, najczęściej glicerolu lub sorbitolu, i wody, w wyniku czego powstaje TPS (Khan i in., 2017, Li i in., 2011). Biotworzywa wytworzone z TPS wykazują wady ograniczające komercyjne zastosowanie. Są to słabe właściwości mechaniczne oraz wysoki stopień krystaliczności. Biotworzywa produkowane z TPS są sztywne i kruche (Agarwal i in., 2021, García-Guzmán i in., 2022). Polimer jest silnie higroskopijny, co prowadzi do zmniejszenia wytrzymałości i stabilności biotworzyw produkowanych na bazie skrobi (Su i in., 2022). Ponadto, biotworzywa charakteryzują się przepuszczalnością pary wodnej i nie zabezpieczają produktów przed wilgocią i utratą wilgoci (Putri i in., 2023). Aby poprawić właściwości użytkowe wprowadza się dodatki, np. wosk pszczeli (Diyana i in., 2021), wermikulit (Rodríguez Cueto i in., 2023) lub tworzy się blendy z innymi polimerami, np. polilaktydem (PLA) (Martinez Villadiego i in., 2022).

Celuloza jest polimerem wykorzystywanym do produkcji biotworzyw, który otrzymywany jest w wyniku bezpośredniej ekstrakcji z biomasy. Celuloza jest pozyskiwana z trzciny cukrowej (Shabbirahmed i in., 2022), bawełny (Rumi i in., 2021), słomy ryżowej (Laya i in., 2022), odpadów rolniczych (Seo i in., 2018). Ze względu na lepszą przetwarzalność, w porównaniu do czystego polimeru, do produkcji biotworzyw wykorzystywane są pochodne, takie jak octan celulozy (Yadav i Hakkarainen, 2021) lub karboksymetyloceluloza (Rahman i in., 2021). Celuloza jest stosowana jako wypełniacz polepszający właściwości biotworzyw, a np. dodatek włókien celulozowych do żywic epoksydowych poprawia właściwości mechaniczne i zwiększa odporność materiału na pękanie (Bach i in., 2020; Le Hoang i in., 2018). W przypadku materiałów opakowaniowych, dodatek celulozy zwiększa właściwości barierowe przed przenikaniem tlenu i wilgoci (Wang i in., 2018).

Synteza z monomerów pochodzenia biologicznego rozpoczyna się od przetworzenia biomasy (m.in. roślin lub odpadów rolno-spożywczych) w celu uzyskania monomeru do polimeryzacji. Przykładem jest produkcja polilaktydu (PLA) z kwasu mlekowego (Abdel-Rahman i in., 2013). Kwas mlekowy jest wytwarzany podczas fermentacji kukurydzy, ziemniaków czy trzciny cukrowej (Auras i in., 2004), a następnie, poddawany polimeryzacji (Pang i in., 2010). PLA, ze względu na swoje właściwości, jest jednym z pierwszych biotworzyw, którego produkcję skomercjalizowano (Rasal i in., 2010). Obecnie znajduje szerokie zastosowanie w różnych dziedzinach, od produkcji biodegradowalnych opakowań (Mustăţea i in., 2019), poprzez druk 3D (Subramaniam i in., 2019), po inżynierię biomedyczną i medycynę (Hamad i in., 2015). Aby poprawić właściwości mechaniczne PLA (m.in. wytrzymałość na rozciąganie, granicę plastyczności) lub/oraz obniżyć cenę produkcji polimeru, często stosuje się blendy PLA np. ze skrobią, celulozą, czy włóknem węglowym (Li i in., 2023).

Poli(bursztynian butylenu) (PBS) jest polimerem syntetyzowanym z monomerów pochodzenia biologicznego, który początkowo był produkowany z nieodnawialnych paliw kopalnych (Xu i Guo, 2010). Obecnie PBS jest wytwarzany z surowców odnawialnych, takich jak trzcina cukrowa czy melasa (Ratshoshi i in., 2021), odpady rolno-spożywcze (Gadkari i in., 2021), organiczna frakcja odpadów komunalnych (Khoshnevisan i in., 2020). Produkcja PBS obejmuje fermentację surowców pochodzących z biomasy do kwasu bursztynowego, a następnie polimeryzację z 1,4-butanodiolem (Aliotta i in., 2022). Biotworzywa wytworzone na bazie PBS charakteryzują się dobrymi właściwościami termomechanicznymi oraz fizycznymi (Barletta i in., 2022).

Biotworzywa są syntetyzowane również przez mikroorganizmy (bakterie, grzyby), których szlaki metaboliczne pozwalają na wytwarzanie biopolimerów jako substancji zmagazynowanych wewnątrzkomórkowo. Najpowszechniejszymi polimerami syntetyzowanymi przez bakterie są polihydroksykwasy (polihydroksyalkaniany, PHA), które charakteryzują się właściwościami zbliżonymi do konwencjonalnych tworzyw sztucznych (Sabapathy i in., 2020). Hodowle mikroorganizmów do produkcji PHA są prowadzone w reaktorach okresowych (typu *batch* i *fed-batch*) z wykorzystaniem mieszanych kultur mikroorganizmów (Tsanh i in., 2019). Kumulacja PHA w komórkach mikroorganizmów następuje przy nadmiarze organicznych związków węglowych oraz ograniczonej dostępności składników odżywczych, takich jak azot czy fosfor. W takich warunkach mikroorganizmy syntezują i akumulują PHA jako źródło energii (El-malek i in., 2020).

W związku ze wzrastającą produkcją biotworzyw i szerokim ich zastosowaniem pojawiają się problemy związane z gospodarowaniem odpadami biotworzyw w aspekcie gospodarki cyrkulacyjnej, której celem jest minimalizacja zużycia surowców, ilości powstających odpadów oraz maksymalizacja efektywnego zarządzania zasobami poprzez jak najdłuższe utrzymywanie materiałów i produktów w użyciu (Morseletto, 2020). Wyzwaniem jest wybór metody przygotowania biotworzyw do recyklingu oraz rodzaju recyklingu.

Na etapie zbierania, odpady z biotworzyw mogą być gromadzone selektywnie łącznie z odpadami z tworzyw sztucznych i przetworzone w procesie recyklingu mechanicznego, chemicznego lub poddane spaleniu (Soroudi i Jakubowicz, 2013). Obecność biotworzyw w strumieniu odpadów z tworzyw sztucznych poddanych recyklingowi mechanicznemu może powodować obniżenie jakości recyklatu. Udział nawet > 0.1% PLA w strumieniu PET wpływa negatywnie na recykling mechaniczny (Briassoulis i in., 2021). W porównaniu do innych polimerów PLA ma niską stabilność termiczną i podczas recyklingu mechanicznego ulega degradacji termicznej, pogarszając właściwości fizyczne i mechaniczne recyklatu (Fredi i Dorigato, 2021). W związku z tym, że recykling mechaniczny biotworzyw, zwłaszcza opakowań do żywności, wiąże się z kosztownym etapem sortowania lub doczyszczania oraz mniejszą przetwarzalnością i jakością recyklatu, poszukuje się innych metod recyklingu. Ze względu na potencjalnie wysoką biodegradowalność biotworzyw oraz priorytety w hierarchii sposobów postępowania z odpadami, odpady z biotworzyw powinny być zbierane wraz z bioodpadami i przetwarzane w procesach recyklingu organicznego, w tym kompostowania (Bernat i in., 2022) lub fermentacji metanowej (Bernat i in., 2023). W recyklingu organicznym coraz powszechniej stosowana jest fermentacja beztlenowa, nie tylko ze względu na produkcję metanu, ale również innych substratów wykorzystywanych do syntezy chemicznej, jak również ze względu na możliwość przyrodniczego wykorzystania pofermentu. Metody recyklingu biotworzyw szczegółowo opisano w publikacji wchodzącej w skład dysertacji (Zaborowska i Bernat, 2023).

W związku z możliwością selektywnej zbiórki biotworzyw wraz z bioodpadami, a następnie zastosowania fermentacji metanowej jako procesu recyklingu organicznego, konieczne jest określenie biodegradowalności biotworzyw w warunkach beztlenowych.

Dostępne dane literaturowe wskazują, że nawet biotworzywa, które są oznaczone jako biodegradowalne nie zawsze efektywnie ulegają biodegradacji (Bátori i in., 2018). Ponadto, producenci stosują różnego rodzaju dodatki (plastyfikatory, stabilizatory, barwniki) poprawiające właściwości użytkowe biotworzyw, często nie podając szczegółowych informacji na temat ich składu. Rodzaje i ilości dodatków mogą determinować biodegradowalność biotworzyw oraz ramy czasowe biodegradacji.

Większość danych literaturowych dotyczy biodegradacji biotworzyw w glebie, kompoście i środowisku wodnym (Emadian i in., 2017), a przebieg procesu zależy od rodzaju stosowanych polimerów (tj. ich masy cząsteczkowej, krystaliczności czy rodzaju grup funkcyjnych) oraz parametrów technologicznych (tj. temperatury, wilgotności, pH) (Ahmed i in., 2018; Folino i in., 2020). Wskazuje się jednak, że ze względu na długi czas biodegradacji biotworzyw (Bernat i in., 2021) konieczna może być obróbka wstępna. Może to zwiększyć powierzchnię biotworzyw, co skutkuje szybszą biodegradacją i wzrostem produkcji metanu (Benn i Zitomer, 2018; Mu i in., 2021). W dostępnej literaturze brakuje holistycznej oceny efektywności beztlenowej biodegradacji komercyjnie dostępnych biotworzyw, która dostarczyłaby danych na temat biodegradowalności i warunków biodegradacji poszczególnych typów biotworzyw.

W dysertacji przedstawiono wieloaspektową analizę wpływu temperatury oraz obróbki wstępnej na beztlenową biodegradację biotworzyw w procesie fermentacji metanowej. Oceny efektywności biodegradacji dokonano na podstawie wskaźników biodegradowalności (biologicznych, fizycznych i chemicznych) biotworzyw podczas mezofilnej i termofilnej biodegradacji w warunkach beztlenowych.

Tak zrealizowana koncepcja badań dostarczyła danych o biodegradowalności wybranych biotworzyw w warunkach beztlenowych. Pozwoliła na przygotowanie wytycznych i wskazanie kierunków recyklingu organicznego biotworzyw. Dane te są niezbędne do planowania gospodarki bioodpadami z udziałem biotworzyw.

2. Cel i hipotezy badawcze

Przyjęcie skutecznej strategii oraz praktyki gospodarowania odpadami biotworzyw, w tym wykorzystania recyklingu organicznego, wymaga monitorowania procesu i tworzenia bazy danych o biodegradowalności biotworzyw w warunkach tlenowych, jak i beztlenowych. W cyklu publikacji, składających się na osiągnięcie naukowe przedstawiono holistyczną ocenę biodegradowalności, w warunkach beztlenowych, biotworzyw oznaczonych jako biodegradowalne.

Celem badań była wieloaspektowa ocena efektywności beztlenowej biodegradacji biotworzyw na podstawie wskaźników i) biologicznych, określających ilość powstającego biogazu lub metanu na podstawie testów respirometrycznych, ii) fizycznych, określających zmiany struktury powierzchni i właściwości mechaniczne biotworzyw, iii) chemicznych, wskazujących na zmiany struktury chemicznej (grupy funkcyjne) biotworzyw, w zależności od warunków temperaturowych i zastosowania wstępnej obróbki biotworzyw.

Zakres badań obejmował:

1. wybór i charakterystykę biotworzyw oznaczonych jako biodegradowalne,
2. ocenę biodegradowalności biotworzyw w warunkach beztlenowych w zależności od warunków temperaturowych i zastosowania wstępnej obróbki biotworzyw, jako wskaźniki przyjęto:
    - wydajność biogazu lub metanu, stałe kinetyczne produkcji biogazu (PB) lub metanu (PM) (stała szybkości oraz szybkość PB lub PM), oraz przydatność biotworzyw do produkcji biogazu i kofermentacji z bioodpadami,
    - zmiany powierzchni (makro- i mikroskopowe lub topografię) oraz właściwości mechaniczne (wytrzymałość na rozciąganie, wydłużenie materiału przy zerwaniu) i termiczne (skaningowa kalorymetria różnicowa, DSC),
    - zmiany struktury chemicznej (grupy funkcyjne) na podstawie analizy spektrofotometrycznej (spektroskopia fourierowska w podczerwieni, FTIR),
    - stopień biodegradacji biotworzyw rozumiany jako stosunek wyznaczonej eksperymentalnie wydajności biogazu lub metanu do teoretycznej produkcji metanu (TPM).

Zweryfikowano następujące hipotezy badawcze:
H #1: warunki temperaturowe beztlenowej biodegradacji wpływają na biodegradowalność biotworzyw,
H #2: obróbka wstępna biotworzyw wpływa na biodegradowalność w warunkach beztlenowej mezofilnej lub termofilnej biodegradacji.

Wyznaczone wartości wskaźników beztlenowej biodegradowalności biotworzyw mają kluczowe znaczenie w gospodarowaniu biodegradowalnymi odpadami komunalnymi, w tym bioodpadami, jak i działaniami na rzecz zrównoważonego rozwoju. Pozwalają na projektowanie i optymalizowanie beztlenowego przetwarzania biotworzyw w skali technicznej.

3. Rodzaje biotworzyw i założenia metodyczne beztlenowej biodegradacji

Do oceny biodegradowalności stosowano 5 rodzajów biotworzyw, tj. folie (F) na bazie i) skrobi (F_S), ii) polilaktydu (F_PLA), iii) celulozy (F_Cel) i iv) poli(bursztynianu butylenu) (F_PBS)) oraz jednorazowe sztywne (S) kubki do napojów na bazie PLA (S_PLA). Charakterystykę biotworzyw przedstawiono w tabeli 1. Symbole i skróty biotworzyw oraz parametry beztlenowej biodegradacji stosowane w opisie poniżej przedstawiono w tabeli 1.

Tabela 1. Charakterystyka biotworzyw

	F_S	F_PLA	F_Cel	F_PBS	S_PLA
Główny komponent biotworzywa	skrobia	polilaktyd	celuloza	poli(bursztynian butylenu)	polilaktyd
Właściwość materiału	miękki (folia, F)				sztywny (S)
Sucha masa organiczna (s.m.o.)	99,27	99,87	99,59	89,87	99,90
Skład elementarny					
C (% s.m.)	55,36	57,56	40,67	55,93	49,56
H (% s.m.)	6,90	6,88	6,67	7,03	44,48
O (% s.m.)	37,64	34,86	49,38	36,31	5,56
N (% s.m.)	–	–	1,91	0,74	–
Właściwości mechaniczne					
Wytrzymałość na rozciąganie (MPa)	16,59	20,79	74,75	25,15	–
Wydłużenie, ε (%)	122,16	218,16	8,13	10,23	–

Tabela 2. Parametry beztlenowej biodegradacji biotworzyw

	F_S	F_PLA	F_Cel	F_PBS	S_PLA
Warunki temperaturowe beztlenowej biodegradacji biotworzyw					
Mezofilne (M)	F_S$_{M}$	F_PLA$_{M}$	F_Cel$_{M}$	F_PBS$_{M}$	S_PLA$_{M}$
Termofilne (T)	F_S$_{T}$	F_PLA$_{T}$	F_Cel$_{T}$	F_PBS$_{T}$	S_PLA$_{T}$
Rodzaj obróbki wstępnej biotworzyw do biodegradacji mezofilnej lub termofilnej					
Alkaliczna (A)	F_S$_{T\_A}$	F_PLA$_{T\_A}$	F_Cel$_{M\_A}$	F_PBS$_{M\_A}$	S_PLA$_{T\_A}$
Hydrotermiczna (HT)	–	–	–	–	S_PLA$_{T\_HT}$

Do określenia efektywności mezofilnej lub termofilnej biodegradowalności biotworzyw wyznaczonej na podstawie wskaźników biologicznych tj. wydajności biogazu lub metanu (L/kg s.m.o.) wykorzystywano system OxiTop (P2) oraz AMPTS II (P3-P5). Inokulum stanowił przefermentowany osad ściekowy z zamkniętej komory fermentacyjnej. Początkowe obciążenie ładunkiem związków organicznych z biotworzyw wynosiło 4 kg s.m.o./m^3.

Stosowano obróbkę wstępną biotworzyw do beztlenowej biodegradacji: chemiczną (alkaliczną, 0,1 M KOH, 2 h w temperaturze pokojowej) lub hydrotermiczną (H_2O, 2 h, 90°C).

Do określenia mezofilnej lub termofilnej biodegradowalności biotworzyw wyznaczonej na podstawie wskaźników fizycznych przeprowadzono statyczne próby rozciągania (wytrzymałość na rozciąganie i wydłużenie przy zerwaniu) zgodnie z normą ISO (ISO 527-2:2012, ISO 527-3:2019) z wykorzystaniem TA.HD.Plus (Stable Microsystems, Surrey, UK). Zmiany mikroskopowe biotworzyw analizowano za pomocą mikroskopu polaryzacyjnego Nikon eclipse50i (Nikon, Tokio, Japonia), mikroskopu cyfrowego (Keyence VHX-7000, Japonia) lub binokularu (Delta Optical). Topografię materiału określono z wykorzystaniem mikroskopu cyfrowego (Keyence VHX-7000, Japonia) i profilometru Mitutoyo (Mitutoyo, Japonia). Analizę spektrofotometryczną FTIR wykonano przy użyciu spektrofotometru Perkin Elmer Spectrum Two (Perkin Elmer Co., USA). Zastosowano następujące parametry pomiarowe: zakres spektralny 4000–400 cm^{-1}, rozdzielczość 4 cm^{-1}, temperatura pokojowa. Właściwości termiczne biotworzyw oceniono przy użyciu różnicowego kalorymetru skaningowego DSC Phoenix 204 F1 metodą hit flow (Netzsch, Niemcy). Mierzonym parametrem był swobodny przepływ ciepła. Zastosowano temperaturę od 30°C do 200°C z szybkością ogrzewania 5°C/min. Skład elementarny biotworzyw określono przy użyciu analizatora elementarnego Flash 2000 (Thermo Scientific, Włochy).

4. Weryfikacja hipotez badawczych

Jedną z dwóch stosowanych metod recyklingu organicznego (biorecyklingu) w systemie gospodarki bioodpadami jest fermentacja metanowa. Technologia jest atrakcyjna ze względu na możliwości pozyskiwania biogazu lub metanu. W cyklu publikacji przedstawiono wyniki biodegradowalności testowanych biotworzyw w beztlenowych warunkach mezofilnych i/lub termofilnych jak również po obróbce wstępnej biotworzyw do beztlenowej biodegradacji (P2-P5).

H #1: warunki temperaturowe beztlenowej biodegradacji wpływają na biodegradowalność biotworzyw

Na podstawie analizy wartości wskaźników biodegradowalności wykazano, że warunki temperaturowe wpływają na biodegradowalność testowanych biotworzyw (P2-P5).

Biodegradowalność biotworzyw w warunkach mezofilnych

Na podstawie wskaźników biologicznych biodegradowalności biotworzyw w warunkach mezofilnych wykazano, że w czasie 365 dni F_PLA$_{M}$ oraz F_S$_{M}$, pomimo oznaczeń jako biodegradowalne, nie uległy biodegradacji w warunkach beztlenowych. Fragmenty biotworzyw pozostały widoczne przez cały czas badań (P2). W przypadku biodegradacji obu folii notowano 65 dniową lag fazę (fazę opóźnienia) w produkcji biogazu (PB). Po 175 oraz 200 dniach biodegradacji uzyskano 90% maksymalnej (kumulacyjnej) PB z F_PLA$_{M}$ oraz F_S$_{M}$, ale maksymalna produkcja biogazu wynosiła jedynie odpowiednio 25,2 i 30,4 L/kg s.m.o. Zakładając 50% zawartość metanu w biogazie (na podstawie równania Buswell i Mueller (1952)) można określić, że produkcja metanu była 2-krotnie mniejsza niż produkcja biogazu (ok. 12 i ok. 15 L/kg s.m.o.) i stanowiła ok. 2,1% oraz 2,5% teoretycznej produkcji metanu (TPM).

Po roku beztlenowej biodegradacji F_PLA$_{M}$ w warunkach mezofilnych analiza mikroskopowa (powiększenie 100x) nie wykazała zmian powierzchni. W przypadku powierzchni F_S$_{M}$ widoczne były pojedyncze pęknięcia, szczeliny, wskazujące na początkową fazę degradacji i dezintegracji materiału. Niewielkie, obserwowane po 365 dniach biodegradacji, zmiany w topografii powierzchni F_S$_{M}$ wskazują na zmniejszenie grubości foli (P2).

Folia F_PBS$_{M}$ była widoczna w inokulum przez 100 dni biodegradacji. Intensywna produkcja metanu trwała do 10. dnia biodegradacji. Podczas procesu nie wystąpiła lag faza, a kumulacyjna produkcja metanu wynosiła 25,5 L/kg s.m.o., czyli około 4,3% TMP. Folia F_Cel$_M$ była widoczna w inokulum jedynie przez 2 pierwsze dni biodegradacji. Produkcja metanu w tym czasie wyniosła 134 L/kg s.m.o., co stanowiło 43% kumulacyjnej produkcji metanu. Po 2 dniach materiał uległ dezintegracji, rozpuszczeniu, i nie był identyfikowany gołym okiem. Pomimo, że folia nie była widoczna, to metan był produkowany do 7. dnia badań. Po 7 dniach uzyskano maksymalną produkcję metanu z F_Cel$_M$ wynoszącą 311 L/kg s.m.o. (77,3% TMP) (P5). Na podstawie wskaźników fizycznych (wytrzymałość na rozciąganie, wydłużenie przy zerwaniu (ε)) wykazano, że F_PBS$_M$ utraciła właściwości mechaniczne po 35 dniach biodegradacji, natomiast folia F_Cel$_{M,}$ po 2 dniach. Wyjściowa wytrzymałość na rozciąganie folii F_Cel wynosiła około 75 MPa i w ciągu dwóch dni biodegradacji stopniowo spadała do 18 MPa. Wytrzymałość na rozciąganie F_PBS wynosiła ok. 25 MPa. Podczas pierwszych 9 dni biodegradacji wartość spadła ponad 2-krotnie, w 35 dniu do ok. 5 MPa. Wartość parametru ε folii F_Cel wynosiła 8% i w ciągu 2 dni mezofilnej biodegradacji beztlenowej uległa 5,3-krotnemu obniżeniu. Wartość ε F_PBS wynosiła około 10% i zmniejszała się w czasie 9 dni beztlenowej biodegradacji do ok. 1,4%. Wartość ta utrzymywała się do 35 dnia badań.

Wyniki analizy spektrofotometrycznej FTIR, jako wskaźnika biodegradowalności, wykazały, że w warunkach mezofilnej biodegradacji F_PLA$_M$, F_S$_M$, F_PBS$_M$, oraz F_Cel$_M$ nie tworzyły się nowe grupy funkcyjne, ale intensywność pików odpowiadających poszczególnym grupom funkcyjnym wzrosła, co wskazywało na postępującą degradację biotworzyw (P2, P5).

Podsumowując, wskaźniki biologiczne tj. produkcja biogazu lub metanu, dostarczają cennych informacji o biodegradowalności biotworzyw. W warunkach mezofilnych wydajność biogazu lub metanu zależała od rodzaju biotworzywa. Beztlenowa biodegradacja F_PLA, F_S oraz F_PBS zachodziła w nieznacznym stopniu, z niewielką produkcją biogazu (2,1-4,3% TMP). Materiały te w procesie ko-fermentacji z bioodpadami mogłyby obniżyć wydajność powstającego biogazu. F_Cel uległa biodegradacji w warunkach beztlenowych, a wydajność produkcji metanu z F_Cel stanowiła ponad 70% TMP. Uzyskane wyniki wydajności biogazu lub metanu w warunkach mezofilnych pozwoliły na uszeregowanie biotworzyw od najbardziej biodegradowalnego:

F_Cel$_M$ >> F_PBS$_M$ > F_S$_M$ ≥ F_PLA$_M$.

Biorąc pod uwagę PB lub PM należy stwierdzić, że przydatność biotworzyw, z wyjątkiem F_CelM, do produkcji biogazu lub metanu była technologicznie niezasadna.

Wykazano zależność pomiędzy biologicznymi i fizycznymi wskaźnikami biodegradowalności biotworzyw. Biodegradowalność określona na podstawie wydajności biogazu lub metanu w warunkach mezofilnych korespondowała ze wskaźnikiem fizycznym tj. wartością wydłużenia przy zerwaniu. Wydajność biogazu lub metanu z biotworzyw F_S oraz F_PLA, charakteryzujących się wysoką wartością wydłużenia, była niska. Można przypuszczać, że dodatki stosowane do polepszenia właściwości użytkowych folii, w tym ich elastyczności (wysokie wartości wydłużenia), obniżają biodegradowalność i wydajności biogazu lub metanu. W przypadku F_Cel oraz F_PBS charakteryzujących się niższymi wartościami wydłużenia, wydajność biogazu lub metanu była wyższa.

Biotworzywa, z wyjątkiem F_Cel$_{M}$, były widoczne w inokulum przez okres beztlenowej biodegradacji. Wyniki biodegradowalności na podstawie obserwacji makro- i mikroskopowych (wskaźniki fizyczne) wskazują na brak biodegradacji biotworzyw (F_S$_{M}$, F_PBS$_{M}$, F_PLA$_{M}$) przy HRT 20-30 dni, a tym samym brak możliwości ich kofermentacji np. z bioodpadami. Dodatkowo, w przypadku kofermentacji z bioodpadami, biotworzywa stanowiłby zanieczyszczenie pofermentu.

Biodegradowalność biotworzyw w warunkach termofilnych

W warunkach termofilnych folie F_PLA$_{T}$ oraz F_S$_{T}$ pozostawały widoczne w inokulum przez 100 dni biodegradacji (P3). W produkcji metanu zarówno z F_PLA$_{T}$, jak i z F_S$_{T}$ wystąpiła 6-7 dniowa lag faza. Metan był intensywnie produkowany w pierwszych 15 dniach termofilnej biodegradacji. Kumulacyjna produkcja metanu (PM) z F_PLA$_{T}$ wynosiła 34,5 L/kg s.m.o. (ok. 6% TPM). Szybkość produkcji metanu wynosiła 13,6 L/(kg s.m.o·d). Podczas biodegradacji folii F_S$_{T}$ powstało 32,7 L metanu z kg s.m.o. (6% TPM), szybkość produkcji wynosiła 17.6 L/(kg s.m.o. d). Zmiany (pęknięcia, szczeliny) na powierzchni F_S$_{T}$ oraz F_PLA$_{T}$ pojawiły się odpowiednio po 45. i 59. dniu biodegradacji. Do 59. dnia możliwy był również pomiar właściwości mechanicznych F_PLA$_{T}$. Wyjściowa wytrzymałość na rozciąganie F_PLA wynosiła ok. 21 MPa. Podczas termofilnej biodegradacji wytrzymałość materiału spadała i w 59. dniu wynosiła ok. 3,6 MPa. W przypadku F_S$_{T}$ najbardziej intensywny spadek wytrzymałości na rozciąganie, z 16,6 MPa do 11,1 MPa, obserwowano w ciągu pierwszych 10 dni procesu, a następnie notowano systematyczny spadek do 5,9 MPa. Pomiar wytrzymałości na rozciąganie F_S$_{T}$ był możliwy do 39. dnia biodegradacji, wartość tego parametru zmniejszyła się prawie 3-krotnie w porównaniu z materiałem wyjściowym. Pomimo zbliżonych wartości wytrzymałości na rozciąganie F_PLA oraz F_S, wartość ε F_PLA była prawie 2-krotnie większa niż F_S (odpowiednio ok. 220% i ok. 120%). Najbardziej intensywny spadek ε podczas biodegradacji zarówno F_PLA$_T$, jak i F_S$_T$ miał miejsce do 30. dnia, po tym czasie wartość pozostawała na zbliżonym poziomie. W ostatnim możliwym dniu pomiaru, ε F_PLA$_T$ oraz F_S$_T$ wynosiło odpowiednio 7% i 10% (P4).

Fragmenty F_PBS$_T$ były widoczne do 14 dnia, w którym uzyskano ponad 87% kumulacyjnej PM. Pomimo, że od 14. dnia materiał nie był widoczny w inokulum, metan był nadal wytwarzany przez kolejne 10 dni (P5). Po ok. 25 dniach termofilnej biodegradacji F_PBS$_T$, PM ustabilizowała się na poziomie 180 L/kg s.m.o (30.2% TMP). Fragmenty F_Cel$_T$ pozostawały widoczne w inokulum jedynie przez 2 dni biodegradacji, w tym czasie łatwo ulegały rozrywaniu oraz obserwowano powstawanie mikropęknięć na ich powierzchni. Podczas 4. pierwszych dni uzyskano prawie 100% kumulacyjnej PM wynoszącej 319.5 L/kg s.m.o. (79.3% TMP).

Wytrzymałość na rozciąganie i ε folii F_Cel wynosiły odpowiednio 75 MPa oraz 8%. Już po 12 godzinach odnotowano spadek tych wartości o 70% i 80%. Po dwóch dniach beztlenowej biodegradacji wytrzymałość na rozciąganie F_Cel$_T$ wynosiła 5,1 MPa, a ε 1,7% (P5).

Fragmenty S_PLA$_T$ były widoczne w inokulum przez 66 dni beztlenowej biodegradacji (P4). W tym czasie obserwowano 12-dniową lag fazę. 90% kumulacyjnej PM (406,18 L/kg s.m.o.) powstało do 66 dnia eksperymentu, a szybkość procesu wynosiła 7,9 L/(kg s.m.o.·d). Druga faza PM trwała do 75 dnia (mimo, że fragmenty S_PLA$_T$ były niewidoczne w inokulum) i zachodziła z 2-krotnie mniejszą szybkością tj. 3,9 L/(kg s.m.o.·d). Kumulacyjna PM wynosiła 453,0 L/kg s.m.o, co stanowiło 97% TPM. Od 7. dnia obserwowano zmiany powierzchni, materiał zmienił kolor z przezroczystego na biały, natomiast pęknięcia materiału pojawiły się po 23. dniu biodegradacji beztlenowej (P4).

W warunkach termofilnej biodegradacji F_PLA$_T$, F_S$_T$, F_PBS$_T$, F_Cel$_T$ oraz S_PLA$_T$ wyniki analizy spektrofotometrycznej FTIR wykazały wzrost intensywności pików odpowiadających poszczególnym grupom funkcyjnym, natomiast nie tworzyły się nowe grupy funkcyjne (P2, P4, P5).

Uzyskane wyniki wydajności metanu w warunkach termofilnych pozwoliły na uszeregowanie biotworzyw od najbardziej biodegradowalnego:
S_PLA$_T$ > F_Cel$_T$ > F_PBS$_T$ > F_PLA$_T$ ≥ F_S$_T$.

Podsumowując, w warunkach termofilnych biotworzywa uległy biodegradacji, a wydajność metanu z S_PLA_T, F_Cel_T, F_PBS_T była wysoka. Należy brać jednak również pod uwagę czas, w którym została wyprodukowana maksymalna ilość metanu. Uzyskanie najwyższej wartości kumulacyjnej PM z folii S_PLA_T (prawie 100% TPM) wymagało aż 75 dni. Zatem, uwzględniając zarówno wydajność metanu, jak i czas osiągnięcia maksymalnej produkcji metanu, z technologicznego punktu widzenia biotworzywa, z wyjątkiem F_Cel_T oraz F_PBS_T, nie powinny być poddawane termofilnej fermentacji metanowej czy np. kofermentacji z bioodpadami. Fragmenty F_Cel_T oraz F_PBS_T przestały być widoczne w inokulum po odpowiednio 2 i 14 dniach. Pozostałe biotworzywa pozostawały widoczne do 66. (S_PLA_T) i 100. (F_PLA_T, F_S_T) dnia beztlenowej biodegradacji (P4). W skali technicznej, przy HRT 20-30 dni fermentacji metanowej, poferment byłby nieustabilizowany a biotworzywa stanowiłyby jego zanieczyszczenie.

Biodegradowalność biotworzyw w warunkach mezofilnych vs termofilnych

Niezależnie od warunków temperaturowych beztlenowej biodegradacji, PM z F_Cel_T oraz z F_Cel_M była zbliżona (319,5-311,4 L/kg s.m.o.). Natomiast w warunkach termofilnych odnotowano ponad 2,5-krotny wzrost szybkości PM, co przekładało się na skrócenie czasu, w którym uzyskano maksymalną PM (5-6 vs 7-8 dni). Niezależnie od warunków temperaturowych, F_Cel, była widoczna w inokulum jedynie przez 2 dni procesu, a najbardziej intensywny spadek właściwości mechanicznych obserwowano do 12 h biodegradacji.

W warunkach termofilnych uzyskano skrócenie czasu (ze 100 do 14 dni), w którym folia F_PBS była widoczna oraz ponad 80% wzrost PM. Odnotowano również 2-krotny wzrost szybkości PM. Niezależnie od warunków temperaturowych, pomiar właściwości mechanicznych F_PBS możliwy był przez 35 dni.

Niezależnie od warunków temperaturowych obserwowano niekompletną degradację F_PLA oraz F_S. Zastosowanie temperatury termofilnej wpłynęło na skrócenie lag fazy podczas PM lub PB, spowodowało niewielki wzrost PM, a uszkodzenia powierzchni materiałów następowały szybciej.

Weryfikując hipotezę #1 wykazano, że:

- zarówno w warunkach mezofilnych, jak i termofilnych biodegradowalność określona na podstawie wartości wskaźników biologicznych (wydajności biogazu lub metanu) zależała od rodzaju biotworzyw,

- niezależnie od warunków temperaturowych biodegradacji wydajność metanu z F_Cel była zbliżona; wydajność metanu była wysoka, materiał ulegał biodegradacji, fragmenty nie były widoczne w inokulum,
- w warunkach termofilnych nastąpił 2-krotny wzrost szybkości PM i ponad 80% wzrost wydajności metanu z F_PBS,
- wydajność metanu z F_PBS w warunkach mezofilnych, oraz z F_PLA oraz F_S, niezależnie od warunków temperaturowych, była niewielka, co wskazuje na niską biodegradowalność biotworzyw,
- niezależnie od warunków temperaturowych wyniki analizy spektrofotometrycznej FTIR, wykazały wzrost intensywności pików odpowiadających grupom funkcyjnym, co wskazywało na postępującą degradację biotworzyw, nie obserwowano powstawania nowych grup funkcyjnych,
- warunki termofilne przyspieszały fragmentację F_Cel, F_PBS, F_PLA oraz F_S, w krótszym czasie następowały uszkodzenia powierzchni biotworzyw,
- biotworzywa charakteryzujące się wysoką wartością wydłużenia miały niską wydajność biogazu lub metanu,
- przydatność biotworzyw do produkcji biogazu lub metanu była technologicznie niezasadna z wyjątkiem folii F_Cel, niezależnie od warunków temperaturowych, oraz folii F_PBS w warunkach termofilnych.

H #2: zastosowanie wstępnej obróbki wpływa na biodegradowalność biotworzyw podczas beztlenowej mezofilnej lub termofilnej biodegradacji

Wykazano, że zastosowanie obróbki wstępnej przed beztlenową mezofilną lub termofilną biodegradacją nie wpływa na biodegradowalność biotworzyw ocenianą na podstawie wskaźników biologicznych, natomiast wpływa na zmiany powierzchni, właściwości mechanicznych oraz struktury chemicznej biotworzyw (P2-P5).

Wstępna obróbka biotworzyw przed mezofilną beztlenową biodegradacją

Podczas prowadzenia procesu biodegradacji w warunkach termofilnych F_PBS oraz F_Cel uległy biodegradacji w czasie, który może być stosowany podczas fermentacji metanowej w skali technicznej (20-30 dni), co oznacza, że w tym przypadku nie ma uzasadnienia stosowania obróbki wstępnej. Obróbkę wstępną F_PBS oraz F_Cel stosowano jedynie przed mezofilną beztlenową biodegradacją (P5).

Alkaliczna obróbka wstępna F_PBS i F_Cel spowodowała wzrost heterogeniczności powierzchni F_PBS$_{M\_A}$ i F_Cel$_{M\_A}$. Folia F_PBS$_{M\_A}$ była widoczna w inokulum przez 100 dni prowadzenia procesu, podczas których obserwowano przejaśnienia w strukturze i zmniejszanie się grubości materiału. Maksymalna produkcja metanu wynosiła 29,3 L/kg s.m.o (4,9% TPM), a początkowa szybkość PM 14,6 L/(kg s.m.o.·d). Ostatni możliwy pomiar właściwości mechanicznych materiału był możliwy 35. dnia procesu, po tym czasie F_PBS$_{M\_A}$ rozpadała się przy dotknięciu. Do 9. dnia następował największy spadek wytrzymałości na rozciąganie oraz ε, po tym czasie wartości parametrów pozostawały na stałym poziomie.

Fragmenty F_Cel$_{M\_A}$ były widoczne w inokulum przez pierwsze 2 dni termofilnej biodegradacji, w czasie tym powstało 176 L/kg s.m.o. metanu (56% maksymalnej PM). Pomimo, że folia była niewidoczna w inokulum to produkcja metanu zachodziła jeszcze przez kolejne 5-6 dni. Maksymalna PM oraz początkowa szybkość PM wynosiły odpowiednio 315,0 L/kg s.m.o (78,2% of TMP) i 161,7 L/(kg s.m.o.·d). Pomiar właściwości mechanicznych był możliwy do 2. dnia, po tym czasie F_Cel$_{T\_A}$ łatwo ulegała rozrywaniu, a na powierzchni pojawiły się mikropęknięcia (P5).

W warunkach mezofilnej biodegradacji F_PLA$_{M\_A}$, F_S$_{M\_A}$, F_PBS$_{M\_A}$, oraz F_Cel$_{M\_A}$ wyniki analizy spektrofotometrycznej FTIR wykazały, że nie powstawały nowe grupy funkcyjne, obserwowano natomiast wzrost intensywności pików odpowiadających poszczególnym grupom funkcyjnym. Pomimo że biotworzywa nie zmieniły swojego składu chemicznego, następowała degradacja (P2, P5).

Wstępna obróbka biotworzyw przed termofilną beztlenową biodegradacją

Podczas prowadzenia procesu biodegradacji w warunkach mezofilnych (365 dni) jak i termofilnych (100 dni) F_S i F_PLA nie uległy biodegradacji. Obróbkę wstępną F_S i F_PLA stosowano jedynie przed termofilną beztlenową biodegradacją (P2, P3).

Podczas 15 dni biodegradacji beztlenowej (w tym lag faza trwająca 4 dni), produkcja metanu z F_PLA$_{T\_A}$ i F_S$_{T\_A}$ wynosiła 47,5 L/kg s.m.o (F_PLA$_{T\_A}$) i 58,6 L/kg s.m.o (F_S$_{T\_A}$) i zachodziła z szybkością odpowiednio 17,6 L/(kg s.mo.·d) i 27,1 L/(kg s.mo.·d). Wartości PM stanowiły jedynie ok. 8%-10% TPM, co wskazuje na niską biodegradowalność biotworzyw (P3).

Fragmenty biotworzyw były widoczne w inokulum przez 100 dni procesu. Obserwowana powierzchnia folii ulegała uszkodzeniom oraz następował wzrost chropowatości powierzchni biotworzyw. Po 45 dniach (F_S$_{T\_A}$) oraz 59 dniach (F_PLA$_{T\_A}$) termofilnej biodegradacji obserwowano pierwsze zmiany makroskopowe powierzchni (pęknięcia, szczeliny). Pomiar właściwości mechanicznych F_PLA$_{T\_A}$

i F_S$_{\_A}$ był możliwy przez odpowiednio 28 oraz 35 dni. Wytrzymałość na rozciąganie F_PLA$_{T\_A}$ po 7 dniach spadła z ok. 20 MPa do ok. 18 MPa i utrzymywała się na zbliżonym poziomie do 20 dnia, następnie do 28 dnia notowano gwałtowny spadek wartości do ok. 8 MPa. W przypadku F_S$_{\_A}$, najbardziej intensywny spadek wartości wytrzymałości na rozciąganie (z ok. 17 MPa do ok. 10 MPa) nastąpił do 10. dnia. Wartość tego wskaźnika uległa obniżeniu do ok. 5,5 MPa (w 35. dniu eksperymentu) i był to ostatni możliwy pomiar (P3).

Materiał S_PLA$_{T}$ w warunkach termofilnych ulegał biodegradacji w czasie 75 dni, stąd aby zintensyfikować proces zaproponowano wstępną obróbkę alkaliczną i hydrotermiczną (P4). Podczas beztlenowej biodegradacji S_PLA$_{T\_A}$ nie wystąpiła lag faza. Do 5. dnia biodegradacji, PM zachodziła z szybkością 11,16 L/(kg s.m.o.·d), co było związane z uwolnieniem do roztworu łatwobiodegradowalnych związków organicznych po obróbce wstępnej (odnotowano wzrost stężenia ChZT w roztworze alkalicznym). Następnie obserwowano 10-dniowe plateau, po którym ponownie nastąpiła PM z szybkością 7,72 L/(kg s.m.o.·d). Fragmenty S_PLA$_{T\_A}$ były widoczne przez 60 dni, podczas których powstało 90% maksymalnej PM tj. 448 L/kg s.m.o. Dalsza PM (pozostałe 10%) zachodziła do 70. dnia, z szybkością 2,53 L/(kg s.m.o.·d). Zastosowanie alkalicznej obróbki wstępnej spowodowało pojawienie się licznych rys w strukturze S_PLA$_{T\_A}$. Od 7. dnia, materiał zmienił kolor na biały, a pierwsze pęknięcia na powierzchni pojawiły się 14. dnia. W kolejnych dniach materiał ciemniał, szczeliny się pogłębiały, stawał się coraz bardziej kruchy, nieliczne fragmenty były obecne do 60. dnia beztlenowej biodegradacji.

Produkcja metanu z S_PLA$_{T\_HT}$ po hydrotermicznej obróbce wstępnej zachodziła z 5-dniową lag fazą. Fragmenty pozostawały widoczne w inokulum przez 50 dni, podczas których powstało 90% maksymalnej PM. PM zachodziła w dwóch fazach. W pierwszej, trwającej 50 dni, podczas której fragmenty materiału były widoczne, szybkość PM wynosiła 8,35 L/(kg s.m.o.·d). W drugiej fazie, metan był jeszcze produkowany do 60. dnia, ale z mniejszą szybkością, 2,20 L/(kg s.m.o.·d). Maksymalna PM z S_PLA$_{T\_HT}$ wynosiła 448 L/kg s.m.o. Wstępna obróbka hydrotermiczna spowodowała nieliczne, niewielkie zmiany (mikropęknięcia) na powierzchni materiału. Od 7. dnia beztlenowej biodegradacji zmienił się kolor na biały i pojawiły się pojedyncze szczeliny i pęknięcia, które pogłębiały się wraz z czasem. Od 23. dnia, S_PLA$_{T\_HT}$ zaczął zmieniać kolor na ciemniejszy, stawał się coraz bardziej kruchy, nieliczne fragmenty były obecne w inokulum do 50 dnia. Największe zmiany w strukturze S_PLA$_{T\_A}$ i S_PLA$_{T\_HT}$ nastąpiły w fazie intensywnej produkcji metanu (P4).

Wyniki analizy spektrofotometrycznej FTIR wykazały, że w warunkach termofilnej biodegradacji _PLA$_{T\_A}$, F_S$_{T\_A}$, F_PBS$_{T\_A}$, F_Cel$_{T\_A}$, S_PLA$_{T\_HT}$ oraz S_PLA$_{T\_A}$ nie powstawały nowe grupy funkcyjne, co wskazuje na fakt, że skład chemiczny biotworzyw nie uległ zmianie. Obserwowano wzrost intensywności pików odpowiadających poszczególnym grupom funkcyjnym, co wskazywało na postępującą degradację biotworzyw

Beztlenowa biodegradacja biotworzyw bez obróbki wstępnej vs z obróbką wstępną biotworzyw przed beztlenową biodegradacją

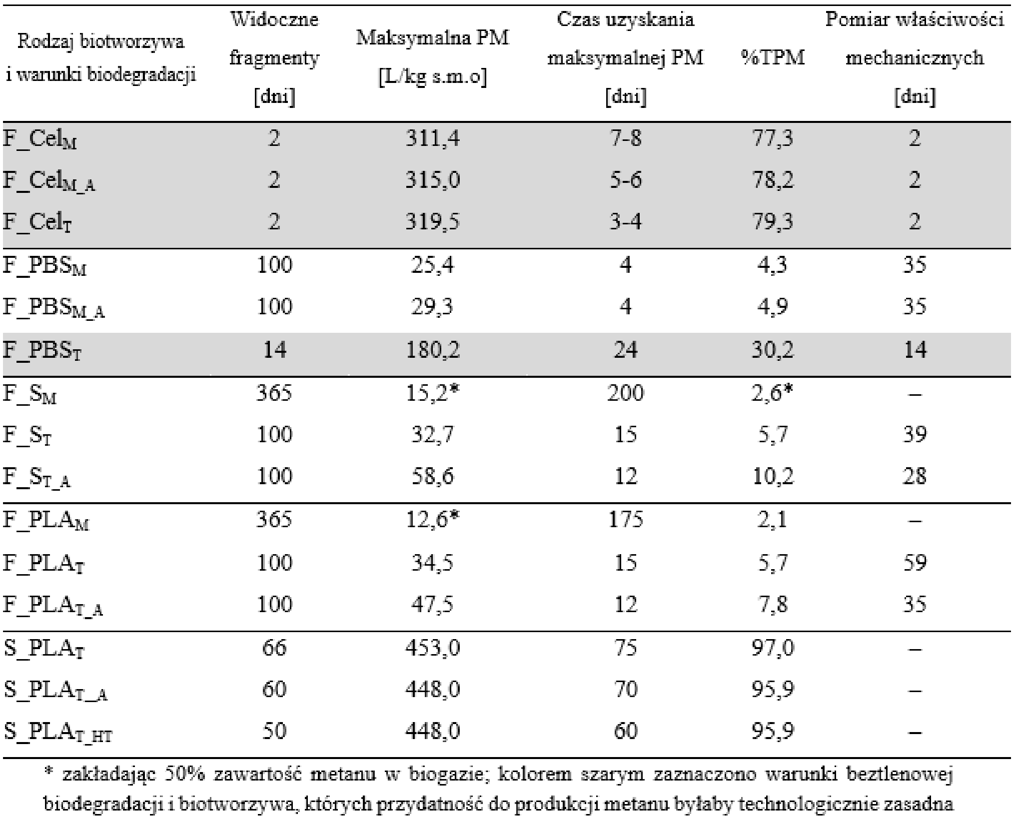
Obróbka wstępna biotworzyw przed beztlenową mezofilną (F_PBS, F_Cel) lub termofilną (F_PLA, F_S) biodegradacją nie powodowała zwiększenia PM, przyspieszyła natomiast utratę właściwości mechanicznych biotworzyw w porównaniu do biotworzyw nie poddanych obróbce wstępnej. Obróbka wstępna F_PLA oraz F_S spowodowała wzrost chropowatości powierzchni w porównaniu do biotworzyw bez obróbki wstępnej. Niezależnie od zastosowania obróbki wstępnej przed mezofilną degradacją F_PBS oraz przed termofilną degradacją F_PLA, F_S, S_PLA, czas biodegradacji biotworzyw był kilkukrotnie dłuższy niż biodegradacji bioodpadów, co wskazuje na brak możliwości kofermentacji. Obróbka wstępna alkaliczna S_PLA$_{T\_A}$ skróciła lag fazę i czas, w którym osiągnięto maksymalną PM w porównaniu do biodegradacji S_PLA$_{T}$ bez obróbki wstępnej; po hydrotermicznej obróbce wstępnej S_PLA$_{T\_HT}$ czas, w którym osiągnięto maksymalną PM był najkrótszy, a metan był wytwarzany z 1,1-krotnie wyższą szybkością w porównaniu do biodegradacji bez obróbki wstępnej; produkcja metanu nie zależała od zastosowania i rodzaju obróbki wstępnej materiału do beztlenowej biodegradacji. Przydatność do produkcji biogazu lub metanu biotworzyw poddawanych obróbce wstępnej, z wyjątkiem F_Cel$_{M\_A}$, S_PLA$_{T\_A}$ i S_PLA$_{T\_HT}$, była nieistotna; nie ma uzasadnienia technologicznego ani ekonomicznego stosowania wstępnej obróbki biotworzyw do beztlenowej biodegradacji. Obróbka wstępna alkaliczna nie miała wpływu na powstawanie nowych grup funkcyjnych podczas biodegradacji biotworzyw, obserwowano wzrost intensywności pików odpowiadających poszczególnym grupom funkcyjnym, co wskazywało na postępującą biodegradację biotworzyw. Biorąc pod uwagę długi czas, po którym uzyskano maksymalną PM z S_PLA$_{T\_A}$ i S_PLA$_{T\_HT}$, pomimo wysokiej wydajności metanu, nie ma technologicznego uzasadnienia kofermentacji z bioodpadami.

Weryfikując hipotezę #2 wykazano, że:

- wstępna obróbka biotworzyw przed beztlenową mezofilną lub termofilną biodegradacją nie wpłynęła na biodegradowalność ocenianą na podstawie wskaźników biologicznych, natomiast wpływała na zmiany powierzchni oraz właściwości mechaniczne biotworzyw,
- po wstępnej obróbce biotworzywa szybciej traciły właściwości mechaniczne,
- niezależnie od zastosowania wstępnej obróbki, czas biodegradacji biotworzyw był kilkukrotnie dłuższy niż bioodpadów, co wskazuje na brak możliwości wspólnej kofermentacji z bioodpadami,
- niezależnie od warunków temperaturowych oraz zastosowania obróbki wstępnej, wyniki analizy spektrofotometrycznej FTIR wykazały wzrost intensywności pików odpowiadających grupom funkcyjnym, co wskazywało na postępującą biodegradację biotworzyw, natomiast nie obserwowano powstawania nowych grup funkcyjnych.

W tabeli 3 zestawiono wydajność metanu z biotworzyw bez lub po wstępnej obróbce przed beztlenową mezofilną lub termofilną biodegradacją.

Tab. 3. Parametry beztlenowej mezofilnej lub termofilnej biodegradacji biotworzyw



Rodzaj biotworzywa i warunki biodegradacji	Widoczne fragmenty [dni]	Maksymalna PM [L/kg s.m.o]	Czas uzyskania maksymalnej PM [dni]	%TPM	Pomiar właściwości mechanicznych [dni]
F_Cel$_{M}$	2	311,4	7-8	77,3	2
F_Cel$_{M\_A}$	2	315,0	5-6	78,2	2
F_Cel$_{T}$	2	319,5	3-4	79,3	2
F_PBS$_{M}$	100	25,4	4	4,3	35
F_PBS$_{M\_A}$	100	29,3	4	4,9	35
F_PBS$_{T}$	14	180,2	24	30,2	14
F_S$_{M}$	365	15,2*	200	2,6*	–
F_S$_{T}$	100	32,7	15	5,7	39
F_S$_{T\_A}$	100	58,6	12	10,2	28
F_PLA$_{M}$	365	12,6*	175	2,1	–
F_PLA$_{T}$	100	34,5	15	5,7	59
F_PLA$_{T\_A}$	100	47,5	12	7,8	35
S_PLA$_{T}$	66	453,0	75	97,0	–
S_PLA$_{T\_A}$	60	448,0	70	95,9	–
S_PLA$_{T\_HT}$	50	448,0	60	95,9	–

* zakładając 50% zawartość metanu w biogazie; kolorem szarym zaznaczono warunki beztlenowej biodegradacji i biotworzywa, których przydatność do produkcji metanu byłaby technologicznie zasadna

5. Spis literatury

Abd El-malek, F., Khairy, H., Farag, A., Omar, S., 2020. The sustainability of microbial bioplastics, production and applications. *International Journal of Biological Macromolecules*, *157*, 319-328.

Abdel-Rahman, M.A., Tashiro, Y., Sonomoto, K., 2013. Recent advances in lactic acid production by microbial fermentation processes. *Biotechnology Advances*, *31*(6), 877-902.

Agarwal, S., Singhal, S., Godiya, C.B., Kumar, S., 2021. Prospects and applications of starch based biopolymers. *International Journal of Environmental Analytical Chemistry*, 1-20.

Ahmed, T., Shahid, M., Azeem, F., Rasul, I., Shah, A. A., Noman, M., Hameed, A., Manzoor, N., Muhammad, S., 2018. Biodegradation of plastics: current scenario and future prospects for environmental safety. *Environmental Science and Pollution Research*, *25*, 7287-7298.

Ali, S.S., Elsamahy, T., Abdelkarim, E.A., Al-Tohamy, R., Kornaros, M., Ruiz, H.A., Zhao, T., Li, F., Sun, J., 2022. Biowastes for biodegradable bioplastics production and end-of-life scenarios in circular bioeconomy and biorefinery concept. *Bioresource Technology*, *363*, 127869.

Aliotta, L., Seggiani, M., Lazzeri, A., Gigante, V., Cinelli, P., 2022. A brief review of poly (butylene succinate)(PBS) and its main copolymers: synthesis, blends, composites, biodegradability, and applications. *Polymers*, *14*(4), 844.

Arikan, E.B., Bilgen, H.D., 2019. Production of bioplastic from potato peel waste and investigation of its biodegradability. *International Advanced Researches and Engineering Journal*, *3*(2), 93-97.

Astolfi, M.L., Marconi, E., Lorini, L., Valentino, F., Silva, F., Ferreira, B.S., Canepari, S., Majone, M., 2020. Elemental concentration and migratability in bioplastics derived from organic waste. *Chemosphere*, *259*, 127472.

Atiwesh, G., Mikhael, A., Parrish, C.C., Banoub, J., Le, T.A.T., 2021. Environmental impact of bioplastic use: A review. *Heliyon*, *7*(9), 07918.

Auras, R., Harte, B., Selke, S., 2004. An overview of polylactides as packaging materials. *Macromolecular bioscience*, *4*(9), 835-864.

Bach, Q.V., Manh Vu, C., 2020. Bacterial cellulose filled epoxy resin-based green composites: fabrication and characterization. *Composite Interfaces*, *27*(7), 645-662.

Barletta, M., Aversa, C., Ayyoob, M., Gisario, A., Hamad, K., Mehrpouya, M., Vahabi, H., 2022. Poly(butylene succinate) (PBS): materials, processing, and industrial applications. *Progress in Polymer Science*, *132*, 101579.

Bátori, V., Åkesson, D., Zamani, A., Taherzadeh, M.J., Horváth, I.S., 2018. Anaerobic degradation of bioplastics: A review. *Waste Management*, *80*, 406-413.

Benn, N., Zitomer, D., 2018. Pretreatment and anaerobic co-digestion of selected PHB and PLA bioplastics. *Frontiers in Environmental Science*, *5*, 93.

Bernat, K., Kulikowska, D., Wojnowska-Baryła, I., Kamińska, A., 2022). Can the biological stage of a mechanical-biological treatment plant that is designed for mixed municipal solid waste be successfully utilized for effective composting of selectively collected biowaste? *Waste Management*, *149*, 291-301.

Bernat, K., Kulikowska, D., Wojnowska-Baryła, I., Zaborowska, M., Pasieczna-Patkowska, S., 2021. Thermophilic and mesophilic biogas production from PLA-based materials: Possibilities and limitations. *Waste Management*, *119*, 295-305.

Bernat, K., Le, T.C.T., Zaborowska, M., Kulikowska, D., 2023. Pre-Treatment of separately collected biowaste as a way to increase methane production and digestate stability. *Energies*, *16*(3), 1264.

Briassoulis, D., Pikasi, A., Hiskakis, M., 2021. Recirculation potential of post-consumer/industrial bio-based plastics through mechanical recycling. Techno-economic sustainability criteria and indicators. *Polymer Degradation and Stability*, *183*, 109217.

Buswell, A.M.; Mueller, H.F. ,1952. Mechanism of methane fermentation. *Industrial & Engineering Chemistry, 44*, 550–552.

Dang, B.T., Bui, X.T., Tran, D.P., Ngo, H.H., Nghiem, L. D., Hoang, T.K.D., Nguyen, P.T., Nguyen, P.T., Vo, T.K.Q., Lin, C., Lin, K.Y.A., Varjani, S., 2022. Current application of algae derivatives for bioplastic production: A review. *Bioresource Technology*, *347*, 126698.

de Azevedo, L.C., Rovani, S., Santos, J.J., Dias, D.B., Nascimento, S.S., Oliveira, F.F., Silva, L.G.A., Fungaro, D.A., 2020. Biodegradable films derived from corn and potato starch and study of the effect of silicate extracted from sugarcane waste ash. *ACS Applied Polymer Materials*, *2*(6), 2160-2169.

Diyana, Z.N., Jumaidin, R., Selamat, M.Z., Suan, M.S.M., 2021. Thermoplastic starch/beeswax blend: Characterization on thermal mechanical and moisture absorption properties. *International Journal of Biological Macromolecules*, *190*, 224-232.

Dyrektywa Parlamentu Europejskiego i Rady (UE) 2019/904 z dnia 5 czerwca 2019 r. w sprawie zmniejszenia wpływu niektórych produktów z tworzyw sztucznych na środowisko, Directive (EU) 2019/904 of the European Parliament and of the Council of 5 june 2019 on the reduction of the impact of certain plastic products on the environment

Emadian, S.M., Onay, T.T., Demirel, B., 2017. Biodegradation of bioplastics in natural environments. *Waste Management*, *59*, 526-536.

Folino, A., Karageorgiou, A., Calabrò, P.S., Komilis, D., 2020. Biodegradation of wasted bioplastics in natural and industrial environments: A review. *Sustainability*, *12*(15), 6030.

Fredi, G., Dorigato, A., 2021. Recycling of bioplastic waste: A review. *Advanced Industrial and Engineering Polymer Research*, *4*(3), 159-177.

Gadkari, S., Kumar, D., Qin, Z. H., Lin, C.S.K., Kumar, V., 2021. Life cycle analysis of fermentative production of succinic acid from bread waste. *Waste Management*, *126*, 861-871.

García-Guzmán, L., Cabrera-Barjas, G., Soria-Hernández, C.G., Castaño, J., Guadarrama-Lezama, A. Y., Rodríguez Llamazares, S., 2022. Progress in starch-based materials for food packaging applications. *Polysaccharides*, *3*(1), 136-177.

Hamad, K., Kaseem, M., Yang, H.W., Deri, F., Ko, Y.G., 2015. Properties and medical applications of polylactic acid: A review. *Express Polymer Letters*, *9*(5).

Ismail, N.A., Mohd Tahir, S., Yahya, N., Abdul Wahid, M.F., Khairuddin, N.E., Hashim, I., Hasim, I., Rosli, N., Abdullah, M.A., 2016. Synthesis and characterization of biodegradable starch-based bioplastics. w: *Materials Science Forum*, vol. 846, Trans Tech Publications Ltd. pp. 673-678.

Jogi, K., Bhat, R., 2020. Valorization of food processing wastes and by-products for bioplastic production. *Sustainable Chemistry and Pharmacy*, *18*, 100326.

Khan, B., Bilal Khan Niazi, M., Samin, G., Jahan, Z., 2017. Thermoplastic starch: A possible biodegradable food packaging material - a review. *Journal of Food Process Engineering*, *40*(3), e12447.

Khoshnevisan, B., Tabatabaei, M., Tsapekos, P., Rafiee, S., Aghbashlo, M., Lindeneg, S., Angelidaki, I., 2020. Environmental life cycle assessment of different biorefinery platforms valorizing municipal solid waste to bioenergy, microbial protein, lactic and succinic acid. *Renewable and Sustainable Energy Reviews*, *117*, 109493.

Krishnamurthy, A., Amritkumar, P., 2019. Synthesis and characterization of eco-friendly bioplastic from low-cost plant resources. *SN Applied Sciences*, *1*(11), 1432.

Laya, S., Shamina, S., Moossa, P.P., 2022. Production of bioplastic from rice straw cellulose, *The Pharma Innovation Journal, SP-11*(9), 1742-1744.

Le Hoang, S., Vu, C.M., Pham, L.T., Choi, H.J., 2018. Preparation and physical characteristics of epoxy resin/bacterial cellulose biocomposites. *Polymer Bulletin*, *75*, 2607-2625.

Li, H., Huneault, M.A., 2011. Comparison of sorbitol and glycerol as plasticizers for thermoplastic starch in TPS/PLA blends. *Journal of Applied Polymer Science*, *119*(4), 2439-2448.

Li, X., Lin, Y., Liu, M., Meng, L., Li, C., 2023. A review of research and application of polylactic acid composites. *Journal of Applied Polymer Science*, *140*(7), 53477.

Liang, Y., Tan, Q., Song, Q., Li, J., 2021. An analysis of the plastic waste trade and management in Asia. *Waste Management*, *119*, 242-253.

Marichelvam, M.K., Jawaid, M., Asim, M., 2019. Corn and rice starch-based bio-plastics as alternative packaging materials. *Fibers*, *7*(4), 32.

Martinez Villadiego, K., Arias Tapia, M.J., Useche, J., Escobar Macías, D., 2022. Thermoplastic starch (TPS)/polylactic acid (PLA) blending methodologies: a review. *Journal of Polymers and the Environment*, *30*(1), 75-91.

Miraj, S.S., Parveen, N., Zedan, H.S., 2021. Plastic microbeads: small yet mighty concerning. *International Journal of Environmental Health Research*, *31*(7), 788-804.

Morseletto, P., 2020. Targets for a circular economy. *Resources, Conservation and Recycling*, *153*, 104553.

Mu, L., Zhang, L., Ma, J., Zhu, K., Chen, C., Li, A., 2021. Enhanced biomethanization of waste polylactic acid plastic by mild hydrothermal pretreatment: Taguchi orthogonal optimization and kinetics modeling. *Waste Management*, *126*, 585-596.

Mustățea, G., Ungureanu, E.L., Belc, N., 2019. Polylactic acid (PLA) for food packaging applications - a short overview. *Annals. Food Science and Technology*, *20*(1), 9-14.

Nanda, N., Bharadvaja, N., 2022. Algal bioplastics: current market trends and technical aspects. *Clean Technologies and Environmental Policy*, *24*(9), 2659-2679.

Otoni, C. G., Azeredo, H.M., Mattos, B.D., Beaumont, M., Correa, D.S., Rojas, O.J., 2021. The food-materials nexus: Next generation bioplastics and advanced materials from agri-food residues. *Advanced Materials*, *33*(43), 2102520.

Pang, X., Zhuang, X., Tang, Z., Chen, X., 2010. Polylactic acid (PLA): research, development and industrialization. *Biotechnology Journal*, *5*(11), 1125-1136.

Pohare, M.B., Bhor, S.A., Patil, P.K., 2017. Sugarcane for economical bioplastic production. *Pop Kheti*, *5*(1), 20-23.

Prata, J.C., da Costa, J.P., Lopes, I., Duarte, A.C., Rocha-Santos, T., 2020. Environmental exposure to microplastics: An overview on possible human health effects. *Science of the total environment*, *702*, 134455.

Putri, T. R., Adhitasari, A., Paramita, V., Yulianto, M.E., Ariyanto, H.D., 2023. Effect of different starch on the characteristics of edible film as functional packaging in fresh meat or meat products: A review. *Materials Today: Proceedings*, In Press, https://doi.org/10.1016/j.matpr.2023.02.396.

Rahman, A., Miller, C.D., 2017. Microalgae as a source of bioplastics. W: *Algal green chemistry*, Eds.: Rastogi R.P, Madamwar D., Pandey A., pp. 121-138. Elsevier.

Rahman, M.S., Hasan, M.S., Nitai, A.S., Nam, S., Karmakar, A.K., Ahsan, M. S., Shiddky, M.J.A., Ahmed, M.B., 2021. Recent developments of carboxymethyl cellulose. *Polymers*, *13*(8), 1345.

Rasal, R.M., Janorkar, A.V., Hirt, D.E., 2010. Poly(lactic acid) modifications. *Progress in Polymer Science*, 35(3), 338–356.

Ratshoshi, B.K., Farzad, S., Görgens, J.F., 2021. Techno-economic assessment of polylactic acid and polybutylene succinate production in an integrated sugarcane biorefinery. *Biofuels, Bioproducts and Biorefining*, *15*(6), 1871-1887.

Rodríguez Cueto, Y., Montemayor, S.M., Rodríguez González, F.J., Mondragón Chaparro, M., 2023. High performance thermoplastic starch/vermiculite bionanocomposites. W: *Green-Based Nanocomposite Materials and Applications,* Eds.: Avalos Belmontes, F., González, F.J., López-Manchado, M.Á., pp. 81-99, Cham. Springer International Publishing.

Rosenboom, J.G., Langer, R. Traverso, G., 2022. Bioplastics for a circular economy. *Nature Reviews. Materials, 7*(2), 117-137

Rumi, S.S., Liyanage, S., Abidi, N., 2021. Conversion of low-quality cotton to bioplastics. *Cellulose*, *28*, 2021-2038.

Sabapathy, P.C., Devaraj, S., Meixner, K., Anburajan, P., Kathirvel, P., Ravikumar, Y., Zabed, H.M., Qi, X., 2020. Recent developments in Polyhydroxyalkanoates (PHAs) production - a review. *Bioresource Technology*, *306*, 123132.

Seo, Y.R., Kim, J. W., Hoon, S., Kim, J., Chung, J.H., Lim, K.T., 2018. Cellulose-based nanocrystals: sources and applications via agricultural byproducts. *Journal of Biosystems Engineering*, *43*(1), 59-71.

Shabbirahmed, A.M., Haldar, D., Dey, P., Patel, A.K., Singhania, R.R., Dong, C.D., Purkait, M.K. 2022. Sugarcane bagasse into value-added products: a review. *Environmental Science and Pollution Research*, *29*(42), 62785-62806.

Soroudi, A., Jakubowicz, I., 2013. Recycling of bioplastics, their blends and biocomposites: a review. *European Polymer Journal*, *49*(10), 2839-2858.

Su, C.Y., Li, D., Wang, L.J., Wang, Y., 2022. Biodegradation behavior and digestive properties of starch-based film for food packaging–a review. *Critical Reviews in Food Science and Nutrition*, 1-23.

Subramaniam, S.R., Samykano, M., Selvamani, S.K., Ngui, W.K., Kadirgama, K., Sudhakar, K., Idris, M.S., 2019. 3D printing: overview of PLA progress. w: *AIP conference proceedings*, vol. 2059, AIP Publishing LLC., 020015

Sultan, N.F.K., Johari, W.L.W., 2017. The development of banana peel/corn starch bioplastic film: a preliminary study. *Bioremediation Science and Technology Research*, *5*(1), 12-17.

Tejaswini, M.S.S.R., Pathak, P., Ramkrishna, S., Ganesh, P.S., 2022. A comprehensive review on integrative approach for sustainable management of plastic waste and its associated externalities. *Science of the Total Environment*, *825*, 153973.

Tsang, Y. F., Kumar, V., Samadar, P., Yang, Y., Lee, J., Ok, Y.S., Song, H., Kim, K.H., Kwon, E.E., Jeon, Y.J., 2019. Production of bioplastic through food waste valorization. *Environment International*, *127*, 625-644.

Tsang, Y. F., Kumar, V., Samadar, P., Yang, Y., Lee, J., Ok, Y.S., Song, H., Kim, K.H., Kwon, E.E., Jeon, Y.J., 2019. Production of bioplastic through food waste valorization. *Environment International*, *127*, 625-644.

Walker, S., Rothman, R., 2020. Life cycle assessment of bio-based and fossil-based plastic: A review. *Journal of Cleaner Production*, *261*, 121158.

Wang, J., Gardner, D. J., Stark, N. M., Bousfield, D. W., Tajvidi, M., Cai, Z. (2018). Moisture and oxygen barrier properties of cellulose nanomaterial-based films. *ACS Sustainable Chemistry Engineering*, *6*(1), 49-70.

Xu, J., Guo, B. H., 2010. Microbial succinic acid, its polymer poly (butylene succinate), and applications. *Plastics from Bacteria: Natural Functions and Applications*, 347-388.

Yadav, N., Hakkarainen, M., 2021. Degradable or not? Cellulose acetate as a model for complicated interplay between structure, environment and degradation. *Chemosphere*, *265*, 128731.

Zaborowska, M., Bernat, K., 2023. The development of recycling methods for bio-based materials–A challenge in the implementation of a circular economy: A review. *Waste Management and Research, 41*(1), 68-80.

Zanchetta, E., Damergi, E., Patel, B., Borgmeyer, T., Pick, H., Pulgarin, A., Ludwig, C., 2021. Algal cellulose, production and potential use in plastics: challenges and opportunities. *Algal Research*, *56*, 102288.

Zoungranan, Y., Lynda, E., Dobi-Brice, K.K., Tchirioua, E., Bakary, C., Yannick, D. D., 2020. Influence of natural factors on the biodegradation of simple and composite bioplastics based on cassava starch and corn starch. *Journal of Environmental Chemical Engineering*, *8*(5), 104396.

Review Article

WM&R

Waste Management & Research
2023, Vol. 41(1) 68–80

DOI: 10.1177/0734242X221105432
journals.sagepub.com/home/wmr
SAGE

The development of recycling methods for bio-based materials – A challenge in the implementation of a circular economy: A review

Magdalena Zaborowska and Katarzyna Bernat

Abstract

This review focuses on the characteristics of the most widely used biopolymers that contain starch, polylactic acid, cellulose and/or polybutylene succinate. Because worldwide production of bio-based materials has grown dynamically, their waste is increasingly found in the existing waste treatment plants. The development of recycling methods for bio-based materials remains a challenge in the implementation of a circular economy. This article summarizes the recycling methods for bio-based materials, which, in the hierarchy of waste management, is much more desirable than landfilling. Several methods of recycling are available for the end-of-life management of bio-based products, which include mechanical (reuse of waste as a valuable raw material for further processing), chemical (feedstock recycling) and organic (anaerobic digestion or composting) ones. The use of chemical or mechanical recycling is less favourable, more costly and requires the improvement of systems for separation of bio-based materials from the rest of the waste stream. Organic recycling can be a sustainable alternative to those two methods. In organic recycling, bio-based materials can be biologically treated under aerobic or anaerobic conditions, depending on the characteristics of the materials. The choice of the recycling method to be implemented depends on the economic situation and on the properties of the bio-based products and their susceptibility to degradation. Thus, it is necessary to label the products to indicate which method of recycling is most appropriate.

Keywords

Biopolymers, organic recycling, mechanical recycling, chemical recycling, composting, anaerobic digestion, biodegradation

Received 9th November 2021, accepted 14th May 2022 by Editor in Chief Arne Ragossnig.

Introduction

Recently, because of plastic pollution, petroleum-based polymers (conventional plastics) are increasingly being replaced by biopolymers that retain the properties and utility of conventional plastics. These products have many environmental benefits, and one such benefit is as follows: bio-based polylactic acid (PLA) has four times lower carbon footprint than petroleum-based polypropylene. In general, one metric tonne of bio-based products generates from 0.8 to 3.2 times less CO_2 than petroleum-derived plastic (Abraham et al., 2021). In 2019, biopolymers constituted 0.3% (1.174 million tonnes) of total plastic production, and their market share is expected to grow rapidly by 2030, even up to 40% (PlasticsEurope, 2019; Zhao et al., 2020). According to the European Standard (EN 16575), a bio-based product is one that is wholly or partly derived from biomass. The content of renewable resources in bio-based products can range from 20% to 100% (Biron, 2020), and it can be measured using the radiocarbon method and elemental analysis (EN 16785) or using ^{14}C measurement (EN 16640; ISO 16620). Bio-based products are widely used in the production of packaging (~60%) and in agriculture and horticulture (13%). Biopolymers, which are most widely used for rigid and flexible packaging, contain starch, PLA and/or polybutylene succinate (PBS). For this reason, this review focuses on the characteristics of these biopolymers.

Because the production of bio-based materials is developing very dynamically, waste generated from these materials is increasingly found in the existing mechanical–biological treatment plants. Thus, this review aims to provide an insightful overview of the recycling method of waste from bio-based products. Bio-based products can be (i) mechanically or chemically recycled with conventional petroleum-based plastics, (ii) treated via organic recycling with biowaste, (iii) incinerated (energy recovery) or (iv) landfilled. However, incineration of bio-based products should only be used when other methods cannot be implemented, and landfilling should be avoided (it is banned in many countries) (Ioannidou et al., 2020). It is important to determine the effect of bio-based products on recycling, a method

Department of Environmental Biotechnology, University of Warmia and Mazury in Olsztyn, Olsztyn, Poland

Corresponding author:
Magdalena Zaborowska, Department of Environmental Biotechnology, University of Warmia and Mazury in Olsztyn, Sloneczna 45G, Olsztyn 10-709, Poland.
Email: magdalena.zaborowska@uwm.edu.pl

which is consistent with the requirements of a circular economy. Moreover, due to the increasing production of bio-based products, it is necessary to establish effective methods for recycling them, which has been still a challenge in the waste treatment systems.

Types and properties of commonly used biopolymers

Starch, a natural polymer, is becoming widely used in the production of bio-based products (44% of global production of biodegradable polymers) due to its abundance, low cost and biodegradability. It consists of approximately 20–25% of linear/helical amylose and 75–80% of branched amylopectin. Depending on its biological origin, starch has various crystalline structures (Zhao et al., 2020) and may undergo thermal degradation before reaching its melting point (Storz and Vorlop, 2013). Due to its poor mechanical properties (i.e. low tensile strength, high brittleness), starch must be processed before it is used for production (Sorrentino et al., 2007; Zhao et al., 2020). Methods of starch processing include mechanical shearing under heat or addition of plasticizers (typically water or glycerol). During these processes, the crystalline structure of the starch is destroyed, and thermoplastic starch (TPS) is formed (Rodriguez-Gonzalez et al., 2004; Van Soest et al., 1996). TPS is very hydrophilic, and humidity weakens its structure. Therefore, to improve its properties, sorbitol can be used as a plasticizer (Li and Huneault, 2011), and in commercial products, TPS is often blended with other polymers (e.g. PLA, polycaprolactone (PCL) or low-density polyethylene) (Mazerolles et al., 2019). However, starch is not compatible with other hydrophobic polymers; thus, starch content typically ranges from around 25% to 30% (Storz and Vorlop, 2013), whereas plasticizer content may range from 10% to 50% (Nafchi et al., 2013). However, adding too much of plasticizer decreases melt viscosity.

PLA is another important polymer used for the production of bio-based products. There are two main methods to produce PLA at industrial scale: direct polycondensation of lactic acid (LA) (Laonuad et al., 2010) or ring-opening polymerization (ROP) through the lactide (cyclic dimer of LA) (Murariu and Dubois, 2016). Since the first method has many disadvantages, such as difficulties in purifying and water removal; the necessity of using a relatively large reactor; change in colour; racemization; and production of only low to intermediate molecular weight PLA, the ROP method is mainly used in practice (Gruber et al., 2000; Lasprilla et al., 2012). LA used for PLA production can be obtained by chemical synthesis or fermentation. Currently, fermentation by bacteria and fungi is the most popular and desirable method because it uses renewable agricultural resources, such as sugar cane, corn and cassava (John et al., 2006; Nampoothiri et al., 2010). However, the yield of LA produced by fungi is lower than that produced by bacteria. The microorganisms responsible for LA production are the following: *Lactococcus, Enterococcus, Streptococcus, Leuconostoc, Weissella*, some *Lactobacilli* and *Lactobacillus brevis*. For LA production, batch, fed batch, or continuous fermentation can be used; the first two processes produce a high concentration of LA, whereas the third has a higher productivity (Ghaffar et al., 2014; Nampoothiri et al., 2010; Riaz et al., 2018). Recently, worldwide production of PLA has increased to the point where it accounts for 24% of the biodegradable polymer market. This increase is due to its desirable properties, such as high mechanical strength, high modulus and transparency. In general, the mechanical properties of PLA are similar to those of polystyrene. However, PLA has some disadvantages, such as high sensitivity to moisture; low flexibility, ductility, impact and resistance; and resistance to hydrolysis. To improve the properties of PLA, plasticization, copolymerization and blending with other materials are employed (Karamanlioglu et al., 2017a; Lamberti et al., 2020; Murariu and Dubois, 2016). PLA can be either semi-crystalline or amorphous. The higher the crystallinity of PLA, the better its mechanical properties and thermal behaviour. Therefore, the degradation rate of crystalline PLA is lower than that of amorphous PLA (Zhang et al., 2012).

Another commonly used biodegradable polymer is PBS, a semi-crystalline polyester that is synthesized via polycondensation of succinic acid and 1-4-butanediol. It should be emphasized that PBS can be bio based or petroleum based. Recently, bio-based PBS, produced by fermenting renewable sources such as glucose or sucrose, has been extensively investigated. The mechanical properties of PBS are similar to those of polypropylene and low-density polyethylene (Liminana et al., 2018; Tokiwa et al., 2009). Due to its high processability and chemical resistance and its good thermal properties, the polymer is increasingly used for packaging. PBS is easily biodegradable because it has a flexible backbone and contains readily hydrolysable ester bonds, which can be degraded by microorganisms or enzymes (Pan et al., 2018).

Cellulose is an abundant natural polymer that can be obtained from plants, wood or bacteria. The most effective bacterial species for cellulose production is *Komagataeibacter xylinus*. Bacterial cellulose has higher purity than plant-based cellulose, but its production is economically disadvantageous. Generally, cellulose has very good properties for production of bio-based materials, such as hydrophilicity, flexibility, mouldability and crystallinity (Gorgieva and Trček, 2019; Ummartyotin and Manuspiya, 2015). Moreover, it biodegrades in few weeks or months in natural environments. Celluloses biodegrade due to the enzymatic activity of bacteria and fungi, which breaks down lignocelluloses into sugars (Houfani et al., 2020).

Mechanical recycling of bio-based material

In mechanical recycling, plastics are recycled into secondary raw materials, and in contrast to organic and chemical recycling or incineration, the structure of the polymer and its value as a feedstock and its polymerization energy are preserved (Niaounakis, 2013; Resch-Fauster et al., 2017). However, mechanical recycling of bio-based products with conventional plastics may deteriorate the quality of the plastic recyclable, but recycling of bio-based material in a separate stream requires a critical mass of biopolymers, at least 200 million kg per year (Cornell, 2007). Moreover, the mechanical recycling of bio-based products involves potential costs and logistical problems connected with their recovery and separation.

Several methods have been proposed for identifying and sorting bio-based products from the plastic stream, for example, manual sorting (based on the markers and labels), separation by density differences or separation using optical systems (based on near-infrared (NIR)) (Niaounakis, 2019, 2013). For example, PLA, which is the polymer that has been most intensively investigated with regard to mechanical recyclability, can be sorted by NIR with an accuracy of 98%. However, sight separation or separation based on density does not allow easy sorting of PLA from polyethylene terephthalate (PET). And PET recycling can be negatively affected by a PLA content of even 0.1% (Briassoulis et al., 2021b). Based on life cycle assessment, mechanical recycling of PLA has a lower environmental impact than chemical recycling or composting.

However, the properties of recycled PLA are undesirable, due to its tendency to undergo thermal degradation (De Andrade et al., 2016). After mechanical recycling, bio-based products exhibit decreased molecular weight, intrinsic viscosity, thermal stability and microhardness. PBS and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)/poly(butylene adipate-co-terephthalate) (PBAT) are not suited for mechanical recycling, due to its significant losses of mechanical properties and changes in their molecular structure. Although industrial mechanical recycling of bio-based cellulose acetate butyrate does not affect its mechanical properties, it does affect its molecular structure, and after recycling, the polymer emits an undesirable odour (Resch-Fauster et al., 2017).

Because mechanical recycling of bio-based materials causes a significant molecular degradation of polymers, various methods have been proposed to improve the quality of bio-based material recyclates (Beltrán et al., 2019a; Lamberti et al., 2020; Soroudi and Jakubowicz, 2013). One of them is to blend recycled materials with chain extenders to increase the molecular weight of bio-based polymers and to improve the quality of the recyclate (Niaounakis, 2013; Resch-Fauster et al., 2017; Zhao et al., 2007). For example, after three extrusion cycles of mechanical recycling of polyhydroxybutyrate (PHB), its mechanical properties had deteriorated, and its degree of crystallinity had increased. However, Fourier transform infrared spectroscopy and thermogravimetric analysis did not reveal any significant changes in the chemical structure of PHB. Therefore, to improve the PHB recyclability and to slow the degradation process, mixing PHB with virgin polymers or incorporation of stabilizers and/or chain extenders was proposed (Rivas et al., 2017). Similarly, blending mechanically recycled PLA with a chain extender and an organic peroxide improves its viscosity, thermal stability and microhardness. However, the effectiveness of this method and the quality of the recirculate depend on the degradation state of the recycled PLA material and the amount of additives (Beltrán et al., 2019b). To increase the molecular weight and intrinsic viscosity of PLA, the recycled polymer can also be mechanically blended with virgin polymer (Beltrán et al., 2017).

The literature shows that bio-based polymers can be mechanically recycled, but they must first be separated from the conventional plastic waste stream, where they can significantly reduce the recyclate quality. Therefore, it is necessary to improve the systems for separating bio-based materials from the rest of the waste stream.

Chemical recycling of bio-based material

In chemical recycling, polymers are chemically broken down into smaller molecules and separated from contaminants (monomers and/or oligomers). Chemical recycling allows for the reproduction of the same polymers, which may reduce the use of virgin materials for plastic production or new products. However, due to high energy inputs, this process is not common at industrial scale (Norrrahim et al., 2013; Rahimi and García, 2017). There are a few techniques for chemical recycling, such as hydrolysis (partial or complete), thermal degradation (pyrolysis), alcoholysis and dry-heat depolymerization (Niaounakis, 2019). The final product of chemical recycling depends on the material that is recycled and on the methods that are used. PHB hydrolysis produces mainly 3-hydroxybutyric acid and crotonic acid (Yu et al., 2005), and PLA hydrolysis produces LA. Hydrolysis of PLA proceeds via bulk erosion and requires high temperatures (170–200°C) and pressure (0.7–1.6 MPa). The time of PLA hydrolysis can be reduced by increasing the process temperature. For example, increasing the temperature from 180°C to 190°C can reduce the time of hydrolysis from 80 to 45 minutes (Cristina et al., 2016; Tsuji et al., 2008). However, if the temperature is raised too high (<250°C), LA will decompose (Tsuji et al., 2003). At lower temperatures, the rate of PLA hydrolysis can be increased by including NaOH in the process (Chauliac et al., 2020). Producing LA by hydrolysing PLA consumes less energy than producing LA from corn, but the chemical recycling process has a larger environmental footprint than mechanical recycling of PLA (Cristina et al., 2016; Majgaonkar et al., 2021).

Alcoholysis has been proposed as another method of chemically recycling bio-based products. During alcoholysis of PHB, alkyl esters can be obtained. For example, methanolysis of PHB using Brønsted–Lewis acidic ionic liquid as a catalyst produces methyl 3-hydroxybutyrate (Song et al., 2018). Alcoholysis of PLA produces alkyl lactates that correspond to the alcohol that is used, that is, methyl lactate (Whitelaw et al., 2011), ethyl lactate or butyl lactate (Hirao et al., 2010; Majgaonkar et al., 2021). Both methyl lactate and ethyl lactate can be used as green alternatives to conventional solvents (Aparicio and Alcalde, 2009; Pereira et al., 2011) in applications like membrane preparation (Rasool et al., 2020).

Another method of chemical recycling is thermal degradation (pyrolysis). During thermal degradation of polyhydroxyalkanoate (PHA) and PHBV, crotonic acid and 2-pentanoic acid can be produced (Ariffin et al., 2010). Mamat et al. (2014) found that the yield of crotonic acid was 63%, 30% higher than that of conventional synthesis from petrochemicals. The end products from thermal degradation of these polymers can be used as a feedstock for the copolymerization of poly(crotonic acid-*co*-acrylic acid), which can be employed as an enzyme-stabilizing agent and hydrogel for biosorbents, wastewater treatment and agriculture. Yang et al. (2014) investigated the microwave-assisted recycling of PHB with the use of green solvents (water, methanol and ethanol) under alkaline conditions, and obtained 3-hydroxybutanoic acid, 3-methoxybutanoic acid and crotonic acid. They found that, with this method, a higher rate can be achieved at a lower temperature than that used in pure thermal degradation of PHB. Generally, the end products of PHB recycling can be used as chain extenders, plasticizers and coatings, as well as for painting (Don and Liao, 2018). Pyrolysis has also been proposed as a novel method for recycling starch-based materials to produce sulfonated catalysts (SO_3H– catalyst) and other chemicals, for example, terephthalic acid, which may be used as a monomer in polyester synthesis (Samorì et al., 2021).

Organic recycling of bio-based materials with the use of most common biological treatment methods

Based on the hierarchy of waste management, organic recycling is a priority option, after material recovery (Briassoulis et al., 2021a). According to EU Packaging and Packaging Waste Directive 94/62/EC, organic recycling is defined as an ‘aerobic (composting) or anaerobic (biomethanization) treatment, under controlled conditions and using microorganisms’. Thus, because waste from bio-based products can be found in biowaste streams, recommended method of their treatment should be anaerobic digestion (AD) or composting. Nevertheless, not all bio-based products are biodegradable or compostable. It should be emphasized that even non-biodegradable bio-based products (e.g. soy-based polyurethanes) are also considered to be beneficial for reducing carbon emissions and environmental impact. However, biodegradable or compostable products are most desirable in the context of organic recycling. The term biodegradable indicates that 90% of the organic matter is converted to CO_2 within 6 months in composting conditions or a minimum of 50% of the organic matter is converted to biogas (based on the theoretical biogas production) within 2 months (EN 13432; ISO 18606). Compostable means that the material can be processed by industrial composting (EN 13432 (for packaging) or EN 14995 (for non-packaging plastic)).

Biodegradable bio-based products degrade in the presence of microorganisms into biomass and water and, depending on the conditions (anaerobic or aerobic), into biogas or carbon dioxide (Bonten, 2019; Kale et al., 2007b). In both processes, microorganisms (bacteria, archaea and fungi) are involved, and it is well known that thermophilic conditions improve degradation. For example, PLA is rapidly hydrolysed at temperatures at or above 55–62°C and at high relative humidity (>60%) (Karamanliogluet al., 2017b). For precise insight into organic recycling, the processes of biodegradation of bio-based polymers should be described.

Biodegradation of bio-based products

Biodegradation of biodegradable bio-based products is caused by the enzymatic activity of selected groups of microorganisms that create a biofilm on the product. As a result of this process, the polymers break down into smaller molecules and can be further metabolized by microorganisms. However, to allow them to fit into the active sites of enzymes, the polymer chains should be conformationally flexible. Moreover, microorganisms can attack only specific functional groups at specific sites of the polymers (Kale et al., 2007b).

Generally, in the process of biodegradation of biopolymers, four stages are involved: (i) biodeterioration, (ii) depolymerization, (iii) bioassimilation and (iv) mineralization. The first stage may result in oxidation processes or formation of a microbial biofilm on the surface or/and inside a polymeric material (Haider et al., 2019; Lucas et al., 2008).

Next, during depolymerization/fragmentation, the macromolecular chains of the polymers are broken down into oligomers and monomers. This step, depending on the polymer and the environment in which it is degrading, may occur as a result of abiotic or biotic reactions, or a combination of both. The abiotic process, which is the hydrolysis or photochemical scission of the backbone of the polymer, occurs as a result of mechanical, physical and chemical factors. Hydrolysis is the most common mechanism of polymer degradation and consists of the dissociation of the bonds of the polymer backbone in the presence of water. Hydrolysis depends on various external factors, such as temperature or pH, and may occur via bulk or surface erosion. In bulk erosion, the loss of strength and the structural properties of the polymer are due to diffusion of water into the amorphous parts of the biopolymer. This process occurs when the rate of diffusion of water exceeds the rate of the hydrolysis reaction. In surface erosion, the degradation of the biopolymer begins at the exterior surface and progresses towards the interior material. In this case, the rate of hydrolysis exceeds the rate of diffusion of water into the polymer matrix or catalyst, for example, enzymes cannot penetrate the polymer matrix (Burkersroda et al., 2002; Haider et al., 2019; Kabir et al., 2020).

Biotic reactions during depolymerization of polymers consist of catalysis by extracellular enzymes secreted by microorganisms, for example, α-amylases (which attack starches) or lysosome (which attacks chitin). These enzymes break down the polymer chains, producing products that can easily cross through microbial membranes and be assimilated by microorganisms (Laycock et al., 2017). Other examples of common enzymes that mediate the degradation of polymers, especially with those with hydrolysable bonds (e.g. esters, amides and glycosidic bonds), are hydrolases, depolymerases and peroxidases (Gan and Zhang, 2019; Meereboer et al., 2020). For example, PLA can be degraded by lipase esterase and alcalase (Rittié and Perbal, 2008), whereas starch-based polymers can be broken down by, for example, α-amylases, β-amylases, glucoamylases and α-glucosidases. During depolymerization, the polymers lose their properties, particularly their molar mass and strength, and the contact surface between the microorganisms and the polymers increases (Chandra and Rustgi, 1998; Kliem et al., 2020).

Next, bioassimilation, in which the oligomers and monomers formed in the previous stage are transported to the cells of microorganisms and then assimilated, is followed by mineralization. The end products of biodegradation are biomass and water, and either CO_2 in aerobic conditions or CH_4 and CO_2 in anaerobic conditions. CO_2 and CH_4 are formed as a result of the conversion of polymer-derived carbon and the incorporation of polymer-derived carbon into microbial biomass.

During complete biodegradation, the original substrate should be completely converted into gaseous products and salts (Agarwal, 2020; Luckachan and Pillai, 2011; Swift, 1995). However, there are many factors that affect the biodegradation of bio-based products. First, there are factors that are intrinsic to the polymers themselves, that is, their origin and chemical/physical properties (e.g. chemical structure, molecular weight, surface area, crystallinity, hydrophobicity/hydrophilicity, copolymer composition) (Kabir et al., 2020; Tokiwa et al., 2009). Easier-to-biodegrade polymers have lower crystallinity, a shorter chain and less complex formulas (Emadian et al., 2017). For example, Kolstad et al. (2012) found that amorphous PLA is more susceptible to degradation under anaerobic conditions than semi-crystalline PLA. Second, there are environmental factors that affect the biodegradation of bio-based products. The most important are pH, temperature, moisture, sunlight, oxygen content and the presence of competent microbial degraders. Numerous microorganisms (bacteria, streptomycetes and fungi) that can hydrolyse some bio-based products have been isolated from different terrestrial and aquatic environments. For example, several bacteria and fungi that are found in compost can produce hydrolases, which enable them to degrade PBS, polybutylene succinate adipate (PBSA), PCL, PHB and PLA (Urbanek et al., 2020). Similarly, Actinomycetes in compost (Micromonospora, Nocardia and Streptomycetes) can decompose TPS.

Aerobic conditions/composting

Biodegradable bio-based products can be composted in both home and industrial conditions. Biodegradability of some bio-based materials under aerobic conditions is shown in Table 1. In aerobic degradation/composting, biological decomposition of organic matter occurs, which is performed by microorganisms, and CO_2, H_2O and composts are generated. Worth noting is the fact that some bio-based products with a high melting point and a high glass transition temperature (e.g. PLA or PHB) require elevated temperatures (>50°C) for hydrolysis and degradation to begin, which is not achieved during home composting (Meereboer et al., 2020; Urbanek et al., 2020). Although TPS, PCL and PHB may degrade in home composting, the degree of degradation is lower than that in industrial composting (Narancic et al., 2018).

For example, the degree of sample disintegration of starch-based products in home-composting conditions was 6.7–14.1% (Adamcová et al., 2019), but PLA, PBS and polyhydroxyoctanoate did not degrade in such conditions (Narancic et al., 2018). After 12 weeks (84 days) in real composting conditions, commercial starch and starch/PCL-based materials were about 70% degraded, and fractures, breaches, cavities and holes had appeared in their surface (Adamcová et al., 2018).

During composting (58 ± 1°C) of PHBV and PBSA foils, both bio-based materials broke into small pieces after 40 days. These foils were 100% mineralized after about 80 days of composting (Salomez et al., 2019). Films based on gelatin, chitosan and sodium caseinate completely disintegrated during 5 days of composting at 58 ± 2°C (Bonilla and Sobral, 2020). However, 20 days of thermophilic phase was not sufficient to ensure PLA and starch/PBAT degradation (Ruggero et al., 2021). This may have been caused challenges with composting bio-based materials in industrial conditions, where the thermophilic phase lasts 14–21 days. The suggested solution was to recirculate the bio-based material macro-residues after refining treatment.

It should be kept in mind that, although the polymer in bio-based materials is biodegradable, the additives used in producing the material are often not biodegradable. As a result, these additives may accumulate in the final compost (Sintim et al., 2019).

For example, an antimicrobial gluten-based material that was improved with cinnamaldehyde addition showed good biodegradability under composting conditions and the final compost did not have any ecotoxic effect on tomato plants. However, the presence of residual cinnamaldehyde prevented organic recycling of the material (Balaguer et al., 2015).

After composting of starch-based bags at 65 ± 2°C for 21 days, the material was not distinguishable in the final compost. Moreover, the compost did not show any ecotoxic effect during a phytotoxicity test and the results were even better than those of the control (cellulose). However, after composting PLA-based water bottles in these conditions, the material was found in the compost in the form of tiny crystallized pieces (<2 mm). PLA degraded to water-soluble LA, which reduced the pH of the compost and had negative effects on the seed germination and germination indexes. Therefore, the degradation of PLA may change the acidity of environments (Bandini et al., 2020).

The effectiveness of composting of bio-based products depends on environmental factors, such as the temperature or pH. For example, under mesophilic conditions (25°C and 37°C), PLA fabric and films did not degrade even after 210 days of bench-scale composting and only 10% of the theoretical amount of CO_2 was produced. Under thermophilic conditions (60°C), in contrast, the mineralization degree was 90% and the fastest CO_2

Table 1. Biodegradability of bio-based materials under aerobic conditions.

Materials	Conditions	Inoculum	Time (days)	Biodegradability (%)	Literature
Home composting					
Starch-based products	Average temperature: 36.9°C	Synthetic waste	365	6.7–14.1	Adamcová et al. (2019)
PCL	ISO 14855 at 28°C	Mature compost	88	<100*	Narancic et al. (2018)
TPS			90	<100*	
PLA films	Initial water content 52%	Sheep manure and sawdust (5:1 (w/w))	330	Low degree	Rudnik and Briassoulis (2011)
Bench scale/laboratory scale					
PBS/PCL films	Not given	Compost culture solution	60	32.67**	Huang et al. (2016)
Starch/glycerol foam	ISO 14855 with adaptation (room temperature)	Stabilized and matured organic compost	47	34	Taiatele et al. (2020)
PBAT/starch film				38	
PLA films	Real composting conditions	Peat, wood chips and biowaste	60	99	Itävaara et al. (2002)
PLA non-woven fabrics				48 and 73	
Starch-based products	58°C	Synthetic waste	84	93.5–98.7	Adamcová et al. (2019)
PHB pellet	ISO 14855	Mature green compost	70–90	100	Salomez et al. (2019)
PBS pellet					
Gelatin-based films	ISO 20200	Synthetic waste	5	100	Bonilla and Sobral (2020)
Chitosan-based film					
Sodium caseinate-based films					
Gluten-based material improved with cinnamaldehyde	ISO 20200	2- to 4-month-old compost from MSW treatment plant	4	100	Balaguer et al. (2015)
PHB films	ISO 20200	Synthetic solid waste imbued with soil sourced from an active dumpsite	40	100	Adorna et al. (2021)
PHB/cellulose/calcium carbonate films			30–50		
PLA	ASTM D5338-15	Food waste compost	98 ± 5	90	Kalita et al. (2021a)
		Water hyacinth-based compost	100 ± 5		
		Paper mill sludge	110 ± 5		
PLA-based strips	ASTM D5338	Compost prepared from paper mill sludge, dry leaves, cow dung and saw dust	140 days	90	Kalita et al. (2020)
Full-scale composting					
PBAT-based films		Dairy manure solids, broiler litter, yard wastes, animal bedding and fish carcasses	126	>99***	Sintim et al. (2019)
PLA/PHA-based films				97***	
Starch-based products		3-month-old mature compost	84	70***	Adamcová et al. (2018)
Starch/PCL products					

*Expressed as a percentage of biodegradation of cellulose.

**Weight loss.

***Macroscopic degradation/visual assessment.

PBAT, poly(butylene adipate-co-terephthalate); PCL, polycaprolactone; PHA, polyhydroxyalkanoate; PHB, polyhydroxybutyrate; PBS, polybutylene succinate; PLA, polylactic acid; TPS, thermoplastic starch.

production took place (Itävaara et al., 2002) Ruggero et al. (2020) found that, during composting of MaterBi®, the starch and additives were intensively degraded in the initial phase of the process, as shown by the decrease in their weight and activation energy. However, another component of the material, PBAT, which is a synthetic aromatic-aliphatic co-polyester with a more complex molecular structure, did not degrade them. However, it did degrade in the next phase of composting, and its degradation rate was not reduced by the decrease in temperature and humidity at the start of the maturation phase. Hosni et al. (2019) composted PCL, PHB, PLA and PBS at 25°C, 37°C and 50°C. At the highest temperature, all of the polymers degraded, and PCL, which completely degraded after 91 days, had the fastest rate of degradation. However, only PCL and PHB degraded under all temperature conditions, and PLA and PBS did not significantly degrade at 25°C and 37°C.

The share of bio-based products is an important factor during composting. For an efficient process, the share of PLA should be less than 30% (w/w) because larger amounts can decrease the pH, due to the disintegration of PLA to LA, and suppress microbial growth (Ghorpade et al., 2001). Addition of 50% (v/v) PLA (as PLA-based food containers) caused the ratio to decrease from ca. 6.5 to 3.5 pH and affected fungal diversity and community structure in compost (Karamanlioglu et al., 2017a).

The compostability of bio-based products depends on their composition and thickness (Soni et al., 2009). The thickness of certified compostable PLA and PBS should not exceed 3000 μm and 120 μm, respectively (Reichert et al., 2020). The biodegradation of bio-based products may be affected by changes in their composition. For example, in composting conditions, a composite of PBS and PCL degraded faster than pure PBS and PCL (Huang et al., 2016), whereas pure PHB and PLA disintegrated faster than a blend of these substances and PBAT (Tabasi and Ajji, 2015). Cadar et al. (2012) reported that, under controlled composting conditions, the biodegradation degree of PLA copolymer increased as the amount of LA in the material was increased. Those authors also reported that the degrees of biodegradation of commercially available and synthesized PLA were about 70% after 110 days of composting with 2-month-old mature compost from organic domestic waste. Both PBSA copolymer and PBS homopolymer biodegraded in composting conditions (58 ± 2°C), as shown by decreases in their molar mass and increases in their crystallinity, but PBSA was more susceptible to biodegradation than PBS (Puchalski et al., 2018). Moreover, pure PBS required 75 days to disintegrate under composting conditions, whereas composites of PBS with cellulose disintegrated 10 days faster (Platnieks et al., 2020). Kalita et al. (2021b) composted neat PLA granules and PLA biocomposites (PLA/chitosan, PLA/cellulose nanocrystal and PLA/gum arabic) with food waste as compost. The percent biodegradation of the neat polymer was 94.2% during 136 days of measurement, whereas that of the composites ranged from 80.5% to 97% during 120–145 days. They also found that *Bacillus flexus* was involved in biodegradation of PLA-based biocomposites.

Generally, the amorphous part of the polymers degrades faster than the crystalline part. For example, Kale et al. (2007a) composted PLA bottles and food containers made of 96% and 94% L-lactide, respectively, for 30 days. The PLA bottles had a lower degradation rate than the containers due to their higher degree of crystallinity. The authors observed first-order degradation kinetics and linear degradation trends for both PLA materials. Similarly, Sedničková et al. (2018) concluded that amorphous polymers are more susceptible to biodegradation than crystalline ones.

Sedničková et al. (2018) also found that, in composting conditions, PHB degraded faster than PLA, and minor changes in the composition of the material (e.g. addition of plasticizer) affected the biodegradation rate and time of disintegration. Thus, neat polymers have higher percentages and rates of biodegradation than commercially available ones under both mesophilic and thermophilic conditions (Pattanasuttichonlakul et al., 2018). For example, the presence of nano-titanium dioxide (TiO_2) additives, commonly used as a white pigment in plastic cups and plates, lowers the values of biodegradation of PLA and PBS during composting at 58 ± 2°C and induces lag time (Nobile et al., 2015). Similarly, the addition of chain extenders has an inhibitory effect during composting of PHB and PLA/PBAT, probably due to an increase in the molar mass of the polymer and a slight increase in crystallinity. The use of nanoparticles for bio-based materials production also affects their biodegradation. For example, montmorillonite may promote the hydrolysis of material by facilitating water penetration, but it may also inhibit the diffusion of oligomers for the microorganisms (Freitas et al., 2017). However, Balaguer et al. (2016) found that nanoparticles did not limit the compostability of PLA and that biodegradation was higher after they were added, although these differences were not statistically significant ($p > 0.05$). Finally, chemical modification of TPS and changes in its carbonyl content affect the rate and percentage of TPS biodegradation. During laboratory-scale composting (58 ± 2°C), TPS degraded faster than modified TPS, and its percentage of biodegradation after 56 days of measurement was about 73%, whereas that of modified TPS ranged from about 6% to 66%, depending on its carbonyl content (Du et al., 2008).

Anaerobic conditions/anaerobic digestion

AD is a promising option for treating bio-based products and producing biogas, which is used as a renewable energy source. Moreover, it is noted that AD of some bio-based materials (cellulose, starch, starch/PCL, PLA, PBAT and PHA) has a lower energy footprint than that of home and industrial composting and incineration (Hermann et al., 2011). In addition, some bio-based materials may be more susceptible to AD than to composting; biodegradability under anaerobic conditions is shown in Table 2. For example, as reported by Siracusa et al. (2008), the degradation of PHA occurs much faster under anaerobic conditions than aerobic ones.

However, AD of bio-based products alone may not be effective for a variety of reasons. Inappropriate C/N ratios can be a

Table 2. Biodegradability of bio-based materials under anaerobic conditions.

Material	Temperature (°C)	Time (days)	Biodegradability (%)	Literature
Mesophilic conditions				
Biodegradable coffee capsules	38	100	12–24	Cazaudehore et al. (2021)
PBAT	37 ± 2	126	2.2	Svoboda et al. (2019)
PHB	37	9	90	Yagi et al. (2014)
PCL		277	3–22	
PLA		277	29–49	
PBS		–	0	
Thermophilic conditions				
PLA powder	55	60	80	Yagi et al. (2012)
PLA film		40	75–84	
PHB	55	14	90	Yagi et al. (2013)
PCL		50	80	
PLA		75	75	
PBS		–	0	
Pectin–cellulose-based material	55 ± 1	30	90–94	Bátori et al. (2017)
PBAT	55 ± 2	126	8.3	Svoboda et al. (2019)
PLA	55	31	40.41	Camacho-Muñoz et al. (2020)
TPS			92.11	
TPS/PLA			62.48	
Biodegradable coffee capsules	58	100	47–69	Cazaudehore et al. (2021)
PLA-based foils	55	21	9.0–12.7	Shrestha et al. (2020)
PLA-based foils		35	16.3–18.3	
PLA-based coffee capsules		21	<1	
PLA-based coffee capsules		35	<3	
Plasticized starch	55 ± 1	28	97	Borowski et al. (2020)

PBAT, poly(butylene adipate-co-terephthalate); PBS, polybutylene succinate; PCL, polycaprolactone; PHB, polyhydroxybutyrate; PLA, polylactic acid; TPS, thermoplastic starch.

problem because bio-based materials are rich in carbohydrates and contain little or no nitrogen. Moreover, some bio-based products (e.g. PCL) are mainly degraded by fungi, which are present in compost, but not in AD conditions (Sankhla et al., 2020). Furthermore, it is not always possible to completely degrade bio-based products at the hydraulic retention times (HRTs) commonly used in biogas plants, that is, 20–30 days (Bátori et al., 2018). For example, cellulose film and PLA coffee capsules did not completely degrade and disintegrate during thermophilic AD (55°C) that lasted for a typical operation time for an industrial biogas plant (21 days) or the maximum time of operation for AD of bioplastics (35 days) (Shrestha et al., 2020).

One of the most important of the factors that influence AD efficiency is the process temperature. The process is most often carried out in mesophilic (35–42°C) or thermophilic (45–60°C) conditions (Weiland, 2010), and sometimes in psychrophilic conditions (<20°C) (Safley and Westerman, 1992). In general, the available evidence indicates that the process is more efficient at higher temperatures. For example, Cazaudehore et al. (2021) found that, after 100 days, the methane potential of commercially available coffee capsules made of biodegradable plastics was much higher under thermophilic conditions (257–294 NL CH_4/kg VS) than under mesophilic ones (67–127 NL CH_4/kg VS). Moreover, some polymers require high temperatures for starting hydrolysis, which means that, under mesophilic conditions, they are degraded to a very small extent or not at all. For example, there is almost no biodegradation of PBAT under anaerobic mesophilic (37°C) conditions. Based on biogas production, biodegradation of PBAT after 126 days of measurement under mesophilic and thermophilic conditions was 2.2% and 8.3%, respectively. In addition, the higher temperatures in thermophilic conditions significantly changed the crystallization behaviour of PBAT (Svoboda et al., 2019). Mesophilic biodegradation of a commercially available PLA-based material used in disposable cups only achieved maximal biogas production after 280 days (558–570 L/kg OM), which is not an acceptable time on a technical scale. Even though thermophilic biodegradation of this material reduced the lag phase from 40 to 10 days and enabled maximal biogas production (831–849 L/(kg OM)) to be achieved much faster, the process still lasts almost 40 days, which is much longer than the HRTs used in industrial AD (Bernat et al., 2021). This is consistent with other results in the literature, which indicate that the biodegradation time of PLA in AD is very long, with a low level of process efficiency. For example, after 1 year of mesophilic AD, starch- and PLA-based foils started to degrade; however, only minor structural damage was observed (Zaborowska et al., 2021a). The lag phases of biogas production lasted 60 and 70 days for PLA and starch-based material, respectively. After the lag phase, biogas production started to increase, although very slowly, and it reached only 25.2 and 30.4 L/kg VS for PLA and the starch-based materials, respectively. Although these materials began to lose their mechanical properties faster under thermophilic conditions, only a small amount of methane was produced from the foils by day 50 of thermophilic AD (55°C). In fact, even after 100 days of the process, the materials had only fragmented and were still visible. This indicates that digestate may become contaminated with fragments of these materials (Zaborowska et al., 2021b). Finally, Kolstad et al. (2012) concluded that PLA degradation at low temperature (ca. 20°C) would last many decades and produce very little biogas.

The type of bio-based material is another factor that has a substantial influence on AD efficiency. Yagi et al. (2013, 2014) found that PBS did not biodegrade in AD (irrespective of the temperature) and that the biodegradability rate of bio-based polymers in thermophilic and mesophilic conditions decreased in the following the order: PHB > PCL > PLA and PHB >> PLA > PCL, respectively. Cucina et al. (2021) ranked the biodegradability of some other bio-based materials in this order: PHAs > starch based ⩾ PLA. Yagi et al. (2013, 2014) reported that the temperature did not strongly influence the degradation of PHB, which was 90% degraded during 14 and 9 days under mesophilic and thermophilic conditions, respectively, which means that PHB can be degraded with commonly used HRTs. Bátori et al. (2017) found that a polymer obtained from orange pectin–cellulose waste that also achieves a high degree of biodegradation (90%) within 15 days and has an average methane production of 350 NL/kg COD. It should be emphasized that pectin–cellulose waste is easily biodegradable, hence the short degradation time. Finally, Camacho-Muñoz et al. (2020) reported that a blend of PLA and TPS did not exhibit a lag phase and achieved 65.48% biodegradability in slurry thermophilic AD. In contrast, pure PLA and TPS achieved 40.41% and 92.11% biodegradability, respectively.

Some studies indicate that AD of bio-based products does not occur, or takes place to a limited extent; therefore, to obtain more complete degradation and higher biogas yield, pre-treatment of these products has been proposed. For example, Calabro' et al. (2020) found that only some methods of pre-treating compostable bags made of MaterBi® (Novamont, Italy), biodegradable wine bottle corks and cellulosic plates significantly increased methane production and decreased mass loss. However, the authors showed that mechanical pre-treatment and the type of inoculum (digested sludge from mesophilic or thermophilic) did not affect methane production and mass loss during AD of bio-based materials. Alkaline pre-treatment of PHB and PLA at elevated temperature resulted in decrease in lag phase time and increase in methane production compared to untreated material (Benn and Zitomer, 2018; Venkiteshwaran et al., 2019). PHB pre-treatment (55°C, pH 12) increased methane production from 86% and 91% (Venkiteshwaran et al., 2019). Zaborowska et al. (2021b) found that alkaline pre-treatment of starch and PLA-based foils resulted in increasing in methane production; however, the values were low and constituted only about 8–10% of the theoretical methane production. However, pre-treatment of foils shortened the lag phase of methane production but most of all increased the surface damage and weakened the mechanical properties. Despite determination of mechanical properties is not a common practice, the authors emphasized that it can be considered as valuable indicator of polymers' biodegradability (Zaborowska et al., 2021b). Correspondingly, Hobbs et al. (2019) indicated that alkaline pre-treatment of PLA increased methane production from 756 to 1021 mL of CH_4 in comparison to untreated material. Moreover, the PLA without treatment resulted in only 54% weight reduction. Authors showed that pre-treated PLA may be codigested with food waste in digestion systems. On the contrary, acidic and alkaline chemical pre-treatments at ambient temperature did not affect AD of starch- and PLA-based materials (Battista et al., 2021). Moreover, pre-treatment of PLA at 70°C for 1 hour with no pH control resulted in even less biomethane production than from untreated PLA (Endres and Siebert-Raths, 2011).

Conclusion

The continual development of bio-based products has led to several challenges in waste management. To recycle waste from these products, effective technologies must be found.

Chemical or mechanical recycling is not only a costly process, but also require a thorough separation of bio-based products from the waste stream. It is crucial to sort out bio-based materials from conventional plastics without affecting the recycling of the latter. Therefore, there is a need to develop sophisticated systems to separate waste from bio-based products from mixed waste or plastic waste.

The organic recycling of bio-based products seems to be more sustainable and economically friendly, especially when bio-based products are collected together with biowaste. However, the characteristics of the bio-based products determine the choice of the method of organic recycling, that is, AD or composting. Some bio-based products that biodegrade under composting conditions do not biodegrade under anaerobic ones. Most often, these products are only partially biodegraded under anaerobic conditions, and the time of degradation is very long, which is not acceptable at technical scale. Moreover, because bio-based materials do not produce large quantities of biogas, and they only disintegrate, they may contaminate the digestate. As the choice of recycling method depends on the type of bio-based product, it is highly desirable to label these products to indicate which method of recycling is preferable for them.

Declaration of conflicting interests

The authors declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

Funding

The authors received no financial support for the research, authorship and/or publication of this article.

ORCID iD

Magdalena Zaborowska https://orcid.org/0000-0003-1132-9891

References

Abraham A, Park H, Choi O, et al. (2021) Anaerobic co-digestion of bioplastics as a sustainable mode of waste management with improved energy production: A review. *Bioresource Technology* 322: 124537.

Adamcová D, Radziemska M, Zloch J, et al. (2018) SEM analysis and degradation behavior of conventional and bio-based plastics during composting. *Acta Universitatis Agriculturae et Silviculturae Mendelianae Brunensis* 66: 349–356.

Adamcová D, Zloch J, Brtnický M, et al. (2019) Biodegradation/disintegration of selected range of polymers: Impact on the compost quality. *Journal of Polymers and the Environment* 27: 892–899.

Adorna JA, Ventura RLG, Dang VD, et al. (2021) Biodegradable polyhydroxybutyrate/cellulose/calcium carbonate bioplastic composites prepared by heat-assisted solution casting method. *Journal of Applied Polymer Science* 2021: 51645.

Agarwal S (2020) Biodegradable polymers: Present opportunities and challenges in providing a microplastic-free environment. *Macromolecular Chemistry and Physics* 221: 2000017.

Aparicio S and Alcalde R (2009) The green solvent ethyl lactate: An experimental and theoretical characterization. *Green Chemistry* 11: 65–78.

Ariffin H, Nishida H, Hassan MA, et al. (2010) Chemical recycling of polyhydroxyalkanoates as a method towards sustainable development. *Biotechnology Journal* 5: 484–492.

Balaguer MP, Aliaga C, Fito C, et al. (2016) Compostability assessment of nano-reinforced poly (lactic acid) films. *Waste Management* 48: 143–155.

Balaguer MP, Villanova J, Cesar G, et al. (2015) Compostable properties of antimicrobial bioplastics based on cinnamaldehyde cross-linked gliadins. *Chemical Engineering Journal* 262: 447–455.

Bandini F, Frache A, Ferrarini A, et al. (2020) Fate of biodegradable polymers under industrial conditions for anaerobic digestion and aerobic composting of food waste. *Journal of Polymers and the Environment* 28: 2539–2550.

Bátori V, Åkesson D, Zamani A, et al. (2018) Anaerobic degradation of bioplastics: A review. *Waste Management* 80: 406–413.

Bátori V, Jabbari M, Åkesson D, et al. (2017) Production of pectin-cellulose biofilms: A new approach for citrus waste recycling. *International Journal of Polymer Science* 2017: 9732329.

Battista F, Frison N and Bolzonella D (2021) Can bioplastics be treated in conventional anaerobic digesters for food waste treatment? *Environmental Technology & Innovation* 22: 101393.

Beltrán FR, Barrio I, Lorenzo V, et al. (2017) Mechanical recycling of polylactide: Improvement of the properties of the recycled material. In: *5th international conference on sustainable solid waste management*, Athens.

Beltrán FR, Barrio I, Lorenzo V, et al. (2019a) Valorization of poly (lactic acid) wastes via mechanical recycling: Improvement of the properties of the recycled polymer. *Waste Management & Research* 37: 135–141.

Beltrán FR, Infante C, de la Orden MU, et al. (2019b) Mechanical recycling of poly (lactic acid): Evaluation of a chain extender and a peroxide as additives for upgrading the recycled plastic. *Journal of Cleaner Production* 219: 46–56.

Benn N and Zitomer D (2018) Pretreatment and anaerobic co-digestion of selected PHB and PLA bioplastics. *Frontiers in Environmental Science* 5: 93.

Bernat K, Kulikowska D, Wojnowska-Baryła I, et al. (2021) Thermophilic and mesophilic biogas production from PLA-based materials: Possibilities and limitations. *Waste Management* 119: 295–305.

Biron M (2020) Environmental and engineering data to support eco-design for plastics. In: Biron M (ed.) *A Practical Guide to Plastics Sustainability*. Amsterdam, The Netherlands: Elsevier, pp.209–307.

Bonilla J and Sobral PJ (2020) Disintegrability under composting conditions of films based on gelatin, chitosan and/or sodium caseinate containing boldo-of-Chile leafs extract. *International Journal of Biological Macromolecules* 151: 178–185.

Bonten C (eds) *Plastics Technology: Introduction and Fundamentals*. München, Germany: Carl Hanser Verlag GmbH & Co. KG, 2019.

Borowski G, Klepka T, Pawłowska M, et al. (2020) Effect of flax fibers addition on the mechanical properties and biodegradability of biocomposites based on thermoplastic starch. *Archives of Environmental Protection* 46: 74–82.

Briassoulis D, Pikasi A and Hiskakis M (2021a) Organic recycling of post-consumer/industrial bio-based plastics through industrial aerobic composting and anaerobic digestion-techno-economic sustainability criteria and indicators. *Polymer Degradation and Stability* 190: 109642.

Briassoulis D, Pikasi A and Hiskakis M (2021b) Recirculation potential of post-consumer/industrial bio-based plastics through mechanical recycling-Techno-economic sustainability criteria and indicators. *Polymer Degradation and Stability* 183: 109217.

Burkersroda F, Schedl L and Göpferich A (2002) Why degradable polymers undergo surface erosion or bulk erosion. *Biomaterials* 23: 4221–4231.

Cadar O, Paul M, Roman C, et al. (2012) Biodegradation behaviour of poly (lactic acid) and (lactic acid-ethylene glycol-malonic or succinic acid) copolymers under controlled composting conditions in a laboratory test system. *Polymer Degradation and Stability* 97: 354–357.

Calabro' PS, Folino A, Fazzino F, et al. (2020) Preliminary evaluation of the anaerobic biodegradability of three biobased materials used for the production of disposable plastics. *Journal of Hazardous Materials* 390: 121653.

Camacho-Muñoz R, Villada-Castillo HS and Solanilla-Duque JF (2020) Anaerobic biodegradation under slurry thermophilic conditions of poly (lactic acid)/starch blend compatibilized by maleic anhydride. *International Journal of Biological Macromolecules* 163: 1859–1865.

Cazaudehore G, Monlau F, Gassie C, et al. (2021) Methane production and active microbial communities during anaerobic digestion of three commercial biodegradable coffee capsules under mesophilic and thermophilic conditions. *Science of the Total Environment* 784: 146972.

Chandra R and Rustgi R (1998) Biodegradable polymers. *Progress in Polymer Science* 23: 1273–1335.

Chauliac D, Pullammanappallil PC, Ingram LO, et al. (2020) A combined thermochemical and microbial process for recycling polylactic acid polymer to optically pure l-lactic acid for reuse. *Journal of Polymers and the Environment* 28: 1503–1512.

Cornell DD (2007) Biopolymers in the existing postconsumer plastics recycling stream. *Journal of Polymers and the Environment* 15: 295–299.

Cristina AM, Rosaria A, Sara F, et al. (2016) PLA recycling by hydrolysis at high temperature. In: *VIII international conference on times of polymers and composites: From aerospace to nanotechnology* (eds A Damore, D Acierno and L Grassia), Melville, NY, May 2016, vol.1736. AIP Publishing LLC.

Cucina M, de Nisi P, Tambone F, et al. (2021) The role of waste management in reducing bioplastics' leakage into the environment: A review. *Bioresource Technology* 337: 125459.

De Andrade MFC, Souza PM, Cavalett O, et al. (2016) Life cycle assessment of poly (lactic acid) (PLA): Comparison between chemical recycling, mechanical recycling and composting. *Journal of Polymers and the Environment* 24: 372–384.

Don TM and Liao KH (2018) Studies on the alcoholysis of poly (3-hydroxybutyrate) and the synthesis of PHB-b-PLA block copolymer for the preparation of PLA/PHB-b-PLA blends. *Journal of Polymer Research* 25: 1–10.

Du YL, Cao Y, Lu F, et al. (2008) Biodegradation behaviors of thermoplastic starch (TPS) and thermoplastic dialdehyde starch (TPDAS) under controlled composting conditions. *Polymer Testing* 27: 924–930.

Emadian SM, Onay TT and Demirel B (2017) Biodegradation of bioplastics in natural environments. *Waste Management* 59: 526–536.

EN 13432 Packaging. Requirements for packaging recoverable through composting and biodegradation. Test scheme and evaluation criteria for the final acceptance of packaging. Available at: https://www.en-standard.eu/bs-en-13432-2000-packaging.-requirements-for-packaging-recoverable-through-composting-and-biodegradation.-test-scheme-and-evaluation-criteria-for-the-final-acceptance-of-packaging/ (accesed 14 June 2022).

EN 14995 Plastics - Evaluation of compostability - Test scheme and specifications. Available at: https://www.en-standard.eu/csn-en-14995-plastics-evaluation-of-compostability-test-scheme-and-specifications/ (accesed 14 June 2022).

EN 16575 Bio-based products – Vocabulary. Available at: https://www.en-standard.eu/bs-en-16575-2014-bio-based-products-vocabulary/ (accessed 14 June 2022).

EN 16640 Bio-based products – Bio-based carbon content – Determination of the bio-based carbon content using the radiocarbon method. Available at: https://www.en-standard.eu/csn-en-16640-bio-based-products-bio-based-carbon-content-determination-of-the-bio-based-carbon-content-using-the-radiocarbon-method/ (accessed 14 June 2022).

EN 16785 Bio-based products – Bio-based content – Part 2: Determination of the bio-based content using the material balance method.

Endres HJ and Siebert-Raths A (2011) Engineering Biopolymers: Markets, Manufacturing, Properties and Applications. Germany: Carl Hanser Verlag GmbH & Co. KG.

Freitas ALPDL, Tonini FLR, Calvão PS, et al. (2017) Effect of montmorillonite and chain extender on rheological, morphological and biodegradation behavior of PLA/PBAT blends. *Polymer Testing* 62: 189–195.

Gan Z and Zhang H (2019) PMBD: A comprehensive plastics microbial biodegradation database. *Database* 2019: baz119.

Ghaffar T, Irshad M, Anwar Z, et al. (2014) Recent trends in lactic acid biotechnology: A brief review on production to purification. *Journal of Radiation Research and Applied Sciences* 7: 222–229.

Ghorpade VM, Gennadios A and Hanna MA (2001) Laboratory composting of extruded poly (lactic acid) sheets. *Bioresource Technology* 76: 57–61.

Gorgieva S and Trček J (2019) Bacterial cellulose: Production, modification and perspectives in biomedical applications *Nanomaterials* 9: 1352.

Gruber PR, Drumright RE and Henton DE (2000) Polylactic acid technology. *Advanced Materials* 12: 1841–1846.

Haider TP, Völker C, Kramm J, et al. (2019) Plastics of the future? The impact of biodegradable polymers on the environment and on society. *Angewandte Chemie International Edition* 58: 50–62.

Hermann BG, Debeer L, De Wilde B, et al. (2011) To compost or not to compost: Carbon and energy footprints of biodegradable materials' waste treatment. *Polymer Degradation and Stability* 96: 1159–1171.

Hirao K, Nakatsuchi Y and Ohara H (2010) Alcoholysis of poly (l-lactic acid) under microwave irradiation. *Polymer Degradation and Stability* 95: 925–928.

Hobbs SR, Parameswaran P, Astmann B, et al. (2019) Anaerobic codigestion of food waste and polylactic acid: Effect of pretreatment on methane yield and solid reduction. *Advances in Materials Science and Engineering* 2019: 4715904.

Hosni AAS, Pittman JK and Robson GD (2019) Microbial degradation of four biodegradable polymers in soil and compost demonstrating polycaprolactone as an ideal compostable plastic. *Waste Management* 97: 105–114.

Houfani AA, Anders N, Spiess AC, et al. (2020) Insights from enzymatic degradation of cellulose and hemicellulose to fermentable sugars–a review. *Biomass and Bioenergy* 134: 105481.

Huang J, Cui C, Yan G, et al. (2016) A study on degradation of composite material PBS/PCL. *Polymers and Polymer Composites* 24: 143–148.

Ioannidou SM, Pateraki C, Ladakis D, et al. (2020) Sustainable production of bio-based chemicals and polymers via integrated biomass refining and bioprocessing in a circular bioeconomy context. *Bioresource Technology* 307: 123093.

ISO 16620 Plastics – Biobased content – Part 1: General principles. Available at: https://www.iso.org/standard/63766.html (accesed 14 June 2022).

ISO 18606 Packaging and the environment - Organic recycling. Available at: https://www.iso.org/standard/55874.html (accessed 14 June 2022).

Itävaara M, Karjomaa S and Selin JF (2002) Biodegradation of polylactide in aerobic and anaerobic thermophilic conditions. *Chemosphere* 46: 879–885.

John RP, Nampoothiri KM and Pandey A (2006) Simultaneous saccharification and fermentation of cassava bagasse for L-(+)-lactic acid production using Lactobacilli. *Applied Biochemistry and Biotechnology* 134: 263–272.

Kabir E, Kaur R, Lee J, et al. (2020) Prospects of biopolymer technology as an alternative option for non-degradable plastics and sustainable management of plastic wastes. *Journal of Cleaner Production* 258: 120536.

Kale G, Auras R and Singh SP (2007a) Comparison of the degradability of poly (lactide) packages in composting and ambient exposure conditions. *Packaging Technology and Science* 20: 49–70.

Kale G, Kijchavengkul T, Auras R, et al. (2007b) Compostability of bioplastic packaging materials: An overview. *Macromolecular Bioscience* 7: 255–277.

Kalita NK, Bhasney SM, Kalamdhad A, et al. (2020) Biodegradable kinetics and behavior of bio-based polyblends under simulated aerobic composting conditions. *Journal of Environmental Management* 261: 110211.

Kalita NK, Hazarika D, Kalamdhad A, et al. (2021a) Biodegradation of biopolymeric composites and blends under different environmental conditions: Approach towards end-of-life panacea for crop sustainability. *Bioresource Technology Reports* 15: 100705.

Kalita NK, Sarmah A, Bhasney SM, et al. (2021b) Demonstrating an ideal compostable plastic using biodegradability kinetics of poly (lactic acid) (PLA) based green biocomposite films under aerobic composting conditions. *Environmental Challenges* 3: 100030.

Karamanlioglu M, Preziosi R and Robson GD (2017a) The compostable plastic poly (lactic) acid causes a temporal shift in fungal communities in maturing compost. *Compost Science & Utilization* 25: 211–219.

Karamanlioglu M, Preziosi R and Robson GD (2017b) Abiotic and biotic environmental degradation of the bioplastic polymer poly (lactic acid): A review. *Polymer Degradation and Stability* 137: 122–130.

Kliem S, Kreutzbruck M and Bonten C (2020) Review on the biological degradation of polymers in various environments. *Materials* 13: 4586.

Kolstad JJ, Vink ET, De Wilde B, et al. (2012) Assessment of anaerobic degradation of Ingeo™ polylactides under accelerated landfill conditions. *Polymer Degradation and Stability* 97: 1131–1141.

Lamberti FM, Román-Ramírez LA and Wood J (2020) Recycling of bioplastics: Routes and benefits. *Journal of Polymers and the Environment* 28: 2551–2571.

Laonuad P, Chaiyut N and Ksapabutr B (2010) Poly (lactic acid) preparation by polycondensation method. *Optoelectronics and Advanced Materials-Rapid Communications* 4: 1200–1202.

Lasprilla AJ, Martinez GA, Lunelli BH, et al. (2012) Poly-lactic acid synthesis for application in biomedical devices – A review. *Biotechnology Advances* 30: 321–328.

Laycock B, Nikolić M, Colwell JM, et al. (2017) Lifetime prediction of biodegradable polymers. *Progress in Polymer Science* 71: 144–189.

Li H and Huneault MA (2011) Comparison of sorbitol and glycerol as plasticizers for thermoplastic starch in TPS/PLA blends. *Journal of Applied Polymer Science* 119: 2439–2448.

Liminana P, Garcia-Sanoguera D, Quiles-Carrillo L, et al. (2018) Development and characterization of environmentally friendly composites from poly (butylene succinate) (PBS) and almond shell flour with different compatibilizers. *Composites Part B: Engineering* 144: 153–162.

Lucas N, Bienaime C, Belloy C, et al. (2008) Polymer biodegradation: Mechanisms and estimation techniques–A review. *Chemosphere* 73: 429–442.

Luckachan GE and Pillai CKS (2011) Biodegradable polymers-a review on recent trends and emerging perspectives. *Journal of Polymers and the Environment* 19: 637–676.

Majgaonkar P, Hanich R, Malz F, et al. (2021) Chemical recycling of post-consumer PLA waste for sustainable production of ethyl lactate. *Chemical Engineering Journal* 423: 129952.

Mamat MRZ, Ariffin H, Hassan MA, et al. (2014) Bio-based production of crotonic acid by pyrolysis of poly (3-hydroxybutyrate) inclusions. *Journal of Cleaner Production* 83: 463–472.

Mazerolles T, Heuzey MC, Soliman M, et al. (2019) Development of co-continuous morphology in blends of thermoplastic starch and low-density polyethylene. *Carbohydrate Polymers* 206: 757–766.

Meereboer KW, Misra M and Mohanty AK (2020) Review of recent advances in the biodegradability of polyhydroxyalkanoate (PHA) bioplastics and their composites. *Green Chemistry* 22: 5519–5558.

Murariu M and Dubois P (2016) PLA composites: From production to properties. *Advanced Drug Delivery Reviews* 107: 17–46.

Nafchi MA, Moradpour M, Saeidi M, et al. (2013) Thermoplastic starches: Properties, challenges, and prospects. *Starch-Stärke* 65: 61–72.

Nampoothiri KM, Nair NR and John RP (2010) An overview of the recent developments in polylactide (PLA) research. *Bioresource Technology* 101: 8493–8501.

Narancic T, Verstichel S, Reddy CS, et al. (2018) Biodegradable plastic blends create new possibilities for end-of-life management of plastics but they are not a panacea for plastic pollution. *Environmental Science & Technology* 52: 10441–10452.

Niaounakis M (2013) Physical recycling. In: Niaounakis M (ed.) *Biopolymers: Reuse, Recycling, and Disposal*. Oxford: William Andrew, pp.151–166.

Niaounakis M (2019) Recycling of biopolymers–the patent perspective. *European Polymer Journal* 114: 464–475.

Nobile MR, Cerruti P, Malinconico, et al. (2015) Processing and properties of biodegradable compounds based on aliphatic polyesters. *Journal of Applied Polymer Science* 132: 42481

Norrrahim MNF, Ariffin H, Hassan MA, et al. (2013) Performance evaluation and chemical recyclability of a polyethylene/poly (3-hydroxybutyrate-co-3-hydroxyvalerate) blend for sustainable packaging. *RSC Advances* 3: 24378–24388.

Pan W, Bai Z, Su T, et al. (2018) Enzymatic degradation of poly (butylene succinate) with different molecular weights by cutinase. *International Journal of Biological Macromolecules* 111: 1040–1046.

Pattanasuttichonlakul W, Sombatsompop N and Prapagdee B (2018) Accelerating biodegradation of PLA using microbial consortium from dairy wastewater sludge combined with PLA-degrading bacterium. *International Biodeterioration & Biodegradation* 132: 74–83.

Pereira CS, Silva VM and Rodrigues AE (2011) Ethyl lactate as a solvent: Properties, applications and production processes–a review. *Green Chemistry* 13: 2658–2671.

PlasticsEurope (2019) The circular economy for plastics-a European overview. *Technical report*. Available at: https://www.plasticseurope.org/en/resources/publications/1899-circular-economy-plastics-european-overview (accessed 14 June 2022).

Platnieks O, Gaidukovs S, Barkane A, et al. (2020) Bio-based poly (butylene succinate)/microcrystalline cellulose/nanofibrillated cellulose-based sustainable polymer composites: Thermo-mechanical and biodegradation studies. *Polymers* 12: 1472.

Puchalski M, Szparaga G, Biela T, et al. (2018) Molecular and supramolecular changes in polybutylene succinate (PBS) and polybutylene succinate adipate (PBSA) copolymer during degradation in various environmental conditions. *Polymers* 10: 251.

Rahimi A and García JM (2017) Chemical recycling of waste plastics for new materials production. *Nature Reviews Chemistry* 1: 1–11.

Rasool MA, Van Goethem C and Vankelecom IF (2020) Green preparation process using methyl lactate for cellulose-acetate-based nanofiltration membranes. *Separation and Purification Technology* 232: 115903.

Reichert CL, Bugnicourt E, Coltelli MB, et al. (2020) Bio-based packaging: Materials, modifications, industrial applications and sustainability. *Polymers* 12: 1558.

Resch-Fauster K, Klein A, Blees E, et al. (2017) Mechanical recyclability of technical biopolymers: Potential and limits. *Polymer Testing* 64: 287–295.

Riaz S, Fatima N, Rasheed A, et al. (2018) Metabolic engineered biocatalyst: A solution for PLA based problems. *International Journal of Biomaterials* 2018: 1963024.

Rittié L and Perbal B (2008) Enzymes used in molecular biology: A useful guide. *Journal of Cell Communication and Signaling* 2: 25–45.

Rivas LF, Casarin SA, Nepomuceno NC, et al. (2017) Reprocessability of PHB in extrusion: ATR-FTIR, tensile tests and thermal studies. *Polímeros* 27: 122–128.

Rodriguez-Gonzalez FJ, Ramsay BA and Favis BD (2004) Rheological and thermal properties of thermoplastic starch with high glycerol content. *Carbohydrate Polymers* 58: 139–147.

Rudnik E and Briassoulis D (2011) Degradation behaviour of poly (lactic acid) films and fibres in soil under Mediterranean field conditions and laboratory simulations testing. *Industrial Crops and Products* 33: 648–658.

Ruggero F, Carretti E, Gori R, et al. (2020) Monitoring of degradation of starch-based biopolymer film under different composting conditions, using TGA, FTIR and SEM analysis. *Chemosphere* 246: 125770.

Ruggero F, Onderwater RC, Carretti E, et al. (2021) Degradation of film and rigid bioplastics during the thermophilic phase and the maturation phase of simulated composting. *Journal of Polymers and the Environment* 29: 3015–3028.

Safley LM, Jr and Westerman PW (1992) Performance of a low temperature lagoon digester. *Bioresource Technology* 41: 167–175.

Salomez M, George M, Fabre P, et al. (2019) A comparative study of degradation mechanisms of PHBV and PBSA under laboratory-scale composting conditions. *Polymer Degradation and Stability* 167: 102–113.

Samorì C, Parodi A, Tagliavini E, et al. (2021) Recycling of post-use starch-based plastic bags through pyrolysis to produce sulfonated catalysts and chemicals. *Journal of Analytical and Applied Pyrolysis* 155: 105030.

Sankhla IS, Sharma G and Tak A (2020) Fungal degradation of bioplastics: An overview. In: Singh J and Gehlot P (eds) *New and Future Developments in Microbial Biotechnology and Bioengineering*. Amsterdam: Elsevier, pp.35–47.

Sedničková M, Pekařová S, Kucharczyk P, et al. (2018) Changes of physical properties of PLA-based blends during early stage of biodegradation in compost. *International Journal of Biological Macromolecules* 113: 434–442.

Shrestha A, van-Eerten Jansen MC and Acharya B (2020) Biodegradation of bioplastic using anaerobic digestion at retention time as per industrial biogas plant and international norms. *Sustainability* 12: 4231.

Sintim HY, Bary AI, Hayes DG, et al. (2019) Release of micro-and nanoparticles from biodegradable plastic during in situ composting. *Science of the Total Environment* 675: 686–693.

Siracusa V, Rocculi P, Romani S, et al. (2008) Biodegradable polymers for food packaging: A review. *Trends in Food Science & Technology* 19: 634–643.

Song X, Liu F, Wang H, et al. (2018) Methanolysis of microbial polyester poly (3-hydroxybutyrate) catalyzed by Brønsted-Lewis acidic ionic liquids as a new method towards sustainable development. *Polymer Degradation and Stability* 147: 215–221.

Soni R.K, Soam S and Dutt K (2009) Studies on biodegradability of copolymers of lactic acid, terephthalic acid and ethylene glycol. *Polymer Degradation and Stability* 94: 432–437.

Soroudi A and Jakubowicz I (2013) Recycling of bioplastics, their blends and biocomposites: A review. *European Polymer Journal* 49: 2839–2858.

Sorrentino A, Gorrasi G and Vittoria V (2007) Potential perspectives of bionanocomposites for food packaging applications. *Trends in Food Science & Technology* 18: 84–95.

Storz H and Vorlop KD (2013) Bio-based plastics: Status, challenges and trends. *Landbauforschung* 4: 321–332.

Svoboda P, Dvorackova M and Svobodova D (2019) Influence of biodegradation on crystallization of poly (butylene adipate-co-terephthalate). *Polymers for Advanced Technologies* 30: 552–562.

Swift G (1995) Opportunities for environmentally degradable polymers. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* 32: 641–651.

Tabasi RY and Ajji A (2015) Selective degradation of biodegradable blends in simulated laboratory composting. *Polymer Degradation and Stability* 120: 435–442.

Taiatele I, Dal Bosco TC, Bertozzi J, et al. (2020) Biodegradability assessment of starch/glycerol foam and poly (butylene adipate-co-terephthalate)/starch film by respirometric tests. *Brazilian Journal of Food Technology* 23: e2018248.

Tokiwa Y, Calabia BP, Ugwu CU, et al. (2009) Biodegradability of plastics. *International Journal of Molecular Sciences* 10: 3722–3742.

Tsuji H, Daimon H and Fujie K (2003) A new strategy for recycling and preparation of poly (L-lactic acid): Hydrolysis in the melt. *Biomacromolecules* 4: 835–840.

Tsuji H, Saeki T, Tsukegi T, et al. (2008) Comparative study on hydrolytic degradation and monomer recovery of poly (L-lactic acid) in the solid and in the melt. *Polymer Degradation and Stability* 93: 1956–1963.

Ummartyotin S and Manuspiya H (2015) A critical review on cellulose: From fundamental to an approach on sensor technology. *Renewable and Sustainable Energy Reviews* 41: 402–412.

Urbanek AK, Mirończuk AM, García-Martín A, et al. (2020) Biochemical properties and biotechnological applications of microbial enzymes involved in the degradation of polyester-type plastics. *Biochimica et Biophysica Acta (BBA)-Proteins and Proteomics* 1868: 140315.

Van Soest JJ, Hulleman SHD, De Wit D, et al. (1996) Crystallinity in starch bioplastics. *Industrial Crops and Products* 5: 11–22.

Venkiteshwaran K, Benn N, Seyedi S, et al. (2019) Methane yield and lag correlate with bacterial community shift following bioplastic anaerobic co-digestion. *Bioresource Technology Reports* 7: 100198.

Weiland P (2010) Biogas production: Current state and perspectives. *Applied Microbiology and Biotechnology* 85: 849–860.

Whitelaw EL, Davidson MG and Jones MD (2011) Group 4 salalen complexes for the production and degradation of polylactide. *Chemical Communications* 47: 10004–10006.

Yagi H, Ninomiya F, Funabashi M, et al. (2012) Anaerobic biodegradation of poly (lactic acid) film in anaerobic sludge. *Journal of Polymers and the Environment* 20: 673–680.

Yagi H, Ninomiya F, Funabashi M, et al. (2013) Thermophilic anaerobic biodegradation test and analysis of eubacteria involved in anaerobic biodegradation of four specified biodegradable polyesters. *Polymer Degradation and Stability* 98: 1182–1187.

Yagi H, Ninomiya F, Funabashi M, et al. (2014) Mesophilic anaerobic biodegradation test and analysis of eubacteria and archaea involved in anaerobic biodegradation of four specified biodegradable polyesters. *Polymer Degradation and Stability* 110: 278–283.

Yang X, Odelius K and Hakkarainen M (2014) Microwave-assisted reaction in green solvents recycles PHB to functional chemicals. *ACS Sustainable Chemistry & Engineering* 2: 2198–2203.

Yu J, Plackett D and Chen LX (2005) Kinetics and mechanism of the monomeric products from abiotic hydrolysis of poly [(R)-3-hydroxybutyrate] under acidic and alkaline conditions. *Polymer Degradation and Stability* 89: 289–299.

Zaborowska M, Bernat K, Pszczółkowski B, et al. (2021a) Anaerobic degradability of commercially available bio-based and oxo-degradable packaging materials in the context of their end of life in the waste management strategy. *Sustainability* 13: 6818.

Zaborowska M, Bernat K, Pszczółkowski B, et al. (2021b) Challenges in sustainable degradability of bio-based and oxo-degradable packaging materials during anaerobic thermophilic treatment. *Energies* 14: 4775.

Zhang J, Yan DX, Xu JZ, et al. (2012) Highly crystallized poly (lactic acid) under high pressure. *AIP Advances* 2: 042159.

Zhao JB, Li KY and Yang WT (2007) Chain extension of polybutylene adipate and polybutylene succinate with adipoyl-and terephthaloyl-biscaprolactamate. *Journal of Applied Polymer Science* 106: 590–598.

Zhao X, Cornish K and Vodovotz Y (2020) Narrowing the gap for bioplastic use in food packaging: An update. *Environmental Science & Technology* 54: 4712–4732.

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Magdalena Zaborowska, oświadczam, że mój wkład naukowy w ostateczną wersję poniższej publikacji naukowej wyniósł 70%:

Zaborowska Magdalena, Bernat Katarzyna, 2022. The development of recycling methods for bio-based materials - A challenge in the implementation of a circular economy: A review. *Waste Management Research*, 41(1), 68-80.

Mój udział jako współautora publikacji obejmował:

- ☑ Współautorstwo w przygotowaniu koncepcji pracy
- ☑ Udział w pisaniu pracy
- ☑ Udział w graficznym przedstawieniu wyników
- ☑ Zbieranie materiałów źródłowych
- ☐ Konsultacja i opieka
- ☑ Udział w interpretacji wyników i wnioskowaniu
- ☑ Korekta pracy przed złożeniem do druku

07.07.2023 Magdalena Zaborowska
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Katarzyna Bernat, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 70%:

Zaborowska Magdalena, Bernat Katarzyna, 2022. The development of recycling methods for bio-based materials - A challenge in the implementation of a circular economy: A review. *Waste Management Research*, 41(1), 68-80.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

☒ Współautorstwo w przygotowaniu koncepcji pracy

☒ Udział w pisaniu pracy

☒ Udział w graficznym przedstawieniu wyników

☐ Zbieranie materiałów źródłowych

☒ Konsultacja i opieka

☒ Udział w interpretacji wyników i wnioskowaniu

☒ Korekta pracy przed złożeniem do druku

7.07.2023r. Katarzyna Bernat
data i podpis

sustainability

MDPI

Article

Anaerobic Degradability of Commercially Available Bio-Based and Oxo-Degradable Packaging Materials in the Context of Their End of Life in the Waste Management Strategy

Magdalena Zaborowska [1,*], Katarzyna Bernat [1], Bartosz Pszczółkowski [2], Irena Wojnowska-Baryła [1] and Dorota Kulikowska [1]

[1] Department of Environmental Biotechnology, Faculty of Geoengineering, University of Warmia and Mazury in Olsztyn, ul. Sloneczna 45 G, 10-719 Olsztyn, Poland; bernat@uwm.edu.pl (K.B.); irka@uwm.edu.pl (I.W.-B.); dorotak@uwm.edu.pl (D.K.)

[2] Department of Materials and Machines Technology, University of Warmia and Mazury in Olsztyn, ul. Oczapowskiego 11, 10-719 Olsztyn, Poland; bartosz.pszczolkowski@uwm.edu.pl

* Correspondence: magdalena.zaborowska@uwm.edu.pl; Tel.: +48-89-523-4118; Fax: +48-89-523-4131

Abstract: There are discrepancies concerning the time frame for biodegradation of different commercially available foils labeled as biodegradable; thus, it is essential to provide information about their biodegradability in the context of their end of life in waste management. Therefore, one-year mesophilic (37 °C) anaerobic degradation tests of two bio-based foils (based on starch (F_S), polylactic acid (F_{PLA})) and oxo-degradable material (F_{OXO}) were conducted in an OxiTop system. Biodegradation was investigated by measuring biogas production (BP) and analyzing structural changes with differential scanning calorimetry, polarizing and digital microscopic analyses, and Fourier transform infrared spectroscopy. After 1 year, F_{OXO} had not degraded; thus, there were no visible changes on its surface and no BP. The bio-based materials produced small amounts of biogas (25.2, F_{PLA}, and 30.4 L/kg VS, F_S), constituting 2.1–2.5% of theoretical methane potential. The foil pieces were still visible and only starting to show damage; some pores had appeared in their structure. The structure of F_{PLA} became more heterogeneous due to water diffusing into the structure. In contrast, the structure of F_S became more homogenous although individual cracks and fissures appeared. The color of F_S had changed, indicating that it was beginning to biodegrade. The fact that F_S and F_{PLA} showed only minor structural damage after a one-year mesophilic degradation indicates that, in these conditions, these materials would persist for an unknown but long amount of time.

Keywords: polymers; starch- and polylactic-acid-based material; biogas production; FTIR and microscopic analyses; DSC

Citation: Zaborowska, M.; Bernat, K.; Pszczółkowski, B.; Wojnowska-Baryła, I.; Kulikowska, D. Anaerobic Degradability of Commercially Available Bio-Based and Oxo-Degradable Packaging Materials in the Context of Their End of Life in the Waste Management Strategy. *Sustainability* **2021**, *13*, 6818. https://doi.org/10.3390/su13126818

Academic Editor: Alessio Siciliano

Received: 10 May 2021
Accepted: 14 June 2021
Published: 16 June 2021

1. Introduction

The worldwide use of bioplastics (bio-based products) has been increasing, and it is expected that the share of bio-based products on the plastics market will increase by 40% by 2030 [1]. These products are most often used as food packaging, frozen food containers, milk and juice cartons, disposable tableware, or for agriculture purposes [2]. Bio-based products are wholly or partly of biological origin, e.g., based on lignin, cellulose, or starch. These products contain from 20% up to 100% renewable raw materials and can be both biodegradable and non-biodegradable [3]. However, the most desirable are biodegradable or compostable products, which degrade anaerobically or aerobically in the presence of microorganisms. Among biodegradable bio-based products, starch-based materials and polylactic acid (PLA) are the most common, constituting 44% and 24% of the global production capacity for biodegradable polymers, respectively. Other biopolymers produced at an industrial scale are poly(butylene succinate) (PBS) and poly(butyleneadipateterephthalate) (PBAT), which constitute 23% of the global production capacity, and polyhydroxyalkanoates (PHA), which constitute 6% [4]. PLA can be synthesized from renewable biomass (e.g., molasses, whey, bagasse, potato, tapioca, wheat) via microbial fermentation process by bacteria and fungi [5]. However, the yield of lactic acid produced by fungi is lower than produced by bacteria. The microorganisms used for PLA production are the following: *Lactococcus*, *Enterococcus*, *Streptococcus*, *Leuconostoc*, *Weissella*, some *Lactobacilli*, and *Lactobacillus brevis*. PLA can be produced in batch, fed batch, or continuous fermentation, whereof the first two produce a high concentration of lactic acid and the last one has higher productivity [6–8]. Starch is a natural material, composed of amylose and amylopectin. For bio-based material production, thermoplastic starch (TPS) is the most often used. TPS is formed during, e.g., mechanical shearing under heat or the addition of plasticizers (typically water or glycerol) to starch [9].

Although they should not be confused with bio-based materials, petroleum-based products to which oxidants have been added (i.e., oxo-degradable products) are often classified as biodegradable plastics, and they can degrade via an abiotic–biotic process [10,11]. The additives used in oxo-degradable products facilitate the breakdown of molecular chains, leading to the products' degradation [12]. For example, photodegradation of low-density polyethylene and polypropylene films can be activated using metal oxides (e.g., Fe_2O_3, Cu_xO, ZnO, and TiO_2) as catalysts [13,14].

Biodegradable bio-based products often contain various non-organic additives to increase their thermal stability and mechanical properties. Bio-based materials may contain additives such as stabilizers, plasticizers, fillers, reinforcing agents, colorants, and fire retardants, which influence the biodegradability of these materials [15]. For example, regarding starch-based materials, the most common plasticizers used for the improvement of their thermal stability are polyols (glycerol and sorbitol) [16]. Moreover, to improve their mechanical and thermal properties, sodium silicate [17] or silica [18] can be used. Other common plasticizers used for bio-based material production are glycerol [19], urea [20], or citrate esters [21]. However, these additives decrease both the degree and the rate of degradation of the bio-based products [22]. The complete degradation of bio-based products occurs only under optimized conditions (i.e., optimal temperature, pH), which may be different for different materials. Generally, the large fragments of these products are first fragmented into smaller particles. This fragmentation, as well as incomplete degradation, may cause the biopolymers to be released into the environment as microplastics [23]. Due to the increasing amount of waste from bio-based products, it is necessary to assess the effect of these products on waste management, including organic recycling. Waste from bio-based products can be found in streams of selectively collected plastic waste and biowaste. If bioplastics are handled with conventional plastics, they will likely be recycled or incinerated. However, assuming that they are labeled as bio-based products, they should be collected with biowaste (kitchen waste and green waste). Therefore, it is necessary to carry out the degradation of bio-based products under the process conditions used during the treatment of the biowaste. Mechanical–biological treatment (MBT) plants treat biowaste via anaerobic digestion (AD) and/or aerobic stabilization/composting. In organic recycling of bio-waste, methane fermentation is increasingly used because it improves the economy of MBT plants and provides other benefits like decomposition of organic matter, production of biogas, and reduction of the waste volume. Moreover, the process enables production of naturally used digestate and other substrates for chemical syntheses (e.g., for volatile fatty acids) [24–26]. Therefore, it is important that bio-based products should be completely biodegradable, and after they become a part of compost or digestate in an MBT plant, they should not contaminate these materials.

Due to rapid growth in the amount of bio-based products and their waste, there is a need to determine the optimal conditions for degrading these products, especially under anaerobic conditions. AD can be carried out in MBT plants at mesophilic (35–40 °C) or thermophilic (50–60 °C) temperatures. However, the mesophilic process is more stable and requires a smaller energy input [27]. Generally, anaerobic tests are based on the measurement of biogas or methane production. The principal standard methods for monitoring the anaerobic degradation of bio-based products use mesophilic temperatures. For example, ISO 14853:2016, used to determine the anaerobic biodegradability of plastic materials in an aqueous medium, calls for exposure of the test polymers to sludge at 35 °C ± 2 °C for a period of up to 90 days [28]. This time is longer than the conventional sludge retention time (25 to 30 days) in anaerobic digesters. Massardier-Negotte et al. [29] used ISO 14853 for anaerobic tests and found that, in these conditions, biopolymers (PLA, polycaprolactone, starch/polycaprolactone, and PBAT) degraded slightly or did not degrade.

To determine the degree and rate of anaerobic mesophilic biodegradation of plastic materials, ASTM D5526 may be also used [30]. In this test, the inoculum should be derived from anaerobic digesters operating only with pretreated household waste. Biodegradation should be carried out under dry (>30% total solids (TS)) and static non-mixed conditions. Another test of polymer biodegradability is provided by EN 13432, which defines the requirements for determining the compostability and anaerobic treatability of plastic packaging materials [31]. Zhang et al. [32] carried out mesophilic anaerobic degradation of nine different bioplastics (based on cellulose, starch, and PLA) according to EN13432. They concluded that only four bioplastics showed substantial biodegradability, but less than 20% of their carbon was converted into methane.

In summary, many products on the market are labeled as biodegradable. However, even though various products can be based on the same main component, e.g., starch or PLA, its content in the products can differ. Moreover, manufacturers use various types of additives in different proportions to improve the functional properties of a material. Unfortunately, however, the manufacturers do not provide detailed information on the composition of their products. Most likely, the types and proportions of the additives are the main factors determining the biodegradability of bioplastics and the time frame for their biodegradation. Thus, reports on the degree of biodegradation of different bioplastics during anaerobic treatment differ substantially [33–36]. Moreover, for waste-management and end-of-life considerations, it is essential to provide information on as many as possible of the commercially available materials that are considered biodegradable. Therefore, the aim of this study was to investigate the degradation of selected bio-based and oxo-degradable products (waste disposal bags) during a long-term (1-year) anaerobic mesophilic biodegradation test. Three different commercially available foil materials were studied by observing changes in their structure with the use of polarizing and digital microscopic analyses, Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC).

2. Materials and Methods

2.1. Bio-Based Materials and Oxo-Degradable Material

In the present study, three different commercially available foils were subjected to anaerobic mesophilic (37 °C) degradation. Two of them were bio-based products: BioBag waste bags made from Mater-Bi® material based on starch (F_S) and bags made from polylactic acid (F_{PLA}). The third foil was an oxo-degradable product (F_{OXO}), consisting of conventional polyethylene containing the pro-oxidant additive d2w. Each of the investigated foils was cut to a particle size of 10x10 mm. The characteristics of the materials are presented in Table 1. To improve their functional properties, these products, which were purchased on the commercial public market, may have contained other additives. Unfortunately, however, the manufacturer did not provide details of their composition.

Table 1. Characteristics of the materials used in the experiment.

Material	F_{PLA}	F_{S}	F_{OXO}
Basic characteristics			
VS (% of DM)	99.3	99.9	93.1
COD (g/kg)	71.5	63.9	n.d.
TN (mg/kg)	454.9	408.6	3 766.8
Elemental composition			
Carbon, %	57.56	55.36	n.d.
Hydrogen, %	6.88	6.90	n.d.
Oxygen, %	34.86	37.64	n.d.
Nitrogen, %	0	0	n.d.

n.d., not determined; VS, volatile solids; DM, dry mass; COD, chemical oxygen demand; TN, total nitrogen.

2.2. Measurement of Biogas Production

An anaerobic biodegradation test with measurement of biogas production from bio-based and oxo-degradable foils was performed under mesophilic conditions (37 ± 0.5 °C) with the use of a standard test of gas potential (ISO 14853:2016) with modifications [28]. The measurement lasted 1 year and was carried out in triplicate for each foil with the use of the OxiTop® Control system (WTW Wissenschaftlich-Technische Werkstätten GmbH, Germany), which consists of measuring vessels (bioreactors) with a capacity of 630 mL and measuring heads with built-in pressure sensors. Pressure values obtained from respirometric measurements allowed determination of the volume of biogas produced. To ensure anaerobic conditions, the space above the sample was flushed with nitrogen gas before measurements.

To determine the biogas production from foil, the inoculum (approximately 100 mL) and the foil were introduced into the OxiTop bioreactors. The inoculum was fermented sludge from a closed mesophilic digester chamber from a municipal wastewater treatment plant employing the activated sludge method (north-eastern Poland). The planned initial organic load (OL) was 4 kg VS/m^3, indicating that the doses of foils were 0.4 g. Additionally, biogas production by the inoculum alone was determined. The biogas production of the foils themselves was determined by taking the difference between the amount of biogas generated in the bioreactors with inoculum and foil and the amount of biogas generated in the bioreactors with only inoculum.

Additional glass bottles, with volume identical to those of the bioreactors, were prepared to enable sampling of foil pieces from these bottles. These bottles were prepared in the same manner as the OxiTop vessels, which were used only for measuring biogas production. All the bioreactors and bottles were placed in a thermostatic incubator. Every month during anaerobic biodegradation tests, pieces of F_{S}, F_{PLA}, and F_{OXO} were removed from the inoculum for the microscopic, differential scanning calorimetry (DSC), and FTIR analyses. However, the results of these analyses did not show any changes in comparison with the raw materials during the first year. Changes finally appeared after 1 year, and only these results are shown below.

2.3. Microscopic and FTIR Analysis

The changes on the surface of the bio-based and oxo-degradable materials were analyzed using a Nikon eclipse50i polarizing microscope at a magnification of 100× and digital microscope (Keyence VHX-7000, Osaka, Japan) at a magnification of 1000×. Additionally, the digital microscope allows to determine 3D geometric structure (topography) at the microscale without contact with the investigated foil sample.

The FTIR spectra were collected using a PerkinElmer Spectrum Two (with diamond ATR) brand device within the wavenumber range of 4000–400 cm^{-1} and resolution of 4

cm^{-1} at room temperature and repeated in triplicate for each foil material. Smoothing functions were not employed.

2.4. Differential Scanning Calorimetry Analysis

In the raw foil materials and after 1 year of the degradation, thermal properties of bio-based and oxo-degradable foils were investigated with a differential scanning calorimetry analysis (DSC) on DSC Phoenix 204 F1 differential scanning calorimeter utilizing hit flow method (NETZSCH, Selb, Germany). The measured parameter is free heat flow. Small amounts (ca. 5 mg) of dry samples of each of the foils were placed into aluminum crucibles, sealed, and heated at between 30 °C and 200 °C at a heating rate of 5 °C/min. An empty aluminum crucible was used as reference. The analysis based on the measurement of energy required to establish a zero-temperature difference between the analyzed sample and a reference sample. The thermal characteristics such as the glass transition temperature (Tg), cold crystallization temperature (Tcc), cold crystallization enthalpy (ΔHcc), melting temperature (Tm), and melting enthalpy (ΔHm) were determined from DSC curves.

2.5. Analytical Methods

Volatile solids (VS) as loss on ignition and the contents of COD and TN (as total Kjeldahl nitrogen) in foil materials (if possible) were determined according to APHA [37]. Elemental composition of the materials was determined with the use of Flash 2000 Organic Elemental Analyzer (Thermo Scientific, Milan, Italy).

3. Results and Discussion

3.1. Anaerobic Biodegradation Test of Selected Bio-Based and Oxo-Degradable Materials in OxiTop System

Anaerobic biodegradation of pieces of foils of F_S, F_{PLA}, and F_{OXO} were carried out under mesophilic conditions at 35 °C. The OxiTop system allowed measurement of the volume of biogas (in mL) produced during the anaerobic test. During the analyses of biogas volume (BV) from investigated material, two BV profiles were considered. The inoculum alone (I) represents the first profile. The inoculum with the material (F_S + I, F_{PLA} + I) represents the second profile. The profile of the biogas volume for the material alone is possible to be obtained by subtracting the values of the first profile from the second. As shown in Figure 1, the profiles of biogas volume corresponding to the inoculum alone and to both the inoculum and the foil material were very close to each other. This means that the biogas volume corresponding to the foil material alone would be very low. This was confirmed by the value of BP in liters per kg of organic matter (L/kg VS), that is, the most commonly used units for BP during anaerobic measurements in this kind of system, as the VS content of the foil materials was considered to reflect the organic matter content. The profiles corresponding to the inoculum alone and to both the inoculum and the foil material of F_{OXO} showed no differences indicating lack of degradation; thus, no BV and BP profiles are provided.

The profiles of the biogas volume for the bio-based foil materials of FPLA and FS showed the initial long lag phases. With FS, the lag phase was even longer, lasting 70 days, whereas with FPLA, it lasted 60 days. After the lag phase, BP started to increase very slowly until 160–180 day of the measurements, and then, the biogas volumes remained the same until the end of an almost 400-day anaerobic test. The final biogas production for FPLA and FS was similar: 25.2 and 30.4 L/kg VS, respectively.

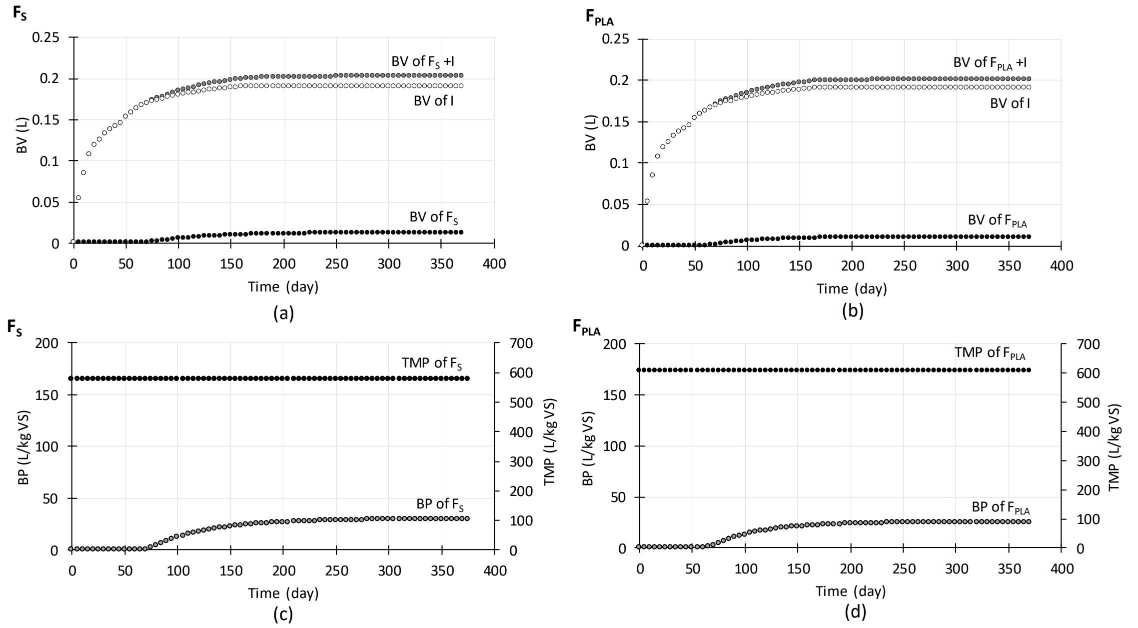


Figure 1. Biogas volume (BV; in L) profiles (a,b) from the inoculum (I) only and bio-based materials with the inoculum (F_S + I, F_{PLA} + I) and biogas production (BP; in L/kg VS) profiles (c,d) during an anaerobic biodegradation test at 35 °C of bio-based materials of F_{PLA} and F_S; the values of theoretical methane potential (TMP) of F_S and F_{PLA} (based on the elemental composition) are also shown; the F_{OXO} did not degrade, and thus, no BP was observed and the profiles are not provided.

Based on the elementary composition of the foil materials, the theoretical amounts of methane (theoretical methane potential, TMP), assuming complete conversion of organics into biogas, were calculated using the Buswell equation [38]:

$$C_aH_bO_c + \left(a - \frac{b}{4} - \frac{c}{2}\right) H_2O \rightarrow \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4}\right) CO_2 + \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4}\right) CH_4 \quad (1)$$

The theoretical molar compositions of the methane that could be obtained from one mole of the tested foil materials were as follows:

- F_{PLA}: $C_{4.40}H_{6.31}O_2 + 1.99\ H_2O \rightarrow 2.71\ CH_4 + 2.08\ CO_2$;
- F_S: $C_{9.83}H_{14.70}O_5 + 1.71\ H_2O \rightarrow 2.58\ CH_4 + 2.03\ CO_2$.

To calculate the mass of methane and carbon dioxide, molar masses were considered. Then, to determine the theoretical volumes of gases, their densities were considered as 0.717 g/L and 1.978 g/L, respectively (at 0 °C, 101 kPa). The values of TMP of F_S and F_{PLA} (based on the elemental composition) are 577 and 610 L/kg VS, and they are also shown in Figure 1 for comparison with the obtained BP. Assuming that methane content in biogas from F_S and F_{PLA} would be ca. 50% [38], the values of methane production (MP) would be two times lower than biogas production, ca. 12 and ca. 15 L/kg VS, respectively.

Most of the studies assumed that the value of TMP is the maximal value of methane that could be obtained. The ratios of MP/TMP for F_S and F_{PLA} are 0.021 and 0.025. Thus, F_S and F_{PLA} produced methane in amounts constituting only 2.1% and 2.5%, respectively, of the TMP values.

There are discrepancies concerning the time frame for the biodegradation of different biopolymers, and most researchers have not provided information on biogas yield. Bátori et al. [36] found that some biopolymers, such as starch, cellulose, pectin, and poly(hydroxyalkanoate), can be degraded at hydraulic retention times commonly used in biogas plants. Shin et al. [39] reported that 89% of poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHB/HV; 92/8, *w*/*w*) could be degraded within 20 days under anaerobic mesophilic conditions. Similarly, Noda et al. [33] found that 80% of 14-C-labeled poly(3-hydroxybutyrate-*co*-3-hydroxyoctanate) biodegraded after 25 days under anaerobic conditions at 37 °C.

Yagi et al. [35] found that during mesophilic (37 °C) anaerobic degradation, PHB was over 90% biodegraded in 10 days, whereas PLA was only 7% biodegraded in 90 days, and PBS did not degrade. Kolstad et al. [34] tested the degradability of a commercially available PLA product at two temperatures: 21 °C (under simulated landfill conditions) and 35 °C. The duration of the tests was 13 months (390 days) and 170 days, respectively. The authors found that, in a year-long psychrophilic test, the amorphous and semicrystalline PLA did not produce a significant volume of biogas. At 37 °C, it was predicted that amorphous PLA would yield approximately 189 L/kg (40% of the theoretical potential), whereas it was observed that the semicrystalline samples did not generate a significant volume of methane.

3.2. Microscopic Analyses and Topography of the Investigated Materials

The small amount of biogas produced by the bio-based materials is connected with the fact that, until 365 days of anaerobic degradation had passed, pieces of the foils were still visible in the inoculum, and these fragments only started to show damage. Polymer degradation can be determined based on the changes in the surface, e.g., formation of holes and/or cracks, and changes in color or roughness parameters. Moreover, thermal properties (DSC) or the results of FTIR analyses can provide information about the structural changes in the material [40].

The foils used in the present study came from commonly available bags for waste collection. Initially, each of the foils had a green color and was smooth. Microscopic analyses at 100-fold magnification showed no changes after 1 year of degradation of the F_{PLA} material, but analyses at 1000-fold revealed some pores in the material structure (Figure 2). Analyses of surface topography indicated that, after long-term anaerobic degradation, the structure of F_{PLA} had become more heterogeneous than that of the raw material (Figure 3). The distance between the valleys and peaks decreased after degradation, which may have been caused by diffusion of water into the material structure and may indicate that the foil’s thickness was gradually decreasing and it was being degraded [41].

In contrast to F_{PLA}, the FS material changed visibly after 1 year of degradation, and individual cracks and fissures were visible in its structure (Figure 2). These changes corresponded to slightly higher biogas production from F_S than from F_{PLA}. A change in the color of the material was also observed. Such changes in the color of a polymer may be considered an important indicator of the biodegradation process [42]. Lee et al. [43] observed that, during anaerobic degradation of a foil consisting of a mixture of PLA and pure lactic acid, its color changed from transparent to white after 10 days of the process, whereas a foil consisting of pure PLA did not change color during this time. In the study present here, the analyses of F_S surface topography indicated that, after degradation, the structure of the material became more homogeneous (Figure 3). The change in the color of the bio-based product may be one of the indicators of the biodegradation of the polymer. Fortunati et al. [44] observed changes of color of the PLA material during composting due to hydrolytic degradation of the polymer, which led to a change in the refraction index. This was caused by water absorption and/or the presence of hydrolysis product. The same results were obtained by Arrieta et al. [45] during composting of PLA and plasticized PLA/PHB films. Moreover, the authors suggested that an increase in lightness of plasticized films may be caused by loss of the plasticizer and the compression of macromolecular chains of polymer. The color change of bio-based products may also correspond to the embrittlement of materials, which is associated with increase in crystallinity [46].

Microscopic analyses of F_{OXO} did not show any changes in the foil’s structure (Figure 2), whereas an analysis of surface topography showed a decrease in the height of the peaks and the depth of the valleys on the material surface (Figure 3). This may have been caused by washing away the pro-oxidant additive.

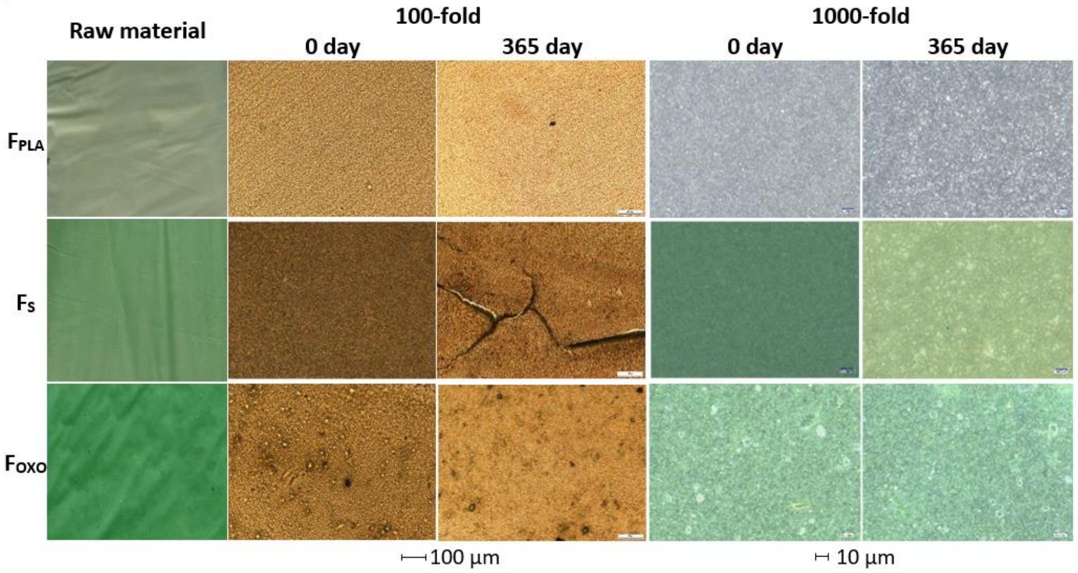


Figure 2. Polarizing and digital microscopic images of raw foil materials and of foil materials after a 365-day anaerobic mesophilic degradation test.

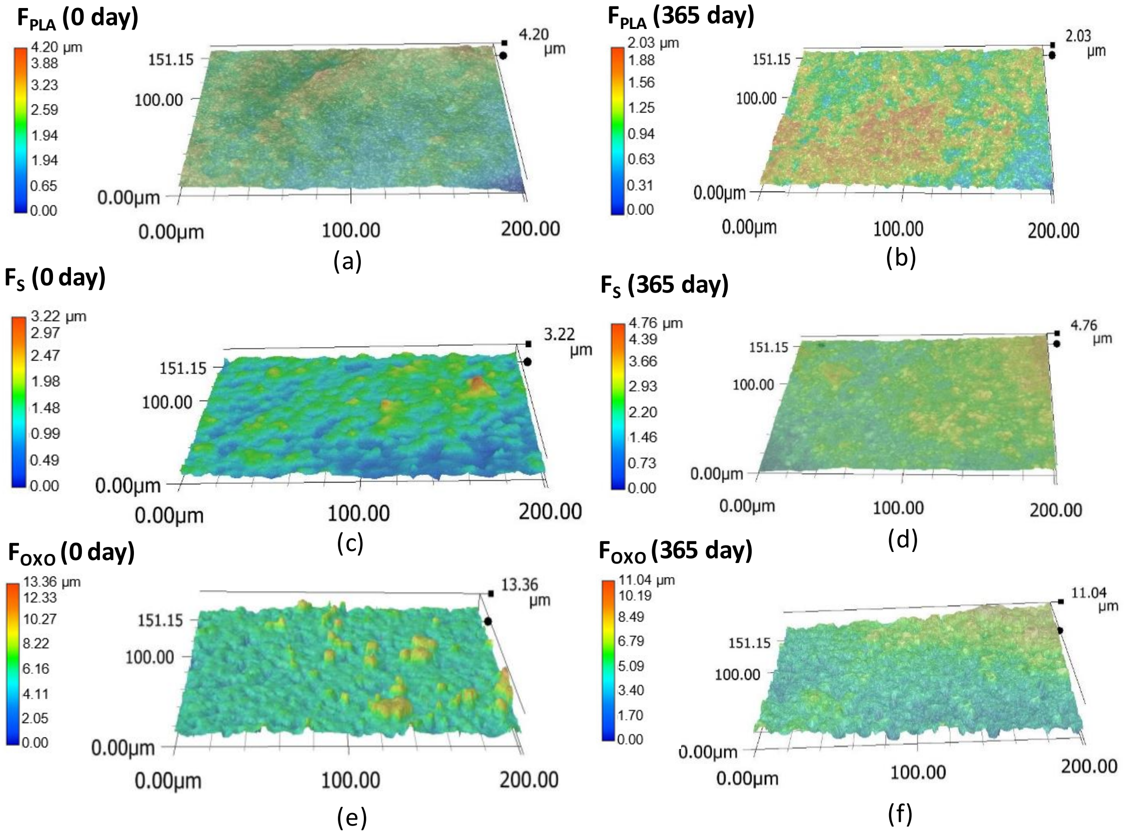


Figure 3. Topography of raw foil materials (a,c,e) and of foil materials after a 365-day (b,d,f) anaerobic mesophilic degradation test.

3.3. Differential Scanning Calorimetry (DSC) Measurements

Regarding the DSC curve of raw foil of F_{PLA} before degradation, the cold crystallization peak was observed at 75 °C. After one-year degradation, this peak was not noted, which may indicate the hydrolysis of F_{PLA} and the rapid increase in polymer matrix crystallinity [47]. A shift in the melting point from 166 °C (F_{PLA} before degradation) to 164 °C

(F_{PLA} after degradation) was observed. Moreover, the enthalpy of the melting process decreased by about 2 J/g. The decrease of F_{PLA} melting point during degradation may be connected with molecular mass reduction [48]. The glass transition temperature increased after degradation from 55 °C to 66 °C, and no enthalpy changes were observed (Figure 4).

Regarding raw foil of F_S before degradation, the three melting points at 64 °C, 118 °C, and at 152.8 °C were observed (Figure 4). Aldas et al. [49] reported that the melting point in starch-based material Mater-Bi at 56.3 °C and 107.3 °C corresponded to poly(ε-caprolactone) (PCL) and poly(butylene adipate-co-terephthalate) (PBAT) addition, respectively. Whereas a melting point at ca. 150.3 °C refers to the melting of the plasticized starch fraction [49,50]. Abdullah et al. [51] found that glass transition temperature and melting temperature of starch-based bioplastics decrease with the decrease of starch to glycerol ratio (glycerol is a common plasticizer for producing starch-based bio-based products). In the presented study, after one-year degradation of F_S, a shift of all peaks of the DSC curve was observed. However, the area under both curves was similar, which indicated no enthalpy changes for F_S before degradation and after the process.

DSC analyses for F_{OXO} material (in raw material and after one-year degradation) showed typical DSC curves of polyethylene, without substantial changes due to pro-oxidant additive. Contant-Rodrigo [52], during thermal characterization of polypropylene with the addition of pro-oxidant, also showed that the additive did not modify the DSC curve. In the presented study, the DSC curve of the material after the long-term degradation did not change. Melting process was in the range from 114 °C to ca. 128 °C. The melting point was observed at 124 ± 0.1 °C. A slightly lower melting point value (117–119 °C) was obtained by Benitez et al. [53] for linear low-density polyethylene.

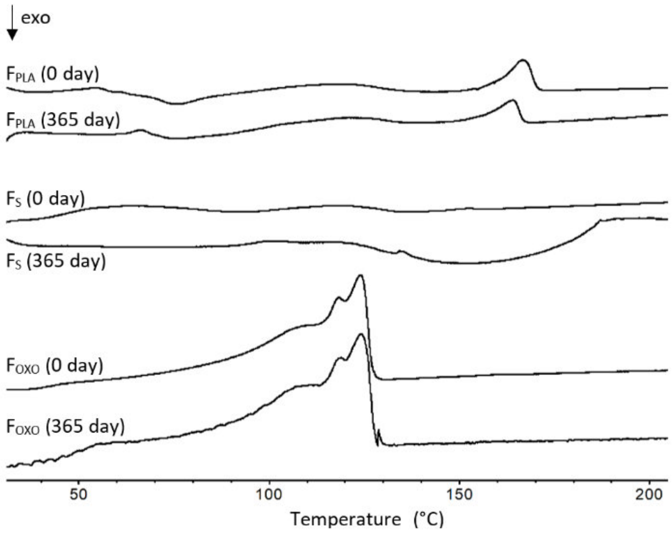


Figure 4. The DSC curves of raw foil materials and of foil materials after a 365-day anaerobic mesophilic degradation test.

3.4. FTIR Spectra

The FTIR spectra of investigated foils allowed to detect their chemical composition before and after long-term degradation (Figure 5). The spectrum of raw material of F_{PLA} showed typical bands for pure PLA. The peak between 3612 and 3000 cm^{-1} indicated hydrogen-bonded (intra- and intermolecular) -OH groups. The bands located at 2964–2880 cm^{-1} corresponded to asymmetric and symmetric vibrations of the $-CH_3$ groups. The peak at 1710 cm^{-1} represented asymmetric stretching of carbonyl C=O groups by lactide [45,54], which may indicate the amorphous phase of PLA. The peaks at 1263, 1133, and 1098 cm^{-1} corresponded to stretching vibrations of the C-O-C and -CH-O- groups. The band at 931 cm^{-1} combined contributions of both $-CH_3$ rocking and deformation of the carboxylic -OH···H groups [55]. At 874 and 727 cm^{-1}, the $O-CH-CH_3$, esters and/or C-C, and rocking vibrations of -CH_3 groups were noted. After one-year anaerobic degradation, no shifts or new peaks appeared in FTIR spectra of F_{PLA}. However, the intensity of all bands increased, indicating minor degradation. The increase in peak corresponding to carbonyl C=O groups is associated with the increase in the number of carboxylic end groups in the polymer chain due to hydrolytic degradation [45].

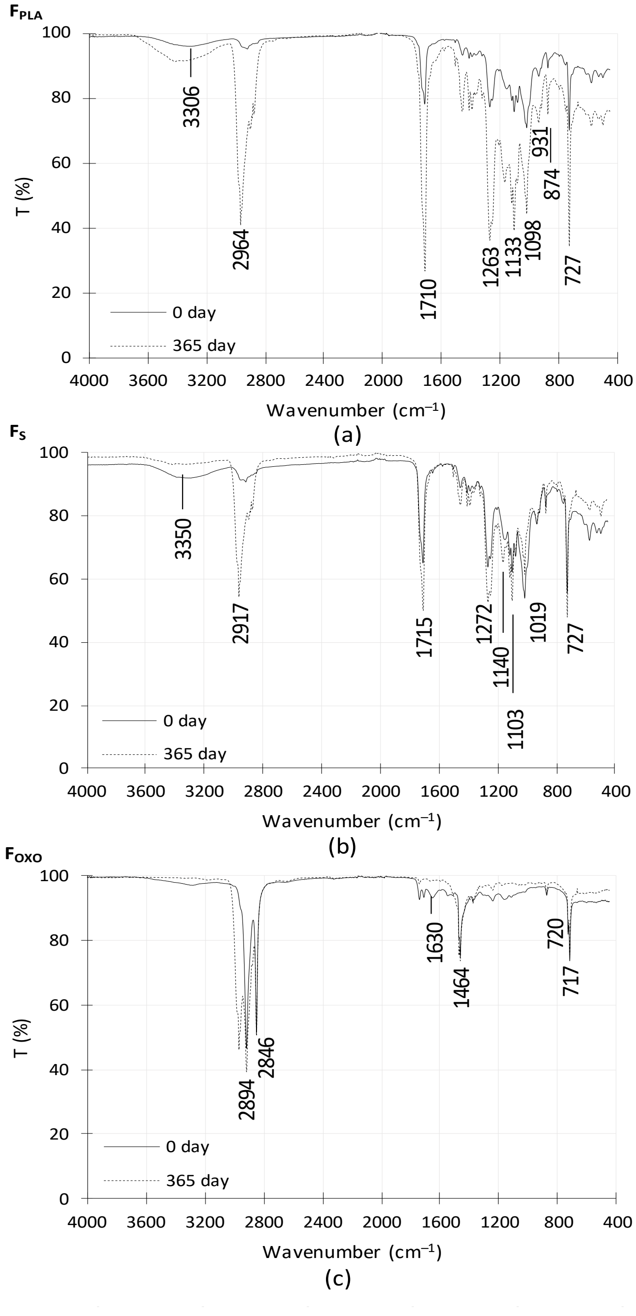


Figure 5. FTIR spectra of raw foil materials and of foil materials after a 365-day anaerobic mesophilic degradation test; (a) F_{PLA}, (b) F_S, (c) F_{OXO}.

Infrared spectra for the raw material of F_S exhibited bands characteristic of plasticized starch. Over the one-year anaerobic degradation, no new peaks appeared in the IR spectra, and transmittance across all peaks slightly changed, indicating minor degradation. The peaks between 3600 and 3100 cm^{-1} and between 1270 and 900 cm^{-1} related to O–H stretching groups and to C-O stretching and hydrogen bonding peaks, respectively. Peaks at 1140 and 1103 cm^{-1}, indicated the C–O stretching of the C–O–H group, which is a typical starch group in hydrogen bonding. The peak at 1016 cm^{-1} corresponded to the C–O stretching of the C–O–C group of the starch glycosidic bonds [56]. The peak located at 727 cm^{-1} represented four or more adjacent methylene ($–CH_2–$) groups. The bands at 2917 cm^{-1} corresponded to C–H stretching in aliphatic and aromatic groups. The bands at 1715, 1272 cm^{-1}, and 1019 cm^{-1} corresponded to the carbonyl groups C=O, the C–O link, and the stretching of phenylene groups, respectively.

Regarding F_{OXO}, the FTIR spectrum was typical for polyethylene. The difference was a small band at 1630 cm^{-1} corresponding to a double bond (or aromatic rings), which was indicated probably as a result of surface antioxidant addition. This band was not noted after 365 days of anaerobic degradation, and the F_{OXO} spectrum was as for pure PE. This means that antioxidant additive was washed away or assimilated by bacteria [57]. The peaks located at 2894 and 2846 cm^{-1} belong to C–H stretching asymmetric and symmetric vibrations. The band at 1464 cm^{-1} related to CH_2 scissoring groups, whereas the bands at 720 cm^{-1} and 717 cm^{-1} indicated CH_2 rocking vibration.

In summary, due to the development of the market of bio-based products, their waste may appear in the waste management system. As was mentioned, such kind of waste can be found in different streams, i.e., mixed municipal waste and selectively collected plastic waste or biowaste. Given the priorities in the waste management hierarchy, bio-based products should be collected with biowaste and biologically treated. Thus, researchers and future studies should focus on searching for the most optimal conditions for biodegradation of bio-based products and potential microorganisms that have the capability to degrade these polymers. The knowledge about the microbiological community structure involved in the biodegradation and the pathways of biodegradation of bio-based materials during composting or anaerobic digestion would provide valuable information. For waste management and end-of-life scenarios, it is essential to provide as much information as possible to create a database on the biodegradability of commercially available bio-based materials. This information may also be useful for assessing regulations for the management of bio-based materials.

4. Conclusions

During one year under mesophilic anaerobic conditions, F_{OXO} did not degrade (no biogas was produced). Moreover, no microscopic changes were found in the foil structure. The bio-based materials (F_S and F_{PLA}) produced small amounts of biogas, 25.2 and 30.4 L/kg VS for F_{PLA} and F_S, respectively, whereas TMP indicated that even 610 and 577 L/kg VS could be obtained. The structure of bio-based foils started to show damage. However, the individual cracks and fissures were visible in the structure of F_S. This indicates that they were in the initial phase of degradation. Although the manufacturers labeled these commercially available bio-based products as biodegradable, this study found that they did not disintegrate even after 1 year of mesophilic anaerobic degradation, indicating that the foils would persist for an unknown but lengthy amount of time. Thus, providing guidelines for bio-based foil treatment remains a challenge in waste management.

Author Contributions: Conceptualization, M.Z. and K.B.; methodology, M.Z., K.B., and B.P.; formal analysis, K.B., I.W.-B., and D.K.; validation, M.Z. and B.P.; investigation, M.Z. and K.B.; resources, M.Z., K.B., I.W.-B., and D.K.; data curation, M.Z. and K.B.; writing—original draft preparation, M.Z., K.B., I.W.-B., and D.K.; writing—review and editing, M.Z., B.P., K.B., I.W.-B., and D.K.; visualization, M.Z. and B.P.; supervision, K.B.; funding acquisition, K.B., I.W.-B., and D.K. All authors have read and agreed to the published version of the manuscript.

Funding: We are grateful for the financial support of the Ministry of Science and Higher Education, Poland (statutory project No. 29.610.024-110).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Zhao, X.; Cornish, K.; Vodovotz, Y. Narrowing the gap for bioplastic use in food packaging: An update. *Environ. Sci. Technol.* **2020**, *54*, 4712–4732.
2. Emadian, S.M.; Onay, T.T.; Demirel, B. Biodegradation of bioplastics in natural environments. *Waste Manag.* **2017**, *59*, 526–536.
3. Biron, M. Environmental and engineering data to support eco-design for plastics. In *A Practical Guide to Plastics Sustainability*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 209–307.
4. European Bioplastic 2019. Bioplastics Packaging-Combining Performance with Sustainability-Materials and Market Development in the Packaging Segment. Fact Sheet European Bioplastic. Available online: www.european-bioplastic.org (accessed on 4 May 2021).
5. John, R.P.; Nampoothiri, K.M.; Pandey, A. Simultaneous saccharification and fermentation of cassava bagasse for L-(+)-lactic acid production using Lactobacilli. *Appl. Biochem. Biotechnol.* **2006**, *134*, 263–272.
6. Riaz, S.; Fatima, N.; Rasheed, A.; Riaz, M.; Anwar, F.; Khatoon, Y. Metabolic engineered biocatalyst: A solution for PLA based problems. *Int. J. Biomater.* **2018**, *2018*, 1963024.
7. Nampoothiri, K.M.; Nair, N.R.; John, R.P. An overview of the recent developments in polylactide (PLA) research. *Bioresour. Technol.* **2010**, *101*, 8493–8501.
8. Ghaffar, T.; Irshad, M.; Anwar, Z.; Aqil, T.; Zulifqar, Z.; Tariq, A.; Kamran, M.; Ehsan, N.; Mehmood, S. Recent trends in lactic acid biotechnology: A brief review on production to purification. *J. Radiat. Res. Appl. Sci.* **2014**, *7*, 222–229.
9. Rodriguez-Gonzalez, F.J.; Ramsay, B.A.; Favis, B.D. Rheological and thermal properties of thermoplastic starch with high glycerol content. *Carbohydr. Polym.* **2004**, *58*, 139–147.
10. Nikolić, M.A.L.; Gauthier, E.; Colwell, J.M.; Halley, P.; Bottle, S.E.; Laycock, B.; Truss, R. The challenges in lifetime prediction of oxodegradable polyolefin and biodegradable polymer films. *Polym. Degrad. Stab.* **2017**, *145*, 102–119.
11. Ojeda, T.F.M.; Dalmolin, E.; Forte, M.M.C.; Jacques, R.J.S.; Bento, F.M.; Camargo, F.A.O. Abiotic and biotic degradation of oxo-biodegradable polyethylenes. *Polym. Degrad. Stab.* **2009**, *94*, 965–970.
12. Napper, I.E.; Thompson, R.C. Environmental deterioration of biodegradable, oxo-biodegradable, compostable, and conventional plastic carrier bags in the sea, soil, and open-air over a 3-year period. *Environ. Sci. Technol.* **2019**, *53*, 4775–4783.
13. Sivan, A. New perspectives in plastic biodegradation. *Curr. Opin. Biotechnol.* **2011**, *22*, 422–426.
14. Shawaphun, S.; Manangan, T.; Wacharawichanant, S. Thermo- and photo- degradation of LDPE and PP films using metal oxides as catalysts. In *Proceedings of the Advanced Materials Research*; Trans Tech Publications Ltd.: Bach, Switzerland, 2010; Volume 93–94, pp. 505–508.
15. Arrieta, M.P.; Samper, M.D.; Aldas, M.; López, J. On the use of PLA-PHB blends for sustainable food packaging applications. *Materials* **2017**,*10*, 1008.
16. Souza, A.C.; Benze, R.; Ferrão, E.S.; Ditch, C.; Coelho, A.C.V.; Tadini, C.C. Cassava starch biodegradable films: Influence of glycerol and clay nanoparticles content on tensile and barrier properties and glass transition temperature. *LWT Food Sci. Technol.* **2012**, *46*, 110–117.
17. de Azevedo, L.C.; Rovani, S., Santos, J.J.; Dias, D.B.; Nascimento, S.S.; Oliveira, F.F.; Silba, L.G.A, Fungaro, D.A. Biodegradable films derived from corn and potato starch and study of the effect of silicate extracted from sugarcane waste ash. *ACS Appl. Polym. Mater.* **2020**, *2*, 2160–2169.
18. Oluwasina, O.O.; Akinyele, B.P.; Olusegun, S.J.; Oluwasina, O.O.; Mohallem, N.D. Evaluation of the effects of additives on the properties of starch-based bioplastic film. *SN Appl. Sci.* **2021**, *3*, 1–12.
19. Martin, O.; Avérous, L. Poly(lactic acid): Plasticization and properties of biodegradable multiphase systems. *Polymers* **2001**, *42*, 6209–6219.
20. Felix, M.; Perez-Puyana, V.; Romero, A.; Guerrero, A. Development of protein-based bioplastics modified with different additives. *J. Appl. Polym. Sci.* **2017**, *134*, 45430.
21. Ljungberg, N.; Wesslén, B. Preparation and properties of plasticized poly(lactic acid) films. *Biomacromolecules* **2005**, *6*, 1789–1796.
22. Shen, M.; Song, B.; Zeng, G.; Zhang, Y.; Huang, W.; Wen, X.; Tang, W. Are biodegradable plastics a promising solution to solve the global plastic pollution? *Environ. Pollut.* **2020**, *263*, 114469.
23. Shruti, V.C.; Kutralam-Muniasamy, G. Bioplastics: Missing link in the era of microplastics. *Sci. Total Environ.* **2019**, *697*, 134139.
24. Fernández-Domínguez, D.; Astals, S.; Peces, M.; Frison, N.; Bolzonella, D.; Mata-Alvarez, J.; Dosta, J. Volatile fatty acids production from biowaste at mechanical-biological treatment plants: Focusing on fermentation temperature. *Bioresour. Technol.* **2020**, *314*, 123729.
25. Capson-Tojo, G.; Rouez, M.; Crest, M.; Steyer, J.P.; Delgenès, J.P.; Escudié, R. Food waste valorization via anaerobic processes: A review. *Rev. Environ. Sci. Biotechnol.* **2016**, *15*, 499–547.
26. Dahiya, S.; Kumar, A.N.; Shanthi Sravan, J.; Chatterjee, S.; Sarkar, O.; Mohan, S.V. Food waste biorefinery: Sustainable strategy for circular bioeconomy. *Bioresour. Technol.* **2018**, *248*, 2–12.

27. Lin, L.; Xu, F.; Ge, X.; Li, Y. Improving the sustainability of organic waste management practices in the food-energy-water nexus: A comparative review of anaerobic digestion and composting. *Renew. Sustain. Energy Rev*. **2018**, *89*, 151–167.
28. ISO 14853:2016, Plastics–Determination of the Ultimate Anaerobic Biodegradation of Plastic Materials in an Aqueous System–Method by Measurement of Biogas Production. Available online: https://www.iso.org/standard/67804.html (accessed on 4 May 2021).
29. Massardier-Nageotte, V.; Pestre, C.; Cruard-Pradet, T.; Bayard, R. Aerobic and anaerobic biodegradability of polymer films and physico-chemical characterization. *Polym. Degrad. Stab*. **2006**, *91*, 620–627.
30. ASTM D5526, Standard Test Method for Determining Anaerobic Biodegradation of plastic Materials under Accelerated Landfill Conditions. Available online: https://www.astm.org/Standards/D5526.htm (accessed on 4 May 2021).
31. EN 13432 Standard, Requirements for Packaging Recoverable through Composting and Biodegradation—Test Scheme and Evaluation Criteria for the Final Acceptance of Packaging. Available online: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32001D0524 (accessed on 4 May 2021).
32. Zhang, W.; Heaven, S.; Banks, C.J. Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste. *Polym. Degrad. Stab*. **2018**, *147*, 76–88.
33. Noda, I.; Lindsey, S.B.; Caraway, D. *NodaxTM Class PHA Copolymers: Their Properties and Applications*; Springer: Berlin/Heidelberg, 2010; pp. 237–255.
34. Kolstad, J.J.; Vink, E.T.H.; De Wilde, B.; Debeer, L. Assessment of anaerobic degradation of IngeoTM polylactides under accelerated landfill conditions. *Polym. Degrad. Stab*. **2012**, *97*, 1131–1141.
35. Yagi, H.; Ninomiya, F.; Funabashi, M.; Kunioka, M. Mesophilic anaerobic biodegradation test and analysis of eubacteria and archaea involved in anaerobic biodegradation of four specified biodegradable polyesters. *Polym. Degrad. Stab*. **2014**, *110*, 278–283.
36. Bátori, V.; Åkesson, D.; Zamani, A.; Taherzadeh, M.J.; Sárvári Horváth, I. Anaerobic degradation of bioplastics: A review. *Waste Manag*. **2018**, *80*, 406–413.
37. Greenberg, A.E.; Clesceri, L.S.; Eaton, A.D. *Standard Methods for the Examination of Water and Wastewater*, 18th ed., APHA: Washington, DC, USA, 1992.
38. Buswell, A.M.; Mueller, H.F. Mechanism of Methane Fermentation. *Ind. Eng. Chem*. **1952**, *44*, 550–552.
39. Shin, P.K.; Kirn, M.H.; Kim, J.M. Biodegradability of degradable plastics exposed to anaerobic digested sludge and simulated landfill conditions. *J. Environ. Polym. Degrad*. **1997**, *5*, 33–39.
40. Lucas, N.; Bienaime, C.; Belloy, C.; Queneudec, M.; Silvestre, F.; Nava-Saucedo, J.E. Polymer biodegradation: Mechanisms and estimation techniques—A review. *Chemosphere* **2008**, *73*, 429–442.
41. Sevim, K.; Pan, J. A model for hydrolytic degradation and erosion of biodegradable polymers. *Acta Biomater*. **2018**, *66*, 192–199.
42. Zimmermann, M.V.G.; Brambilla, V.C.; Brandalise, R.N.; Zattera, A.J. Observations of the effects of different chemical blowing agents on the degradation of poly(lactic acid) foams in simulated soil. *Mater. Res*. **2013**, *16*, 1266–1273.
43. Lee, J.C.; Moon, J.H.; Jeong, J.H.; Kim, M.Y.; Kim, B.M.; Choi, M.C.; Kim, J.R.; Ha, C.S. Biodegradability of poly(lactic acid) (PLA)/lactic acid (LA) blends using anaerobic digester sludge. *Macromol. Res*. **2016**, *24*, 741–747.
44. Fortunati, E.; Armentano, I.; Iannoni, A.; Barbale, M.; Zaccheo, S.; Scavone, M.; Visai, L.; Kenny, J.M. Newmultifunctional poly(lactide acid) composites: Mechanical, antibacterial, and degradation properties. *J. Appl.Polym. Sci.* **2012**, *124*, 87–98.
45. Arrieta, M.P.; López, J.; Rayón, E.; Jiménez, A. Disintegrability under composting conditions of plasticized PLA–PHB blends. *Polym. Degrad. Stab*. **2014**, *108*, 307–318.
46. Kliem, S.; Kreutzbruck, M.; Bonten, C. Review on the biological degradation of polymers in various environments. *Materials* **2020**, *13*, 4586.
47. Ebadi-Dehaghani, H.; Barikani, M.; Borhani, S.; Bolvardi, B.; Khonakdar, H.A.; Jafari, S.H. Biodegradation and hydrolysis studies on polypropylene/polylactide/organo-clay nanocomposites. *Polym Bull*. **2016**, *73*, 3287–3304.
48. Hakkarainen, M.; Karlsson, S.; Albertsson, A.C. Rapid (bio)degradation of polylactide by mixed culture of compost microorganisms—low molecular weight products and matrix changes. *Polymer* **2000**, *41*, 2331–2338.
49. Aldas, M.; Ferri, J.M.; Lopez-Martinez, J.; Samper, M.D.; Arrieta, M.P. Effect of pine resin derivatives on the structural, thermal, and mechanical properties of Mater-Bi type bioplastic. *J. Appl. Polym. Sci*. **2019**, *137*, 48236.
50. Correa, A.C.; Carmona, V.B.; Simão, J.A.; Capparelli Mattoso, L.H.; Marconcini, J.M. Biodegradable blends of urea plasticized thermoplastic starch (UTPS) and poly(ε-caprolactone) (PCL): Morphological, rheological, thermal and mechanical properties. *Carbohydr. Polym*. **2017**, *167*, 177–184.
51. Abdullah, A.H.D.; Putri, O.D.; Sugandi, W.W. Effects of starch-glycerol concentration ratio on mechanical and thermal properties of cassava starch-based bioplastics. *J. Sains Mater. Indones*. **2019**, *20*, 162.
52. Contat-Rodrigo, L. Thermal characterization of the oxo-degradation of polypropylene containing a pro-oxidant/pro-degradant additive. *Polym. Degrad. Stab*. **2013**, *98*, 2117–2124.
53. Benítez, A.; Sánchez, J.J.; Arnal, M.L.; Müller, A.J.; Rodríguez, O.; Morales, G. Abiotic degradation of LDPE and LLDPE formulated with a pro-oxidant additive. *Polym. Degrad. Stab*. **2013**, *98*, 490–501.
54. Ruggero, F.; Onderwater, R.C.A.; Carretti, E.; Roosa, S.; Benali, S.; Raquez, J.M.; Gori, R.; Lubello, C.; Wattiez, R. Degradation of film and rigid bioplastics during the thermophilic phase and the maturation phase of simulated composting. *J. Polym. Environ*, **2021**, 1–14. https://doi.org/10.1007/s10924-021-02098-2.
55. Socrates, G. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*; John Wiley & Sons: Hoboken, NJ, USA, 2004.

56. Azevedo, H.S.; Gama, F.M.; Reis, R.L. In vitro assessment of the enzymatic degradation of several starch based biomaterials. *Biomacromolecules* **2003**, *6*, 1703–1712.
57. Bandini, F.; Frache, A.; Ferrarini, A.; Taskin, E.; Cocconcelli, P.S.; Puglisi, E. Fate of biodegradable polymers under industrial conditions for anaerobic digestion and aerobic composting of food waste. *J. Polym. Environ.* **2020**, *28*, 2539–2550.

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Magdalena Zaborowska, oświadczam, że mój wkład naukowy w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Anaerobic degradability of commercially available bio-based and oxo-degradable packaging materials in the context of their end of life in the waste management strategy. *Sustainability*, 13(12), 6818.

Mój udział jako współautora publikacji obejmował:

- ☒ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☒ Udział w graficznym przedstawieniu wyników
- ☒ Udział w planowaniu badań
- ☒ Prowadzenie badań i analiz laboratoryjnych
- ☐ Konsultacja i opieka
- ☒ Udział w interpretacji wyników i wnioskowaniu
- ☒ Korekta pracy przed złożeniem do druku

07.07.2023 Magdalena Zaborowska
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Katarzyna Bernat, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Anaerobic degradability of commercially available bio-based and oxo-degradable packaging materials in the context of their end of life in the waste management strategy. *Sustainability*, 13(12), 6818.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☒ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☒ Udział w graficznym przedstawieniu wyników
- ☒ Udział w planowaniu badań
- ☐ Prowadzenie badań i analiz laboratoryjnych
- ☒ Konsultacja i opieka
- ☒ Udział w interpretacji wyników i wnioskowaniu
- ☒ Korekta pracy przed złożeniem do druku

7.07.2023r. Katarzyna Bernat

data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Bartosz Pszczółkowski, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Anaerobic degradability of commercially available bio-based and oxo-degradable packaging materials in the context of their end of life in the waste management strategy. *Sustainability*, 13(12), 6818.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☐ Współautorstwo w przygotowaniu koncepcji pracy
- ☐ Udział w pisaniu pracy
- ☒ Udział w graficznym przedstawieniu wyników
- ☐ Udział w planowaniu badań
- ☒ Prowadzenie badań i analiz laboratoryjnych
- ☐ Konsultacja i opieka
- ☒ Udział w interpretacji wyników i wnioskowaniu
- ☐ Korekta pracy przed złożeniem do druku

07.07.2023 ....
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Irena Wojnowska-Baryła, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Anaerobic degradability of commercially available bio-based and oxo-degradable packaging materials in the context of their end of life in the waste management strategy. *Sustainability*, 13(12), 6818.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

☐ Współautorstwo w przygotowaniu koncepcji pracy

☒ Udział w pisaniu pracy

☐ Udział w graficznym przedstawieniu wyników

☐ Udział w planowaniu badań

☐ Prowadzenie badań i analiz laboratoryjnych

☒ Konsultacja i opieka

☐ Udział w interpretacji wyników i wnioskowaniu

☐ Korekta pracy przed złożeniem do druku

6.07.2023 Wojnowska-B
……………………………………
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Dorota Kulikowska, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Anaerobic degradability of commercially available bio-based and oxo-degradable packaging materials in the context of their end of life in the waste management strategy. *Sustainability*, 13(12), 6818.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☐ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☐ Udział w graficznym przedstawieniu wyników
- ☐ Udział w planowaniu badań
- ☐ Prowadzenie badań i analiz laboratoryjnych
- ☒ Konsultacja i opieka
- ☐ Udział w interpretacji wyników i wnioskowaniu
- ☐ Korekta pracy przed złożeniem do druku

..06.07.2023...........................

data i podpis

Article

Challenges in Sustainable Degradability of Bio-Based and Oxo-Degradable Packaging Materials during Anaerobic Thermophilic Treatment

Magdalena Zaborowska [1,*], Katarzyna Bernat [1], Bartosz Pszczółkowski [2], Irena Wojnowska-Baryła [1] and Dorota Kulikowska [1]

[1] Department of Environmental Biotechnology, Faculty of Geoengineering, University of Warmia and Mazury in Olsztyn, 10-719 Olsztyn, Poland; bernat@uwm.edu.pl (K.B.); irka@uwm.edu.pl (I.W.-B.); dorotak@uwm.edu.pl (D.K.)

[2] Department of Materials and Machines Technology, University of Warmia and Mazury in Olsztyn, ul. Oczapowskiego 11, 10-719 Olsztyn, Poland; bartosz.pszczolkowski@uwm.edu.pl

* Correspondence: magdalena.zaborowska@uwm.edu.pl; Tel.: +48-89-523-4118; Fax: +48-89-523-4131

Abstract: Although the manufacturers labelled commercially available bio-based products as biodegradable, there are discrepancies concerning the time frame for their sustainable biodegradation and methane production. Starch-based, polylactic acid-based and oxo-degradable foils were anaerobically treated in thermophilic condition (55 °C, 100 days). The effect of alkaline pretreatment on foils degradation was also investigated. To examine changes in their mechanical and physical properties, static tensile tests and microscopic analyses, FTIR and surface roughness analyses were conducted. Despite the thermophilic condition, and the longer retention time compared to that needed for biowaste, a small amount of methane was produced with bio-based foils, even after pretreatment (ca. 30 vs. 50 L/kg VS) and foils only lost functional and mechanical properties. The pieces of bio-based materials had only disintegrated, which means that digestate may become contaminated with fragments of these materials. Thus, providing guidelines for bio-based foil treatment remains a challenge in waste management.

Keywords: biopolymers; starch- and polylactic acid-based material; methane production; surface roughness; tensile strength; FTIR and microscopic analyses

Citation: Zaborowska, M.; Bernat, K.; Pszczółkowski, B.; Wojnowska-Baryła, I.; Kulikowska, D. Challenges in Sustainable Degradability of Bio-Based and Oxo-Degradable Packaging Materials during Anaerobic Thermophilic Treatment. *Energies* **2021**, *14*, 4775. https://doi.org/10.3390/en14164775

Academic Editor: Gabriele Di Giacomo

Received: 1 July 2021
Accepted: 30 July 2021
Published: 5 August 2021

1. Introduction

Bio-based products are defined as entirely or partially biological in origin. Among the bio-based products, biodegradable polymers (biopolymers) play an important role. Biopolymers can be degraded by microorganisms into water and biomass, and depending on whether oxygen is present, into carbon dioxide under aerobic conditions, or into carbon dioxide and methane under anaerobic conditions. In recent years, the share of biopolymers on the market has been increasing and, in 2019, 1.174 million tons were produced at a global level. Further increases in the share of these plastics on the market are expected (i.e., 1.334 million tons by 2024) [1,2].

One of the most known biopolymers is polylactide (PLA), which is produced by the polymerization of lactic acid via the fermentation of dextrose derived from carbohydrate-rich crops, such as potatoes or corn. PLA is widely used because of its properties, including its biodegradability, biocompatibility, high elastic modulus, transparency and mechanical strength [3]. The other commonly used natural polymer (meaning that it is produced directly in nature) is starch, which is, more specifically, a reserve polysaccharide composed of amylopectin (75−80%) and amylose (20−25%). Starch is used due to its abundance, inexpensiveness, and biodegradability. It is known that, on the market, apart from biopolymers, oxo-degradable polymers are still used in some countries [4]. They contain pro-degradants (e.g., d2w® or TDPA (totally degradable plastic additives)), usually produced from cobalt, manganese, and iron compounds, which should ensure the polymer decomposition. Some authors indicate that oxo-degradable polymers may be partially biodegradable, e.g., with mineralization level of 12.4% after three months of incubation with compost [5].

Among the bio-based and oxo-degradable products present on the market, the most popular are materials used for food packaging or waste bags for biowaste collection. Because they are labelled as biodegradable, these products should be separately collected, together with biowaste. Thus, most of the waste from these products is eventually gathered and processed, aerobically or anaerobically, in mechanical–biological treatment plants (MBT installations), or via a combination of the two methods. Because the share of biodegradable polymers in the stream of selectively collected biowaste will likely continue to increase, it is important to better understand the mechanisms and characteristics of their degradation. Most studies have focused on the biodegradation of biopolymers under environmental conditions, i.e., in soil, compost, and aquatic environments [6]. In aerobic conditions, the characteristics of the process depend on the types of polymers involved (i.e., their molecular weight, crystallinity or type of functional groups) and environmental factors (i.e., temperature, moisture, pH, and presence of oxygen) [7,8]. However, knowledge concerning the possibility of polymer degradation under anaerobic conditions is limited, especially in the context of commonly used methods for the treatment of biowaste. Therefore, it is necessary to determine the conditions that facilitate biodegradation of bio-based and oxo-degradable products and the characteristics of this process. Anaerobic processes seem to be especially profitable because they produce methane, which can be used for energy generation. However, because of amount of time needed for methane production from bio-based products [9], pretreatment is needed. The use of pretreatment may increase the surface area of the material, resulting in more rapid degradation and improved methane production [10]. For example, Yu et al. [11] reported over 70% abiotic degradation of PHB at 70 °C in 4 M sodium hydroxide after 4 h of treatment. However, the treatment of PHB in acidic solutions of sulfuric acid (0.05–2 M) at 70 °C for up to 14 h did not result in abiotic degradation. Myung et al. [12] observed the near complete abiotic degradation of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) at 60 °C in 0.1 M sodium hydroxide after 18 h of treatment.

In conclusion, despite many commercial products on the market being labeled as biodegradable, their detailed compositions are not provided by manufacturers. The content of the polymer and various types of additives in the products can differ, but most likely, the composition affects the biodegradability of polymers and the time frame for their biodegradation, especially in the context of their end-of-life considerations in waste management. Thus, in the present study, degradability and methane production (MP) from commercially available bio-based foils based on starch (FS), polylactic acid (PLA), and additionally oxo-degradable product (OXO), was analyzed. Moreover, alkaline pretreatment was used to check the acceleration of the process. Microscopic and FTIR analyses, and determination of the functional properties of the surfaces and the mechanical properties of the materials (static tensile tests) were also performed. Determination of the mechanical properties of material, as another indicator of its degradation, is not a common practice.

2. Materials and Methods

2.1. Bio-Based and Oxo-Degradable Materials Used in the Experiment

In the experiment, commonly available waste bags made of bio-based materials and oxo-degradable material were used. As bio-based materials, BioBag waste bags made from Mater-Bi® material based on starch (FS) and bags made from polylactic acid (PLA) were used. The oxo-degradable waste bag (OXO) was made from petroleum-based polyethylene containing d2w pro-degradant additive. The characteristics of the materials are as follows:

- PLA (the VS content of 99.3 % DM, 71.5 g COD/kg DM, 454.9 mg N_{tot}/kg DM);
- FS (the VS content of 99.9 % DM, 63.9 g COD/kg DM, 408.6 mg N_{tot}/kg DM);

- OXO (the VS content of 93.1 % DM, 3766.8 mg N_{tot}/kg DM (COD was not possible to determine)).

The products were obtained from the commercial public market; thus, they may have contained other additives, improving their functional properties but, unfortunately, the manufacturer did not report their detailed composition. The waste bags were shredded to a particle size of 10 × 10 mm.

Two sets of experiments were carried out. In the first, all materials (PLA, FS, OXO) were used without pretreatment. In the second set, PLA, FS and OXO were pretreated with 0.1 M potassium hydroxide (KOH) for 2 h; pretreatment was performed at ambient temperature (PLA_{KOH}, FS_{KOH}, OXO_{KOH}). After 2 h, the mixture was neutralized with hydrochloric acid. Solubilized PLA ($PLA_{solubilized}$) and FS ($FS_{solubilized}$) were used as control samples. Each material was solubilized with the use of 1 M KOH for 24 h. The OXO material did not solubilize under these conditions.

2.2. Measurement of Methane Production (MP) under Thermophilic Conditions

The anaerobic degradation test of bio-based and oxo-degradable products was carried out in thermophilic conditions (55 °C). The experiment was carried out in a methane potential analysis device (Automatic Methane Potential Test System, AMPTS II, Bioprocess Control, Sweden AB) for 100 days. The device consisted of reactors with a volume of 630 mL. The reactors were mixed at a speed of 80 rpm for 1 min every hour. To each reactor, 200 mL of inoculum and the appropriate amount of material was added to ensure a starting organic load of 4 kg VS/m^3. Anaerobic conditions were achieved by flushing each reactor with pure nitrogen for 2 min. The inoculum was obtained from a closed chamber for the mesophilic anaerobic digestion of sewage sludge. Thermophilic preincubation of the inoculum was carried out at 55 °C for 14 days. The dry mass (DM) content of the inoculum was approximately 1.7%, whereas VS constituted 69.5% of DM.

The anaerobic degradation test was based on determining the volume of methane produced online. The measurement of MP with each material and inoculum, and with inoculum alone was performed in triplicate. In order to not disturb the MP in the AMPTS II, additional glass bottles were prepared for sampling for microscopic analysis, and roughness and static tensile tests. These bottles had the same volume as the reactors used in the AMPTS II and were dosed with the same amount of inoculum and material, and placed in a thermostatic incubator at 55 °C. When the fragments of bio-based and oxo-degradable materials were collected for analysis, they were cleaned with distilled water.

Based on the anaerobic degradation test in the methane potential system, the biodegradation degree (BD) was assumed. The BD of the bio-based materials (PLA, FS, PLA_{KOH} and FS_{KOH}) during anaerobic treatment at 55 °C was calculated as the ratio of the cumulative MP from the material (after pretreatment (treated) or without pretreatment (untreated)) to the cumulative MP from the material after its solubilization. The cumulative MP from the solubilized material was assumed to be the maximal MP from this material under the experimental conditions. For the OXO material, which did not solubilize, the BD was not determinable.

Methane production (MP) followed pseudo first-order kinetics, and can be described with this equation:

$$C_{t,CH4} = C_{CH4} \cdot (1 - e^{kCH4}\ t) + C_{0,CH4}, \tag{1}$$

where $C_{t;CH4}$ (L/kg VS) is the cumulative MP at time t (days) of anaerobic measurement; C_{CH4} (L/kg VS) is the maximal MP; $C_{0,CH4}$ (L/kg VS) is the initial MP; k_{CH4} (d^{-1}) is the kinetic coefficient of MP.

The rate of MP is the product of C_{CH4} and k_{CH4}.

The values of C_{CH4}, $C_{0,CH4}$ and k_{CH4} were obtained by nonlinear regression analysis with Statistica software, version 13.0 (StatSoft, Tulsa, OK, USA).

2.3. Microscopic and FTIR Analysis

During anaerobic degradation tests, pieces of FS, PLA, OXO, PLA_{KOH}, FS_{KOH}, and OXO_{KOH} were removed from the inoculum and cleaned with distilled water for the microscopic analysis, and the roughness and static tensile tests.

The changes on the surface of the bio-based and oxo-degradable materials were analyzed using a Nikon eclipse50i (Nikon, Tokyo, Japan) polarizing microscope at a magnification of 10×. Pictures were taken at 0, 20, 45, 59 and 100 days.

The FTIR spectra (with three replicates for each foil material) were obtained using a Perkin Elmer Spectrum Two (with diamond ATR) (Perkin Elmer, Waltham, MA, USA) brand device having a resolution of 4 cm^{-1} within the wavenumber range of 4000–400 cm^{-1} at room temperature.

2.4. Functional Properties of the Surface

The geometric structure of the surface and the functional properties of the fragments of foils (five replications) were performed with the profile method (PN-ISO 3274) using a Mitutoyo Surftest SJ-210 profilometer (Mitutoyo, Kawasaki, Japan) with a diamond measuring tip with a point angle of 60° and a stylus radius of 2 µm. The measured length for each material consisted of five elementary sections that were 0.8 mm long. The changes in amplitude (arithmetical mean roughness value (Ra), mean square surface profile deviation (Rq)) were determined. The Abbott–Firestone curves [13] were used to determine the reduced peak height without bearing properties (Rpk); the roughness core height (roughness core profile), characterizing the surface bearing properties (Rk); the reduced valleys depth, characterizing the ability of the surface to hold liquids (Rvk); total height of the roughness profile (Rt) and the percentage of the peaks and valleys (Mr1, Mr2, respectively). A detailed description is given in [14].

2.5. Static Tensile Tests

Static tensile tests (tensile strength at break and elongation at break) were performed according to ISO standard (ISO 527-2:2012, ISO 527-3:2019) with the use of a TA.HD.Plus (Stable Microsystems, Surrey, UK). Five replicate samples of foils were used for the measurements until they were too fragile for analysis, and it was impossible to place them in the tensile test device. The samples were subjected to a tensile force at a constant speed until the moment of fracture.

2.6. Analytical Methods

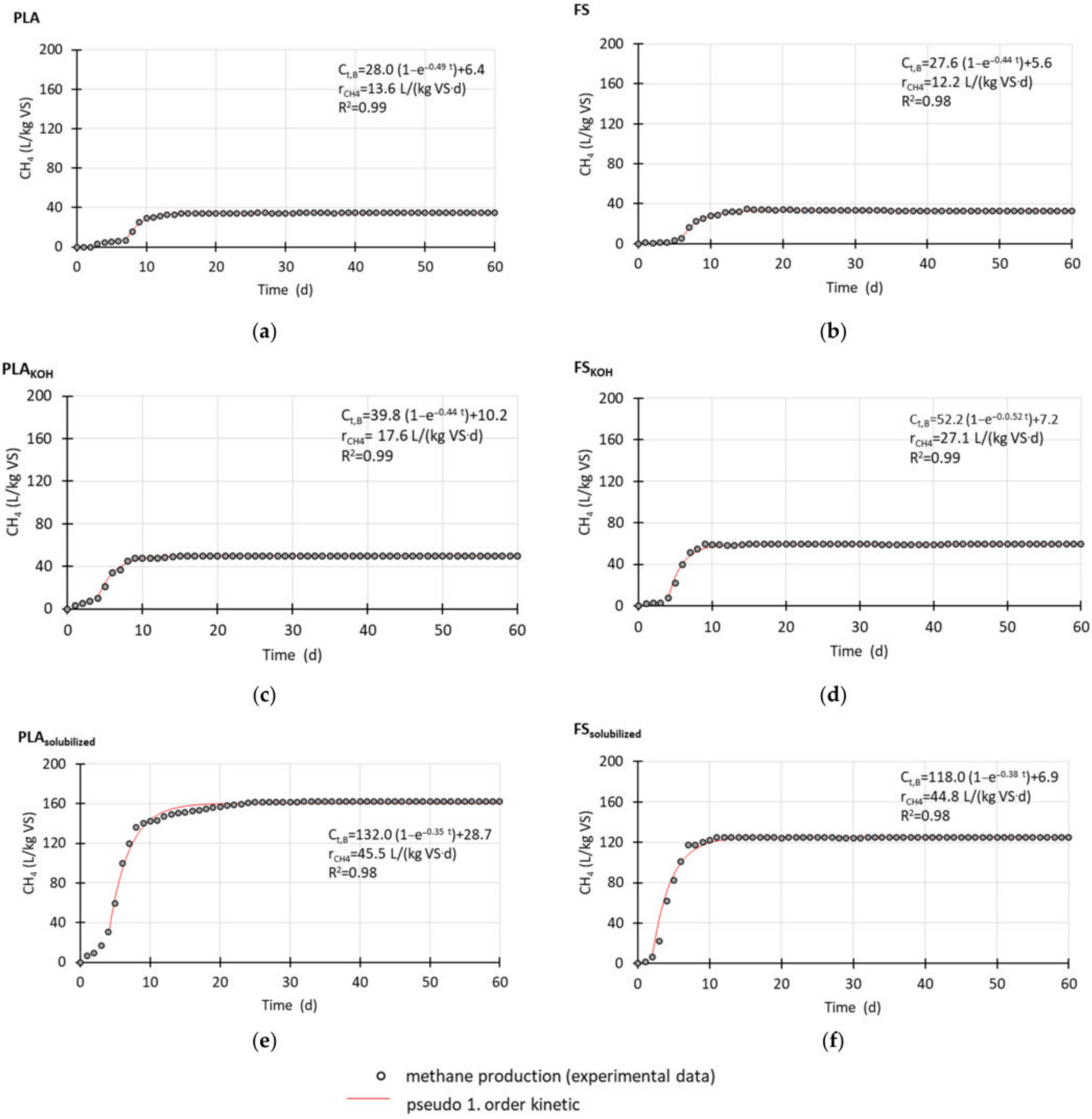
The volatile substance (VS) content of the FS, PLA and OXO materials was determined as loss after ignition at 550 °C. The chemical oxygen demand (COD) of these materials and the content of nitrogen (Kiejdahl nitrogen) were also determined. All physicochemical analyses were performed according to Greenberg et al. [15]. Flash 2000 Organic Elemental Analyzer (Thermo Scientific, Milan, Italy) was used to determine elemental composition of bio-based materials according to the manufacturer's protocol.

3. Results and Discussion

3.1. Methane Production during Anaerobic Test

Biodegradation anaerobic of pieces of waste bags made of PLA, FS, OXO, and also the materials after pretreatment (PLA_{KOH}, FS $_{KOH}$, and OXO_{KOH}) were carried out under thermophilic conditions at 55 °C. The MP analysis tool allowed measurement of the volume of methane (in mL) produced online. Two MP profiles are considered during the analyses of each material: the first profile corresponds to the inoculum alone, and the second, to both the inoculum and the material. By subtracting the values of the first profile from the second, the profile of the methane volume for the material alone is obtained. In the present study, the VS content of the materials was considered to reflect the organic matter content, and the MP was shown as L/kg VS (Figure 1). To improve the readability of the figure, 60 days of measurements are shown, although the time of measurements was ca.

100 days. The OXO material did not degrade; thus, no MP was observed, and the profiles are not provided.



(a) (b) (c) (d) (e) (f)

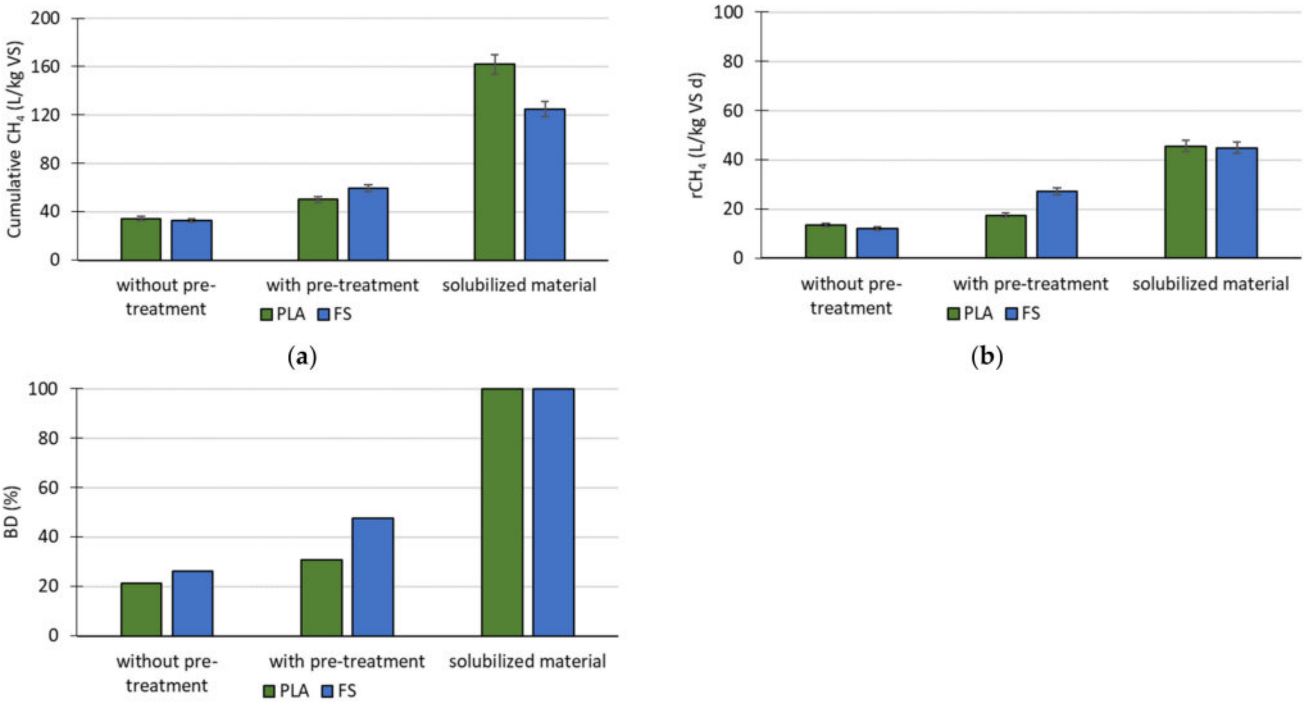
Figure 1. Methane production profiles during an anaerobic degradation test at 55 °C of bio-based materials made of PLA and FS without pretreatment (**a**,**b**), of these materials with pretreatment (**c**,**d**), and solubilized materials (**e**,**f**); to improve the readability of the figure, 60 days of measurements are shown, although the time of measurements was ca. 100 days.

Regarding bio-based materials made of PLA and FS without pretreatment, lag phases in MP were observed. With FS, the lag phase was shorter, lasting 6 days, whereas with PLA, it lasted 7 days. After the lag phase, MP increased until day 15 or 16 of measurements. Then, the methane volumes remained the same until the end of the anaerobic test, which lasted almost 100 days, and the final methane volumes for PLA and FS were similar, 34.5 and 32.7 L/kg VS, respectively.

After pretreatment, the lag phases shortened to 4 days for both PLA_{KOH} and FS_{KOH}, and after this time, intensive MP took place. After the lag phase, during next 6 days of measurement, PLA_{KOH} produced 47.5 L/kg VS, whereas FS_{KOH} produced almost 25% more, 58.6 L/kg VS.

When solubilized materials were investigated in anaerobic degradation tests, it was found that MP started from the beginning of the measurements. After 15 and 12 days of the measurements with $PLA_{solubilized}$ and $FS_{solubilized}$, respectively, MP reached maximum. Despite the fact that PLA needed a longer time to obtain maximum MP, the final value was 1.3 times higher than MP with FS (162 L/kg VS for $PLA_{solubilized}$ vs. 125 L/kg VS for $FS_{solubilized}$).

Cumulative MP after 100 days of anaerobic treatment of PLA and FS, without pretreatment, with pretreatment, and the solubilized materials, is shown in Figure 2a. To summarize, cumulative MP was similar with both materials without pretreatment. After pretreatment, cumulative MP with PLA_{KOH} and FS_{KOH} increased almost 40% and 80%, respectively; with the solubilized materials, it was highest. However, the values were much lower than with pure PLA and pure starch materials.



(**a**) (**b**)

(**c**)

Figure 2. Cumulative methane production after 100 days of anaerobic degradation of PLA and FS (**a**), the rate of methane production (**b**), and the biodegradation degree (BD) (**c**).

Methane production proceeded with first-order kinetics, and the model fit the experimental data well ($R^2 = 0.98–0.99$). The kinetic models and the initial rates of MP are shown in Figure 1.

The rates of MP, summarized in Figure 2b, corresponded with the cumulative MP with untreated and treated materials. However, the rates of MP with both solubilized materials were similar, despite the difference in cumulative MP.

It was assumed that the solubilized materials ($PLA_{solubilized}$ and $FS_{solubilized}$, i.e., control samples) produced the maximal methane volume, and this equaled 100% of the biodegradation degree (BD) of these materials. For PLA without pretreatment and FS without pretreatment, BD was higher for FS, but for both of the materials, it did not exceed 26% in comparison with solubilize materials. The BD of PLA_{KOH} FS_{KOH} increased to 30 and 47.5%, respectively (Figure 2c).

It should be emphasized that, during the long-term anaerobic biodegradation test, the pieces of the materials were still visible in the inoculum, and they did not disintegrate, as shown by the microscopic analyses.

The elemental compositions of the bio-based products, PLA and FS, were determined (Table 1).

Table 1. Elemental composition, empirical formula, and theoretical methane production (TMP) of foil materials (PLA, FS) and of pure polymers (pure PLA, pure FS).

Characteristics	Pure PLA	PLA	Pure FS	FS
Empirical formula	$C_3H_4O_2$	$C_{4.4}H_{6.31}O_2$	$C_6H_{10}O_5$	$C_{9.8}H_{14.7}O_5$
Elemental composition				
Carbon, % TS	50.00	57.56	44.44	55.36
Hydrogen, % TS	5.56	6.88	6.17	6.90
Oxygen, % TS	44.44	34.86	49.38	37.64
Methane production				
* TMP, L/kg	467	610	413	577
** MP, L/kg	–	162	–	125

* TMP calculated using the Buswell equation [16]; ** cumulative methane production (MP) after 100 days of anaerobic thermophilic treatment of solubilized PLA and FS.

PLA contained more carbon and less oxygen than S. The hydrogen content of both foils was about 6.9%. However, it must be emphasized that both foils (PLA, FS) contained more C and H than pure PLA and pure FS, with lower content of O.

The FS foil material is described by the manufacturer as consisting mainly (as much as 85% or more) of modified thermoplastic starch that is biodegradable and compostable [17]. On the basis of the elementary composition of the foil materials and pure polymers (pure PLA, pure FS), the theoretical amounts of methane (TMP) and carbon dioxide that could be obtained, assuming complete conversion of organics into biogas, were calculated using the Buswell equation [16]:

$$C_aH_bO_c + \left(a - \frac{b}{4} - \frac{c}{2}\right) H_2O \rightarrow \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4}\right) CO_2 + \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4}\right) CH_4 \quad (2)$$

The TMP values of pure PLA and pure FS were approximately 1.3–1.4-times lower than those of the PLA and FS foils, due to the lower carbon and hydrogen contents of the pure materials (Table 1). As for the cumulative MP during anaerobic digestion at 55° C, PLA and FS produced more than two-times less methane than $PLA_{solubilized}$ and $FS_{solubilized}$. However, even solubilized materials produced methane in amounts constituted only 27% and 22%, respectively, of the TMP values. The small amount of methane produced by all the bio-based materials is connected with the fact that, until 100 days of anaerobic degradation had passed, pieces of the foils were still visible in the inoculum, and these fragments only disintegrated when they were touched.

The results concerning anaerobic treatment of starch-based material are scarce. For example, Mohee et al. [18] found that the cumulative methane production from starch-based material was of 245 mL over 32 days of batch digestion assays. The value was much higher than that obtained in the present study; however, the authors did not provide the initial doses of the material. Therefore, it is not known what the methane production was per 1 g VS, and the efficiency of the process cannot be estimated.

Studies with PLA are more numerous, however, most of them are carried out with the used of pure polymer, not with commercially available foil materials. Itävaara et al. [19] found that at temperatures of 37 °C during 40 days of measurements PLA degradation was not higher than 5%. They reported 60% of PLA degradation after 100 days of an anaerobic test without providing more specific information. Under thermophilic conditions, about 60% of PLA was also degraded, but after 40 days. Contrarily, the results of Yagi et al. [20] showed that PLA biodegradability was 80–91% in aquatic conditions at a thermophilic temperature. In another study, Yagi et al. [21] found approximately 60% biodegradability of PLA powder of 90% in 60 days under thermophilic conditions. However, these studies focused on the biodegradation degree but without determination of the efficiency of methane production. The recovery of energy from municipal waste one of the main key points of the strategy of circular economy. Thus, it is important to determine the biogas potential of packaging materials (foils) considered to be biodegradable. This was done in the present study.

3.2. Changes in the Structure of Tested Materials—Microscopic Analysis

At the beginning, the foil pieces of the investigated materials looked like typical foil waste bag materials, and all of them were green in color and smooth.

Microscopic images of the structure of untreated and treated foils were present in Figure 3. Regarding the structure of FS, the changes were visible from the 28th day of degradation, whereas changes in the structure of PLA were visible from about the 59th day. When the changes became apparent, there were individual cracks and fissures in the structure. After this time, the cracks and fissures had become deeper and more numerous on the surface. Unfortunately, both of the bio-based materials did not disintegrate completely, and they were still visible until almost 100 days of anaerobic treatment. The use of the pretreatment step did not facilitate the process of disintegration of the bio-based foils. The visible changes, in the form of cracks and fissures, appeared on the surface of foils around the same time as in the variant without pretreatment. However, the pretreatment step caused the foil pieces to become severely weakened and fragile, so that they crumbled when touched after a shorter time of degradation.

As mentioned, the OXO foil did not produce methane, and microscopic analyses did not show any structural changes even after the pretreatment step.

3.3. Changes in the Mechanical Properties of the Materials

During the anaerobic degradation test, the mechanical properties of the foils before and after the pretreatment were investigated. The results of tensile strength are presented in Figure 4a,b. Regarding the untreated OXO material, the tensile strength decreased by about 17.5 ± 6.8% in the first 10 days of the experiment. Then, until the end of the test, the tensile strength remained at a similar level. The initial decrease could result from the presence of the oxo-degradant, which may weaken the mechanical properties of polyethylene (PE) under thermophilic conditions [22,23].

Regarding the bio-based products without pretreatment, a decrease in tensile strength was observed, which indicated that degradation was progressing (Figure 4). It was possible to measure the tensile strength of FS until to the 39th day of the anaerobic degradation test, at which point the tensile strength had decreased by almost three fold. After this time, the foil was too brittle to be subjected to the strength test and it was not possible to place particles of FS in the measuring device. During the first 10 days, the tensile strength decreased sharply, from 16.6 ± 0.8 MPa in the raw material, to 11.1 ± 0.7 MPa. After this time, the tensile strength continued to decrease steadily, and after 39 days, it reached 5.9 ± 0.9 MPa (Figure 4a).

Tensile strength measurements of PLA were possible until the 59th day of the test, which means that, in this regard, the material was more resistant than FS.

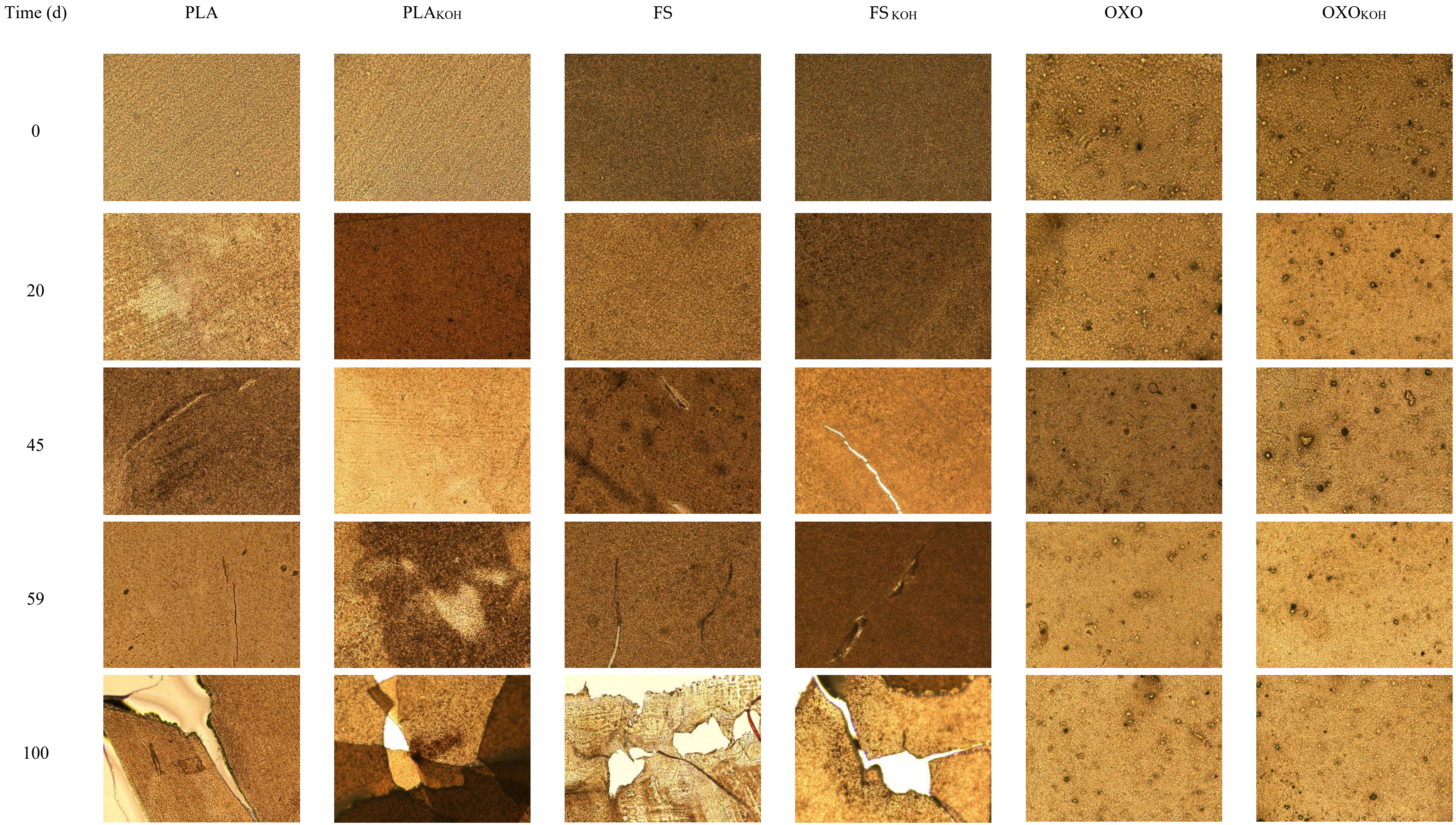


Figure 3. Microscopic images of the structure of untreated and treated foil materials during anaerobic thermophilic degradation test.

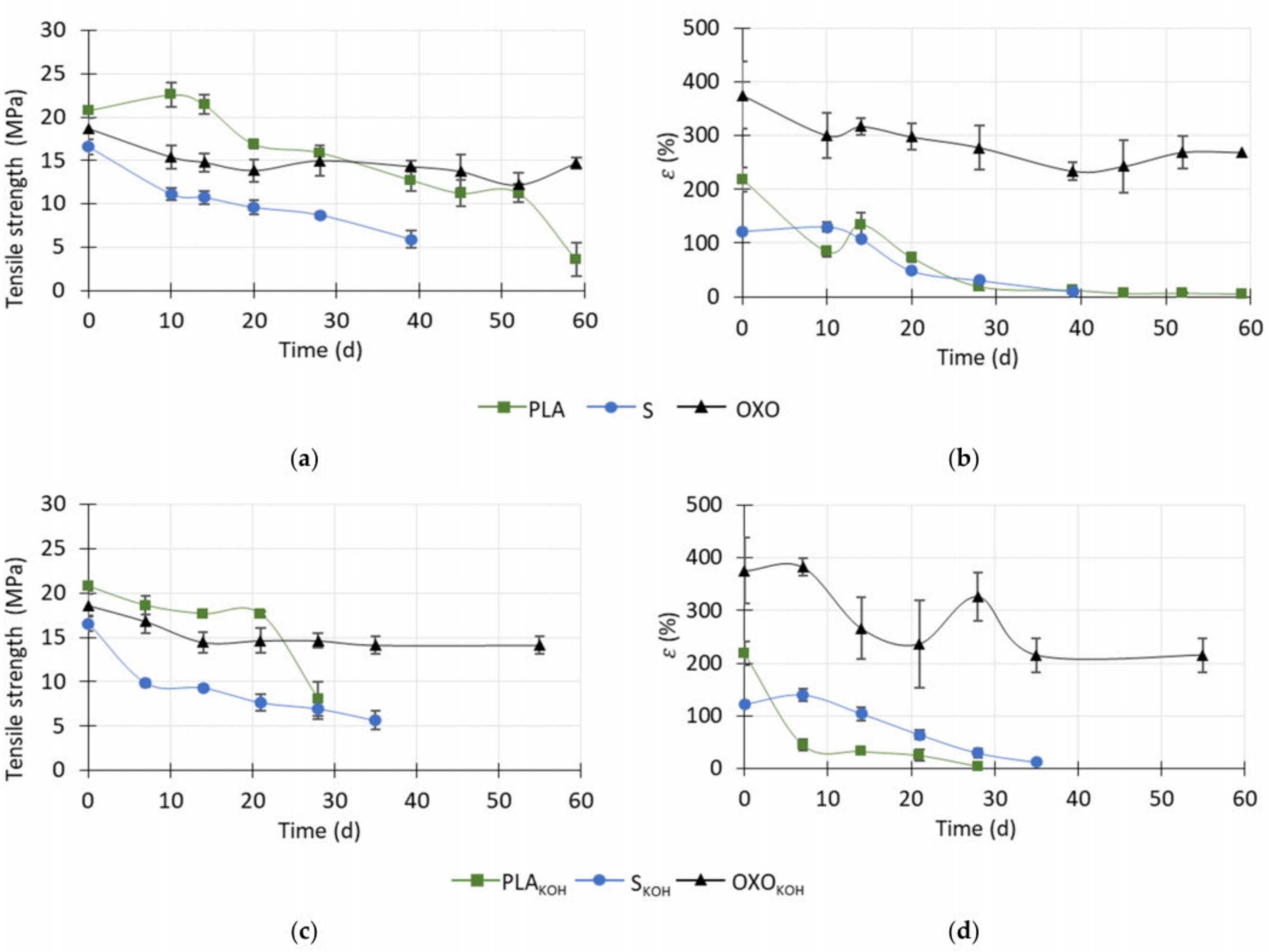


Figure 4. Changes in the mechanical properties (tensile strength and elongation at break ε) during an anaerobic degradation test of untreated foils (**a**,**b**) and foils after pretreatment with KOH (**c**,**d**).

Up to day 14 of the experiment, the tensile strength of PLA increased by about 9% because the material stiffened. Vasile et al. [24] carried out burial soil degradation of pure PLA and found that, after an initial decrease in tensile strength by about 14% on day 50, the material stiffened slightly, corresponding to a tensile strength increase after 100 days. After 150 days, the tensile strength decreased again. Stiffening of PLA may be caused by the water diffusing into the amorphous region of the material and random scission of ester bonds. This causes an increase in the degree of crystallinity during the degradation process. Next, after the degradation of the amorphous regions, degradation proceeds towards the center of the crystalline parts [25,26].

In the present study, the tensile strength of the PLA continuously decreased from day 14 to day 52 of the test, reaching 11.3 ± 1.0 MPa. On the last day, the PLA material was still collectible for the test, and the tensile strength was 3.6 ± 2.0 MPa, which was almost six times lower than in the raw/starting material (Figure 4a).

Rajesh et al. [27] carried out the soil burial degradation of pure PLA for 90 days at room temperature. Before starting degradation, the tensile strength of the material was 50 MPa and, during their study, it decreased by 26.5% (to ca. 38 MPa). Compared to the present study, the reduction in tensile strength was much smaller, but the tensile strength values were much higher. It should be emphasized that those authors conducted their degradation tests under aerobic conditions at room temperature, and they used pure PLA, which has greater tensile strength than the material used in the study presented here. The decrease in the tensile strength of bio-based products during degradation tests may be caused by the diffusion of water into the polymer matrix, causing hydrolysis to begin faster [28].

Then, as a result of breaking the secondary bonds (hydrogen, van der Waals bonds), the polymer is weakened, and the long polymer chains are converted to chains of low molecular weight. Then, the covalent bonds between the monomers are broken, which continues until the polymer is completely degraded [29].

The elongation at break (ε) of PLA, FS and OXO was also determined (Figure 4b,d). The value of ε for OXO material slightly decreased during the first 10 days of the degradation test, but over the next few days, only the small changes were noted. However, it should be emphasized that the initial ε of OXO was the highest of all the tested materials (375%), in contrast to its tensile strength, which was similar to that of the other foil materials.

Generally, the ε value of FS and PLA decreased as anaerobic degradation progressed. Despite the fact that the tensile strengths of both materials were similar, the elongation at the break of PLA was almost two-times higher than that of FS (ca. 220% and ca. 120%, respectively). However, in the case of PLA foil, a rapid initial decrease in ε (to ca. 85%) corresponded to the initial increase in tensile strength (from ca. 21 to ca. 23 MPa). The material may have stiffened due to an increase in its degree of crystallinity, which caused its tensile strength to increase. Then, at ca. 15 days, its elongation at break increased to 135%, which may have been caused by the breakdown of the secondary bonds between the polymer chains. From day 14 to day 45, the ε value decreased, reaching ca. 7%, which was only 3.2% of the initial value. The ε value then remained the same until the 59th day of the test, when the last measurement of this characteristic was possible. Regarding FS, its ε value increased by about 6% (from ca. 122%) during the first 10 days of measurement. This might have been caused by the polymer absorbing water. Then, at day 39, when the last measurement was possible, ε had decreased to ca. 10 ± 2% (Figure 4b,d).

The tensile strength and ε of KOH-pretreated OXO were virtually the same as those of OXO that had not been pretreated. Initially, the tensile strength slowly decreased, and after the 14th it was 22 ± 6% lower than the initial value. Then, the tensile strength and ε remained the same until the end of the degradation test. However, it should be emphasized that the KOH-pretreatment of OXO increased the standard deviation of the ε values (Figure 4c,d).

In contrast, pretreatment weakened the mechanical properties of both bio-based materials. Moreover, the time during which it was possible to determine the mechanical properties of these two foils was shorter with pretreatment than without pretreatment (for PLA_{KOH}, reduced from 52 to 28 days; for FS_{KOH}, from 39 to 35 days).

After 7 days of anaerobic degradation of PLA_{KOH}, the tensile strength decreased by about 11 ± 4% in comparison to the raw material (ca. 21 MPa). No temporary stiffness was observed, unlike the PLA, which was not pretreated. This lack of stiffness was also confirmed by the fact that, during this time, elongation at break decreased rapidly to 45%, which was almost two-times lower than the value obtained during the first days with the untreated PLA. Until 21 days of the test, the tensile strength remained at a similar level, while ε decreased slightly. Then, at 28 days, the tensile strength and ε decreased to ca. 8 MPa and 5%, respectively. With regard to both FS and FS_{KOH}, the tensile strength decreased sharply to ca. 10 MPa within the first 10 days of degradation.

In general, the decrease in elongation at the break of both the pretreated bio-based products and those without pretreatment was caused by an increase in the stiffness and a decrease in the flexibility of those materials. Similarly, Vasile et al. [24] reported that the tensile strength and elongation at break of pure PLA materials and PLA biocomposites decreased during soil burial biodegradation. The authors stated that, as the time of degradation progressed, the stiffness of the investigated materials increased.

3.4. Changes in the Surface Roughness of the Foils

During anaerobic degradation, the surface roughness of the foils decreased. Measurements of roughness were carried out to days 59 and 53 of degradation of the untreated and treated foils, respectively. After this time, the foils were too brittle to be analyzed.

During the first 9 days of anaerobic degradation, the Ra, Rq and Rt values of untreated PLA decreased, corresponding to a decrease in the roughness core (Rk). In addition, the reduced valley depth (Rvk) also decreased. Taken together, the decreases in these values indicated that the roughness of the PLA decreased, which may be due to the diffusion of the inoculum into the polymer matrix and water adsorption by the polymer. From day 9 to day 20, the Ra, Rq, Rt values increased, and on day 28, these values were similar to values noted in the raw material. In contrast, the Rpk value decreased until day 4, and then until day 14, it increased more than 2-times, and then remained at a similar level until the end of the measurements (Figures 5 and 6).

Until day 45, the the Ra, Rq, Rt values for PLA decreased again by about 1.4–1.5 times compared to the raw material, which was probably related to the secondary diffusion of water into the material structure. This also may indicate a gradual decrease in the thickness of the foil. The percentage of the peaks and valleys (Mr1 and Mr2) remained at a same level until day 45, then slightly decreased.

Regarding the FS foil, the Ra, Rq and Rt values increased during the first days of the anaerobic testing, which may indicate that the top layer of the material quickly dissolved. The structure of the material then became more complex and non-homogeneous. The roughness (Ra, Rq, Rt, Rk) of foil FS decreased to the 39th day of the analysis, and after this time, it remained at a constant level. However, the total height of the profile (Rt) increased, which may mean that larger random height peaks occurred in the structure, which are characteristic of damage to the surface structure.

Regarding the OXO foil, the roughness indicators did not display any differences up to day 14, and then, on day 20, all of these values except Mr1 and Mr2 increased 1.7–2.3-times. After day 20, all roughness indicators decreased. However, on the 59th day of degradation, the Ra, Rq, Rt, Rk, Rpk and Rvk values increased, which may have been related to the removal of oxo-additives from the surface structure. During the degradation test, the value of Mr1 decreased slightly, while that of Mr2 remained at a similar level (Figures 5 and 6).

Generally, after the pretreatment with KOH, the roughness of the bio-based materials decreased. This may be due to degradation of the external layers of the foils. However, the MR2 and MR1 values remained at a level similar to that in the untreated materials (Figures 5 and 6).

The pretreatment caused the initial weakening of the surface structure of the PLA. After the pretreatment with KOH, binding of PLA and KOH might have taken place, which would have created a layer that partially blocked the pores in the structure, resulting in the lack of change in the roughness indicators. The slight fluctuations in their values may have resulted from the damage to the surface of the materials after pretreatment. The Ra, Rq, Rt, Rk, Rpk and Rvk values decreased on day 53 of the anaerobic test. This may indicate that particles were rinsed out of the material into the inoculum. Moreover, the lower Rk value indicated a decrease in the roughness core, which could be connected with damage to the top layer of the material. At this time, the material defragmented when it was touched and further determination of the surface roughness was not possible. In contrast, Luo et al. [30] found that, in compost conditions, the neat PLA did not present significant changes on the surface after 5 days biodegradation, but after 20 days, the surface roughness increased. This could be owned to the hydrolysis of PLA and microorganism activities. With increasing incubation time, the cracks and voids became substantially deep and large.

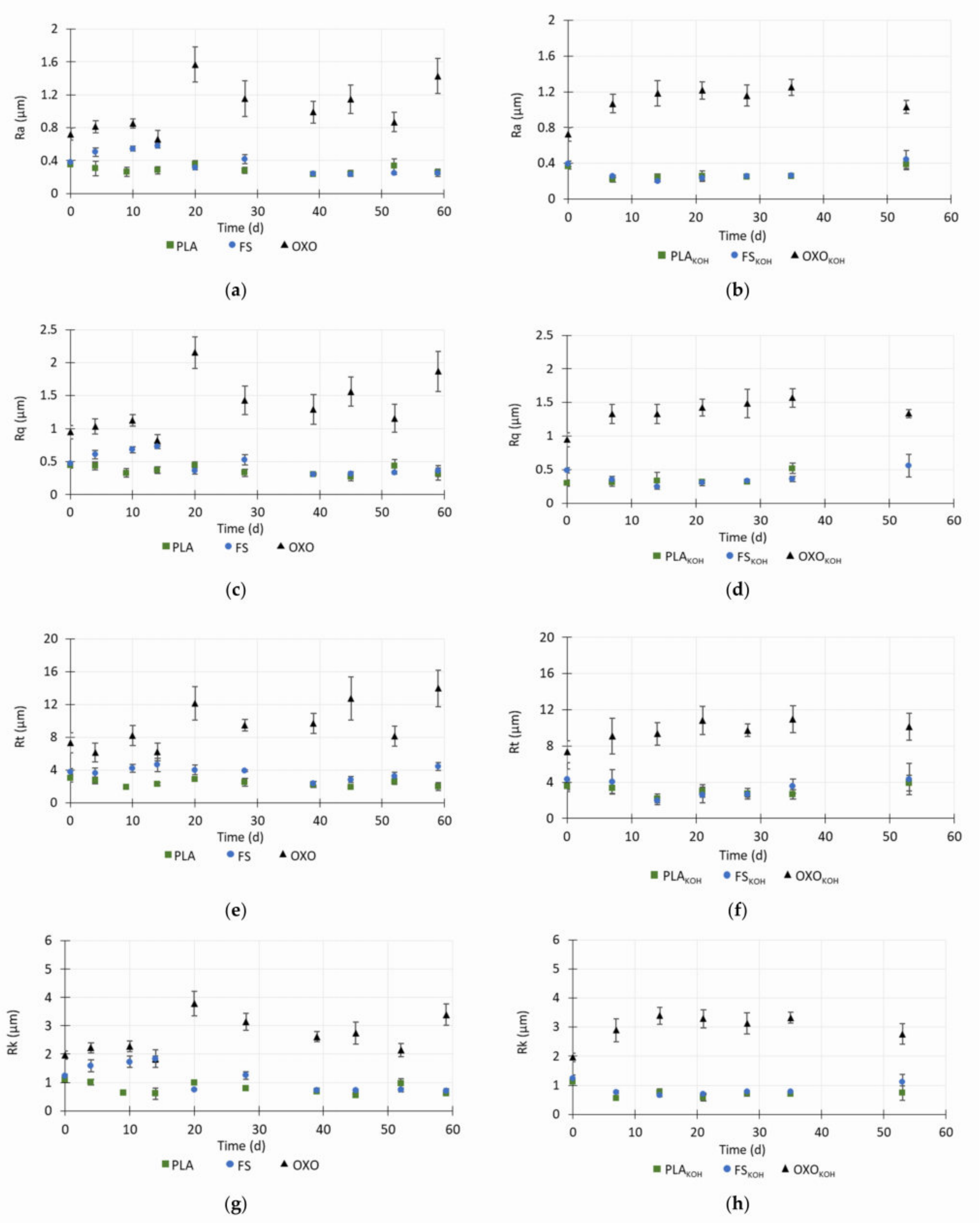
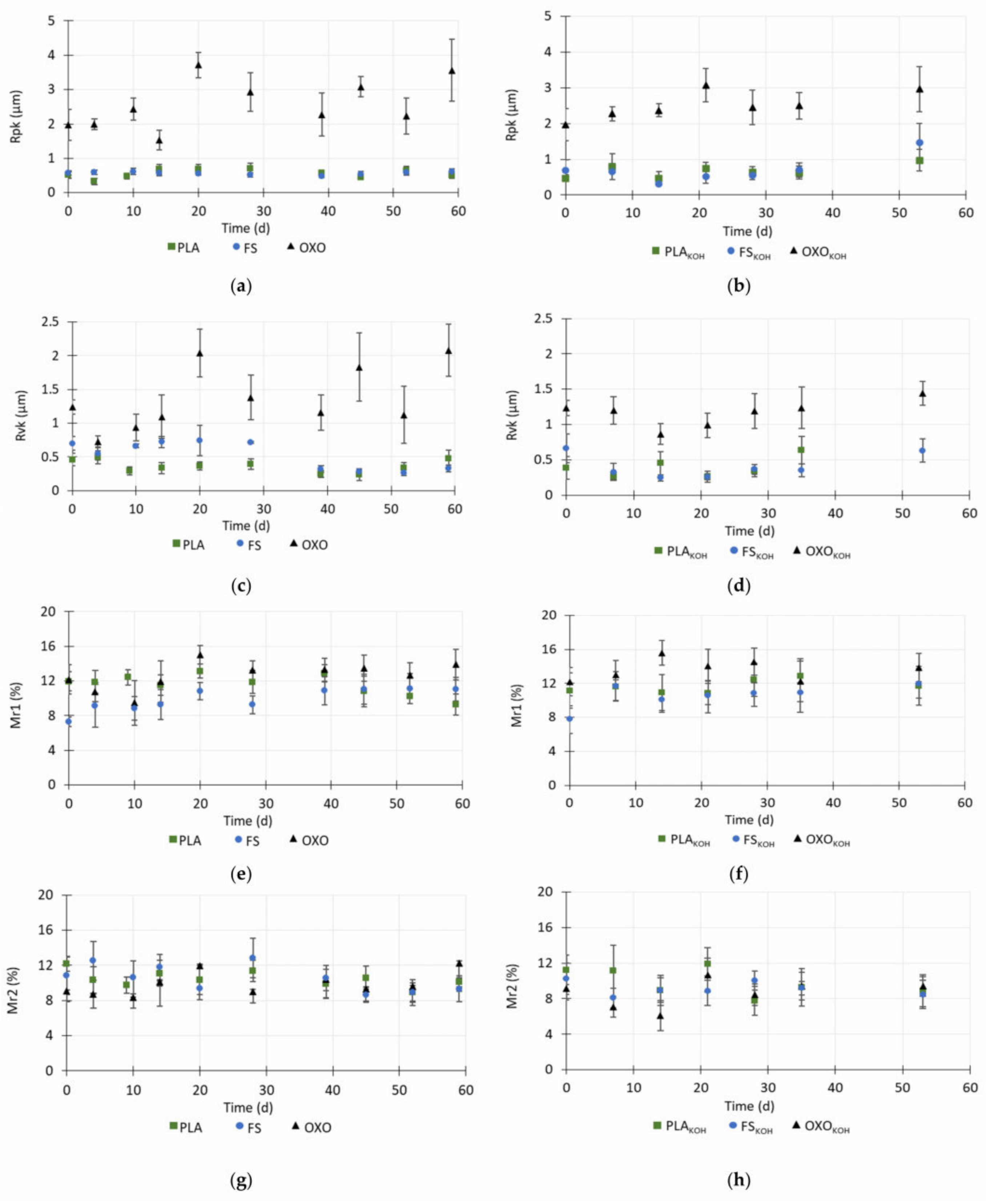


Figure 5. The surface roughness indicators (arithmetical mean roughness value (Ra), mean square surface profile deviation (Rq), the roughness core height (roughness core profile) (Rk), total height of the roughness profile (Rt)) during an anaerobic degradation test of untreated foils (PLA, FS, OXO) (**a**,**c**,**e**,**g**) and foils after pretreatment with KOH (PLA_{KOH}, FS_{KOH}, OXO_{KOH}) (**b**,**d**,**f**,**h**).



(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

(**g**) (**h**)

Figure 6. The surface roughness indicators (the reduced peak height without bearing properties (Rpk), the reduced valleys depth (Rvk); the percentage of the peaks and valleys (Mr1, Mr2, respectively)) during an anaerobic degradation test of untreated foils (PLA, FS, OXO) (**a**,**c**,**e**,**g**) and foils after pretreatment with KOH (PLA$_{KOH}$, FS$_{KOH}$, OXO$_{KOH}$) (**b**,**d**,**f**,**h**).

After the KOH pretreatment, the roughness indicators of the FS were lower than those of the untreated material, and they decreased with time until 14 days of the anaerobic test had passed, indicating rapid initial degradation of S. The changes in the values of the roughness indicators corresponded to changes in the MP profile. The lag phase of MP lasted only 4 days and was shorter with pretreated material than with untreated foil, and after this time methane started to be produced rapidly until day 15.

Cumulative MP was higher with treated FS than with the untreated material. Between 15 and 35 days of the test, the roughness indicators did not change much. On day 53, these values differed from what was observed on the other days. This was connected with the non-homogenous structure of S_{KOH} and the presence of small, deep micropores on the surface, which increased the roughness indicator values.

The pretreatment of OXO foil caused the initial values of its roughness indicators to be higher than those of the untreated material. This might have been caused by rapid removal of oxo-additives from the surface structure of OXO. It should be emphasized that the OXO was very rough and heterogenous in its structure. The polymer was not damaged during the anaerobic test, even after the pretreatment, and the changes in its roughness resulted from this heterogenous structure and degradation of the oxo-additive.

3.5. Changes in the Structure of Bio-Based and Oxo-Degradable Foil Materials—FTIR Analysis

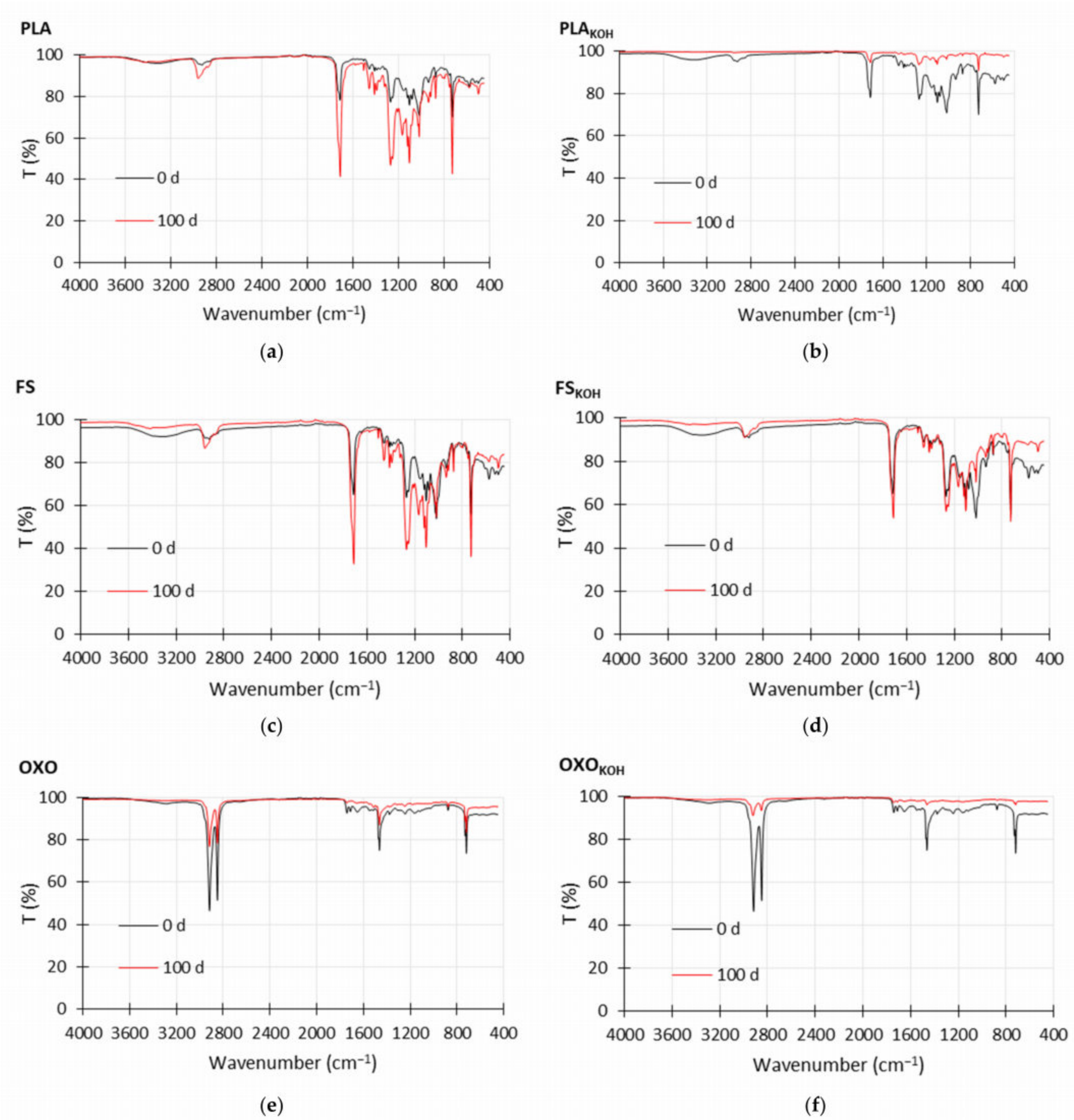
Regarding the raw PLA foil material, the FTIR analysis showed typical peaks for pure PLA. Hydrogen-bonded (intra- and intermolecular) -OH groups corresponded to the band at 3371 cm^{-1}. The asymmetric and symmetric vibrations of the $-CH_3$ groups were represented by the bands located at 3000–2850 cm^{-1}. The strong band at 1713 cm^{-1} indicated asymmetric stretching of carbonyl C=O groups, which may correspond to the amorphous phase of PLA.

In contrast, if a weak band is observed at ~1720 cm^{-1}, it may be assigned to C=O stretching of the crystalline phase of PLA [31]. The bands at 1271, 1104, and 1019 cm^{-1} corresponded to stretching vibrations of the C-O-C and -CH-O- groups. The band at 930 cm^{-1} combined contributions of both $-CH_3$ rocking and deformation of the carboxylic -OH … H groups [32]. The $O-CH-CH_3$, esters and/or C-C and rocking vibrations of $-CH_3$ groups were noted at 874 and 727 cm^{-1}, respectively (Figure 7).

With the untreated PLA foil material, the intensity of all bands increased after ca. 100 days of the anaerobic thermophilic test, except the one corresponding to -OH (at 3371 cm^{-1}), which indicated PLA degradation. For example, the intensity of the peak at 1713 cm^{-1} increased, which corresponds to a larger amount of carbonyl C=O groups, which are terminal groups in PLA chains. This indicates that the molecular weight of the PLA chains decreased. Although high molecular weight PLA is insoluble in water, during the degradation process, water diffuses into the polymer matrix, causing the hydrolysis of the ester groups of the amorphous phase. As a result, short-chain soluble carboxyl-terminated oligomers and monomers are formed and penetrate the aqueous environment. This causes an increase in the number of carboxyl chain ends, which was shown by the greater intensity of the peak corresponding to this group [33,34].

On the contrary, with PLA foil pretreated with KOH, the intensity of all bands decreased. However, in both cases biodegradation took place, which was confirmed by the weakness of the mechanical properties of the material and MP.

However, the time during which it was possible to determine the mechanical properties of PLA_{KOH} was 28 days, which was almost 2 two times shorter than that during which the properties of PLA could be determined. Pretreatment influenced the mechanical properties more than biogas production.



(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

Figure 7. FTIR spectra of untreated foil materials (PLA, FS, OXO) (**a**,**c**,**e**) and foil materials after pretreatment with KOH (PLA_{KOH}, FS_{KOH}, OXO_{KOH}) (**b**,**d**,**f**) before and after 100 days of anaerobic degradation at 55 °C.

Vasile et al. [24] found that, during the degradation of PLA and its composite in soil burial conditions, degradation included the ester groups destroyed by hydrolysis.

In the present study, the intensity of the ATR-FT-IR spectra decreased due to hydrolytic degradation. These results are consistent with those in the literature, Maharana et al. [35] concluded that chain scission of the PLA main chain takes place where the ester bonds are located, leading to the formation of oligomers.

Regarding the raw FS foil material, the bands at 2915 cm^{-1} indicated C–H stretching in aliphatic and aromatic groups (Figure 7). The bands at 1715 and 1272 cm^{-1} corresponded to C=O groups and C–O bonds found in ester linkages. The peak at 1019 cm^{-1} was caused by the stretching of phenylene groups. The band at 727 cm^{-1} indicated four or more adjacent methylene (–CH_2–) groups. The FTIR spectra of FS foil contained bands characteristic of plasticized starch. The peaks between 3558–3100 cm^{-1} and between 1269–900 cm^{-1} corresponded to O–H stretching groups and to C-O stretching and hydrogen bonding peaks, respectively. The peaks recorded at 1140 and 1103 cm^{-1} corresponded to C–O stretching in the C–O–H group. At 1016 cm^{-1}, evidence of C–O stretching in the C–O–C group of the starch anhydroglucose ring could be seen. After 100 days of anaerobic degradation of untreated FS foil material, the bands in the FTIR spectrum were almost identical to those in the spectrum of the raw material, and no new peaks were formed. Only the intensity of the spectra increased.

Regarding the treated FS foil material, the bands in the FTIR spectrum and their intensities were even more similar to those in the spectrum obtained from the raw material. It should be emphasized that pretreatment weakened the mechanical properties of the material more rapidly, and FS_{KOH} produced 80% more methane than FS. Thus, the FTIR spectrums that were obtained after degradation of FS and FS_{KOH} differed.

The FTIR spectra of OXO and OXO_{KOH} were typical of PE (Figure 7). The bands at 2849 and 2846 cm^{-1} corresponded to C–H stretching asymmetric and symmetric vibrations, whereas the band at 1464 cm^{-1} was due to scissoring CH_2 groups. The bands at 720 cm^{-1} and 717 cm^{-1} were caused by CH_2 rocking vibrations. A small band was noted at 1630 cm^{-1}, related to a double bond (or aromatic rings), probably due to some surface antioxidant additive. The spectra obtained from the material after 100 days of anaerobic treatment displayed lower intensity peaks. The band at 1630 cm^{-1} was not observed, which means that the antioxidant additive was washed away or assimilated by bacteria and the spectrum was from pure PE [36]. As a result of the disappearance of the additive, the OXO chains shortened, which slightly weakened the mechanical properties of the material. Degradation of modified polyethylene can proceed via two mechanisms (i) hydro-biodegradation and (ii) oxo-biodegradation, depending on the two additives, starch or pro-oxidant, used in the synthesis polymer [37]. Starch blend polyethylene contains starch inclusions which makes the material hydrophilic and, therefore, microbial amylase enzymes can easily access, attack and remove this part.

Polyethylene with pro-oxidant additive can be photodegraded and chemically degraded, and low molecular weight products are sequentially oxidized [38,39].

4. Conclusions

Because the share of usable polymers has increased in municipal waste streams, it is necessary to the determine the degradability of these materials, which is the current challenge of organic recycling strategies. It was shown that untreated and treated OXO did not degrade; thus, there was no methane production and no visible changes on the surface or in the mechanical properties. Untreated bio-based foils began to lose mechanical properties by day 50 of the anaerobic thermophilic degradation test; the pieces were still visible even after 100 days, and they only disintegrated when touched. Cumulative MP reached only 34 L/kg VS. After pretreatment, cumulative MP increased to 47.5 L/kg VS (PLA_{KOH}) and 58.6 L/kg VS (FS_{KOH}). However, these values constituted only 8–10% of the theoretical MP. Pretreatment of bio-based foils increased surface damage and weakened their mechanical properties (tensile strength, elongation at break). This means that the pieces of bio-based materials may contaminate digestate at municipal waste treatment plant.

Author Contributions: Conceptualization, M.Z. and K.B.; methodology, M.Z., K.B., and B.P.; formal analysis, K.B., I.W.-B., and D.K.; validation, M.Z. and B.P.; investigation, M.Z., B.P., and K.B.; resources, M.Z., K.B., I.W.-B., and D.K.; data curation, M.Z. and K.B.; writing—original draft preparation, M.Z., K.B., B.P., and D.K.; writing—review and editing, M.Z., B.P., K.B., I.W.-B., and D.K.; visualization, M.Z. and B.P.; supervision, K.B.; funding acquisition, K.B., I.W.-B., and D.K. All authors have read and agreed to the published version of the manuscript.

Funding: We are grateful for the financial support of the Ministry of Science and Higher Education, Poland (statutory project No. 29.610.024-110). Publication (Open Access) of this research was financially co-supported by Minister of Science and Higher Education in the range of the program entitled "Regional Initiative of Excellence" for the years 2019–2022, Project No. 010/RID/2018/19, amount of funding 12,000,000 PLN.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References

1. Plastics Europe. Plastics—The Facts 2019. An Analysis of European Plastics Production, Demand and Waste Data. Available online: https://www.plasticseurope.org/application/files/9715/7129/9584/FINAL_web_version_Plastics_the_facts2019_14102019.pdf (accessed on 30 June 2021).
2. Zhao, X.; Cornish, K.; Vodovotz, Y. Narrowing the Gap for Bioplastic Use in Food Packaging: An Update. *Environ. Sci. Technol.* **2020**, *54*, 4712–4732. [CrossRef]
3. Mallegni, N.; Phuong, T.V.; Coltelli, M.-B.; Cinelli, P.; Lazzeri, A. Poly(lactic acid) (PLA) Based Tear Resistant and Biodegradable Flexible Films by Blown Film Extrusion. *Materials* **2018**, *11*, 148. [CrossRef]
4. Abdelmoez, W.; Dahab, I.; Ragab, E.M.; Abdelsalam, O.A.; Mustafa, A. Bio-and oxo-degradable plastics: Insights on facts and challenges. *Polym. Adv. Technol.* **2021**, *32*, 1981–1996. [CrossRef]
5. Ojeda, T.F.; Dalmolin, E.; Forte, M.M.; Jacques, R.J.S.; Bento, F.M.; Camargo, F.A. Abiotic and biotic degradation of oxo-biodegradable polyethylenes. *Polym. Degrad. Stab.* **2009**, *94*, 965–970. [CrossRef]
6. Emadian, S.M.; Onay, T.T.; Demirel, B. Biodegradation of bioplastics in natural environments. *Waste Manag.* **2017**, *59*, 526–536. [CrossRef] [PubMed]
7. Artham, T.; Doble, M. Biodegradation of Aliphatic and Aromatic Polycarbonates. *Macromol. Biosci.* **2007**, *8*, 14–24. [CrossRef] [PubMed]
8. Ahmed, T.; Shahid, M.; Azeem, F.; Rasul, I.; Shah, A.A.; Noman, M.; Hameed, A.; Manzoor, N.; Manzoor, I.; Muhammad, S. Biodegradation of plastics: Current scenario and future prospects for environmental safety. *Environ. Sci. Pollut. Res.* **2018**, *25*, 7287–7298. [CrossRef] [PubMed]
9. Bernat, K.; Kulikowska, D.; Wojnowska-Baryła, I.; Zaborowska, M.; Pasieczna-Patkowska, S. Thermophilic and mesophilic biogas production from PLA-based materials: Possibilities and limitations. *Waste Manag.* **2021**, *119*, 295–305. [CrossRef]
10. Benn, N.; Zitomer, D. Pretreatment and Anaerobic Co-digestion of Selected PHB and PLA Bioplastics. *Front. Environ. Sci.* **2018**, *5*, 93. [CrossRef]
11. Yu, J.; Plackett, D.; Chen, L.X. Kinetics and mechanism of the monomeric products from abiotic hydrolysis of poly[(R)-3-hydroxybutyrate] under acidic and alkaline conditions. *Polym. Degrad. Stab.* **2005**, *89*, 289–299. [CrossRef]
12. Myung, J.; Strong, N.I.; Galega, W.M.; Sundstrom, E.R.; Flanagan, J.C.; Woo, S.-G.; Waymouth, R.; Criddle, C.S. Disassembly and reassembly of polyhydroxyalkanoates: Recycling through abiotic depolymerization and biotic repolymerization. *Bioresour. Technol.* **2014**, *170*, 167–174. [CrossRef]
13. Abbott, E.J.; Firestone, F.A. Specifying surface quality: A method based on accurate measurement and comparison. *Spie MS* **1995**, *107*, 63.
14. Pszczółkowski, B.; Bramowicz, M.; Rejmer, W.; Chrostek, T.; Senderowski, C. The influence of the processing temperature of polylactide on geometric structure of the surface using FDM technique. *Arch. Metall. Mater.* **2021**, *66*, 181–186. [CrossRef]
15. Greenberg, A.E.; Clesceri, L.S.; Eaton, A.D. *Standard Methods for the Examination of Water and Wastewater*, 18th ed.; APHA: Washington, DC, USA, 1992.
16. Buswell, A.M.; Mueller, H.F. Mechanism of Methane Fermentation. *Ind. Eng. Chem.* **1952**, *44*, 550–552. [CrossRef]
17. Aldas, M.; Ferri, J.M.; Lopez-Martinez, J.; Samper, M.D.; Arrieta, M.P. Effect of pine resin derivatives on the structural, thermal, and mechanical properties of Mater-Bi type bioplastic. *J. Appl. Polym. Sci.* **2019**, *137*. [CrossRef]
18. Mohee, R.; Unmar, G.; Mudhoo, A.; Khadoo, P. Biodegradability of biodegradable/degradable plastic materials under aerobic and anaerobic conditions. *Waste Manag.* **2008**, *28*, 1624–1629. [CrossRef]
19. Itävaara, M.; Karjomaa, S.; Selin, J.-F. Biodegradation of polylactide in aerobic and anaerobic thermophilic conditions. *Chemosphere* **2002**, *46*, 879–885. [CrossRef]
20. Yagi, H.; Ninomiya, F.; Funabashi, M.; Kunioka, M. Anaerobic biodegradation tests of poly(lactic acid) and polycaprolactone using new evaluation system for methane fermentation in anaerobic sludge. *Polym. Degrad. Stab.* **2009**, *94*, 1397–1404. [CrossRef]

21. Yagi, H.; Ninomiya, F.; Funabashi, M.; Kunioka, M. Anaerobic Biodegradation Tests of Poly(lactic acid) under Mesophilic and Thermophilic Conditions Using a New Evaluation System for Methane Fermentation in Anaerobic Sludge. *Int. J. Mol. Sci.* **2009**, *10*, 3824–3835. [CrossRef]
22. Corti, A.; Muniyasamy, S.; Vitali, M.; Imam, S.H.; Chiellini, E. Oxidation and biodegradation of polyethylene films containing pro-oxidant additives: Synergistic effects of sunlight exposure, thermal aging and fungal biodegradation. *Polym. Degrad. Stab.* **2010**, *95*, 1106–1114. [CrossRef]
23. Yashchuk, O.; Portillo, F.; Hermida, E. Degradation of Polyethylene Film Samples Containing Oxo-Degradable Additives. *Procedia Mater. Sci.* **2012**, *1*, 439–445. [CrossRef]
24. Vasile, C.; Pamfil, D.; Râpă, M.; Darie-Niţă, R.N.; Mitelut, A.C.; Popa, E.E.; Popescu, P.A.; Draghici, M.C.; Popa, M.E. Study of the soil burial degradation of some PLA/CS biocomposites. *Compos. Part B Eng.* **2018**, *142*, 251–262. [CrossRef]
25. De Jong, S.; Arias, E.; Rijkers, D.T.; van Nostrum, C.; Bosch, J.K.-V.D.; Hennink, W. New insights into the hydrolytic degradation of poly(lactic acid): Participation of the alcohol terminus. *Polymer* **2001**, *42*, 2795–2802. [CrossRef]
26. Elsawy, M.; Kim, K.-H.; Park, J.-W.; Deep, A. Hydrolytic degradation of polylactic acid (PLA) and its composites. *Renew. Sustain. Energy Rev.* **2017**, *79*, 1346–1352. [CrossRef]
27. Rajesh, G.; Prasad, A.R.; Gupta, A. Soil Degradation Characteristics of Short Sisal/PLA Composites. *Mater. Today Proc.* **2019**, *18*, 1–7. [CrossRef]
28. Sevim, K.; Pan, J. A model for hydrolytic degradation and erosion of biodegradable polymers. *Acta Biomater.* **2018**, *66*, 192–199. [CrossRef]
29. Lv, S.; Zhang, Y.; Gu, J.; Tan, H. Physicochemical evolutions of starch/poly (lactic acid) composite biodegraded in real soil. *J. Environ. Manag.* **2018**, *228*, 223–231. [CrossRef]
30. Luo, Y.; Lin, Z.; Guo, G. Biodegradation Assessment of Poly (Lactic Acid) Filled with Functionalized Titania Nanoparticles (PLA/TiO2) under Compost Conditions. *Nanoscale Res. Lett.* **2019**, *14*, 56. [CrossRef]
31. Silva, R.D.N.; Oliveira, T.A.; Da Conceição, I.D.; Araque, L.M.; Alves, T.S.; Barbosa, R. Evaluation of hydrolytic degradation of bionanocomposites through fourier transform infrared spectroscopy. *Polimeros* **2018**, *28*, 348–354. [CrossRef]
32. Socrates, G. *Infrared and Raman Characteristic Group Frequencies*, 3rd ed.; John Wiley and Sons, Ltd.: Chichester, UK, 2004; Volume 35, ISBN 978-0-470-09307-8.
33. Gupta, A.; Kumar, V. New emerging trends in synthetic biodegradable polymers—Polylactide: A critique. *Eur. Polym. J.* **2007**, *43*, 4053–4074. [CrossRef]
34. Middleton, J.C.; Tipton, A.J. Synthetic biodegradable polymers as orthopedic devices. *Biomaterials* **2000**, *21*, 2335–2346. [CrossRef]
35. Maharana, T.; Mohanty, B.; Negi, Y. Melt–solid polycondensation of lactic acid and its biodegradability. *Prog. Polym. Sci.* **2009**, *34*, 99–124. [CrossRef]
36. Bandini, F.; Frache, A.; Ferrarini, A.; Taskin, E.; Cocconcelli, P.S.; Puglisi, E. Fate of Biodegradable Polymers Under Industrial Conditions for Anaerobic Digestion and Aerobic Composting of Food Waste. *J. Polym. Environ.* **2020**, *28*, 2539–2550. [CrossRef]
37. Shah, A.A.; Hasan, F.; Hameed, A.; Ahmed, S. Biological degradation of plastics: A comprehensive review. *Biotechnol. Adv.* **2008**, *26*, 246–265. [CrossRef]
38. Bonhomme, S.; Cuer, A.; Delort, A.-M.; Lemaire, J.; Sancelme, M.; Scott, G. Environmental biodegradation of polyethylene. *Polym. Degrad. Stab.* **2003**, *81*, 441–452. [CrossRef]
39. Yamada-Onodera, K.; Mukumoto, H.; Katsuyaya, Y.; Saiganji, A.; Tani, Y. Degradation of polyethylene by a fungus, Penicillium simplicissimum YK. *Polym. Degrad. Stab.* **2001**, *72*, 323–327. [CrossRef]

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Magdalena Zaborowska, oświadczam, że mój wkład naukowy w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Challenges in sustainable degradability of bio-based and oxo-degradable packaging materials during anaerobic thermophilic treatment. *Energies*, 14(16), 4775.

Mój udział jako współautora publikacji obejmował:

- ☒ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☒ Udział w graficznym przedstawieniu wyników
- ☒ Udział w planowaniu badań
- ☒ Prowadzenie badań i analiz laboratoryjnych
- ☐ Konsultacja i opieka
- ☒ Udział w interpretacji wyników i wnioskowaniu
- ☒ Korekta pracy przed złożeniem do druku

07-07-2023 Magdalena Zaborowska

data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Katarzyna Bernat, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Challenges in sustainable degradability of bio-based and oxo-degradable packaging materials during anaerobic thermophilic treatment. *Energies*, 14(16), 4775.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☒ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☒ Udział w graficznym przedstawieniu wyników
- ☒ Udział w planowaniu badań
- ☐ Prowadzenie badań i analiz laboratoryjnych
- ☒ Konsultacja i opieka
- ☒ Udział w interpretacji wyników i wnioskowaniu
- ☒ Korekta pracy przed złożeniem do druku

7.07.2023r. Katarzyna Bernat
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Bartosz Pszczółkowski, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Challenges in sustainable degradability of bio-based and oxo-degradable packaging materials during anaerobic thermophilic treatment. *Energies*, 14(16), 4775.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☐ Współautorstwo w przygotowaniu koncepcji pracy
- ☐ Udział w pisaniu pracy
- ☒ Udział w graficznym przedstawieniu wyników
- ☐ Udział w planowaniu badań
- ☒ Prowadzenie badań i analiz laboratoryjnych
- ☐ Konsultacja i opieka
- ☒ Udział w interpretacji wyników i wnioskowaniu
- ☐ Korekta pracy przed złożeniem do druku

07.04.2023 ....
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Irena Wojnowska-Baryła, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Challenges in sustainable degradability of bio-based and oxo-degradable packaging materials during anaerobic thermophilic treatment. *Energies*, 14(16), 4775.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☐ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☐ Udział w graficznym przedstawieniu wyników
- ☐ Udział w planowaniu badań
- ☐ Prowadzenie badań i analiz laboratoryjnych
- ☒ Konsultacja i opieka
- ☐ Udział w interpretacji wyników i wnioskowaniu
- ☐ Korekta pracy przed złożeniem do druku

6.07.2023 I. Wojnowska
…………………………………………
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Dorota Kulikowska, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Wojnowska-Baryła Irena, Kulikowska Dorota, 2021. Challenges in sustainable degradability of bio-based and oxo-degradable packaging materials during anaerobic thermophilic treatment. *Energies*, 14(16), 4775.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☐ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☐ Udział w graficznym przedstawieniu wyników
- ☐ Udział w planowaniu badań
- ☐ Prowadzenie badań i analiz laboratoryjnych
- ☒ Konsultacja i opieka
- ☐ Udział w interpretacji wyników i wnioskowaniu
- ☐ Korekta pracy przed złożeniem do druku

06.07.2023
data i podpis

Waste Management 155 (2023) 40–52

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Multi-faceted analysis of thermophilic anaerobic biodegradation of poly (lactic acid)-based material

Magdalena Zaborowska [a], [*], Katarzyna Bernat [a], Bartosz Pszczółkowski [b], Agnieszka Cydzik-Kwiatkowska [a], Dorota Kulikowska [a], Irena Wojnowska-Baryła [a]

[a] *Department of Environmental Biotechnology, Faculty of Environmental Sciences, University of Warmia and Mazury in Olsztyn, Słoneczna Str. 45G, Olsztyn, Poland*
[b] *Department of Materials and Machines Technology, Faculty of Technical Sciences, University of Warmia and Mazury in Olsztyn, Oczapowskiego Str. 11, Olsztyn, Poland*

ARTICLE INFO

Keywords:
Bio-based polymer
Differential scanning calorimetry
Fourier-transform infrared spectroscopy
Microscopic and microbial analyses
The topography of PLA structure

ABSTRACT

Currently, the production of bio-based polymeric materials, of which poly(lactic acid) (PLA) is the most popular, has been increasing, causing the growth of PLA waste in municipal waste. Thus, it is necessary to develop sustainable methods for treating it. Methane production, resulting from anaerobic digestion (AD), is a potential end-of-life scenario for PLA waste that needs to be investigated. To obtain high efficiency of AD, thermophilic fermentation was applied, and to overcome low rates of biodegradation, hydrothermal (HT) and alkaline (A) pretreatments were used. For a deep insight into the process, differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), and microscopic and microbial analyses (based on 16S rDNA) were applied. For both untreated (PLA) and pretreated (PLA_{HT}, PLA_{A}) samples a high maximal methane production (MP) of 453 L/kg volatile solids (VS) was obtained, almost 100 % of the theoretical methane yield from PLA. The use of pretreatment allowed shortening of the time for obtaining maximal MP, especially the hydrothermal pretreatment, which shortened the overall time of MP 1.3-fold, and methane was produced at an almost 10 % higher rate (8.35 vs 7.79 L/(kg VS·d)). However, DSC and microscopic analyses revealed that, in all cases, methane was intensively produced i) after the reduction of the molecular mass of the PLA material and ii) also when PLA pieces were not visible. This should be considered when designing the operational time for the AD process. Parallel to the gradual biodegradation of PLA, the abundances of *Firmicutes*, *Thermotogae*, and *Euryarcheota* increased. With PLA_{HT}, *Syntrophobacteraceae*, *Thermoanaerobacteraceae*, and methanogens were identified as potential key thermophilic PLA biodegraders.

1. Introduction

One of the solutions for reducing the release of petroleum-based plastics into the environment is replacing them with bio-based materials. Nowadays, among bio-based materials, those based on polylactic acid (PLA) are the most common (Kervran et al. 2022). Due to its desirable mechanical properties, similar to polystyrene or polyethylene terephthalate, or even better (Hamad et al., 2015), PLA is increasingly widely used in different industries, which results in an increasing amount of waste from PLA-based products. Due to the high content of readily biodegradable organic matter in PLA materials (PLA-ms), organic recycling (anaerobic digestion (AD) or composting) should be the most desirable option. AD seems to be the most attractive method because it allows for organic matter decomposition and the production of valuable biogas.

Studies on the treatment conditions of PLA-ms are carried out because they are crucial for waste management in the context of the circular economy. It is necessary to determine and monitor its biodegradability and characterize the limits and bottlenecks during degradation to find and develop sustainable treatment methods. However, so far, most of the studies have focused on PLA-ms biodegradability based on a single degradation parameter, i.e. only respiration index, biogas, or methane production (MP). Microbial analyses during PLA-ms degradation, especially in anaerobic conditions, are not numerous. Furthermore, analyses of structural material changes are scarce, even though all the analyses mentioned here should be performed together for deeper insight into the process and a better understanding of PLA anaerobic biodegradation (AnB). Therefore, in this study, a holistic approach was

---

[*] Corresponding author.
E-mail address: magdalena.zaborowska@uwm.edu.pl (M. Zaborowska).

https://doi.org/10.1016/j.wasman.2022.10.031
Received 16 August 2022; Received in revised form 13 October 2022; Accepted 26 October 2022
Available online 5 November 2022

applied for the assessment of the PLA-m biodegradability, and not only the amount of methane was determined, but also the kinetics of its production. Moreover, changes in microbial composition and the structure of the biodegrading material were analyzed.

So far, studies on microorganisms involved in PLA biodegradation have mainly been carried out during composting or in a soil environment. One of the approaches during PLA biodegradation is to enrich the number of interesting microbes or to apply crude enzymes produced by microorganisms. The first reported PLA degrader was *Bacillus brevis*, isolated from soil (Tomita et al., 1999). Other PLA-degrading bacteria that have been isolated include *Paenibacillus amylolyticus* (Akutsu-Shigeno et al., 2003), *Bacillus pumilus* (Bonifer et al., 2019), *Stenotrophomonas pavanii*,*Pseudomonas geniculate* (Bubpachat et al., 2018), *Pseudomonas* sp. MYK1, and *Bacillus* sp. MYK2 (Kim et al., 2017). Most PLA degraders isolated from soil or compost belonged to actinomycetes Butbunchu and Pathom-Aree, (2019) and the dominant genus is *Amycolatopsis*, including, for example, *Amycolatopsis thailandensis* sp. nov. (strain CMU-PLA07) (Chomchoei et al., 2011), *Amycolatopsis oliviviridis* sp. nov. (Penkhrue et al., 2018), or *Amycolatopsis* sp. SCM_MK2-4 (Penkhrue et al., 2015). PLA degradation by various bacteria and fungi has not been as extensively studied as in the case of actinomycetes (Qi et al., 2017). Among filamentous fungi such as *Aspergillus ustus, A. sydowii, A. fumigatus, Paecilomyces lilicanus, and Penicillium verrucosum*, *A. ustus* and *P. verrucosum* were most active during PLA foil degradation (Szumigaj et al., 2008).

Effective fungal degradation of PLA has also been studied using *Tritirachium album* (Jarerat and Tokiwa, 2001), or *Parengyodontium album* VKM F-3028 and *A. calidoustus* VKM F-2909 (Antipova et al., 2018). Regarding enzyme application, Masaki et al. (2005) reported degradation of PLA with purified lipase from the yeast *Cryptococcus* sp. strain S-2. Bacteria that can degrade PLA produce mostly proteases and lipases and belong mainly to the genera *Bacillus*, *Pseudomonas*, and *Stenotrophomonas*.

Although research on microorganisms responsible for PLA biodegradation has been carried out for several years, it mainly concerned aerobic conditions, and focused on the application of pure microbial cultures or crude enzymes. Such an approach gives an idea of which selected microorganisms/enzymes are most useful in PLA biodegradation but does not provide information about their performance under technological conditions, where mixed microbial consortia with complex intra-species relationships are used. Therefore, it is advisable to determine microbiome changes during biodegradation of commercially available PLA-ms by mixed microbial consortia.

AD, which allows for organic matter decomposition and the production of valuable biogas, seems to be the most attractive method of organic recycling. This method can be used for various organic wastes which may differ in biodegradability, which in turn affects the effectiveness of biogas production. Different pretreatment methods (hydrothermal, physical, or chemical) are used to increase the susceptibility to anaerobic degradation of hard-to-degrade materials (e.g., lignocellulosic waste). The pretreatment step before AD has also been tested for some bio-based materials, but the results are contradictory. Most of the studies showed enhancement of methane production, but there are also reports of little/no impact on the effectiveness of AD (Yagi et al., 2009, Mu et al., 2021, Hobbs et al., 2019).

In the present study, to increase the efficiency/rate of the biodegradation process, abiotic hydrolysis of PLA-m was applied. During hydrolysis, complex organic compounds are converted to low molecular weight products, which can be assimilated by microorganisms (Gorrasi and Pantani, 2018).

Other important indications of polymer biodegradation are structural microscopic changes, such as deep, numerous cracks and fissures (Zaborowska et al., 2021), or colour changes (Lee et al., 2016) with time. Indications may also be obtained based on thermal properties (differential scanning calorimetry, DSC) and Fourier-transform infrared spectroscopy (FTIR). Changes in DSC-thermograms may suggest an increase in the crystallinity of PLA and a rapid reduction of molecular mass (Luo et al., 2019). This takes place because PLA crystalline regions are less susceptible to hydrolysis than less ordered amorphous regions due to the hindered diffusion of water, and consequently, the crystalline regions are also less susceptible to degradation (Reeve et al., 2002; Hakkarainen, 2002). Based on FTIR spectra, a decrease in the polymeric molecular weight may also be determined.

Some studies have reported that mesophilic anaerobic PLA degradation takes place to a limited extent (Kolstad et al., 2012; Zhang et al., 2018; Shrestha et al., 2020). Degradation occurs but requires hydraulic retention times that are much longer than those conventionally employed at the technical scale (Bernat et al., 2021; Yagi et al., 2009, 2013). Therefore, in this study, a pretreatment step was applied to increase the susceptibility of PLA-m to microbial degradation. To assess the impact of pretreatment on biodegradation of PLA-m, multi-faceted analyses were done which is crucial in the context of organic recycling of waste from PLA-m. Data on the yields and rates of MP from PLA-m (the most important technological parameters for AD process design) were combined with the characteristics of the degrading material based on DSC, FTIR, and microscopic analyses. This approach shows the relationship between changes in the structure of the biodegrading material and MP. Moreover, microbial analyses (based on 16S rDNA) were applied to determine the effect of pretreatment of PLA-m on the microbiome during thermophilic AnB.

2. Materials and methods

2.1. PLA-m used in the experiment

PLA-based cups obtained from the commercial public market were used. The manufacturer does not disclose the detailed composition of the cups, but they may contain other additives that improve their functional properties. PLA characteristics were as follows: the contents of volatile solids (VS) were 99.3 % dry matter (DM), chemical oxygen demand (COD) was 71.5 g COD/kg DM, nitrogen (Kiejdahl nitrogen, Ntot) was 454.9 mg Ntot/kg DM). Elemental composition of PLA-m was 49.56 % C, 44.48 % O, 5.56 %H, 0 % N. The cups were cut to a particle size of 10x10 mm.

2.2. Organisation of the experiment

Three sets of experiments were carried out. In set 1, PLA-m were used without pretreatment (PLA). In set 2 and 3, PLA-m were pretreated. In set 2 hydrothermal pretreatment (2 h, 90 °C) (PLA_{HT}), whereas in set 3, alkaline pretreatment (2 h, 0.1 M KOH, ambient temperature) (PLA_A) were used. Before MP determination in set 3, the samples were neutralized with hydrochloric acid.

2.3. AnB test of PLA-m

To assess the MP of the PLA-m during a 100-day degradation test in 55 °C, an Automatic Methane Potential Test System (AMPTS II) was employed. The biogas produced in the bioreactors flows through a CO_2 absorber and then through an automatic methane volume meter.

The inoculum was fermented sludge from the technical-scale closed mesophilic digester chamber at the local municipal wastewater treatment plant (north-eastern Poland). Thermophilic preincubation of the inoculum was carried out at 55 °C for 14 days. The DM content of the inoculum was 2.1 %, and vS constituted 71.6 % of the DM.

The inoculum (200 mL) was introduced to 500 mL-bioreactors. For a starting organic load of 4 kg VS/m^3 about 0.8 g of PLA-m was used, taking into account that the substrate had an organic matter content of almost 100 %. An inoculum:PLA ratio was 1:250 (w/w), of 1:5.25 (g DM: g DM), of 1:3.76 (g VS:g VS).

Each bioreactor was flushed with pure nitrogen for 2 min, and placed in a thermostatic incubator and mixed by a multifunctional agitation system (80 rpm/min every hour).

The MP was determined as the methane volume produced online. The MP of the inoculum alone and of the inoculum with the substrate were measured in triplicate. To determine the MP of the PLA-m itself, the MP of the inoculum alone was subtracted from that of the inoculum with the substrate.

The additional glass bottles that were identical to the AMPTS II bioreactors were dosed with the same amount of inoculum and substrate and were placed at 55 °C. These bottles were prepared for sampling PLA-m and biomass for analysis without disturbing the measurement of MP in the bioreactors. When the fragments of PLA-m were sampled for further analysis, they were cleaned with distilled water.

2.4. Analytical methods

The DM content of the inoculum at 105 °C, the vS contents of the inoculum and PLA-m as at 550 °C, and the COD and Ntot of the PLA-m were determined (Greenberg et al., 1992). Flash 2000 Organic Elemental Analyzer (Thermo Scientific, Milan, Italy) was used to determine the elemental composition of PLA-m according to the manufacturer's protocol.

2.5. Microscopic analysis

The microscopic analysis of surface of PLA-m using a polarizing microscope (Nikon eclipse50i, 100 ×) and digital microscope (Keyence VHX-7000, Japan, 1000 ×). The latter determined 3D geometric PLA structure (topography) at the microscale without contact with the material. Pictures were taken up to 66, 60, and 46 days, respectively for PLA, PLA_A and PLA_{HT}, because after this time the pieces were too crumbled to further analyze.

2.6. FTIR and DSC analysis

In the untreated and pretreated PLA pieces and in materials collected after 23 days of biodegradation and the last possible day of sampling, FTIR and DSC analyses were performed.

The FTIR spectra (with three replicates) were obtained using a Perkin Elmer Spectrum Two (with diamond ATR) brand device having a resolution of 4 cm^{-1} within the wavenumber range of 4000–400 cm^{-1} at room temperature. Smoothing functions were not employed. The average FTIR spectra were shown in the graphical form.

Thermal properties of PLA-m were assessed with the use of a DSC Phoenix 204 F1 differential scanning calorimeter utilizing the hit flow method (Netzsch). The measured parameter was free heat flow. Small amounts (ca. 5 mg) of dry samples were placed into aluminum crucibles, sealed, and heated between 30 °C and 200 °C at a heating rate of 5 °C/min. An empty aluminum crucible was used as a reference. The analysis was based on the measurement of the energy required to establish a zero-temperature difference between the analyzed sample and a reference sample. The thermal characteristics such as the glass transition temperature (Tg), cold crystallization temperature (Tc), melting temperature (Tm), and melting enthalpy (ΔHm) were determined from DSC curves.

2.7. Microbial analysis

Biomass from inoculum alone and from inoculum and PLA-m after 14, 38, and 60 days of AnB in each experimental set were taken into a sterile falcon and subjected to molecular analysis. In the notation that will be used here, the subscript indicates the application or not of the pretreatment method, and after the underscore, the day of the collection is given. For example, $PLA_{HT\_}14d$ means the biomass collected during biodegradation of PLA_{HT} on the 14th day. After centrifugation for 15 min at 8000 rpm (MPW-380 centrifuge, MPW), 500 μL of the wet sludge was taken from the bottom of the falcon. DNA isolation was performed using the FastDNA®SPIN Kit for Soil (MP Biomedical). The quantity and quality of DNA were assessed spectrophotometrically (NanoDrop, Thermo Scientific) and by agarose electrophoresis. The DNA was amplified using a primer set 515F/806R (GTGCCAGCMGCCGCGGTAA/GGACTACHVGGGTWTCTAAT) targeting the V4 region of the bacterial 16S rDNA gene (Caporaso et al., 2011). Sequencing was performed in Research and Testing Laboratory (USA, MiSeq Illumina Platform). The obtained sequences were analyzed bioinformatically as described in Jachimowicz et al. (2022) and deposited in the NCBI Sequence Read Archive (experiment entitled "Effect of PLA pretreatment on the microbial community during anaerobic digestion", accession: PRJNA857548).

2.8. Statistical methods

Statistical and metagenomic analysis of microbiome data obtained during anaerobic PLA biodegradation was conducted using MicrobiomeAnalyst (Dhariwal et al., 2017; Chong et al., 2020; $p < 0.05$). To maintain the highest possible precision for each sample, the number of reads obtained during sequencing was not normalized before the calculation of diversity indices (McMurdie and Holmes, 2014).

3. Results and discussion

3.1. MP from PLA-m

The authors' previous study (Bernat et al., 2021) showed that, during 280-day mesophilic AnB of PLA-m (37 °C), biogas was produced. However, the maximal biogas production was 1.5-times lower than that obtained at 58 °C. The time needed for mesophilic biodegradation was not acceptable in anaerobic chambers at technical scale. However, if waste from PLA-m was collected with mixed municipal waste and then landfilled, long-term biogas production from the materials would take place under landfill conditions. Bernat et al. (2021) also revealed that at 58 °C (the temperature imposed by the standards for degradation of polymers), the PLA-m required 40 days to biodegrade, which was longer than the time for municipal biowaste degradation. In commonly used technical-scale thermophilic anaerobic digesters, e.g., for biowaste treatment, the temperature is maintained at 54–55 °C. Thus, to overcome the low rates of biodegradation, pretreatments of PLA-m (PLA_A, PLA_{HT}) were used prior to thermophilic AD at 55 °C in the present study.

In each set, methane was produced intensively until PLA pieces were visible in the inoculum. This coincided with 90 % of maximal MP. Then, when the material was not visible, the remaining volume of methane was produced (Fig. 1).

Pretreatment reduced the length of the lag phase, during which methane was not produced, the time during which PLA pieces were visible, the time to reach 90 % of total MP, and the overall time of MP. With PLA, methane was not produced during the first 12 days.

After this lag phase, intensive MP took place, during which two phases were distinguished. In both phases, MP over time was described with a zero order kinetic model. According to this model, the rate constant equals the rate of MP (rCH_4).

During the first phase, from the end of the lag phase to day 66, 406.18 L/kg vS of methane were produced, which constituted 90 % of total MP. The second phase of MP lasted until day 75, when the methane volume plateaued. The rate of MP was 2-times higher in the first phase than in the second one (7.9 L/(kg VS•d) vs 3.9 L/(kg VS•d)). The maximal MP was ca. 453 L/kg vS.

With PLA_A, no lag phase was observed, the overall time of MP was 1.1-fold shorter than with PLA, and the time during which PLA pieces were visible was 10 % shorter. After 2 h of alkaline pretreatment, organic compounds, expressed as COD, were released, and the organics concentration was 2844 mg COD/L. Thus, until day 5, methane was produced at a rate of 11.16 L/(kg VS•d). The lack of a lag phase and the high initial rate of MP might be related to the availability of soluble

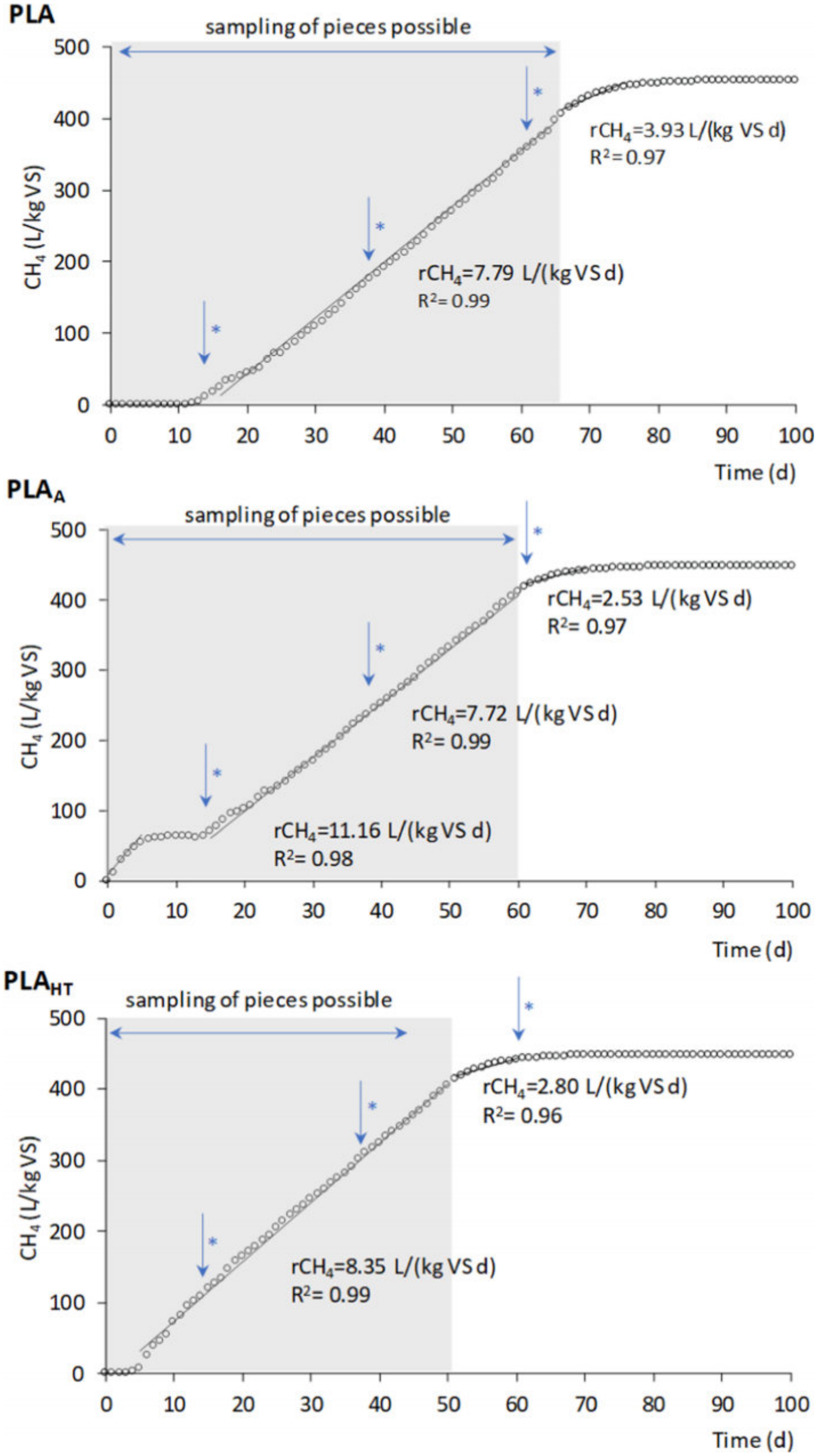


Fig. 1. Methane production from untreated PLA, and pretreated PLA (PLA_A, PLA_{HT}); vertical arrows with * indicate biomass sampling for the microbial community analyses; the gray area represents the time necessary to reach 90% of the maximal methane production; horizontal arrows indicate the time during which PLA, PLA_A, PLA_{HT} pieces were visible and sampling for DSC, FTIR, and microscopic analyses was possible.

organics to microorganisms.

The subsequent plateau of MP for 10 days might be due to the depletion of these compounds. From the 15th day, methane started to be produced again, and two further phases of MP were distinguished. During the first phase, which lasted until day 60, the pieces of PLA were still visible and 90 % of total methane (ca. 405 L/kg VS) was produced. The rate of MP, 7.72 L/(kg VS•d), was similar to that obtained during MP of PLA. However, the pieces of PLA_A were visible for a shorter time than those of PLA. The final phase of MP with PLA_A lasted to day 70 and the rate was 2.53 L/(kg VS•d). At this point MP plateaued, reaching its maximal value of ca. 448 L/kg vS.

Compared to MP from PLA, hydrothermal pretreatment reduced the lag phase by 60 % (to 5 days), shortened the overall time of MP 1.3- fold, and reduced the time that PLA-m was visible by 25 %. In the first phase, 90 % of total MP was achieved, and during this time, PLA_A pieces were still visible. This phase was the shortest (50 days) and methane was produced at the highest rate of the three variants – 8.35 L/(kg VS•d). Between days 50 and 60, the remaining methane was produced at a rate of 2.20 L/(kg VS•d), after which, MP plateaued to ca. 448 L/kg vS Thus, hydrothermal pretreatment most effectively increased the rate of the MP from PLA-m and shortened the time necessary to reach maximal MP. However, the use of both pretreatments did not affect the maximal amount of MP that was obtained (Fig. 1).

In a previous study, Bernat et al. (2021) investigated PLA degradation, but the temperature was higher (58 °C) and production of biogas, not methane, was determined. It was found that degradation proceeded in two phases, first with intensive biodegradation, and second, with lower biogas production. The maximal cumulative biogas production reached after 40 days was approximately 850 L/kg vS Moreover, the experimentally observed value of MP from PLA was similar to the theoretical maximum methane production from pure PLA, 467 L CH_4/kg pure PLA, which was determined with the use of Buswell's equation based on substrate elemental composition (Buswell and Mueller, 1952).

The authors suggested that a slightly lower MP value may result from the fact that commercially available PLA-m may contain additives, which improve properties but reduce MP by making the material less biodegradable. As mentioned, a process temperature of 58 °C is imposed by the standards for degradation of polymeric materials but is not commonly used in thermophilic full-scale digesters, which are operated at up to 55 °C for economic reasons.

Because some studies have indicated that bio-based material degradation does not occur, or takes place to a limited extent, now more studies have focused on testing how a pretreatment influences degradation. For example, Benn and Zitomer (2018) studied the influence of thermal alkaline ($\geq$55 °C, pH $\geq$ 10, $\geq$24 h) pretreatment on anaerobic mesophilic (35.7 °C ± 2.1 %) degradation of commercial PHB- and PLA-based materials. Pretreatment reduced the lag phase up to 60 and 90 % for PHB and PLA, respectively. PLA did not produce methane, whereas after pretreatment 22 ± 6 % of the material was converted to methane (average 79 ± 8 mL CH_4 per g of theoretical oxygen demand). In the case of PHB, pretreatment increased methane conversion from 67 ± 19 % to 91 ± 4 %. Those results indicated that, in mesophilic conditions, it is expedient to apply pretreatment only in the case of PHB. Similarly, Battista et al. (2021) showed that under mesophilic conditions at 37 °C, neither acidic (HCl, pH 2, 48 h) nor basic (NaOH, pH 12, 48 h) pretreatment of PLA- and starch-based materials conducted at room temperature improved their biodegradation. Moreover, specific methane production decreased by around 20 % compared to the untreated materials. Hobbs et al. (2019) investigated a 15-day alkaline PLA pretreatment (pH > 11.5, 21 °C) which resulted in near complete solubilization of the material. Despite the application of this long-term pretreatment methane production at mesophilic conditions (37 ± 1 °C) increased only by 26 %.

Samitthiwetcharong and Chavalparit (2019) found that alkaline pretreatment of PLA films (0.5 M NaOH, 60 h) before mesophilic AD ensured an increase in MP (148 L/kg VS_{added}) in comparison to untreated PLA, from which a negligible amount of methane was produced. The applied mesophilic conditions were advantageous from an energetic point of view, but the obtained MP was much lower than in the present study.

The results of a recent study by Mu et al. (2021) showed that, under mesophilic conditions, PLA-m (cutlery ground to powder) was hard to biodegrade and only 50.5 ± 0.5 mL CH_4/g vS was obtained after 146 days. In thermophilic conditions the authors obtained 410.3 ± 0.5 mL CH_4/g vS after 90 days, but the PLA was in the form of powder, which can be considered mechanical pretreatment. The authors proposed the use of hydrothermal and alkali pretreatment of PLA (120–240 °C, 10–120 min, NaOH 0–10 %) prior to mesophilic biodegradation. They revealed that MP of 460.1 ± 25.0 mL/g vS could be achieved, but the pretreatment temperature needed to be at least 200 °C, which increase the energy consumption and cost of the digestion process (Mu et al. 2021). Samitthiwetcharong et al. (2017) found that for more efficient PLA film degradation under mesophilic conditions, the application of alkaline conditions (NaOH) had a more significant effect than thermal pretreatment. The authors suggested that the most optimal conditions for pretreatment were 0.5 M of NaOH, 60 °C, and 24 h. In these conditions, biogas production was 3.7-times higher than from untreated material (215.47 mL/g vS vs 58.28 mL/g VS). The combination of thermal-alkaline pretreatment increased PLA degradation from 4.32 % to 20.14 % (Samitthiwetcharong et al. 2017).

For most previously mentioned results of studies on bio-based materials, methane fermentation was carried out under mesophilic, not thermophilic, conditions, and the results of the aforementioned studies concerned pretreatment prior to mesophilic fermentation. However, these results indicated that mesophilic fermentation was not effective, regardless of the pretreatment used. Therefore, in the present study, as in the previous work (Bernat et al., 2021), a different approach was used including i) the use of thermophilic conditions for methane production from PLA-m and ii) the use of pretreatment to increase the rate of methane production, which may shorten the retention time in the digesters at technical scale. This study has confirmed that this is the right approach because, in thermophilic conditions, the effectiveness of MP from PLA-m was almost 100 % (compared to the theoretical methane yield from PLA), and the use of pretreatment allowed shortening of the time necessary to obtain maximal MP.

3.2. *Changes in the surface of PLA-m*

The biodegradation of bio-based materials is accompanied by changes in the surface of the material (Figs. 2-3; microscopic images of material sampled more frequently are provided Supplementary Materials (Tab. 1–3.SM)). Changes in the surface homogeneity, the formation of defects in the structure (holes, cracks), as well as visible changes in color or tarnishing are a sign of the loss of the original properties of the polymer and its degradation.

As mentioned, the intensive production of methane occurred until pieces of PLA-m were visible in the inoculum. Initially, the untreated material was transparent, hard, and smooth. The use of alkaline pretreatment (PLA_A) resulted in the appearance of numerous scratches in the structure of the material, and the release of organic compounds from the PLA_A surface was noted which was confirmed by the increase in COD concentration.

The hydrothermal pretreatment (PLA_{HT}) caused only a few randomly occurring signs of structural damage (microcracks). Regardless of the pretreatment method, the material remained transparent. From the 7th day, in each set, the color of PLA-m changed from transparent to opaque. Moreover, individual cracks and fissures appeared on the PLA_{TH} surface. In contrast, Lee et al. (2016) observed no changes in the color of pure PLA film during mesophilic AnB. However, the addition of lactic acid to the film caused an increase in biodegradability and the color changed from transparent to white after 10 days. Changes in PLA colors have been noted by Fortunati et al. (2011) during the composting of PLA and

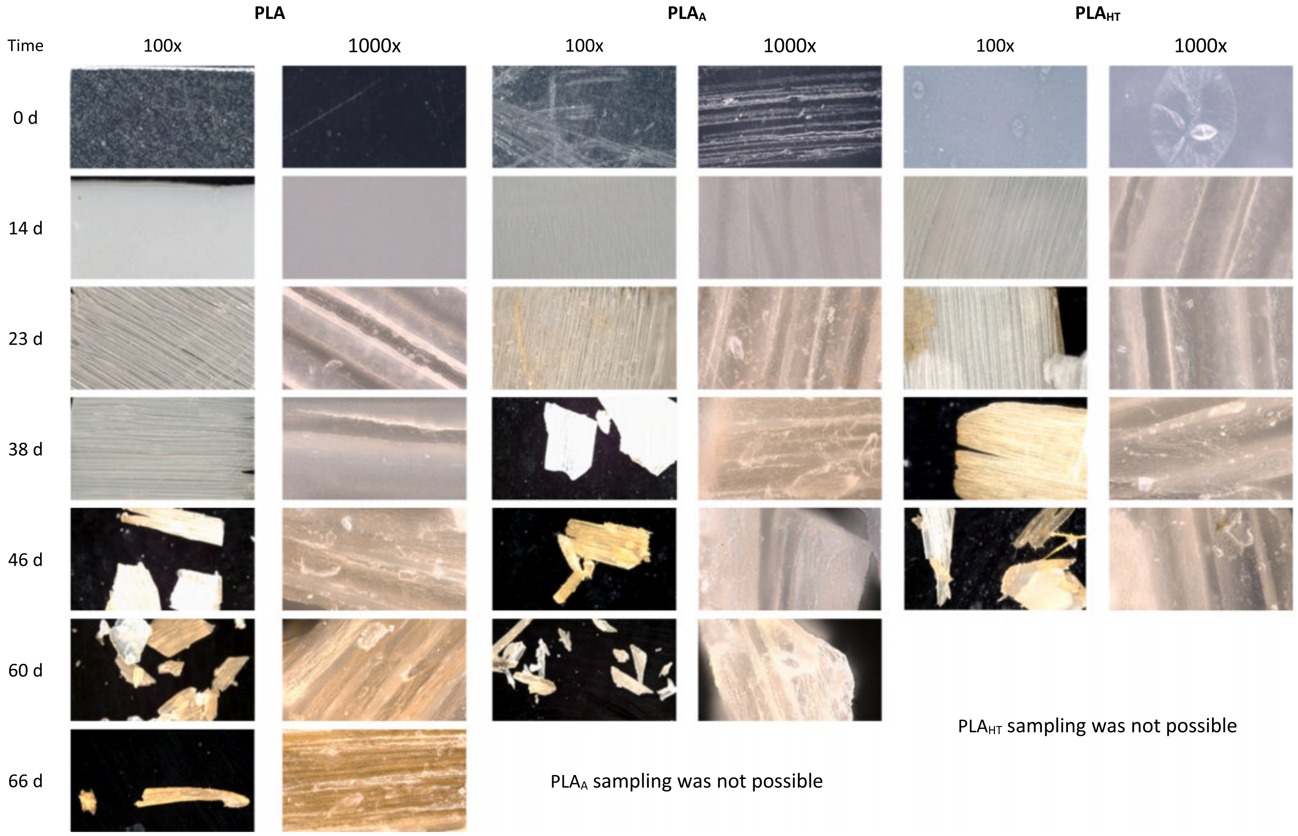


Fig. 2. Digital microscopic images of untreated and pretreated PLA structure during anaerobic thermophilic (55 °C) biodegradation (100x and 1000x magnification) (microscopic images of the material at other sampling times are provided in the Supplementary Materials (Tab. 2.SM)).

its composites. The authors observed changes in the colors to opaque on the 7th day of the process, while the first deformation of the surface and fractures appeared from day 14. They suggested that color changes may indicate the hydrolytic degradation of the polymer matrix as a result of water absorption and/or the presence of products formed during the process. Hydrolytic degradation takes place in both, aerobic and anaerobic conditions. Moreover, changing the color of PLA to white-opaque may be related to material embrittlement due to crystallinity increase (Kliem et al., 2020).

In the present study, although the lag phase of PLA finished on day 12, the structural changes were not visible until day 14. The changes appeared in the period between 14 and 23 days, and at 23 d, deep cracks and fissures appeared (Fig. 2; Tab. 1–2.SM – Supplementary Materials). However, the analysis of the surface topography of PLA showed numerous peaks and valleys (Fig. 3; Tab. 3.SM – Supplementary Materials) which was accompanied by a MP. This means that organics were eluted from the material and served as an energy source for microorganisms. On day 14 of the microscopic analyses, cracks and fissures in the structure of PLA$_A$ become visible, whereas in the PLA$_{HT}$, they had become deeper and more numerous. Analysis of the surface of both pretreated materials showed that from the 14th day, peaks and valleys disappeared from the structure, and longitudinal microcracks were formed. The shape of the cracks appearing during degradation may be related to the manufacturing process of the cups. From day 23, in each set, PLA pieces darkened and weakened. Then, the most crucial changes in the structures of both untreated and pretreated PLA occurred, which corresponded to the most intense MP. The surface topography analysis revealed numerous cracks and fissures in each set (Figs. 2-3; Tab. 1–3.SM – Supplementary Materials). Benn and Zitomer (2018) found that pretreatment caused visible surface erosion, and increased porosity and surface area, which may facilitate enzymatic degradation of the polymer. Therefore, the hydrolysis rate may increase, resulting in an increase in the rate of methanogenesis (Venkiteshwaran et al., 2019). Samitthiwetcharong and Chavalparit (2019) found that pretreatment of PLA increased its porosity and increased its availability to microorganisms or enzymes.

PLA-m was visible in the inoculum for the longest time, up to 66 days. The last possible day to sample the PLA$_A$ was day 60, whereas PLA$_{HT}$ pieces were fragile and crumbled when touched at day 46. After 66, 60, and 46 days, respectively, the PLA, PLA$_A$, and PLA$_{HT}$ materials had crumbled too much for further analysis and were almost invisible in the inoculum.

3.3. FTIR spectra and DSC curves for PLA-m

The FTIR spectra are shown in Fig. 4 a,c,e. The FTIR spectra showed typical bands for poly(lactic acid), which were similar to those reported in the literature (Arrieta et al., 2014; Kumar et al., 2019). The bands at 2998 cm^{-1} and 2920 cm^{-1} correspond to $–CH_3$ and $–CH_2–$ groups, respectively. At 1455 cm^{-1}, signs of symmetric deformation and scissor vibrations of $–CH_2–$ groups are noticeable, whereas the bands at 1383 cm^{-1} and 1358 cm^{-1} correspond to asymmetric and symmetric deformations of $–CH_3–$ groups. The peak at 1748 cm^{-1} indicates asymmetric stretching of the $C{=}O$ group in lactide (Fortunati et al., 2012). At 1209 cm^{-1} and 1043 cm^{-1}, stretching vibrations of the C–O–C and –CH–O– groups can be seen. The peaks at 956 cm^{-1} and 920 cm^{-1} indicate $–CH_3$ rocking and deformation of carboxylic –OH···H groups. The peaks at 870 cm^{-1} ($O–CH–CH_3$) and 755 cm^{-1} (rocking vibrations of $–CH_3$ groups) correspond to the amorphous and crystalline phases of PLA, respectively (Ruggero et al., 2021).

The PLA$_{HT}$ spectrum did not exhibit changes, and no shift in the formation of peaks was observed. However, after alkaline pretreatment, a new peak at 1585 cm^{-1} appeared, which indicates $C{=}O$ stretching of carboxylic acid salts and may be the result of PLA chain hydrolysis (Lee

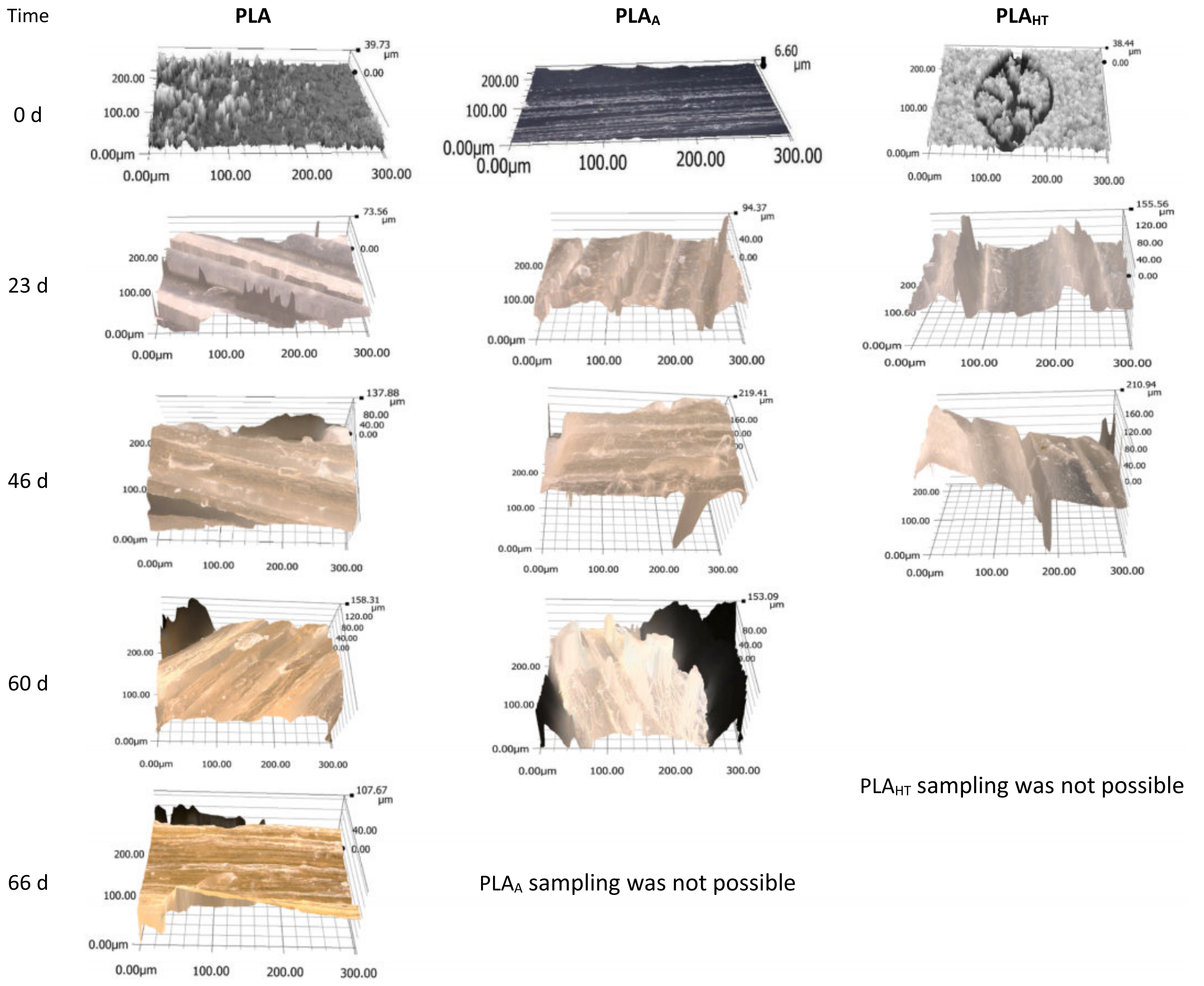


Fig. 3. Digital microscopic images of the topography of untreated (PLA) and pretreated material (PLA$_A$, PLA$_{HT}$) during anaerobic thermophilic (55 °C) biodegradation (microscopic images of the material at other sampling times are provided in the Supplementary Materials (Tab. 3.SM)).

et al., 2016). Moreover, none of the applied pretreatments changed the intensity of the FTIR spectra. After 23 days of PLA$_{HT}$ and PLA$_A$ degradation, new peaks appeared at 3300 cm^{-1}, corresponding to –OH stretching vibrations in carboxylic acids. This may indicate that ester bonds were hydrolyzed (Bernat et al., 2021). Regarding PLA, a new peak at 1585 cm^{-1} was noted at this time. With each set, both on day 23 and on the last day that the material was visible, peaks appeared at ~ 1650 cm^{-1}, which correspond to amides. These peaks may be related to the presence of biofilm on the surface (Socrates, 2001). Although the materials were cleaned with distilled water prior to analysis, their structures were probably so degraded and incrusted with biofilm that it was impossible to remove all of it.

On the last day in each set, when materials were available for analyses, the intensity of the peaks corresponding to carbonyl C═O groups increased. The formation of these groups, which are terminal groups in PLA chains, may be caused by microbial activity and hydrolytic degradation (Arrieta et al., 2014; Fortunati et al., 2011).

Based on the ratios of the FTIR bands at 755 cm^{-1} and 870 cm^{-1}, the crystallinity indexes (CI) of the PLA-m can be calculated (Stoleru et al., 2017). Before degradation, the CI values were 0.97, 0.98, and 0.99 for PLA, PLA$_A$, and PLA$_{HT}$, respectively. This indicates that pretreatments slightly increased PLA crystallinity. Generally, biodegradation proceeds first in the amorphous region of the material because the organized structure of the crystalline part is more resistant to hydrolysis. The amorphous part can be more easily penetrated by water, which leads to the scission of the hydrolyzable ester linkages and to an increase in polymer crystallinity (Elsawy et al., 2017). For example, Stoleru et al. (2017) reported that, during fungal biodegradation of PLA films, the CI of the material increased from 0.531 to 1.942 after 14 days. In the present study, the CI ratios on the final day, when the materials were available for analyses, increased to 0.98 and 1.00 for PLA and PLA$_{HT}$, respectively, whereas that of PLA$_A$ remained unchanged.

Before degradation, the DSC curve for the untreated and pretreated PLA-m showed a Tg peak at 65.5 °C and a Tm at 150.6 °C, with a corresponding enthalpy value of 30.45 J·g^{-1} (Fig. 4b,d,f). Similarly, Sundar et al. (2021) found that neat PLA had a Tm of 156.6 °C with an enthalpy of 30.92 J·g^{-1}. For PLA$_A$, Tg was slightly lower, and Tm was the same as that of untreated PLA. In contrast, for PLA$_{HT}$, Tg and Tm were higher, at 67.0 °C and 151.6 °C, respectively. None of the DSC curves displayed cold crystallization peaks. Similarly, other authors did not observe crystallization peaks in PLA cooling curves, which may indicate that the crystallization rate of PLA was slow (Luyt and Gasmi, 2016; Sundar et al., 2020).

After degradation, the Tg of the PLA did not change, but its Tm decreased to 125 °C. With both pretreated materials, Tg changed to ca. 69 °C, while Tm decreased to 120 °C and 133 °C for PLA$_A$ and PLA$_{HT}$, respectively. These decreases in the Tm are related to a rapid molecular mass reduction (Hakkarainen et al., 2000) and may be caused by

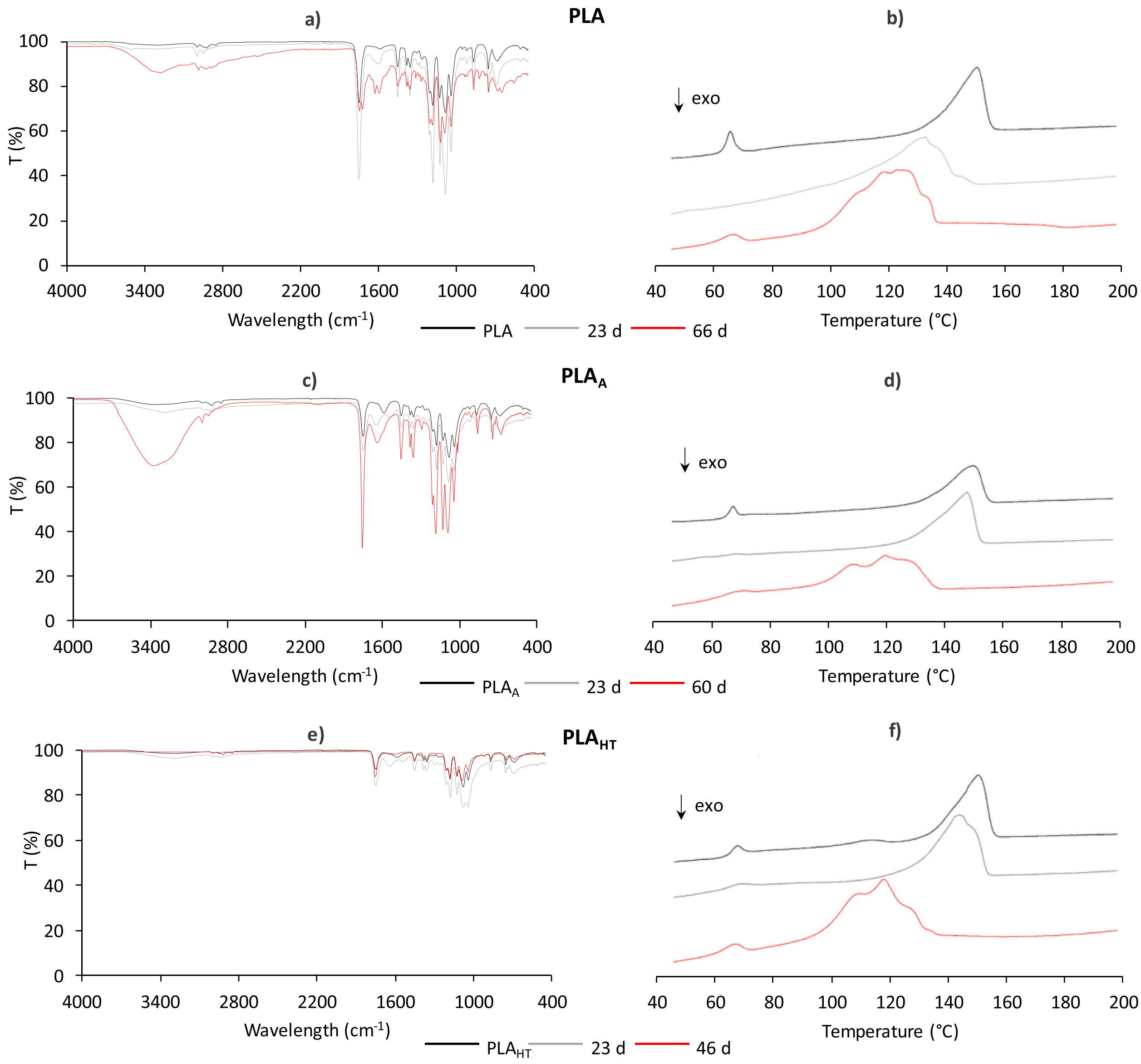


Fig. 4. FTIR spectra (a, c, e) and DSC curves (b, d, f) of untreated PLA and pretreated PLA-based materials (PLA$_A$, PLA$_{HT}$), as well as materials collected after 23 days of biodegradation and on the last possible day of material sampling.

continuing hydrolysis of the crystalline domain of the polymer; this hydrolysis starts mainly with surface erosion (Pantani and Sorrentino, 2013). Luo et al. (2019) reported a slight decrease in the Tg during composting of PLA-m filled with functionalized titanium nanoparticles. Those authors suggested that the Tg decreased due to an increase in molecule mobility caused by hydrolysis and the plasticizing effect of the oligomer fragments and water during biodegradation.

3.4. *Microorganisms in anaerobic PLA degradation*

The microbiome was characterized using 16S rRNA gene amplicon sequencing. After sequencing, over 277 k of high-quality reads were obtained, with an average of 27,715 reads per sample (Table 1). The amount of extracted, high-quality DNA averaged 265 ± 21 ng/μL. Sequencing depth was assessed using rarefaction curves (data not shown), and the number of observed OTUs varied from 120 in the inoculum to 158 in PLA_38d (Table 1). The microbial community was most diverse in samples of pretreated PLA on the 60th day of biodegradation as indicated by the Shannon index.

Table 1
Alpha diversity values of biomass from inoculum alone and from PLA, PLA$_{HT}$, and PLA$_A$, based on amplicon analysis.

Sample	Reads	Observed OTUs	Shannon index
Inoculum	23,532	120	2.51
PLA_14d	15,737	136	2.56
PLA$_{HT}$_14d	23,506	145	2.56
PLA$_A$_14d	31,238	151	2.52
PLA_38d	41,195	158	2.61
PLA$_{HT}$_38d	30,690	152	2.73
PLA$_A$_38d	31,705	155	2.55
PLA_60d	19,016	123	2.44
PLA$_{HT}$_60d	24,743	155	2.91
PLA$_A$_60d	36,461	157	3.08

Principal component analysis (PCA) of beta diversity between the analyzed samples (data not shown) indicated that the time of the experiment explained the largest amount of variation in microbial composition (PERMANOVA, F = 11.98, p < 0.001). Additionally, the application of a pretreatment was also significantly associated with microbial composition, although the amount of variance explained was smaller (PERMANOVA, F = 3.01, $p < 0.05$).

When PLA, $PLA_{HT,}$ and PLA_A samples, were grouped by the time of biodegradation (14 d, 38 d, 60 d), regardless of the application (or not) of pretreatment, the microbial composition changed over time and differed from that in the inoculum (inoculum (0 d)) (Fig. 5a).

At the phylum level, the percent abundances of *Firmicutes* increased substantially, from 2.6 % in the inoculum to an average of 29.1 % on day 60 of PLA biodegradation. Similarly, the abundances of *Thermotogae* and *Euryarcheota* increased, from 1.9 % to 4.6 % and from 0.3 % to 2.7 %, respectively.

The abundance of *Chloroflexi* was highest after 14 days of PLA biodegradation, reaching 18.4 %. The phylum *Chloroflexi* is a diverse group of microorganisms that include, among others, anaerobic organisms that can obtain energy by reducing organic chlorinated compounds *via* dehalogenation (Garrity et al., 2001; Hugenholtz and Stackebrandt, 2004).

During methanogenesis, members of *Chloroflexi* and *Firmicutes* as well as *Bacteroidetes* are the major phyla involved in hydrolysis and acidogenesis (Wang et al., 2018). After 14 days of biodegradation, the abundance of microorganisms belonging to the phylum *Actinobacteria* increased. *Actinobacteria* are among the few microorganisms with potential for PLA degradation (Penkhrue et al., 2015; Panyachanakul et al., 2019), and an increase in their number may indicate intensive PLA degradation, as confirmed by microscopic observation (Fig. 2; Tab.1–3. SM – Supplementary Materials). Additionally, this study identified bacterial genera from other phyla whose abundance was positively correlated with the time of PLA biodegradation (Fig. 1.SMa – Supplementary Materials) such as *Treponema*, *Paludibacter*, *Rubrobacter,* or *Leptolinea.*

Regarding the effect of PLA pretreatment on the microbial community, the average abundances of phyla *Cloacimonetes* (3.5 vs 6.3 %), *Bacteroidetes* (1.9 vs 6.5 %), and *Proteobacteria* (from 3.0 vs 4.7 %) were higher in samples with pretreated PLA than in samples with untreated PLA (Fig. 5b). At the genus level, PLA pretreatment significantly increased the abundances of *Bacteroides*, *Terrimonas*, *Cytophaga*, *Desulfofaba*, *Curvibacter*, *Thermomonas*, and *Flavobacterium* in biomass (Fig. 1. SMb – Supplementary Materials). Most of these genera belong to the phyla *Firmicutes* and *Bacteroidetes,* which were reported to have the highest activity in all methane-producing reactors and are responsible for producing high concentrations of VFAs during the AD process (Guo et al., 2015; Nguyen et al., 2019).

Some studies indicated that the composition of microbial communities during AnB of biodegradable materials closely depends on their composition in the inoculum. For example, Bandini et al. (2020) investigated the dynamics of microbial communities during 23-day thermophilic AnB (55 ± 2 °C) of PLA-based bottles. In the inoculum, which was a mixture of food waste slurry and anaerobic sludge from a thermophilic treatment of an organic fraction of municipal solid waste, the phyla *Bacteroidetes*, *Firmicutes,* and *Proteobacteria* were identified. During degradation, the abundance of these microorganisms increased, which directly resulted from their presence in the inoculum. Cazaudehore et al. (2021) carried out a mesophilic and thermophilic (38 and 55 °C) AnB of commercially available coffee capsules made of biodegradable PLA and starch. They used two different inocula: the mesophilic inoculum was a mixture of grass and sewage sludge; the thermophilic one was a mixture of grass, wheat waste, and sludge. *Bacteroidetes*, *Firmicutes,* and *Chloroflexi* were the major phyla identified in the mesophilic inoculum, whereas Bacteroidetes (49 %), *Thermotogae*

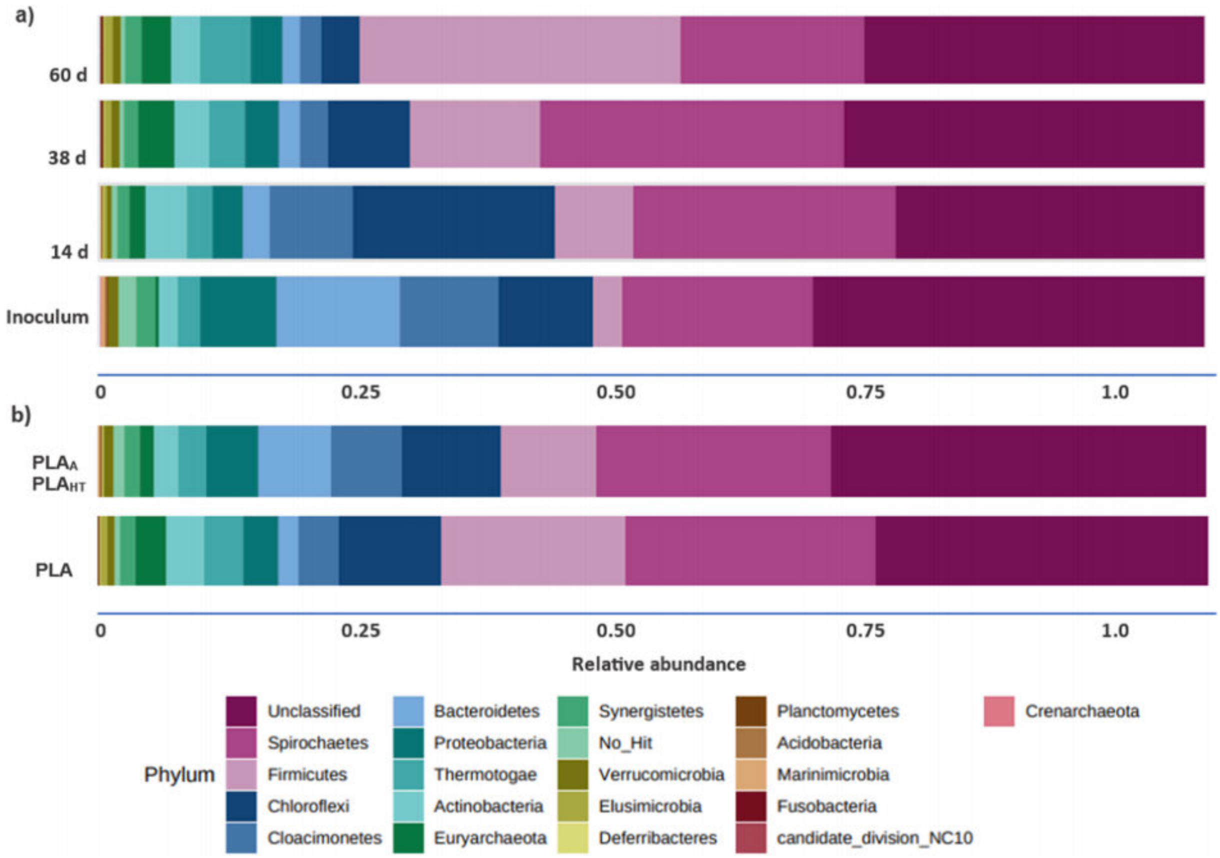


Fig. 5. A stacked bar graph presenting the microbial composition at the phylum level (percent abundance; the 21 most abundant taxa are presented); (a) PLA, PLA_{HT} and PLA_A samples were grouped by the time of biodegradation (14 d, 38 d, 60 d) regardless of the application (or not) of pretreatment and compared with the inoculum (inoculum (0 d)) and (b) samples were grouped by the application (or not) of pretreatment (pretreated PLA (PLA_{HT} and PLA_A) or untreated PLA) regardless of the time of biodegradation.

(27 %) and *Firmicutes* (22 %) predominated in the thermophilic inoculum. These microbes were abundant during the degradation of bioplastic. However, *Firmicutes* increased to 55–85 %, whereas *Bacteroidetes* decreased to<8 %. Moreover, *Tepidimicrobium* sp. was identified as the potential key microorganism during thermophilic AnB of bioplastics. In the present study, it was shown that, after 14 days of AnB, the microbiological structure of the samples to which the inoculum and PLA were dosed was different from that of the samples with inoculum alone (Fig. 6). All the samples to which PLA was added had larger shares of *Lachnospiraceae*, *Methanosaetaceae*, *Kosmotogaceae*, *Ruminococcaceae*, *Prevotellaceae*, *Intracporangiaceae*, *Peptostreptococcaceae*, *Pseudomonadaceae*, *Caldilneaceae*, *Clostridiaceae*, and *Rhodobiaceae*.

Kim et al. (2017) isolated two PLA degrading microorganisms from digester sludge, which were identified with a polymer-film-based

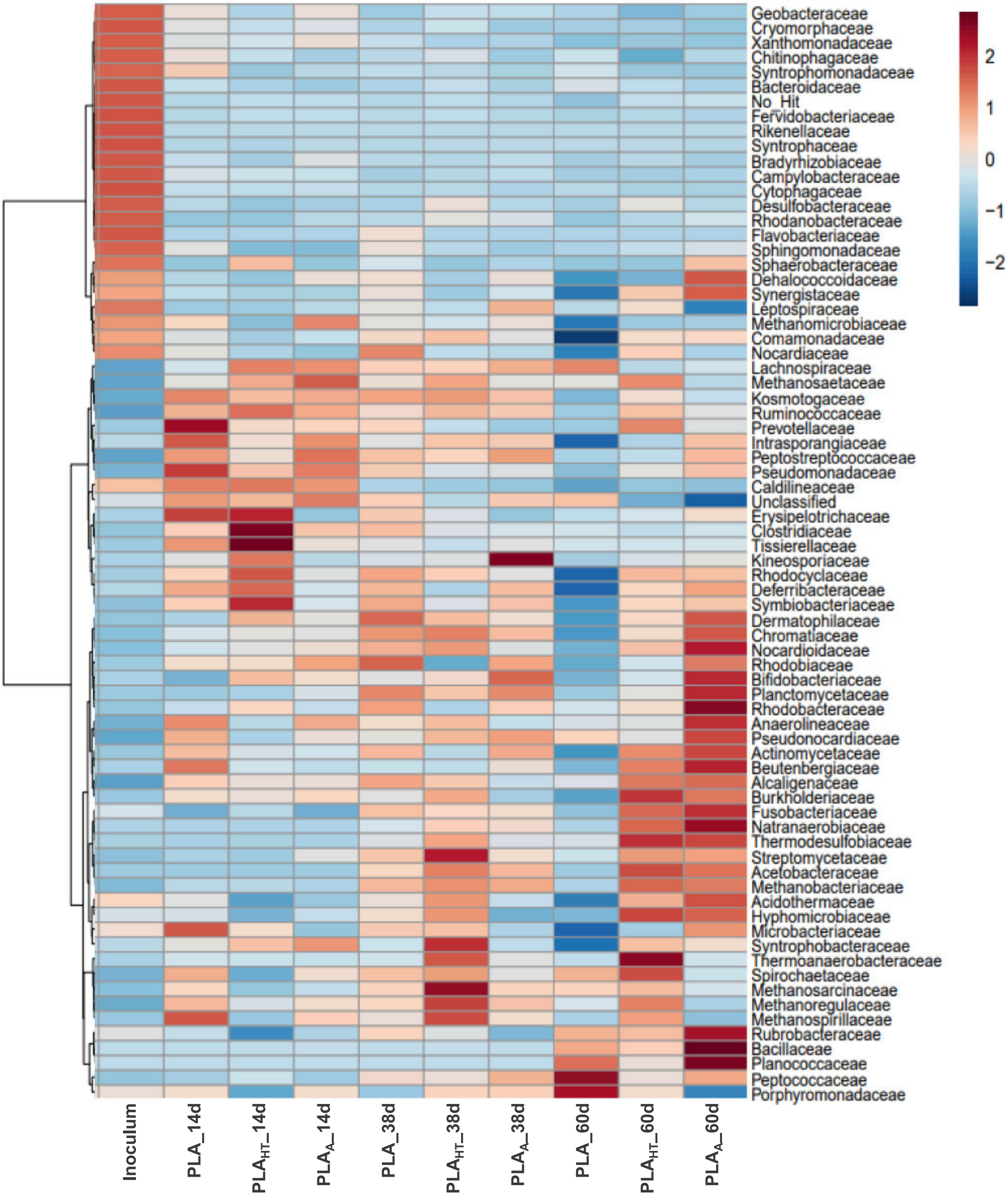


Fig. 6. Heatmap presenting differences between the investigated samples of biomass from inoculum alone and from inoculum and PLA undergoing biodegradation tests in each set (family level, Euclidean distance measure, average algorithm used for clustering).

screening method as *Pseudomonas* sp. MYK1 and *Bacillus* sp. MYK2. The isolates produced more biogas during complete biodegradation of PLA than biodegradation of the initial sludge inoculum. The authors emphasized that the screening method and isolation of PLA-degraders might be a significant stepping-stone for the further application and development of treatment methods for bio-based polymer degradation.

In the PLA_{HT}_14d sample, the abundance of *Clostridiaceae*, *Tissierellaceae*, *Symbiobacteriaceae*, and *Streptomycetaceae* increased substantially. Members of these bacterial groups take part in the first stages of AD and are efficient degraders. *Streptomycetaceae* were also identified as important PLA-degrading players Butbunchu and Pathom-Aree, (2019). The PLA had begun to be degraded, as also indicated by the MP (Fig. 1). Efficient organics degradation and the availability of methane precursors favored the growth of methanogens whose abundance was highest in all samples with PLA on day 38. The PLA_{HT}_38d sample, which had the fastest MP, also had the most diverse and abundant microbial community, including *Thermoanaerobacteraceae*, which can anaerobically degrade carbohydrates (Stackebrandt, 2014), *Syntrophobacteraceae*, which were identified as major acetotrophic sulfate reducers (Liu et al., 2018) and methanogens belonging to *Methanosarcinaceae*, *Methanoregulaceae*, *Methanospirillaceae,* and *Methanosaetaceae*. These four methanogen families were also most numerous in the PLA_{HT}_60d sample.

Among the methanogens, both families that utilize diverse substrates for energy generation and those that use a very limited range of substrates were identified which may have influenced the effectiveness of MP. Members of the family *Methanosarcinaceae* generate energy from methylated amines and methanol, many of those species can grow on H_2/CO_2, and some use acetate, as well as other substrates such as methanethiol, dimethyl sulfide, or carbon monoxide. Members of the families *Methanoregulaceae* and *Methanospirillaceae* use H_2/CO_2 and sometimes formate as substrates for methanogenesis while *Methanosarcinales* use acetate as their sole source of energy (Oren, 2014).

Among the bacteria involved in the biodegradation of PLA and PLA_A, the abundances of *Acetobacteraceae* and *Mathanobacteriaceae* had increased on day 38. However, on day 60, the abundances of these two groups remained high only in samples with PLA_{HT} or PLA_A. In samples with PLA, the shares of *Peptococcaceae* and *Porphyromonadacea* increased. On day 60 of PLA_A biodegradation, the abundance of the families *Rubrobacteraceae*, *Bacillaceae*, *Planococcaceae*, *Dehalococcoidaceae*, *Synergistaceae*, *Nocardioidaceae*, *Bifidobacteriaceae*, *Planctomyceaceae*, *Rhodobacteraceae*, *Anaerolineaceae,* and *Pseudonocardiaceae* increased.

In samples with PLA_{HT} or PLA_A, there was an increase in the share of microorganisms belonging to the families *Actinomycetaceae*, *Beutenbergiaceae*, *Alcaligenaceae*, *Burkholderiaceae*, *Fusobacteriaceae*, *Natranaerobiaceae*, *Thermodesulfobiaceae*, and *Hyphomicrobiaceae* (Fig. 6). Members of *Actinomycetaceae* such as *Actinomadura keratinilytica* strain T16-1 can produce PLA-degrading enzymes. The results of Panyachanakul et al. (2019) concerning PLA degradation with the use of the enzyme from *A. keratinilytica* strain T16-1 indicated that the highest efficiency (89 %) was obtained after 72 h at 60 °C with an agitation speed of 50 rpm and a controlled pH of 8.0.

4. Conclusion

Thermophilic conditions allow MP from both untreated and pretreated PLA-m to reach 453 L/kg vS which is almost 100 % of the theoretical methane yield from PLA. Although, the use of pretreatment prior to AnB of PLA-m shortened the lag phase and the time to reach maximal MP, the use of HT most effectively improved both the time necessary to reach maximal MP (shortening the time by more than 2 weeks in comparison to untreated PLA) and methane was produced with almost 10 % higher rate (8.35 vs 7.79 L/(kg VS·d)).

The FTIR spectra of the PLA-m showed typical bands for poly(lactic acid). On the last day that materials were available, the intensity of the peaks corresponding to carbonyl C=O groups increased, which may reflect the activity of microorganisms and hydrolytic material degradation. The cracks and fissures in PLA structure became deeper and more numerous, which was accompanied by the most intense MP and the most diverse microbial community. Regardless of the application of pretreatment, the abundances of *Firmicutes*, *Thermotogae,* and *Euryarcheota* increased. With PLA_{HT}, the microbial community was the most diverse and abundant, including *Syntrophobacteraceae*, *Thermoanaerobacteraceae*, and methanogens such as *Methanosarcinaceae*, *Methanoregulaceae*, *Methanospirillaceae,* and *Methanosaetaceae*.

As more and more new bio-base products have appeared on the market (especially those labeled as biodegradable), the biodegradability of these materials must be determined to facilitate further waste management. Knowledge of the average time needed for the degradation of various bio-based materials is required to design e.g. the retention time in digesters operated in full-scale conditions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

This research was funded in part by the National Science Centre, Poland (Grant No. 2021/41/N/NZ9/01750). Project financially supported by the Minister of Education and Science under the program entitled “Regional Initiative of Excellence” for the years 2019-2023, Project No. 010/RID/2018/19, amount of funding 12.000.000 PLN.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2022.10.031.

References

Akutsu-Shigeno, Y., Teeraphatpornchai, T., Teamtisong, K., Nomura, N., Uchiyama, H., Nakahara, T., Nakajima-Kambe, T., 2003. Cloning and sequencing of a poly(DL-lactic acid) depolymerase gene from Paenibacillus amylolyticus strain TB-13 and its functional expression in Escherichia coli. Appl. Environ. Microbiol. 69, 2498–2504. https://doi.org/10.1128/AEM.69.5.2498-2504.2003.

Antipova, T.V., Zhelifonova, V.P., Zaitsev, K.V., Nedorezova, P.M., Aladyshev, A.M., Klyamkina, A.N., Kostyuk, S.V., Danilogorskaya, A.A., Kozlovsky, A.G., 2018. Biodegradation of Poly-ε-caprolactones and Poly-l-lactides by Fungi. J. Polym. Environ. 26, 4350–4359. https://doi.org/10.1007/s10924-018-1307-3.

Arrieta, M.P., López, J., Rayón, E., Jiménez, A., 2014. Disintegrability under composting conditions of plasticized PLA–PHB blends. Polym. Degrad. Stab. 108, 307–318. https://doi.org/10.1016/J.POLYMDEGRADSTAB.2014.01.034.

Bandini, F., Frache, A., Ferrarini, A., Taskin, E., Cocconcelli, P.S., Puglisi, E., 2020. Fate of biodegradable polymers under industrial conditions for anaerobic digestion and aerobic composting of food waste. J. Polym. Environ. 28, 2539–2550. https://doi.org/10.1007/s10924-020-01791-y.

Battista, F., Frison, N., Bolzonella, D., 2021. Can bioplastics be treated in conventional anaerobic digesters for food waste treatment? Environ. Technol. Innov. 22, 101393 https://doi.org/10.1016/j.eti.2021.101393.

Benn, N., Zitomer, D., 2018. Pretreatment and anaerobic co-digestion of selected PHB and PLA bioplastics. Front. Environ. Sci. 5, 93. https://doi.org/10.3389/fenvs.2017.00093.

Bernat, K., Kulikowska, D., Wojnowska-Baryła, I., Zaborowska, M., Pasieczna-Patkowska, S., 2021. Thermophilic and mesophilic biogas production from PLA-based materials: possibilities and limitations. Waste Manag. 119, 295–305. https://doi.org/10.1016/j.wasman.2020.10.006.

Bonifer, K.S., Wen, X., Hasim, S., Phillips, E.K., Dunlap, R.N., Gann, E.R., DeBruyn, J.M., Reynolds, T.B., 2019. Bacillus pumilus B12 degrades polylactic acid and degradation is affected by changing nutrient conditions. Front. Microbiol. 10, 2548. https://doi.org/10.3389/fmicb.2019.02548.

Bubpachat, T., Sombatsompop, N., Prapagdee, B., 2018. Isolation and role of polylactic acid-degrading bacteria on degrading enzymes productions and PLA biodegradability at mesophilic conditions. Polym. Degrad. Stab. 152, 75–85. https://doi.org/10.1016/j.polymdegradstab.2018.03.023.

Buswell, A.M., Mueller, H.F., 1952. Mechanism of methane fermentation. Ind. Eng. Chem. 44, 550–552. https://doi.org/10.1021/ie50507a033.

Butbunchu, N., Pathom-Aree, W., 2019. Actinobacteria as promising candidate for polylactic acid type bioplastic degradation. Front. Microbiol. 10, 2834. https://doi.org/10.3389/fmicb.2019.02834.

Caporaso, J.G., Lauber, C.L., Walters, W.A., Berg-Lyons, D., Lozupone, C.A., Turnbaugh, P.J., Fierer, N., Knight, R., 2011. Global patterns of 16S rRNA diversity at a depth of millions of sequences per sample. Proc. Nat. Acad. Sci. USA 108 (supplement_1), 4516–4522. https://doi.org/10.1073/pnas.1000080107.

Cazaudehore, G., Monlau, F., Gassie, C., Lallement, A., Guyoneaud, R., 2021. Methane production and active microbial communities during anaerobic digestion of three commercial biodegradable coffee capsules under mesophilic and thermophilic conditions. Sci. Total Environ. 784, 146972 https://doi.org/10.1016/j.scitotenv.2021.146972.

Chomchoei, A., Pathom-Aree, W., Yokota, A., Kanongnuch, C., Lumyong, S., 2011. Amycolatopsis thailandensis sp. nov., a poly(L-lactic acid)-degrading actinomycete, isolated from soil. Int. J. Syst. Evol. Microbiol. 61, 839–843. https://doi.org/10.1099/ijs.0.023564-0.

Chong, J., Liu, P., Zhou, G., Xia, J., 2020. Using MicrobiomeAnalyst for comprehensive statistical, functional, and meta-analysis of microbiome data. Nat. Protoc. 15, 799–821. https://doi.org/10.1038/s41596-019-0264-1.

Dhariwal, A., Chong, J., Habib, S., King, I.L., Agellon, L.B., Xia, J., 2017. MicrobiomeAnalyst: a web-based tool for comprehensive statistical, visual and meta-analysis of microbiome data. Nucleic Acids Res. 45, W180–W188. https://doi.org/10.1093/nar/gkx295.

Elsawy, M.A., Kim, K.H., Park, J.W., Deep, A., 2017. Hydrolytic degradation of polylactic acid (PLA) and its composites. Renew. Sustain. Energy Rev. 79, 1346–1352. https://doi.org/10.1016/j.rser.2017.05.143.

Fortunati, E., Armentano, I., Iannoni, A., Barbale, M., Zaccheo, S., Scavone, M., Visai, L., Kenny, J.M., 2011. New multifunctional poly(lactide acid) composites: mechanical, antibacterial, and degradation properties. J. Appl. Polym. Sci. 124, 87–98. https://doi.org/10.1002/app.35039.

Fortunati, E., Puglia, D., Santulli, C., Sarasini, F., Kenny, J.M., 2012. Biodegradation of phormium tenax/poly(lactic acid) composites. J. Appl. Polym. Sci. 125, E562–E572. https://doi.org/10.1002/app.36839.

Garrity, G.M., Holt, J.G., Castenholz, R.W., Pierson, B.K., Keppen, O.I., Gorlenko, V.M., 2001. Phylum BVI. Chloroflexi phy. nov., in: Boone, D.R., Castenholz, R.W., Garrity, G.M. (Eds.), Bergey's Manual® of Systematic Bacteriology. Springer, New York, pp. 427–446. doi: 10.1007/978-0-387-21609-6_23.

Gorrasi, G., Pantani, R., 2018. Hydrolysis and biodegradation of poly(lactic acid). Adv. Polym. Sci. 279, 119–151. https://doi.org/10.1007/12_2016_12.

Greenberg, A.E., Clesceri, L.S., Eaton, A.D., 1992. Standard Methods for the Examination of Water and Wastewater. APHA, Washington.

Guo, J., Peng, Y., Ni, B.-J., Han, X., Fan, L., Yuan, Z., 2015. Dissecting microbial community structure and methane-producing pathways of a full-scale anaerobic reactor digesting activated sludge from wastewater treatment by metagenomic sequencing. Microb. Cell Factories 14. https://doi.org/10.1186/s12934-015-0218-4.

Hakkarainen, M., 2002. Aliphatic polyesters: abiotic and biotic degradation and degradation products. Adv. Polym. Sci. 157, 113–138. https://doi.org/10.1007/3-540-45734-8_4.

Hakkarainen, M., Karlsson, S., Albertsson, A.C., 2000. Rapid (bio) degradation of polylactide by mixed culture of compost microorganisms - low molecular weight products and matrix changes. Polymer 41, 2331–2338. https://doi.org/10.1016/S0032-3861(99)00393-6.

Hamad, K., Kaseem, M., Yang, H.W., Deri, F., Ko, Y.G., 2015. Properties and medical applications of polylactic acid: a review. Express Polym. Lett. 9, 435–455. https://doi.org/10.3144/expresspolymlett.2015.42.

Hobbs, S.R., Parameswaran, P., Astmann, B., Devkota, J.P., Landis, A.E., 2019. Anaerobic codigestion of food waste and polylactic acid: effect of pretreatment on methane yield and solid reduction. Adv. Mater. Sci. Eng. 2019, 1–6.

Hugenholtz, P., Stackebrandt, E., 2004. Reclassification of Sphaerobacter thermophilus from the subclass Sphaerobacteridae in the phylum Actinobacteria to the class Thermomicrobia (emended description) in the phylum Chloroflexi (emended description). Int. J. Syst. Evol. Microbiol. 54, 2049–2051. https://doi.org/10.1099/ijs.0.03028-0.

Jachimowicz, P., Nosek, D., Cydzik-Kwiatkowska, A., 2022. Chemical and microbiological changes on the surface of microplastic after long term exposition to different concentrations of ammonium in the environment. Sci. Tot. Environ. 830, 154784 https://doi.org/10.1016/j.scitotenv.2022.154784.

Jarerat, A., Tokiwa, Y., 2001. Degradation of poly(l-lactide) by a fungus. Macromol. Biosci. 1, 134–140. https://doi.org/10.1002/1616-5195(20010601)1:4<136::AID-MABI136>3.0.CO;2-3.

Kervran, M., Vagner, C., Cochez, M., Ponçot, M., Saeb, M.R., Vahabi, H., 2022. Thermal degradation of polylactic acid (PLA)/polyhydroxybutyrate (PHB) blends: a systematic review. Polym. Degrad. Stab. 201 (2022), 109995 https://doi.org/10.1016/j.polymdegradstab.2022.109995.

Kim, M.Y., Kim, C., Moon, J., Heo, J., Jung, S.P., Kim, J.R., 2017. Polymer film-based screening and isolation of polylactic acid (PLA)-degrading microorganisms. J. Microbiol. Biotechnol. 27, 342–349. https://doi.org/10.4014/JMB.1610.10015.

Kliem, S., Kreutzbruck, M., Bonten, C., 2020. Review on the biological degradation of polymers in various environments. Materials (Basel) 13, 4586. https://doi.org/10.3390/ma13204586.

Kolstad, J.J., Vink, E.T.H., De Wilde, B., Debeer, L., 2012. Assessment of anaerobic degradation of IngeoTM polylactides under accelerated landfill conditions. Polym. Degrad. Stab. 97, 1131–1141. https://doi.org/10.1016/j.polymdegradstab.2012.04.003.

Kumar, A., Tumu, V.R., Ray Chowdhury, S., Ramana, R.R., 2019. A green physical approach to compatibilize a bio-based poly (lactic acid)/lignin blend for better mechanical, thermal and degradation properties. Int. J. Biol. Macromol. 121, 588–600. https://doi.org/10.1016/J.IJBIOMAC.2018.10.057.

Lee, J.C., Moon, J.H., Jeong, J.H., Kim, M.Y., Kim, B.M., Choi, M.C., Kim, J.R., Ha, C.S., 2016. Biodegradability of poly(lactic acid) (PLA)/lactic acid (LA) blends using anaerobic digester sludge. Macromol. Res. 24, 741–747. https://doi.org/10.1007/s13233-016-4100-y.

Liu, P., Pommerenke, B., Conrad, R., 2018. Identification of Syntrophobacteraceae as major acetate-degrading sulfate reducing bacteria in Italian paddy soil. Environ. Microbiol. 20, 337–354. https://doi.org/10.1111/1462-2920.14001.

Luo, Y., Lin, Z., Guo, G., 2019. Biodegradation assessment of poly (lactic acid) filled with functionalized titania nanoparticles (PLA/TiO2) under compost conditions. Nanoscale Res. Lett. 14, 1–10. https://doi.org/10.1186/s11671-019-2891-4.

Luyt, A.S., Gasmi, S., 2016. Influence of blending and blend morphology on the thermal properties and crystallization behaviour of PLA and PCL in PLA/PCL blends. J. Mat. Sci. 51, 4670–4681. https://doi.org/10.1007/s10853-016-9784-z.

Masaki, K., Kamini, N.R., Ikeda, H., Iefuji, H., 2005. Cutinase-like enzyme from the yeast Cryptococcus sp. strain S-2 hydrolyzes polylactic acid and other biodegradable plastics. Appl. Environ. Microbiol. 71, 7548–7550. https://doi.org/10.1128/AEM.71.11.7548-7550.2005.

McMurdie, P.J., Holmes, S., 2014. Waste not, want not: why rarefying microbiome data is inadmissible. PLoS Comput. Biol. 10, e1003531.

Mu, L., Zhang, L., Ma, J., Zhu, K., Chen, C., Li, A., 2021. Enhanced biomethanization of waste polylactic acid plastic by mild hydrothermal pretreatment: Taguchi orthogonal optimization and kinetics modeling. Waste Manag. 126, 585–596. https://doi.org/10.1016/j.wasman.2021.03.044.

Nguyen, D., Nitayavardhana, S., Sawatdeenarunat, C., Surendra, K.C., Khanal, S.K., 2019. Chapter 31. Biogas production by anaerobic digestion: status and perspectives. In: Pandey, A., Larroche, C., Dussap, C.-.-G., Gnansounou, E., Khanal, S.K., Ricke, S. (Eds.), Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels. Academic Press, pp. 763–778. https://doi.org/10.1016/B978-0-12-816856-1.00031-2.

Oren A., 2014. The Family Methanosarcinaceae, in: Rosenberg, E., DeLong, E.F., Lory, S., Stackebrandt, E., Thompson, F. (Eds.), The Prokaryotes. Other Major Lineages of Bacteria and The Archaea, 4th ed. Springer Reference, pp. 413–419. doi: 10.1007/978-3-642-38954-2_408.

Pantani, R., Sorrentino, A., 2013. Influence of crystallinity on the biodegradation rate of injection-moulded pol(lactic acid) samples in controlled composting conditions. Polym. Degrad. Stab. 98, 1089–1096. https://doi.org/10.1016/j.polymdegradstab.2013.01.005.

Panyachanakul, T., Sorachart, B., Lumyong, S., Lorliam, W., Kitpreechavanich, V., Krajangsang, S., 2019. Development of biodegradation process for poly(DL-lactic acid) degradation by crude enzyme produced by Actinomadura keratinilytica strain T16–1. Electron. J. Biotechnol. 40, 52–57. https://doi.org/10.1016/j.ejbt.2019.04.005.

Penkhrue, W., Khanongnuch, C., Masaki, K., Pathom-aree, W., Punyodom, W., Lumyong, S., 2015. Isolation and screening of biopolymer-degrading microorganisms from northern Thailand. World J. Microbiol. Biotechnol. 31, 1431–1442. https://doi.org/10.1007/s11274-015-1895-1.

Penkhrue, W., Sujarit, K., Kudo, T., Ohkuma, M., Masaki, K., Aizawa, T., Pathom-Aree, W., Khanongnuch, C., Lumyong, S., 2018. Amycolatopsis oliviviridis sp. Nov., a novel polylactic acidbioplastic-degrading actinomycete isolated from paddy soil. Int. J. Syst. Evol. Microbiol. 68, 1448–1454. https://doi.org/10.1099/ijsem.0.002682.

Qi, X., Ren, Y., Wang, X., 2017. New advances in the biodegradation of Poly(lactic) acid. Int. Biodeterior. Biodegrad. 117, 215–223. https://doi.org/10.1016/j.ibiod.2017.01.010.

Reeve, M.S., McCarthy, S.P., Downey, M.J., Gross, R.A., 2002. Polylactide stereochemistry: effect on enzymic degradability. Macromolecules 27, 825–831. https://doi.org/10.1021/ma00081a030.

Ruggero, F., Onderwater, R.C., Carretti, E., Roosa, S., Benali, S., Raquez, J.M., Gori, R., Lubello, C., Wattiez, R., 2021. Degradation of film and rigid bioplastics during the thermophilic phase and the maturation phase of simulated composting. J. Polym. Environ. 29, 3015–3028. https://doi.org/10.1016/j.aiepr.2021.06.006.

Samitthiwetcharong, S., Chavalparit, O., 2019. Enhancement of methane production from alkaline pretreated poly (lactic acid) waste by the co-digestion process. Int. J. GEOMATE 16, 171–176. doi: 10.21660/2019.56.4773.

Samitthiwetcharong, S., Kullavanijaya, P., Chavalparit, O., 2017. Anaerobic biodegradation of polylactic acid under mesophilic condition using thermal-alkaline pretreatment. doi: 10.1088/1757-899X/222/1/012009.

Shrestha, A., van-Eerten Jansen, M.C.A.A., Acharya, B., 2020. Biodegradation of bioplastic using anaerobic digestion at retention time as per industrial biogas plant and international norms. Sustain 12, 4231. doi: 10.3390/su12104231.

Socrates, G., 2001. Infrared and Raman characteristic Group Frequencies: Tables and Charts. John Wiley & Sons, England.

Stackebrandt, E., 2014. The Family Thermoanaerobacteraceae. In: Rosenberg, E., DeLong, E.F., Lory, S., Stackebrandt, E., Thompson, F. (Eds.), The Prokaryotes. Springer, Berlin, Heidelberg. doi: 10.1007/978-3-642-30120-9_367.

Stoleru, E., Hitruc, E.G., Vasile, C., Oprică, L., 2017. Biodegradation of poly(lactic acid)/chitosan stratified composites in presence of the Phanerochaete chrysosporium fungus. Polym. Degrad. Stab. 143, 118–129. https://doi.org/10.1016/j.polymdegradstab.2017.06.023.

Sundar, N., Kumar, A., Pavithra, A., Ghosh, S., 2020. Studies on semi-crystalline poly lactic acid (PLA) as a hydrophobic coating material on kraft paper for imparting barrier properties in coated abrasive applications. Prog. Org. Coat. 145, 105682 https://doi.org/10.1016/j.porgcoat.2020.105682.

Sundar, N., Stanley, S.J., Kumar, S.A., Keerthana, P., Kumar, G.A., 2021. Development of dual purpose, industrially important PLA–PEG based coated abrasives and packaging materials. J. Appl. Polym. Sci. 138, 50495. https://doi.org/10.1002/app.50495.

Szumigaj, J., Zakowska, Z., Klimek, L., Rosicka-Kaczmarek, J., Bartkowiak, A., 2008. Assessment of polylactide foil degradation as a result of filamentous fungi activity. Pol. J. Environ. Stud. 17, 335–341.

Tomita, K., Kuroki, Y., Nagai, K., 1999. Isolation of thermophiles degrading poly(l-lactic acid). J. Biosci. Bioeng. 87, 752–755. https://doi.org/10.1016/S1389-1723(99)80148-0.

Venkiteshwaran, K., Benn, N., Seyedi, S., Zitomer, D., 2019. Methane yield and lag correlate with bacterial community shift following bioplastic anaerobic co-digestion. Bioresour. Technol. Rep. 7, 100198 https://doi.org/10.1016/j.biteb.2019.100198.

Wang, P., Wang, H., Qiu, Y., Ren, L., Jiang, B., 2018. Microbial characteristics in anaerobic digestion process of food waste for methane production-A review. Bioresour. Technol. 248, 29–36. https://doi.org/10.1016/j.biortech.2017.06.152.

Yagi, H., Ninomiya, F., Funabashi, M., Kunioka, M., 2013. Thermophilic anaerobic biodegradation test and analysis of eubacteria involved in anaerobic biodegradation of four specified biodegradable polyesters. Polym. Degrad. Stab. 98, 2013, 1182–1187. doi: 10.1016/j.polymdegradstab.2013.03.010.

Yagi, H., Ninomiya, F., Funabashi, M., Kunioka, M., 2009. Anaerobic biodegradation tests of poly (lactic acid) and polycaprolactone using new evaluation system for methane fermentation in anaerobic sludge. Polym. Deg. Stab. 94, 1397–1404. https://doi.org/10.1016/j.polymdegradstab.2009.05.012.

Zaborowska, M., Bernat, K., Pszczółkowski, B., Wojnowska-Baryła, I., Kulikowska, D., 2021. Anaerobic degradability of commercially available bio-based and oxo-degradable packaging materials in the context of their end of life in the waste management strategy. Sustainability 13, 6818. https://doi.org/10.3390/su13126818.

Zhang, W., Heaven, S., Banks, C.J., 2018. Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste. Polym. Degrad. Stab. 147, 76–88. https://doi.org/10.1016/j.polymdegradstab.2017.11.005.

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Magdalena Zaborowska, oświadczam, że mój wkład naukowy w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Cydzik-Kwiatkowska Agnieszka, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Multi-faceted analysis of thermophilic anaerobic biodegradation of poly (lactic acid)-based material. *Waste Management*, 155, 40-52.

Mój udział jako współautora publikacji obejmował:

- ☒ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☒ Udział w graficznym przedstawieniu wyników
- ☒ Udział w planowaniu badań
- ☒ Prowadzenie badań i analiz laboratoryjnych
- ☐ Konsultacja i opieka
- ☒ Udział w interpretacji wyników i wnioskowaniu
- ☒ Korekta pracy przed złożeniem do druku

07.07.2023 Magdalena Zaborowska
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Katarzyna Bernat, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Cydzik-Kwiatkowska Agnieszka, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Multi-faceted analysis of thermophilic anaerobic biodegradation of poly (lactic acid)-based material. *Waste Management*, 155, 40-52.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

☒ Współautorstwo w przygotowaniu koncepcji pracy
☒ Udział w pisaniu pracy
☒ Udział w graficznym przedstawieniu wyników
☒ Udział w planowaniu badań
☐ Prowadzenie badań i analiz laboratoryjnych
☒ Konsultacja i opieka
☒ Udział w interpretacji wyników i wnioskowaniu
☒ Korekta pracy przed złożeniem do druku

7.07.2023r. Katarzyna Bernat
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Bartosz Pszczółkowski, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Cydzik-Kwiatkowska Agnieszka, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Multi-faceted analysis of thermophilic anaerobic biodegradation of poly (lactic acid)-based material. *Waste Management*, 155, 40-52.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

☐ Współautorstwo w przygotowaniu koncepcji pracy
☐ Udział w pisaniu pracy
☒ Udział w graficznym przedstawieniu wyników
☐ Udział w planowaniu badań
☒ Prowadzenie badań i analiz laboratoryjnych
☐ Konsultacja i opieka
☒ Udział w interpretacji wyników i wnioskowaniu
☐ Korekta pracy przed złożeniem do druku

07.07.2023 ....
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Agnieszka Cydzik-Kwiatkowska, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Cydzik-Kwiatkowska Agnieszka, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Multi-faceted analysis of thermophilic anaerobic biodegradation of poly (lactic acid)-based material. *Waste Management*, 155, 40-52.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☐ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☐ Udział w graficznym przedstawieniu wyników
- ☐ Udział w planowaniu badań
- ☒ Prowadzenie badań i analiz laboratoryjnych
- ☐ Konsultacja i opieka
- ☒ Udział w interpretacji wyników i wnioskowaniu
- ☐ Korekta pracy przed złożeniem do druku

06.07.23 A Cydzik-Kwiatkowska
……………………………………………
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Dorota Kulikowska, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Cydzik-Kwiatkowska Agnieszka, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Multi-faceted analysis of thermophilic anaerobic biodegradation of poly (lactic acid)-based material. *Waste Management*, 155, 40-52.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

☐ Współautorstwo w przygotowaniu koncepcji pracy

☒ Udział w pisaniu pracy

☐ Udział w graficznym przedstawieniu wyników

☐ Udział w planowaniu badań

☐ Prowadzenie badań i analiz laboratoryjnych

☒ Konsultacja i opieka

☐ Udział w interpretacji wyników i wnioskowaniu

☐ Korekta pracy przed złożeniem do druku

06.07.2023 ……………………

data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Irena Wojnowska-Baryła, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Cydzik-Kwiatkowska Agnieszka, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Multi-faceted analysis of thermophilic anaerobic biodegradation of poly (lactic acid)-based material. *Waste Management*, 155, 40-52.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

☐ Współautorstwo w przygotowaniu koncepcji pracy
☒ Udział w pisaniu pracy
☐ Udział w graficznym przedstawieniu wyników
☐ Udział w planowaniu badań
☐ Prowadzenie badań i analiz laboratoryjnych
☒ Konsultacja i opieka
☐ Udział w interpretacji wyników i wnioskowaniu
☐ Korekta pracy przed złożeniem do druku

7.07.2023 I Wojnowska-
....
data i podpis

Waste Management 168 (2023) 413–422

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Research Paper

Assessment of biodegradability of cellulose and poly(butylene succinate)-based bioplastics under mesophilic and thermophilic anaerobic digestion with a view towards biorecycling

Magdalena Zaborowska[a,*], Katarzyna Bernat[a], Bartosz Pszczółkowski[b], Dorota Kulikowska[a], Irena Wojnowska-Baryła[a]

[a] *Department of Environmental Biotechnology, Faculty of Geoengineering, University of Warmia and Mazury in Olsztyn, 10-719 Olsztyn, Poland*
[b] *Department of Materials and Machines Technology, University of Warmia and Mazury in Olsztyn, 10-719 Olsztyn, Poland*

ARTICLE INFO

Keywords:
Bio-based polymer
Methane production
FTIR/PAS analysis
Kinetics of degradation
Tensile strength
The topography of bioplastic structure

ABSTRACT

Despite the increasing interest in bioplastics, there are still contradictory results on their actual biodegradability, which cause difficulties in choosing and developing appropriate sustainable treatment methods. Two biofoils (based on poly(butylene succinate) (PBS_{37}) and cellulose (Cel_{37})) were anaerobically degraded during 100-day mesophilic (37 °C) and thermophilic (55 °C) tests (PBS_{55}, Cel_{55}). To overcome low degradation rates in mesophilic conditions, alkaline pre-treatment was also used (Pre-PBS_{37}, Pre-Cel_{37}). For comprehensive understanding of biodegradability, not only methane production (MP), but also the structure (topography, microscopic analysis), tensile properties, and FTIR spectra of the materials undergoing anaerobic degradation (AD) analysed.

PBS_{37} and Pre-PBS_{37} were visible in 100-day degradation, and the cumulative MP reached 25.5 and 29.3 L/kg VS, respectively (4.3–4.9% of theoretical MP (TMP)). The biofoils started to show damage, losing their mechanical properties over 35 days. In contrast, PBS_{55} was visible for 14 days (cracks and fissures appeared), cumulative MP was 180.2 L/kg VS (30.2% of the TMP).

Pieces of Cel were visible only during 2 days of degradation, and the MP was 311.4–315.0 L/kg VS (77.3–78.2% of the TMP) at 37 °C and 319.5 L/kg VS (79.3% of the TMP) at 55 °C. The FTIR spectra of Cel and PBS did not show shifts and formation of peaks.

These findings showed differences in terms of the actual biodegradability of the bioplastics and provided a deeper understanding of their behaviour in AD, thus indicating limitations of AD as the final treatment of some materials, and also may support the establishment of guidelines for bioplastic management.

1. Introduction

In recent decades, the global demand for plastics has increased rapidly, resulting in a high amount of waste. The European Union, for example, recorded more than 29 million tonnes of plastic waste in 2020, of which only 30% was recycled and 40% was recovered for energy. However, about 23% of this waste is still sent to landfills, which is more than 6.5 million tonnes (Plastic Europe, 2021). Plastic waste is long-term pollution that requires both mandatory and voluntary measures to minimise its impact on the environment. Growing consumer awareness, pressure from non-governmental organisations, and the need to reduce the accumulation of plastic and microplastics have necessitated the search for sustainable alternatives to plastics, such as bio-based and biodegradable polymers. Among the various polymers, cellulose and its derivatives are some of the most important natural compounds that can be alternatives to conventional plastics due to their potential biodegradability, renewability, relatively good mechanical properties, and low price (Jin et al., 2023). Cellulose-based bioplastic produced from rice straw has been reported to have mechanical properties (tensile strength and elongation) similar to those of polystyrene and plasticized poly(vinyl chloride) in the dry and wet states, respectively (Bilo et al., 2018). Currently, most cellulose is derived from plant resources, e.g., wood (Andreu-Hayles, 2019), hemp (Manian et al., 2021) and tomato residues (Kassab et al., 2020)). It can also be produced by microorganisms, e.g., *Rhizobium*, *Acetobacter*, or *Sarcina* (Chen et al., 2022). It should be noted that despite the chemical similarity of plant and

---

* Corresponding author.
E-mail address: magdalena.zaborowska@uwm.edu.pl (M. Zaborowska).

https://doi.org/10.1016/j.wasman.2023.06.022
Received 3 April 2023; Received in revised form 12 June 2023; Accepted 14 June 2023

microbial cellulose, their mechanical and physical properties are different (Czaja et al., 2007). For example, plant cellulose is characterised by a lower degree of crystallisation and a higher degree of polymerisation than microbial cellulose (de Amorim et al., 2020). Since the latter is chemically pure, it is desirable for certain applications, e.g., in biomedicine and pharmaceutics. In contrast, plant cellulose may contain impurities (e.g., hemicellulose, ash, or pectin) that make it suitable for other applications, such as the paper and textile industries (Naomi et al., 2020).

Cellulose is characterized by strong and highly structured intermolecular hydrogen bonds and is neither meltable nor soluble in water or conventional organic solvents. Therefore, cellulose derivatives are mostly used in commercial applications instead of pure polymers (Bayer et al., 2014; Ashter, 2016). Cellulose is also used as an additive to improve the mechanical and barrier properties of bioplastics (Vilarinho et al., 2018). The main applications of cellulose-based plastics are biodegradable food packaging, especially for short-life products (Quasim et al., 2021). Even though cellulose-based bioplastics have gained much popularity because they are considered biodegradable, among other reasons), there are only a few studies on their actual biodegradability (Nigam et al., 2022).

Another biodegradable material that has recently become a viable substitute for conventional polymers is bio-based poly(butylene succinate) (PBS). For many years, PBS was produced from petrochemical feedstocks, but nowadays the production of the polymer from renewable sources (maize, cassava, or sugarcane) has gained attention (Aliotta et al., 2022). Bio-based PBS is a relatively new polymer on the market, but due to its ease of processing, it has found various applications, from agricultural mulch films, disposable bags or packaging to biomedical materials (Hann et al., 2020). The main obstacle to expanding the use of bio-PBS is its high production cost (Ni et al., 2020). Therefore, in order to reduce the price of the final product, the polymer is blended with other biodegradable materials (Guidotti et al., 2017). The mechanical properties of PBS (tensile and impact strength, moderate stiffness, and hardness) are similar to those of conventional polymers such as polyethylene and polypropylene (Avérous and Kalia, 2016).

Despite growing consumer and industry interest in bio-based and biodegradable plastics, reports on their biodegradability are contradictory. Bio-based and biodegradable materials should be sorted into selectively collected biowaste streams according to their labelling and then processed via organic recycling processes, i.e., anaerobic digestion or composting. However, due to the development of new materials, their recyclability, especially in the AD process, has not been sufficiently investigated, and they may not be compatible with existing recycling infrastructures and processes. A better understanding of the mechanisms of bio-based materials' biodegradation and their properties could lead to finding the most beneficial end-of-life option and reducing their environmentally harmful impact by using the existing recycling infrastructure. It should be noted that the biodegradability of bio-based materials may vary depending on environmental conditions such as temperature, humidity, and presence of light or oxygen (Zaborowska and Bernat, 2023). In addition, bio-based products may have limited degradability, e.g., due to additives that improve their functional properties, e.g., processability, flexibility, or softness (Kemper and Lichtblau 2019). As mentioned, proper disposal of waste from bio-based products involves organic recycling with biowaste. Among organic recycling methods, AD has gained increasing importance due to its favourable energy yield, process duration, odour management and added value of the final product. Pre-treatment techniques such as thermal, chemical, and mechanical processes have been used to improve the rate of anaerobic degradation and increase methane production. These methods cause the breakdown of complex organic compounds into smaller, more accessible compounds that can be better utilized by microorganisms.

The current literature contains little data on the anaerobic degradation (AD) of cellulose- and PBS-based materials as well as the corresponding changes in their mechanical properties during the biodegradation process. In order to address this gap in knowledge, this study was conducted to investigate the AD and methane production from these bio-based materials (commercially available) under different temperatures. The study also provides a comprehensive understanding of the changes that occur in the mechanical properties of the investigated bio-based materials during biodegradation as evidenced by tensile properties, Fourier transform infrared (FTIR) analysis, and microscopic analysis. These findings contribute to a deeper understanding of the behaviour of cellulose- and PBS-based materials during the AD process, which may support the development of more sustainable materials for future use. In the context of their waste management and end-of-life scenarios, the results may also support the establishment of guidelines for bioplastics treatment. Since previous studies have shown that AD of certain bio-based materials (e.g., poly(lactic acid) (PLA)- or starch-based bioplastics) is limited under mesophilic conditions (Bernat et al., 2021; Zaborowska et al., 2021a; Cazaudehore et al., 2021), it was deemed necessary to perform a pre-treatment procedure prior to the mesophilic test to facilitate the methane production (MP) process. To find out whether higher temperatures than those in mesophilic conditions ensure or improve the efficiency of AD and methane production and overcome low degradation rates, thermophilic fermentation was also performed. It is important to compare the degree/rate of biodegradability of different materials considered biodegradable since their treatment under technical conditions requires the same operational conditions (there is no technical possibility of separate processing of different types of bioplastics). Information about large differences in the biodegradability of bioplastics and the low biodegradability and methane production of some bioplastics can help to develop guidelines for the possibility/impossibility of production of packaging considered biodegradable.

2. Materials and methods

2.1. Bioplastics used in the experiment

This study investigated two commercially available bio-based products (bioplastics), cellulose (Cel)- and polybutylene succinate (PBS)-based foils used for food packaging. The Cel- and PBS-based materials had volatile solids (VS) contents of 99.7% and 89.9% dry matter (DM), respectively. The elemental compositions of bioplastics are presented in Table 1. Because these materials come from the public market, they may contain undisclosed additives that could affect their properties and biodegradability.

2.2. Organisation of the experiment

Anaerobic biodegradation of the bioplastics: untreated (Cel_{37}, PBS_{37}) and pre-treated ($Pre\text{-}Cel_{37}$, $Pre\text{-}PBS_{37}$) was investigated under mesophilic conditions. The materials were subjected to pre-treatment with 0.1 M potassium hydroxide (KOH) (the mass ratio of the material to the pure reagent (KOH) was 14.5) for 2 h at room temperature. To find out whether thermophilic conditions improve the rate of anaerobic biodegradation, a higher temperature (55 °C) was also applied (Cel_{55}, PBS_{55}).

2.3. Measurement of methane production (MP) under mesophilic and thermophilic conditions

The MP from PBS- and Cel-based materials was determined with the biomethane potential (BMP) test using the Automated Methane Potential Testing System (AMPTS-II) (Bioprocess control, Sweden) under mesophilic (37 ± 1 °C) and thermophilic (55 ± 1 °C) conditions. Both materials were shredded into 5 mm × 5 mm pieces before BMP test. The AMPTS-II device consists of three units, (sample incubation unit, CO_2-absorbing unit, and gas volume measuring device) and allows online measurement of biomethane flows. The applied starting load was 4 kg VS/m^3 (the substrate to inoculum ratio, expressed as VS/VS, was 0.27)

Table 1
Elemental composition and empirical formula of the materials, molar composition of the biogas, and methane production from materials.

Cellulose-based materials				
Elemental composition (%)				
	Carbon	Hydrogen	Oxygen	Nitrogen
Pure Cel	44.44	6.17	49.38	–
Cel-based material	40.67	6.67	50.75	1.91
The empirical formula and molar composition of the biogas obtained from one mole of material				
Pure Cel	$C_6H_{10}O_5 + H_2O \rightarrow 3\ CH_4 + 3\ CO_2\ (CH_4:CO_2 = 1)$			
Cel-based material	$C_{24.8}H_{48.9}O_{23.3}N + 0.89\ H_2O \rightarrow 2.11\ CH_4 + 2.03\ CO_2 + NH_3\ (CH_4:CO_2 = 1.04)$			
Poly(butylene succinate)-based materials				
Elemental composition (%)				
	Carbon	Hydrogen	Oxygen	Nitrogen
Pure PBS	55.81	6.98	37.21	–
PBS-based material	55.93	7.03	36.31	0.74
The empirical formula and molar composition of the biogas obtained from one mole of material				
Pure PBS	$C_8H_{12}O_4 + 3.00\ H_2O \rightarrow 4.50\ CH_4 + 3.50\ CO_2\ (CH_4:CO_2 = 1.28)$			
PBS-based material	$C_{88.8}H_{133.8}O_{43.2}N + 34.46\ H_2O \rightarrow 50.68\ CH_4 + 38.84\ CO_2 + NH_3\ (CH_4:CO_2 = 1.30)$			
Methane production				
	Pure Cel	Cel-based material	Pure PBS	PBS-based material
*TMP, L/kg VS	415	403	586	596
MP at 37 °C, L/kg VS	–	311.4 (77.3% of TMP)	–	25.5 (4.3% of TMP)
MP at 37 °C, after material pre-treatment, L/kg VS	–	315.0 (78.2% of TMP)	–	29.3 (4.9% of TMP)
MP at 55 °C, L/kg VS	–	319.5 (79.3% of TMP)	–	180.2 (30.2% of TMP)

* TMP calculated using the O'Rourke's equation (Nyns, 1986); MP refers to cumulative MP after 100 days of anaerobic mesophilic treatment at 37 °C and after 40 days of thermophilic treatment at 55 °C.

and the measurement time was 100 and 40 days for mesophilic and thermophilic temperatures, respectively. The inoculum used for the mesophilic test was obtained from the closed mesophilic chamber of the wastewater treatment plant and provided the nutrients needed for the correct course of the process. The inoculum characteristics were pH 7.17 ± 0.10, alkalinity 42.80 ± 1.20 meq/L (2140 ± 60 mg $CaCO_3$/L), total solids (TS) 2.02 ± 0.22%, VS 68.44 ± 0.22% of TS, total nitrogen 36.20 ± 1.30 mg/g TS, total phosphorus 1.86 ± 0.21 mg/g TS, total carbon (TC) 336.5 ± 5.2 mg/g TS, and total organic carbon (TOC) 211.6 ± 6.2 mg/g TS. For the thermophilic test the inoculum was pre-incubated at 55 °C for fourteen days. To maintain anaerobic conditions, the reactors were purged with nitrogen gas for 2 min. Each of the reactors was stirred intermittently at a stirring speed of 80 rpm for 1 min every 30 min. The BMP test was performed in triplicate for each investigated material (untreated and pre-treated) and inoculum only. MP of each of the materials was calculated as the difference between the MP of inoculum combined with material and inoculum alone.

The MP followed pseudo first-order kinetics, according to the following formula:

$$C_{t,CH4} = C_{CH4} \bullet \left(1 - e^{kCH4 \bullet t}\right) \tag{1}$$

where: $C_{t;CH4}$ (L/kg VS) is the cumulative MP at time t (days) of anaerobic biodegradation test; C_{CH4} (L/kg VS) is the maximal MP; k_{CH4} (d^{-1}) is the kinetic coefficient of MP. The values of C_{CH4} and k_{CH4} were obtained by nonlinear regression analysis with Statistica software, version 13.0 (StatSoft, Tulsa, OK, USA).

O'Rourke's equation (Nyns, 1986) was used to determine the theoretical methane potential (TMP) of the foil materials based on their elemental composition, assuming the complete conversion of the organic compounds into biogas:

$$C_aH_bO_cN_d + \left(\frac{4a - b - 2c + 3d}{4}\right)H_2O \rightarrow \left(\frac{4a + b - 2c - 3d}{8}\right)CH_4 + \left(\frac{4a - b + 2c + 3d}{8}\right)CO_2 + dNH_3 \tag{2}$$

In order not to disturb the MP and to allow sampling for additional analyses of the bioplastics, such as FTIR spectroscopy, microscopic analysis, and static tensile tests, additional glass bioreactors with the same amount of inoculum and material as in AMPTS II were set up in parallel for both temperatures. The bioreactors were placed in a thermostatic incubator and mixed twice a day. Pieces of PBS-based material were collected during 100 days at 37 °C and 14 days at 55 °C. In the case of the Cel-based material, the 2nd day was the last possible day of material sampling, regardless of the temperature conditions.

2.4. FTIR spectroscopy, microscopic analysis, and static tensile tests

FTIR was used to evaluate the changes in functional groups of PBS- and Cel-based materials during anaerobic biodegradation. FTIR spectra were recorded with a Perkin Elmer Spectrum Two (with diamond ATR) instrument (Perkin Elmer, Waltham, MA, USA) with a resolution of 4 cm^{-1} in the wavenumber range 4000–400 cm^{-1} at room temperature.

The changes on the surface of the bio-based materials were analysed with a Nikon eclipse50i polarising microscope (Nikon, Tokyo, Japan) at a magnification of 100 × and binocular microscope at a magnification of 1.5× (Delta Optical). The 3D geometric structure (topography) at the microscale was determined with the use of Surface Roughness Contour Measuring Instrument (Mitutoyo Corporation, Kanagawa, Japan).

For analyses of FTIR and structure the following abbreviations were used: untreated (PBS_{37}_100d) and pre-treated (Pre-PBS_{37}_100d) material after 100 days at 37 °C and after 14 days (PBS_{55}_14d) at 55 °C (the last possible day of untreated material sampling under those conditions). In the case of Cel-based material, the 2nd day was the last possible day of material sampling both at 37 °C (untreated (Cel_{37}_2d) and pre-treated material (Pre-Cel_{37}_2d)) and at 55 °C (Cel_{55}_2d).

The changes in the mechanical properties (tensile strength and elongation at break) of the bioplastics during biodegradation were investigated within a static tensile test according to the standard ISO (ISO 527-2:2012; ISO 527-3:2019). The tensile measurement was performed using a TA.HD.Plus (Stable Microsystems, Surrey, UK) for at least five repetitions for samples of each foil. The specimens were subjected to a constant speed tensile force until the moment of fracture. The test was performed every some days until the samples were too fragile for analysis and it was no longer possible to place the samples in the tensile testing machine.

2.5. Analytical methods

The DM (or TS) and VS contents of Cel- and PBS-based materials and inoculum were determined at 105 °C and 550 °C, respectively. Total nitrogen, total phosphorus pH and alkalinity were also determined in the inoculum (Greenberg et al. (1992)). TOC and inorganic carbon (IC) were determined using a Shimadzu Liquid TOC-VCSN. The elemental composition of the foils was analysed using the Flash 2000 Organic Elemental Analyzer (Thermo Scientific, Milan, Italy) according to the manufacturer's instructions.

3. Results and discussion

3.1. Anaerobic biodegradation of Cel- and PBS-based materials based on MP

Based on the experience and results obtained in the previous studies with PLA- and starch-based materials (Bernat et al., 2021; Zaborowska et al., 2021a, 2021b), in the present study, MP was evaluated as an indicator of biodegradation of two other bio-based materials (PBS- and Cel-based foils commercially available on the market) under mesophilic and thermophilic conditions. As our previous study showed limited degradation under mesophilic conditions (Zaborowska et al., 2021a), this led to the proposal to pre-treat the bio-based materials before AD under these conditions.

Regarding the degradation of PBS foil under mesophilic conditions (PBS_{37}), intense MP was noted until day 10, after which no further changes in the amount of methane produced were observed. The maximum cumulative MP was only 25.50 L/kg VS. The kinetic coefficient of MP based on the first-order equation was calculated to be 0.49 d^{-1}, while the initial rate of MP was 12.7 L/(kg VS d). The pieces of PBS_{37} remained visibly present throughout the 100 days of observation (Fig. 1). Pre-treatment before the mesophilic degradation of PBS-based material ($Pre\text{-}PBS_{37}$) only slightly increased the cumulative MP to 29.3 L/kg VS. Moreover, the kinetic coefficient and the initial rate of MP increased to 0.51 d^{-1} and to 14.6 L/(kg VS d), respectively. Pieces of $Pre\text{-}PBS_{37}$ were visible in the inoculum for the 100-day experimental period, similar to the untreated foils. However, progressive degradation of the polymer had occurred, as indicated by the gradual thinning of the material over the course of the process (see also the description of the microscopic analyses). Under thermophilic conditions, MP from PBS material (PBS_{55}) increase markedly. Pieces of foil were visible in the inoculum during the 14 days of degradation, during which more than 87% of the cumulative MP was obtained. Although the material was not visible in the inoculum, methane was still produced for the next 10 days, and then the MP plateaued at 180 L/kg VS. In contrast, the amount of methane produced by the Cel-based material was much higher. Furthermore, regardless of the temperature conditions or the use of pre-treatment, the Cel-based material was consistently visible for only 2 days of biodegradation. Under mesophilic conditions, during these 2 days, the cumulative MP from Cel_{37} and $Pre\text{-}Cel_{37}$ reached 134 and 176 L/kg VS, respectively, which corresponded to 43% and 56% of the maximal cumulative MP, respectively. The rest of the methane from Cel_{37} and $Pre\text{-}Cel_{37}$ was produced by 7–8 days and 5–6 days of measurements, respectively under thermophilic conditions, MP reached 285 L/kg VS, corresponding to 90% of the total cumulative MP.

However, regardless of the conditions of biodegradation, the maximum MP was 312–319 L/kg VS. Nevertheless, the applied conditions did influence the kinetics of the process. The lowest kinetic coefficient and the initial rate of MP were noted with Cel_{37}, 0.44 d^{-1} and 137.3 L/(kg VS d), respectively. The pre-treatment increased the kinetic coefficient and rate of MP from $Pre\text{-}Cel_{37}$ by 16 and 18%, respectively. Under thermophilic conditions, maximum MP from Cel_{55} was attained after 3–4 days, and the highest kinetics values were obtained (a kinetic coefficient and initial rate of MP of 1.1 d^{-1} and 350.9 L/(kg VS d), respectively) (Fig. 1).

The authors' previous studies showed that the biodegradation of bio-based materials is not only affected by the temperature conditions, but also by the type of polymer (i.e. starch, PLA) that is the main component of the material. Moreover, among the various materials that were based on the same type of polymer, e.g., PLA, differences in the degree/rate of their biodegradation were also found.

For example, PLA- and starch-based foils showed negligible decay under mesophilic conditions, produced minimal amounts of biogas, and showed little structural damage after one year of degradation (Zaborowska et al., 2021a). Even under thermophilic conditions, methane was produced with these materials to a limited extent and its amounts constituted only 5% of the theoretical methane potential (TMP). Moreover, both foils lost their mechanical properties but were still visibly intact after 100 days of degradation. Despite the use of pre-treatment, increased surface damage and weakened mechanical properties of the materials (loss of the mechanical properties in a time shorter than 50 days), their MP constituted only 8–10% of the TMP and the pieces of the foils were still visible (Zaborowska et al., 2021b). However, another type of PLA-based material (disposable cups) was completely degraded with high biogas production under anaerobic conditions, albeit in a time frame that is unacceptable for a technical-scale AD. The cumulative biogas production values achieved after 40 days (thermophilic conditions) and 280 days (mesophilic conditions) were 849 L/kg VS and 558 L/kg VS, respectively (Bernat et al., 2021). Furthermore, the use of pre-treatment techniques led to an increase in the rate of MP by almost 10%, and a 1.3-fold reduction in the time needed for achieving the total cumulative MP from PLA cups under thermophilic conditions (Zaborowska et al., 2023).

The elemental compositions of the Cel-and PBS-based foils used in this study were determined. The results were compared with those for pure polymers (consisting only of one type of repeating unit, without any modifications, and containing no additives, fillers, or other substances) and then used for the evaluation of TMP (Table 1). The Cel-based material exhibited around 10% lower carbon content and slightly higher hydrogen and oxygen contents than pure Cel. In contrast, the carbon and hydrogen contents in the PBS-based material were similar to those in the pure polymer. In comparison to pure polymers, nitrogen was detected in both investigated foils, which could be attributed to the presence of additives increasing their usable properties that could have been used in the foil manufacturing process.

Based on the elemental composition of the foils and pure polymers, theoretical amounts of methane and carbon dioxide that could be obtained through the complete conversion of organics to biogas were calculated using O'Rourke's equation (2) (*Materials and methods* section). The molar composition of the biogas from one mole of material was analysed to determine the CH_4:CO_2 ratio. The results showed that the CH_4:CO_2 ratio in the biogas from both bio-based materials was slightly higher than from the pure polymers.

The CH_4:CO_2 ratio in biogas from Cel-based materials was about 30% lower than that from PBS-based materials (regardless of whether a pure polymer or a polymer-based material was used), suggesting that PBS may produce biogas with a higher methane content than cellulose. This corresponds to the TMP value, which was lower in the case of Cel-based materials (403–415 L/kg VS) than in the case of PBS-based materials (586–596 L/kg VS). In the experimental measurements, the MP is lower than the TMP (Zaborowska et al., 2021a, 2021b; Mu et al., 2021). This was also confirmed in the present study. The experimentally determined maximum cumulative MP from the Cel-based material constituted 75–77% of the TMP, which was much higher (311–319 L/kg VS, regardless of the biodegradation conditions) than that from PBS-based material obtained under thermophilic conditions (the highest achieved MP). Even under thermophilic conditions, MP from PBS-based material was about 180 L/kg VS and accounted for only 30% of the TMP (Table 1). Although Cel-based products have gained increasing attention as sustainable alternatives to conventional plastics, research on their biodegradation is scarce. Moreover, the findings are inconsistent and contradictory in terms of their biodegradability and indications of which conditions, mesophilic or thermophilic, are favourable for their degradation. This is because the biodegradability of Cel-based products is affected by their detailed composition, including the cellulose derivatives used in their manufacture. The results of Zhang et al. (2018) confirmed this, as those authors studied the 65-day anaerobic mesophilic degradation (using BMP tests) of Cel-based foils that were certified as compliant with the EN13432 composting standard and therefore considered biodegradable. However, that study did not provide information on the composition the Cel-based foils in terms of the use of additives, such as, e.g., plasticisers and dyes. The following Cel-based foils were used in their study: metallised, heat-sealable, high barrier heat-sealable, non–heat-sealable film and cellulose diacetate foils. Four of the five Cel-based foils produced 374–433 L/kg VS methane, indicating a high degree of mesophilic biodegradation, expressed as solids destruction (88.9–98.3%). However, the cellulose diacetate foil exhibited only 50 L CH_4/kg VS, with a solids destruction of 10.3%. It should be noted that the authors did not specify the time at which maximal MP was found in the BMP tests, as was done in our study, where the maximal

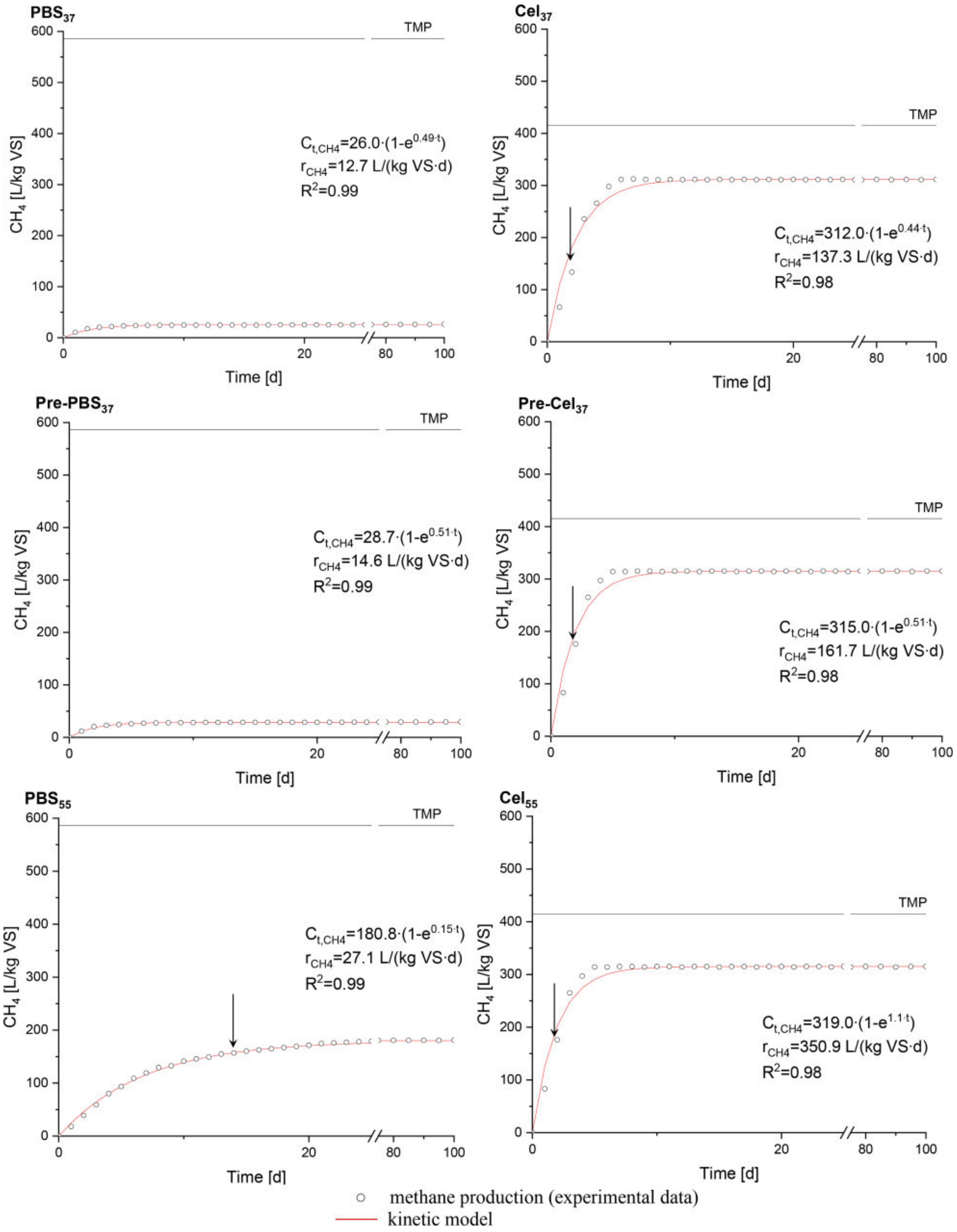


Fig. 1. Methane production from Cel- and PBS-based material during anaerobic mesophilic degradation; untreated material (Cel_{37}, PBS_{37}) and after pre-treatment ($Pre\text{-}Cel_{37}$, $Pre\text{-}PBS_{37}$), and during anaerobic thermophilic degradation (Cel_{55}, PBS_{55}); the values of theoretical methane potential (TMP) (based on the elemental composition) are shown; kinetic models are given; vertical arrows indicate the time during which pieces were visible and sampling was possible.

mesophilic MP of the Cel-based foil was reached within 10 days of measurements. The longer the time needed to reach maximal MP from the investigated material in the BMP tests, the lower the rate of its biodegradation. Assuming that the time to reach maximal MP in the study of Zhang et al. (2018) was around 65 days (total time of the experiment), this means that the Cel-based foils they examined were less biodegradable than the Cel-based foil used in the present study.

Despite the use of a high temperature for anaerobic degradation, Shrestha et al. (2020) reported incomplete degradation of Cel-based foil (commercial packaging material) under thermophilic conditions.

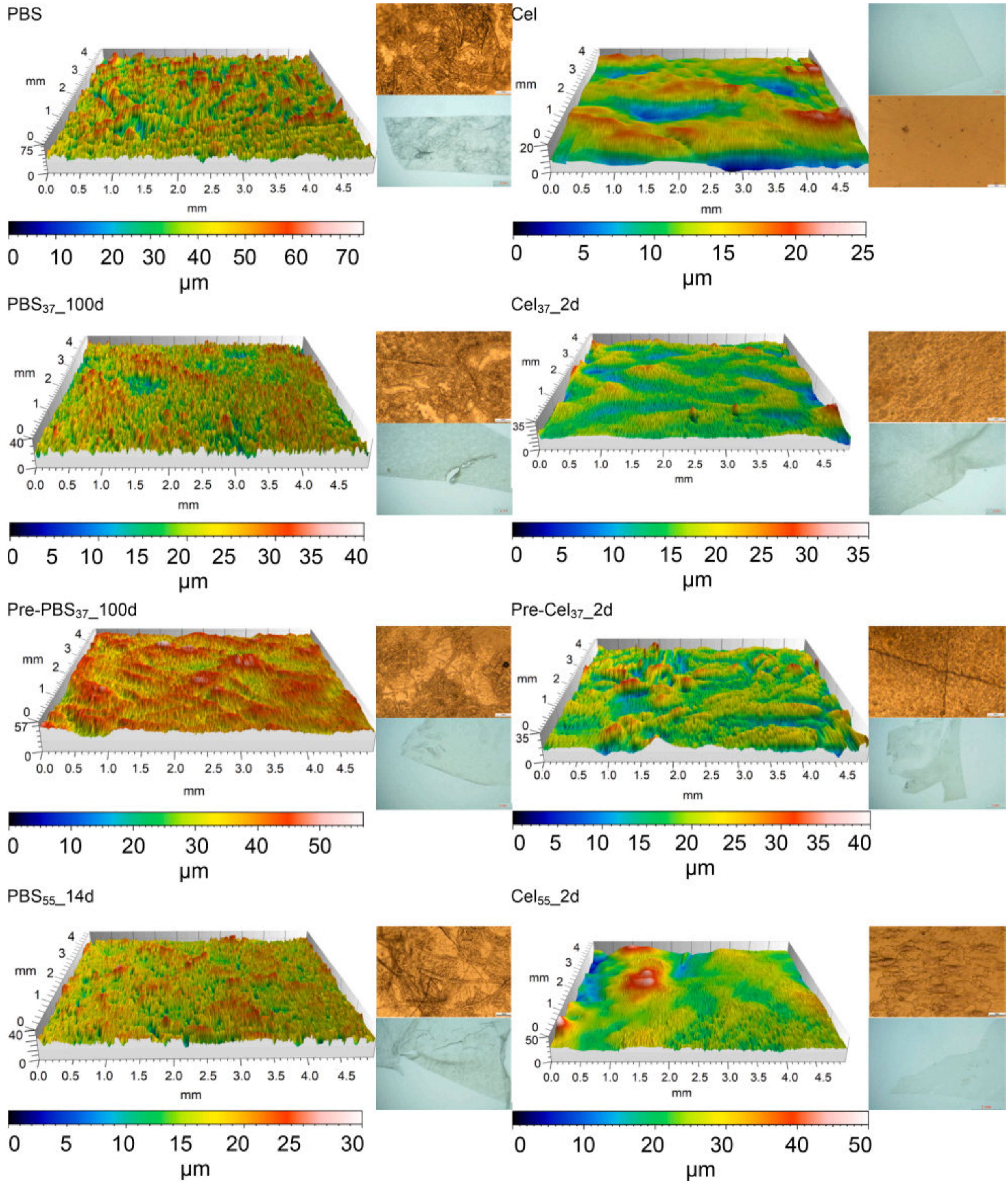


Fig. 2. Topography and microscopic images of PBS-based material (PBS), and these of the PBS-based material (untreated (PBS$_{37}$_100d) and pre-treated (Pre-PBS$_{37}$_100d)) collected after 100 days of mesophilic degradation, and collected after 14 days of thermophilic degradation (the last possible day of material sampling under this conditions (PBS$_{55}$_14d)), and the images of Cel-based material (Cel), and these of the Cel-based material (untreated (Cel$_{37}$_2d) and pre-treated (Pre-Cel$_{37}$_2d)) collected after 2 days of mesophilic degradation, and collected after 2 days of thermophilic degradation (Cel$_{55}$_2d)), in case of Cel-based material, the 2nd day was the last possible day of material sampling.

During 21- and 35-day degradation, those authors measured the biogas potential (BP) from Cel-based foil (three sizes of pieces: 1 × 1, 2 × 2 and 3 × 3 cm) using a gas displacement method for determining the biogas volume. The BP values were 138–195 L/kg VS and 252–283 L/kg VS after 21 and 35 days of measurement, respectively, with higher values for smaller pieces of foil. The methane concentration in the biogas was 41–43% after 35 days. Based on the theoretical BP, the biodegradability of the Cel-based foil was 9.0–12.7% and 16.3–18.3% after 21 and 35 days, respectively, indicating incomplete degradation. In contrast, in the present study, under thermophilic conditions, the Cel-based foil was completely degraded within a few days; the obtained MP was about 320 L/kg VS, which accounted for almost 80% of the TMP. The biodegradation of PBS-based materials under anaerobic conditions has not been extensively studied. One of the available studies is that of Dvorackova et al. (2015). Those authors determined the degree of biodegradation based on the relation of the amount of carbon released in the form of CH_4 and CO_2 to the theoretical amount of carbon in the dry matter of the tested sample. They showed that, regardless of the form of PBS (thin or thick foils, and powder), the material failed to decompose under mesophilic anaerobic conditions (37 °C). Moreover, even under thermophilic (55 °C) conditions, degradation was incomplete. After 120 days, the material degraded to a small extent, reaching 20–23% of the degree of degradation for the powdered PBS and 10–18% of the degree of degradation for PBS foils. The authors observed that assimilation by microorganisms during biodegradation was mainly concentrated in the amorphous region of the PBS.

3.2. Anaerobic biodegradation of Cel- and PBS-based materials based on microscopic and surface analyses

As part of the study of the biodegradation of bioplastics under anaerobic conditions, a microscopic analysis of changes in the bio-based materials was carried out. Surface cracking, pitting or discolouration may indicate that the surface of the bioplastic is being degraded by the microorganisms. Biodegradation can lead to changes in the surface structure, i.e., increased cracks or holes on the surface and an increase in the roughness of the material (Zaborowska et al., 2021b). In the present study, both of the foils were initially smooth and transparent. The morphological changes in the materials' structure before and after degradation were studied and the results are shown in Fig. 2; microscopic images of biofoils sampled more frequently are provided in the Supplementary Materials (Figs. 1-3SM). The Cel-based pieces remained visible in the anaerobic inoculum only during the first two days of the test, when they broke easily and the formation of numerous microcracks on their surface were noted. Analyses of the topography showed that the surface of Pre-Cel_{37} exhibited a high degree of heterogeneity, as evidenced by numerous valleys and hills. Pre-treatment methods are commonly employed prior to anaerobic digestion to facilitate the degradation of polymer chains into smaller, more easily digestible molecules. However, pre-treatment can also alter the surface of the material by changing the surface roughness due to its degradation. A deepening of the valleys was observed in both Cel_{37}_2d and Cel_{55}_2d, indicating possible degradation of the material. The difference between the highest peak and the deepest valley was about 33 μm and 49 μm for the Cel_{37}_2d and Cel_{55}_2d, respectively. This may indicate that Cel_{55} degraded to a greater extent than Cel_{37}.

In contrast to Cel-, the PBS-based material initially displayed a surface topography with numerous peaks and valleys. During biodegradation, the PBS_{37} and Pre-PBS_{37} foils remained visible in the inoculum for 100 days, moreover, low MP took place for up to 10 days. On the contrary, under thermophilic conditions, the PBS_{55} pieces were visible only for 14 days. In these days, microscopic analysis revealed some cracks on the surface of PBS-based pieces. A reduction in the sample thickness was also observed.

However, topography analyses indicated that both pre-treated materials (Pre-PBS_{37}_100d and Pre-Cel_{37}_2d) had the most heterogeneous surfaces among all the analysed samples. Moreover, the degradation was accompanied by a decrease in the number of surface peaks under both mesophilic and thermophilic conditions, indicating a progressive degradation of the material. The results of the present study are consistent with those of previous ones, which have shown that the biodegradation of PBS-based materials under anaerobic conditions is a long-term process that remains incomplete even after 100 days of degradation.

Boonmee et al. (2022) indicated that PBS-based bioplastic buried under a mixture of landfill soil and fermented sludge did not completely disintegrate even after a 90-day period of biodegradation at 61 °C under oxygen-limited conditions, and fragile fragments were still found. In addition, the surface of the samples became increasingly rough after this period, and a few holes and cracks appeared. Dvorackova et al. (2015) reported changes in the surface properties of PBS foil after 113 days of thermophilic anaerobic biodegradation. Those authors noted the presence of deep cracks and holes on the surface and emphasized that the degradation process affected not only the surface of the material but also its interior. Similarly to the results from the present study concerning the impact of pre-treatment on the improvement of anaerobic degradation of PBS, Zaborowska et al. (2021b) found that alkaline pre-treatment, even prior to thermophilic anaerobic degradation, did not improve the disintegration process of different bio-based materials (PLA- and starch-based foils). In that previous study, the only observed effect was an increase in material weakness and brittleness, accompanied by a reduction in surface roughness.

3.3. FTIR spectra of Cel- and PBS-based materials

After 100 days under mesophilic conditions (regardless of the use of pre-treatment), after 14 days of thermophilic biodegradation of PBS, and after 2 days of biodegradation of Cel (regardless of the temperature conditions and the use of pre-treatment), neither the FTIR spectra of Cel nor that of PBS showed a shift and formation of peaks during the biodegradation test, as presented in Fig. 3. The FTIR spectrum of the Cel-based material showed the characteristic bands reported in the literature for cellulose (Abderrahim et al., 2015; Hospodarova et al., 2019). The broad peak between 3500 and 2990 cm^{-1} corresponded to stretching hydroxyl groups and indicated intra- and intermolecular hydrogen bonding in cellulose (Popescu et al., 2011). The band at 2891 cm^{-1} corresponded to CH stretching vibration of hydrocarbons in polysaccharides. The peak 1644 cm^{-1} indicated water absorption in cellulose (Poletto et al., 2011). In the present study, the intensity of this peak increased slightly after degradation. The peaks at 1367, 1314, 1020 and 895 cm^{-1} corresponded to bending and stretching vibrations of –CH, –CH_2, C–O and –OH bonds in cellulose units (Fackler et al., 2011). According to the literature, the band at 895 cm^{-1} is indicative of the amorphous region in cellulose and is characteristic for β-glycosidic bonding between glucose units (Poletto et al., 2014).

Analysis of the FTIR spectrum of the PBS-based material revealed the major functional groups of PBS previously reported in the literature (Abderrahim et al., 2015). The peaks at 3000–2800 and 1329 cm^{-1} corresponded to the asymmetric and symmetric stretching of the –CH– groups. The intense peak at 1713 cm^{-1} indicates the C = O stretching vibration of the carbonyl group, which characterises the ester group in PBS (Muthuraj, et al., 2015). This band can be attributed to the carbonyl stretching of the crystalline domains of PBS (Dong et al., 2004). The peaks between 1312 and 1150 cm^{-1} corresponded to the C–O–C stretching of the ester bonds. The band at 1045 indicated –O–C–C– stretching vibrations (Phua et al., 2013). The peaks at 954 and 919 cm^{-1} correspond to –C–OH bending in the terminal carboxylic acid groups of PBS (de Matos Costa et al., 2020). An absence of changes in the FTIR spectrum of PBS material during biodegradation was also shown by Boonmee et al. (2022) during a 90-day test under oxygen-limited conditions at 61 °C.

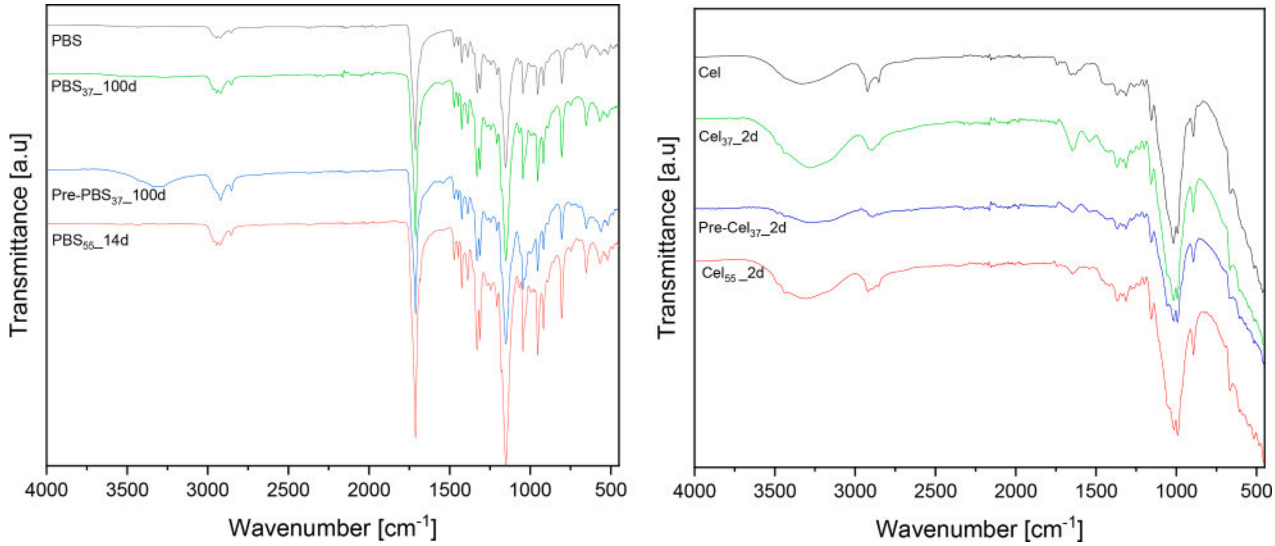


Fig. 3. FTIR spectra of PBS-based material (PBS); these of the PBS-based material (untreated (PBS$_{37}$_100d) and pre-treated (Pre-PBS$_{37}$_100d)) collected after 100 days of mesophilic degradation, and collected after 14 days of thermophilic degradation (the last possible day of material sampling under this conditions (PBS$_{55}$_14d)), and FTIR spectra of Cel-based material (Cel), these of the Cel-based material (untreated (Cel$_{37}$_2d) and pre-treated (Pre-Cel$_{37}$_2d)) collected after 2 days of mesophilic degradation, and collected after 2 days of thermophilic degradation (Cel$_{55}$_2d)), in case of Cel-based material, the 2nd day was the last possible day of material sampling.

3.4. Anaerobic biodegradability of Cel- and PBS-based materials as indicated by changes in their mechanical properties

The mechanical behaviour of the foils during anaerobic biodegradation, such as tensile strength and elongation at break (ε), was evaluated by tensile tests, the results of which are shown in Fig. 4. Foils lost their mechanical properties, which indicated progressive biodegradation. Regarding the Cel -based foils, the tensile test could only be carried out in the first two days of the experiment, regardless of temperature and pre-treatment. After that, the material was not visible in

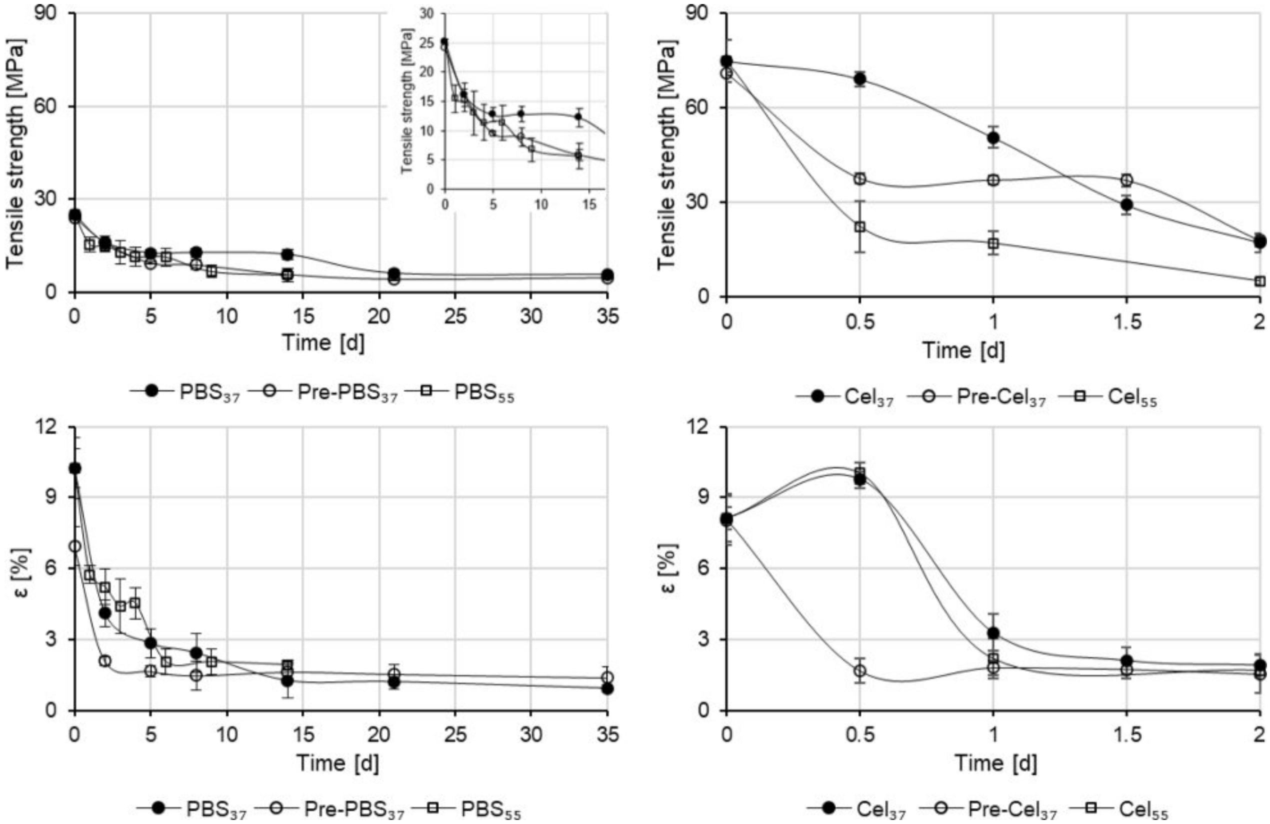


Fig. 4. Changes in the mechanical properties (tensile strength (a, b) and elongation at break ε (c, d)) during anaerobic mesophilic degradation of untreated materials (Cel$_{37}$, PBS$_{37}$) and after pre-treatment (Pre-Cel$_{37}$, Pre-PBS$_{37}$), and during anaerobic thermophilic degradation (Cel$_{55}$, PBS$_{55}$); the mechanical properties were determined for 35 days for the PBS foil, and for 2 days for the Cel foil, so that the x-axes are adapted to this duration.

the inoculum, thus precluding the strength test. The tensile strength of Cel was about 75 MPa and decreased to about 70 MPa after pre-treatment (Pre-Cel) of the material before degradation. Leppänen et al. (2020) report that the tensile strength values of cellulose-based foils can range from 120 MPa for cellophane to 8 MPa for cellulose acetate film. In our study, after 12 h, a decrease in tensile strength was observed, which was greatest (70%) in the foil degraded under thermophilic conditions and lowest (8%) in the foil degraded under mesophilic conditions. Finally (after 2 days), the tensile strength reached the lowest value for Cel_{55}. The elongation at break (ε) of the Cel material was about 8% and did not change after pre-treatment (Pre-Cel). During the first 12 h of anaerobic degradation, a decrease in ε of $Pre\text{-}Cel_{37}$ to about 1.6% was observed, after this time, it remained unchanged. However, the ε of Cel_{37} and Cel_{55} started to decrease from 12 h and reached a stable value after 1 day of biodegradation. Finally (after 2 days), regardless of the temperature conditions and the use of pre-treatment, the ε was about 1.5%, which was 5.3 times lower than the initial value (Fig. 4).

In the present study, the tensile strength of PBS-based foil could be measured up to the 35th day of anaerobic mesophilic degradation with untreated and pre-treated foils. Under thermophilic conditions, measurements were possible up to the 14th day of the test. After that, it was no longer possible to insert foils into the measuring device. This means that the PBS-based material was more resistant to biodegradation than the Cel-based foil. The tensile strength of PBS-based material before degradation was about 25 MPa and slightly decreased after pre-treatment (Pre-PBS). Generally, the mechanical properties of PBS are similar to those of aromatic or semi-aromatic polyesters, such as poly (ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT)); tensile strength ranges from 25 to 35 MPa (Xu and Guo, 2010, Qi et al. 2019). During the first 9 days of biodegradation, regardless of the temperature conditions and the use of pre-treatment, the tensile strength of PBS foil decreased sharply to about 7–12 MPa. After this time, it decreased more slowly. The last measurable value of tensile strength was about 5 MPa. The ε of the PBS-based material was about 10%, which corresponds to the value given in the literature for commercial PBS (Phua et al., 2013, de Matos Costa et al., 2020). For Pre-PBS, the ε decreased to about 7%. Similar to the tensile strength, the ε decreased sharply during the first 9 days of degradation. At this time the greatest decrease, of 4.7-fold, was noted for $Pre\text{-}PBS_{37}$, and the smallest one, of 5.01-fold, for PBS_{55}. From the 9th day, only small changes were observed. Similarly, Zaborowska et al. (2021b) observed a decrease in the mechanical properties of starch- and PLA-based materials during anaerobic thermophilic degradation. The authors found that alkaline pre-treatment shortened the time in which measurements of mechanical properties were possible; however, it should be emphasized that the tested material did not disintegrate during the 100 days of the test. In the present study, it was possible to determine the mechanical properties during the same time regardless of whether the pre-treatment was used or not.

Results concerning the changes in mechanical properties of bioplastics during biodegradation under anaerobic conditions are scarce. Most studies are conducted under aerobic conditions. For example, Mastalygina et al. (2023) degraded bio-based Cel foils (cellophane) in an open-air soil test. The tensile strength and the ε of the material were 90.3 ± 3.8 MPa and 11 ± 1%, respectively, which was similar to the values of the Cel-based foil used in the present study. However, the material lost its integrity in a very short time and degraded completely after 3 months, and thus the authors could not determine changes in its mechanical properties. In another study, Liu et al. (2022) degraded PBS-based material and its copolymers in seawater. They reported a 2-fold decrease in the tensile strength during 250 days. Furthermore, the authors indicated that seawater had a stronger effect on the ε than on the tensile strength. This effect was also observed in the present study with PBS material. Puchalski et al. (2018) found that, during composting, the tensile strength and ε of PBS-based material decreased from 34.8 MPa to 12.7 MPa and from 321.8% to 1.7%, respectively, indicating a strong decrease in the elasticity of the materials.

4. Conclusions

Although there is increasing interest in new bio-based products that have appeared on the market (labeled as biodegradable), there are still some contradictory results about their actual biodegradability. However, for effective waste management, it is crucial to determine the biodegradability of these products, which was done in this study for the tested bio-based materials. The results revealed important differences in their actual biodegradability under anaerobic conditions, indicating that, in some cases, there are significant limitations to using AD for final management.

Cel-based foil produced a large amount of methane (about 310–320 L/kg VS) and degraded rapidly regardless of the temperature conditions and the use of pre-treatment. During mesophilic and thermophilic degradation, fragments were visible for only two days. In contrast, under mesophilic conditions, the PBS-based material degraded slower and produced a much smaller amount of methane (12 times less than the Cel-based foil). Untreated and pre-treated PBS lost their mechanical properties within 35 days, but the pieces were still visible even after 100 days. Under thermophilic conditions, MP increased to 180.2 L/kg VS, indicating an increase in the degradability of PBS. The pieces were visible for only 14 days, and during this time the material lost its mechanical properties. In conclusion, Cel-based material can be effectively treated under anaerobic conditions. Further studies should focus on the challenge of determining if the residues of bioplastics (*microbioplastics*) are present in digestate.

Funding

We are grateful for the financial support of the Ministry of Education and Science, Poland (statutory project No. 29.610.024–110). This research was funded in part by the National Science Centre, Poland (Grant No. 2021/41/N/NZ9/01750).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2023.06.022.

References

Abderrahim, B., Abderrahman, E., Mohamed, A., Fatima, T., Abdesselam, T., Krim, O., 2015. Kinetic thermal degradation of cellulose, polybutylene succinate and a green composite: comparative study. World J. Environ. Eng 3, 95–110.

Aliotta, L., Seggiani, M., Lazzeri, A., Gigante, V., Cinelli, P., 2022. A brief review of poly (butylene succinate)(PBS) and its main copolymers: synthesis, blends, composites, biodegradability, and applications. Polymers 14, 844. https://doi.org/10.3390/polym14040844.

Andreu-Hayles, L., Levesque, M., Martin-Benito, D., Huang, W., Harris, R., Oelkers, R., Lelanda, C., Martin-Fernándeza, J., Anchukaitisa, K.J., Helle, G., 2019. A high yield cellulose extraction system for small whole wood samples and dual measurement of carbon and oxygen stable isotopes. Chemical Geology 504, 53–65. https://doi.org/10.1016/j.chemgeo.2018.09.007.

Ashter, S.A., 2016. Types of biodegradable polymers, in: Ashter, S.A. (Eds.), Plastics Design Library. Introduction to bioplastics engineering. William Andrew Publishing, 2016, pp. 81–151. https://doi.org/10.1016/B978-0-323-39396-6.00005-1.

Avérous, L., Kalia, S., 2016. Biodegradable and biobased polymers for environmental and biomedical applications. John Wiley & Sons. Beverly, MA, USA 2016, 237–239.

Bayer, I.S., Guzman-Puyol, S., Heredia-Guerrero, J.A., Ceseracciu, L., Pignatelli, F., Ruffilli, R., Cingolani, R., Athanassiou, A., 2014. Direct transformation of edible vegetable waste into bioplastics. Macromolecules 47, 5135–5143. https://doi.org/10.1021/ma5008557.

Bernat, K., Kulikowska, D., Wojnowska-Baryła, I., Zaborowska, M., Pasieczna-Patkowska, S., 2021. Thermophilic and mesophilic biogas production from PLA-based materials: Possibilities and limitations. Waste Manage. 119, 295–305. https://doi.org/10.1016/j.wasman.2020.10.006.

Bilo, F., Pandini, S., Sartore, L., Depero, L.E., Gargiulo, G., Bonassi, A., Federici, S., Bontempi, E., 2018. A sustainable bioplastic obtained from rice straw. J. Clean. Prod. 200, 357–368. https://doi.org/10.1016/j.jclepro.2018.07.252.

Boonmee, C., Kositanont, C., Leejarkpai, T., 2022. Degradation behavior of biodegradable plastics in thermophilic landfill soil and wastewater sludge conditions. EREM 78 (1), 57–69. https://doi.org/10.5755/j01.erem.78.1.29502.

Cazaudehore, G., Monlau, F., Gassie, C., Lallement, A., Guyoneaud, R., 2021. Methane production and active microbial communities during anaerobic digestion of three commercial biodegradable coffee capsules under mesophilic and thermophilic conditions. Sci. Total Environ. 784, 146972 https://doi.org/10.1016/j.scitotenv.2021.146972.

Chen, C., Ding, W., Zhang, H., Zhang, L., Huang, Y., Fan, M., Yang, J., Sun, D., 2022. Bacterial cellulose-based biomaterials: From fabrication to application. Carbohydr. Polym. 278, 118995 https://doi.org/10.1016/j.carbpol.2021.118995.

Czaja, W.K., Young, D.J., Kawecki, M., Brown, R.M., 2007. The future prospects of microbial cellulose in biomedical applications. Biomacromolecules 8, 1–12. https://doi.org/10.1021/bm060620d.

de Amorim, J.D.P., de Souza, K.C., Duarte, C.R., da Silva Duarte, I., de Assis Sales Ribeiro, F., Silva, G.S., de Farias, P.M.A., Stingl, A., Costa, A.F.S., Vinhas, G.M., Sarubbo, L.A., 2020. Plant and bacterial nanocellulose: production, properties and applications in medicine, food, cosmetics, electronics and engineering. A review. Environ. Chem. Lett., 18, 851–869. https://doi.org/10.1007/s10311-020-00989-9.

de Matos Costa, A.R., Crocitti, A., Hecker de Carvalho, L., Carroccio, S.C., Cerruti, P., Santagata, G., 2020. Properties of biodegradable films based on poly(butylene succinate) (PBS) and poly(butylene adipate-co-terephthalate) (PBAT) blends. Polymers 12 (10), 2317. https://doi.org/10.3390/polym12102317.

Dong, T., He, Y., Shin, K.M., Inoue, Y., 2004. Formation and Characterization of Inclusion Complexes of Poly (butylene succinate) with α-and γ-Cyclodextrins. Macromol. Biosci. 4 (12), 1084–1091. https://doi.org/10.1002/mabi.200400054.

Dvorackova, M., Svoboda, P., Kostka, L., Pekarova, S., 2015. Influence of biodegradation in thermophilic anaerobic aqueous conditions on crystallization of poly (butylene succinate). Polym. Test. 47, 59–70. https://doi.org/10.1016/j.polymertesting.2015.08.006.

Fackler, K., Stevanic, J.S., Ters, T., Hinterstoisser, B., Schwanninger, M., Salmén, L., 2011. FT-IR imaging microscopy to localise and characterise simultaneous and selective white-rot decay within spruce wood cells. Holzforschung 65, 411–420. https://doi.org/10.1515/hf.2011.048.

Greenberg, A.E., Clesceri, L.S., Eaton, A.D., 1992. Standard Methods for the examination of water and wastewater. APHA, Washington.

Guidotti, G., Soccio, M., Siracusa, V., Gazzano, M., Salatelli, E., Munari, A., Lotti, N., 2017. Novel random PBS-based copolymers containing aliphatic side chains for sustainable flexible food packaging. Polymers 9, 724. https://doi.org/10.3390/polym9120724.

Hann, S., Scholes, R., Lee, T., Ettlinger, S., Jørgensen, H., 2020. Biobased and biodegradable plastics in Denmark. Ind. Biotechnol. 16, 164–175. https://doi.org/10.1089/ind.2020.29213.sha.

Hospodarova, V., Singovszka, E., Stevulova, N., 2019. Characterization of cellulosic fibers by FTIR spectroscopy for their further implementation to building materials. AJAC 9, 303–310. https://doi.org/10.4236/ajac.2018.96023.

ISO 527-2:2012. Plastics -Determination of tensile properties - Part 2: Test conditions for moulding and extrusion plastics.

ISO 527-3:2019 Plastics - Determination of tensile properties - Part 3: Test conditions for films and sheets.

Jin, L., Xu, J., Yang, Q., Huang, Y., Zhang, X., Yao, W., Wang, J., Zhao, Y., Tian, H., He, M., 2023. Fabrication of cellulose/rectorite composite films for sustainable packaging. Int. J. Biol. Macromol. 224, 1471–1477. https://doi.org/10.1016/j.ijbiomac.2022.10.234.

Kassab, Z., Kassem, I., Hannache, H., Bouhfid, R., Qaiss, A.E.K., El Achaby, M., 2020. Tomato plant residue as new renewable source for cellulose production: extraction of cellulose nanocrystals with different surface functionalities. Cellulose 27, 4287–4303. https://doi.org/10.1007/s10570-020-03097-7.

Kemper, B., Lichtblau, D.A., 2019. Extraction of plasticizers: An entire and reproducible quantification method for historical cellulose acetate material. Polym. Test. 80, 106096 https://doi.org/10.1016/j.polymertesting.2019.106096.

Leppänen, I., Vikman, M., Harlin, A., Orelma, H., 2020. Enzymatic degradation and pilot-scale composting of cellulose-based films with different chemical structures. J. Polym. Environ. 28, 458–470. https://doi.org/10.1007/s10924-019-01621-w.

Liu, T.Y., Huang, D., Xu, P.Y., Lu, B., Zhen, Z.C., Zheng, W.Z., Li, X., Ge-Xia, W., Ji, J., 2022. Study on composting and seawater degradation properties of diethylene glycol-modified poly (butylene succinate) copolyesters. e-Polymers 22, 615–626. https://doi.org/10.1515/epoly-2022-0057.

Manian, A.P., Cordin, M., Pham, T., 2021. Extraction of cellulose fibers from flax and hemp: a review. Cellulose 28, 8275–8294. https://doi.org/10.1007/s10570-021-04051-x.

Mastalygina, E., Abushakhmanova, Z., Poletto, M., Pantyukhov, P., 2023. Biodegradation in soil of commercial plastic bags labelled as "biodegradable". Mater. Res. 26, 20220164. https://doi.org/10.1590/1980-5373-MR-2022-0164.

Mu, L., Zhang, L., Ma, J., Zhu, K., Chen, C., Li, A., 2021. Enhanced biomethanization of waste polylactic acid plastic by mild hydrothermal pretreatment: Taguchi orthogonal optimization and kinetics modeling. Waste Manage. 126, 585–596. https://doi.org/10.1016/j.wasman.2021.03.044.

Muthuraj, R., Misra, M., Mohanty, A.K., 2015. Injection molded sustainable biocomposites from poly (butylene succinate) bioplastic and perennial grass. ACS Sustain. Chem. Eng. 3, 2767–2776. https://doi.org/10.1021/acssuschemeng.5b00646.

Naomi, R., Bt Hj Idrus, R., Fauzi, M.B., 2020. Plant- vs. bacterial-derived cellulose for wound healing: a review. IJERPH, 17, 6803. https://doi.org/10.3390/ijerph17186803.

Ni, Y., Richter, G.M., Mwabonje, O.N., Qi, A., Patel, M.K., Woods, J., 2020. Novel integrated agricultural land management approach provides sustainable biomass feedstocks for bioplastics and supports the UK's 'net-zero'target. Environ. Res. Lett. 16, 014023 https://doi.org/10.1088/1748-9326/abcf79.

Nigam, S., Das, A.K., Matkawala, F., Patidar, M.K., 2022. An insight overview of bioplastics produced from cellulose extracted from plant material, its applications and degradation. Environ. Sustain. 1–19 https://doi.org/10.1007/s42398-022-00248-3.

Nyns, E.J., 1986. Biomethanation processes. Microb. Degrad. 8, 207–267.

Phua, Y.J., Chow, W.S., Mohd Ishak, Z.A., 2013. Reactive processing of maleic anhydride-grafted poly (butylene succinate) and the compatibilizing effect on poly (butylene succinate) nanocomposites. EXPRESS Polym. Lett. 7, 40–135. https://doi.org/10.3144/expresspolymlett.2013.31.

Plastic Europe, 2021. Plastics- the facts 2021. An analysis of European plastics production, demand and waste data. Plastic Europe, Brussels, Belgium.

Poletto, M., Pistor, V., Zeni, M., Zattera, A.J., 2011. Crystalline properties and decomposition kinetics of cellulose fibers in wood pulp obtained by two pulping processes. Polym. Degrad. Stab. 96, 679–685. https://doi.org/10.1016/j.polymdegradstab.2010.12.007.

Poletto, M., Ornaghi Junior, H.L., Zattera, A.J., 2014. Native cellulose: structure, characterization and thermal properties. Materials 7, 6105–6119. https://doi.org/10.3390/ma7096105.

Popescu, M.C., Popescu, C.M., Lisa, G., Sakata, Y., 2011. Evaluation of morphological and chemical aspects of different wood species by spectroscopy and thermal methods. J. Mol. Struct. 988, 65–72. https://doi.org/10.1016/j.molstruc.2010.12.004.

Puchalski, M., Szparaga, G., Biela, T., Gutowska, A., Sztajnowski, S., Krucińska, I., 2018. Molecular and supramolecular changes in polybutylene succinate (PBS) and polybutylene succinate adipate (PBSA) copolymer during degradation in various environmental conditions. Polymers 10 (3), 251. https://doi.org/10.3390/polym10030251.

Qasim, U., Osman, A.I., Al-Muhtaseb, A.H., Farrell, C., Al-Abri, M., Ali, M., Vo, D.-V.-N., Jamil, F., Rooney, D.W., 2021. Renewable cellulosic nanocomposites for food packaging to avoid fossil fuel plastic pollution: a review. Environ. Chem. Lett. 19, 613–641. https://doi.org/10.1007/s10311-020-01090-x.

Qi, J., Wu, J., Chen, J., Wang, H., 2019. An investigation of the thermal and (bio) degradability of PBS copolyesters based on isosorbide. Polym. Degrad. Stabil. 160, 229–241. https://doi.org/10.1016/j.polymdegradstab.2018.12.031.

Shrestha, A., van-Eerten Jansen, M.C.A.A., Acharya, B., 2020. Biodegradation of bioplastic using anaerobic digestion at retention time as per industrial biogas plant and international norms. Sustain. 12, 4231. https://doi.org/10.3390/su12104231.

Vilarinho, F., Sanches Silva, A., Vaz, M.F., Farinha, J.P., 2018. Nanocellulose in green food packaging. Crit. Rev. Food Sci. Nutr. 58, 1526–1537. https://doi.org/10.1080/10408398.2016.1270254.

Xu, J., Guo, B.H., 2010. Poly (butylene succinate) and its copolymers: Research, development and industrialization. Biotechnol. J. 5, 1149–1163. https://doi.org/10.1002/biot.201000136.

Zaborowska, M., Bernat, K., 2023. The development of recycling methods for bio-based materials - A challenge in the implementation of a circular economy: A review. Waste Manage. Res. 41, 68–80. https://doi.org/10.1177/0734242X221105432.

Zaborowska, M., Bernat, K., Pszczółkowski, B., Wojnowska-Baryła, I., Kulikowska, D., 2021a. Anaerobic degradability of commercially available bio-based and oxo-degradable packaging materials in the context of their end of life in the waste management strategy. Sustain. 13, 1–14. https://doi.org/10.3390/su13126818.

Zaborowska, M., Bernat, K., Pszczółkowski, B., Wojnowska-Baryła, I., Kulikowska, D., 2021b. Challenges in sustainable degradability of bio-based and oxo-degradable packaging materials during anaerobic thermophilic treatment. Energies 14, 4775. https://doi.org/10.3390/en14164775.

Zaborowska, M., Bernat, K., Pszczółkowski, B., Cydzik-Kwiatkowska, A., Kulikowska, D., Wojnowska-Baryła, I., 2023. Multi-faceted analysis of thermophilic anaerobic biodegradation of poly (lactic acid)-based material. Waste Manage. 155, 40–52. https://doi.org/10.1016/j.wasman.2022.10.031.

Zhang, W., Heaven, S., Banks, C.J., 2018. Degradation of some EN13432 compliant plastics in simulated mesophilic anaerobic digestion of food waste Polym. Degrad. Stabil. 147, 76–88. https://doi.org/10.1016/j.polymdegradstab.2017.11.005.

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Magdalena Zaborowska, oświadczam, że mój wkład naukowy w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Assessment of biodegradability of cellulose and poly(butylene succinate)-based bioplastics under mesophilic and thermophilic anaerobic digestion with a view towards biorecycling. *Waste Management*, 168, 413-422.

Mój udział jako współautora publikacji obejmował:

☒ Współautorstwo w przygotowaniu koncepcji pracy

☒ Udział w pisaniu pracy

☒ Udział w graficznym przedstawieniu wyników

☒ Udział w planowaniu badań

☒ Prowadzenie badań i analiz laboratoryjnych

☐ Konsultacja i opieka

☒ Udział w interpretacji wyników i wnioskowaniu

☒ Korekta pracy przed złożeniem do druku

07.07.2023 Magdalena Zaborowska
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Katarzyna Bernat, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Assessment of biodegradability of cellulose and poly(butylene succinate)-based bioplastics under mesophilic and thermophilic anaerobic digestion with a view towards biorecycling. *Waste Management*, 168, 413-422.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☒ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☒ Udział w graficznym przedstawieniu wyników
- ☒ Udział w planowaniu badań
- ☐ Prowadzenie badań i analiz laboratoryjnych
- ☒ Konsultacja i opieka
- ☒ Udział w interpretacji wyników i wnioskowaniu
- ☒ Korekta pracy przed złożeniem do druku

7.07.2023 r. Katarzyna Bernat
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Bartosz Pszczółkowski, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Assessment of biodegradability of cellulose and poly(butylene succinate)-based bioplastics under mesophilic and thermophilic anaerobic digestion with a view towards biorecycling. *Waste Management*, 168, 413-422.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☐ Współautorstwo w przygotowaniu koncepcji pracy
- ☐ Udział w pisaniu pracy
- ☒ Udział w graficznym przedstawieniu wyników
- ☐ Udział w planowaniu badań
- ☒ Prowadzenie badań i analiz laboratoryjnych
- ☐ Konsultacja i opieka
- ☒ Udział w interpretacji wyników i wnioskowaniu
- ☐ Korekta pracy przed złożeniem do druku

07.07.2023 ……………………………
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Dorota Kulikowska, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Assessment of biodegradability of cellulose and poly(butylene succinate)-based bioplastics under mesophilic and thermophilic anaerobic digestion with a view towards biorecycling. *Waste Management*, 168, 413-422.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☐ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☐ Udział w graficznym przedstawieniu wyników
- ☐ Udział w planowaniu badań
- ☐ Prowadzenie badań i analiz laboratoryjnych
- ☒ Konsultacja i opieka
- ☐ Udział w interpretacji wyników i wnioskowaniu
- ☐ Korekta pracy przed złożeniem do druku

06.07.2023
data i podpis

OŚWIADCZENIE WSPÓŁAUTORA O UDZIALE W PUBLIKACJI

Ja, Irena Wojnowska-Baryła, potwierdzam, że wkład naukowy pierwszego autora (mgr inż. Magdalena Zaborowska) w ostateczną wersję poniższej publikacji naukowej wyniósł 51%:

Zaborowska Magdalena, Bernat Katarzyna, Pszczółkowski Bartosz, Kulikowska Dorota, Wojnowska-Baryła Irena, 2023. Assessment of biodegradability of cellulose and poly(butylene succinate)-based bioplastics under mesophilic and thermophilic anaerobic digestion with a view towards biorecycling. *Waste Management*, 168, 413-422.

Jednocześnie oświadczam, że mój udział jako współautora publikacji obejmował:

- ☐ Współautorstwo w przygotowaniu koncepcji pracy
- ☒ Udział w pisaniu pracy
- ☐ Udział w graficznym przedstawieniu wyników
- ☐ Udział w planowaniu badań
- ☐ Prowadzenie badań i analiz laboratoryjnych
- ☒ Konsultacja i opieka
- ☐ Udział w interpretacji wyników i wnioskowaniu
- ☐ Korekta pracy przed złożeniem do druku

6.07.2023 IWojnowska-B
data i podpis