

Brief Report

# Insights into Seawater Biodegradation of Sustainable Mater-Bi/Poly( $\epsilon$ -caprolactone)-Based Biocomposites Filled with Diisocyanate-Modified Cellulose Particles

Aleksander Hejna <sup>1,2,\*</sup>, Paulina Kosmela <sup>2</sup>, Olga Mysiukiewicz <sup>1</sup> and Mateusz Barczewski <sup>1</sup>

<sup>1</sup> Institute of Materials Technology, Poznan University of Technology, Piotrowo 3, 61-138 Poznań, Poland; olga.mysiukiewicz@put.poznan.pl (O.M.); mateusz.barczewski@put.poznan.pl (M.B.)

<sup>2</sup> Department of Polymer Technology, Gdańsk University of Technology, Narutowicza 11/12, 80-233 Gdańsk, Poland; paulina.kosmela@pg.edu.pl

\* Correspondence: aleksander.hejna@put.poznan.pl

**Abstract:** Due to rapid economic growth, the use of plastics in almost all areas of human life has significantly increased over recent decades, leading to massive pollution. Therefore, works dealing with sustainable and biodegradable polymer materials are vital now. Herein, sustainable Mater-Bi/poly( $\epsilon$ -caprolactone) (PCL)-based biocomposites, filled with diisocyanate-modified cellulose particles, were prepared and subjected to 12-week seawater degradation. Changes in the chemical structure and surface wettability pointed to the increasing hydrophilicity of materials over time, which was limited by diisocyanate modifications. Only minor changes in the thermal performance of analyzed materials have been observed, pointing to the limited biodegradation of the PCL phase. The most significant effects have been related to the composite yellowing due to the filler diisocyanate modifications and surface erosion increasing its roughness. Obtained results pointing to the low degradation rate bring into question the commonly-regarded biodegradable nature of PCL material.

**Keywords:** Mater-Bi; poly( $\epsilon$ -caprolactone); biocomposites; cellulose filler; filler modification; diisocyanates; biodegradation; seawater

**Citation:** Hejna, A.; Kosmela, P.; Mysiukiewicz, O.; Barczewski, M. Insights into Seawater Biodegradation of Sustainable Mater-Bi/Poly( $\epsilon$ -caprolactone)-Based Biocomposites Filled with Diisocyanate-Modified Cellulose Particles. *Environments* **2023**, *10*, 90. <https://doi.org/10.3390/environments10050090>

Academic Editors: Naresh Singhal, Dimitrios Komilis and Spyridoula Gerassimidou

Received: 2 March 2023

Revised: 27 April 2023

Accepted: 20 May 2023

Published: 22 May 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Considering the enormously rapid economic growth of the global economy, the use of plastics in almost all areas of human life has significantly increased over the past decades [1]. In many ways, plastics could be considered salvation for humankind due to their applications in medicine [2–4], food preservation [5–8], energy production and storage [9–11], or water purification [12–14]. Other, maybe less essential, but still important applications include transport [15,16], construction and building materials [17–19], electronics [20,21], or military sectors [22,23]. Depending on the application, plastics and plastic-based materials have a lifetime from hours to years, but irrespectively of the application, their post-use disposal is quite a challenging issue [24]. Conventional, petroleum-based plastics are primarily non-biodegradable, so they have been an environmental burden for many years [25,26]. Therefore, researchers have been working on more sustainable solutions like biodegradable materials and bioplastics [27,28]. Their development has been very rapid over the last few years, which is associated with the increasing human awareness and various law regulations associated with enormous plastic pollution [29]. Among the most victimized by this issue are seas and oceans, which are currently often considered the biggest plastic landfills [30–33]. Such an effect is related to the high hydrolytic resistance of many conventional polymers, which is their great advantage, and, what it seems, an even greater curse [34]. The ideal sustainable plastic material should be characterized by a performance competitive to conventional plastics and be efficiently utilized

after use. Therefore, during the development of more sustainable materials, it is very beneficial to investigate their degradation, both under controlled conditions after their effective collection, e.g., in the composting process [35], as well as in the natural environment, when buried in soil or dumped in any reservoir [36,37].

Mater-Bi materials, commercially available sustainable materials based on thermoplastic starch, are considered biodegradable, which has been repeatedly proven by various researchers [38–44]. In our previous work [45], the soil biodegradation of sustainable Mater-Bi-based composites, filled with brewers' spent grain and additionally modified with isophorone diisocyanate, was investigated. Unfilled Mater-Bi underwent degradation noticeably slower than the prepared composites. However, typically Mater-Bi is applied as a thin film obtained by extrusion blow molding noticeably thinner than compression-molded samples analyzed in the reported work.

The limitation of multiple Mater-Bi materials is their performance, which can be enhanced by blending with other biodegradable polymers or incorporating natural fillers, which would maintain the sustainable character of the material and simultaneously boost its performance. However, various commonly considered biodegradable polymers are often characterized by a slower biodegradation rate than Mater-Bi. Herein, we investigated the exposition of sustainable Mater-Bi/poly( $\epsilon$ -caprolactone)-based biocomposites filled with diisocyanate-modified cellulose particles on seawater environment. The diisocyanates have been applied to enhance the interfacial interactions in prepared materials, a common practice during the development of polymer composites [46–48]. However, enhanced interfacial adhesion often implicates a reduced degradation rate, so the impact of applied modifications on the seawater degradation-induced changes of appearance, chemical structure, surface roughness, and wettability, as well as the thermal properties, have been determined.

## 2. Materials and Methods

### 2.1. Materials

The commercial starch-based biomaterial Mater-Bi NF803 from Novamont SPA (Novara, Italy) was applied as a matrix for prepared composites. It was characterized by a melt flow index (MFI) value of 3.5 g/10 min (150 °C/5 kg) and a melting temperature of 110 °C.

As a second component of the polymer matrix, the poly( $\epsilon$ -caprolactone) Capa 6500 from Perstorp (Malmö, Sweden) was applied. It was characterized by the  $M_w$  = 80,000 g/mol, a melt flow index of 7.0 g/10 min (170 °C/2.16 kg), and a melting temperature of 58–60 °C.

Commercially available cellulose Arbocel® UFC100 from JRS J. Rettenmaier & Söhne GmbH (Rosenberg, Germany) was used as filler for polymer composites. It was characterized by an average particle length of 8  $\mu$ m, an aspect ratio of 4, a bulk density of 160 g/L, and a moisture content of 4.84 wt%.

Two different isocyanates were employed as modifiers of cellulose fillers: methylene diphenyl diisocyanate (MDI), and toluene diisocyanate (TDI), which were acquired from Sigma Aldrich (MO, USA). The purity of MDI was 98%, while for TDI a mixture of 2,4-TDI and 2,6-TDI in the 80/20 ratio was used.

### 2.2. Modifications of UFC100 Filler

Prior to the incorporation into the polymer matrix, cellulose filler was subjected to chemical treatment, which was in detail described in previous works [49,50]. The modification was performed using a GMF 106/2 Brabender batch mixer at room temperature (varied from 21.1 to 23.1 °C), with a rotor speed of 100 rpm. The proper amount of filler was placed in an internal mixer with a calculated amount of diisocyanate (10 wt%), respectively, to the mass of the filler. Mixing was performed for 5 min, and samples were put in hermetic storage bags. Assuming the complete reactivity of the applied modifier

with hydroxyl groups of cellulose, the degree of substitution equals 0.432 and 0.621, respectively, for MDI and TDI. However, the availability of moisture in the surrounding atmosphere during modification and the varying reactivity of isocyanate groups in TDI might affect these values. According to Vilar [51], in 2,4-TDI the reactivity of the isocyanate group at the para position is four times greater than that of the ortho group. Moreover, after the para group is reacted, the reactivity of the ortho group is significantly reduced due to the steric effects. On the other hand, in MDI, the reactivity of both isocyanate groups is similar, so the degree of substitution should be closer to the theoretical value. In our previous work [49], we indirectly investigated changes in the polarity of diisocyanate-modified UFC100 filler. Obtained results indicated that the polarity was reduced more significantly after modification with MDI, which confirms the information given by Vilar [51].

### 2.3. Preparation of Polymer Composites

Composites were prepared using a GMF 106/2 Brabender batch mixer at 140 °C and a rotor speed of 100 rpm. The processing time equaled 6 min, including the 1-min phase of matrix plasticization and 5 min of melt blending with the selected filler. A blend of Mater-Bi and PCL in a 70:30 constant ratio was applied as a matrix. The filler content in each sample was fixed at 30 wt%. Prepared composites were compression molded at 150 °C and 4.9 MPa for 1 min and then kept under pressure at room temperature for another 5 min to enable solidification of the material. Obtained samples were coded as UFC100, MDI, and TDI.

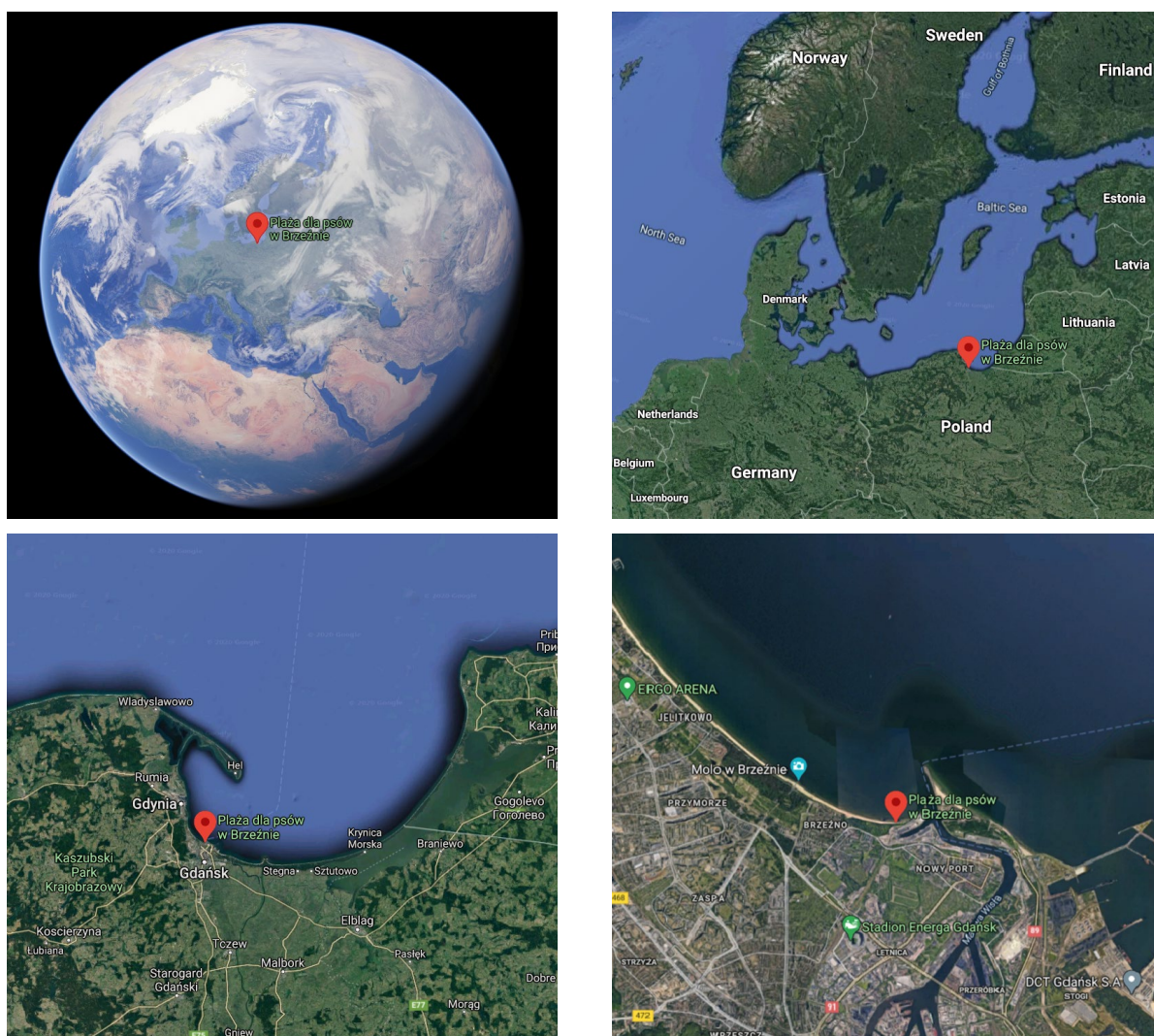
### 2.4. Biodegradation of Prepared Composites

Biodegradation of composites was conducted in simulated seawater immersion conditions. Seawater for the experiments was collected in Gdańsk Bay at Nowy Port Beach (54°24'29" N; 18°39'04" E—see Figure 1) in May 2021, at a 1.5 m depth. Parameters of the collected seawater according to the Institute of Oceanography of the University of Gdańsk are presented in Table 1 [52,53]. The water was used as collected to simulate the natural environment during the degradation of polymer composites.

Samples were placed in a plastic container, which was filled with seawater. Specimens have been placed in separate compartments. Three compartments were used for each sample. Plastic containers were placed outdoors in facing east stand, characterized by open sun exposition. The seawater biodegradation test lasted twelve weeks (from 31 May 2021 to 23 August 2021). After 1, 2, 4, 8, and 12 weeks, samples were retrieved and dried at room temperature before characterization.

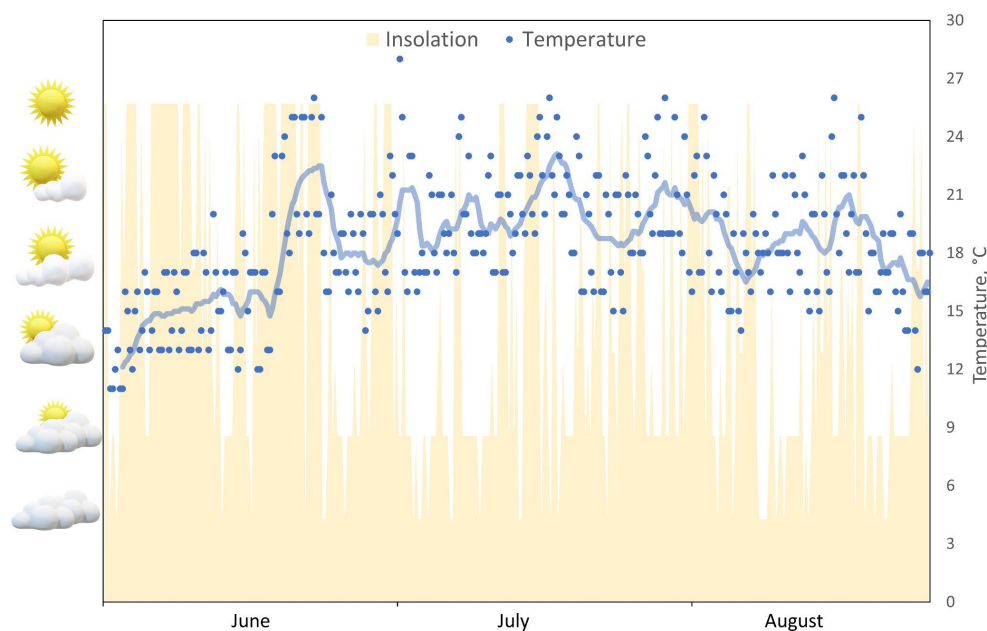
**Table 1.** Parameters of seawater used during degradation analysis.

Water Quality Parameter	Unit	Value	Water Quality Parameter	Unit	Value
Temperature	°C	11.9	Blue-green algae	mg/m <sup>3</sup>	0.0
Salinity	PSU	5.59	Chlorophyll a	mg/m <sup>3</sup>	7.2
N-NH <sub>4</sub>	mg/m <sup>3</sup>	6.4	Chlorophyll b	mg/m <sup>3</sup>	0.49
N-NO <sub>3</sub>	mg/m <sup>3</sup>	18.1	Chlorophyll c	mg/m <sup>3</sup>	0.51
P-PO <sub>4</sub>	mg/m <sup>3</sup>	20.1	Photoprotective carotenoids	mg/m <sup>3</sup>	1.56
Si-SiO <sub>4</sub>	mg/m <sup>3</sup>	531	Photosynthetic carotenoids	mg/m <sup>3</sup>	1.17
Dissolved oxygen	g/m <sup>3</sup>	12.5	Phytoplankton	mg/m <sup>3</sup>	97.2



**Figure 1.** The location of seawater collection for performed degradation analysis with increasing geographic precision from global (upper left), through continental (upper right), and national (bottom left), to local (bottom right) scale.

Figure 2 shows the temperature and insolation over the analyzed period according to the local weather information. All the parameters were noted every six hours. Insolation was expressed on a 0–5 scale, where: 0—very cloudy, 1—cloudy, 2—partly sunny/moderately cloudy, 3—little cloudiness, 4—mostly sunny, and 5—sunny/cloudless.



**Figure 2.** The temperature and insolation over the analyzed period.

### 2.5. Characterization of Prepared Composites

The chemical structure of composites was determined using Fourier transform infrared spectroscopy (FTIR) analysis performed by a Nicolet Spectrometer IR200 from Thermo Fisher Scientific (Waltham, MA, USA). The device had an ATR attachment with a diamond crystal. Measurements were performed with  $1\text{ cm}^{-1}$  resolution in the range from  $4000$  to  $400\text{ cm}^{-1}$ , using 64 scans.

Surface wettability was studied through static water contact angle measurements, using an Ossila L2004 contact angle goniometer (Ossila Ltd., Sheffield, UK) equipped with a camera and Ossila Contact Angle software. Ten contact angle measurements were taken in random positions, putting drops of  $\sim 1\text{ }\mu\text{L}$  distiller water onto the surface of the samples with the aid of a syringe. The average values were calculated and reported.

The roughness of the Mater-Bi and its composites subjected to soil burial was evaluated using an ART300 surface roughness tester from Sunpoc Co. Ltd. (Guiyang, China). The sampling length was  $0.8\text{ mm}$ . The average  $R_a$  value was calculated from five measurements on five different spots on the sample's surface (25 measurements in total).

The thermal properties of the samples were measured by differential scanning calorimetry (DSC) carried out on a DSC 204 F1 Phoenix apparatus from Netzsch (Selb, Germany). Measurements were performed on  $5 \pm 0.2\text{ mg}$  samples in the temperature range of  $-80$  to  $170\text{ }^\circ\text{C}$ , under a nitrogen atmosphere, at a heating rate of  $15\text{ }^\circ\text{C}/\text{min}$ . The heating cycle was performed twice, to erase the thermal history of the samples.

The thermal stability of materials was determined by thermogravimetric analysis (TGA) with the temperature set between  $35\text{ }^\circ\text{C}$  and  $800\text{ }^\circ\text{C}$  at a heating rate of  $15\text{ }^\circ\text{C}/\text{min}$  under a nitrogen flow using a TG 209 F1 Netzsch (Selb, Germany) apparatus. Samples of  $10.0 \pm 0.1\text{ mg}$  and ceramic pans were applied.

## 3. Results

Table 2 presents the appearance of composite samples before and after seawater immersion. Visible changes may be noted, which point to the partial photodegradation of composite surface inducing yellowing of samples [54]. The literature data indicate that the origin of such changes may be associated with the radiation absorption by chromophoric groups and surface erosion [55]. However, diisocyanate-modified samples show a significantly greater extent of visual changes. Such an effect is attributed to the photooxidative

changes in the chemical groups resulting from the presence of diisocyanates in the system [56]. Such an effect is commonly known for polyurethane materials, in which the urethane bond oxidizes to a quinone-imide structure, which is a strong chromophore [57]. It is especially pronounced for aromatic diisocyanates [58]. Moreover, visual changes could be related to the deposition of biofilm on the surface of samples [59].

**Table 2.** The appearance of prepared composite samples before and after seawater degradation.



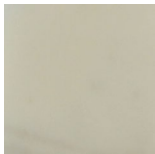
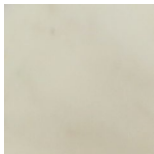

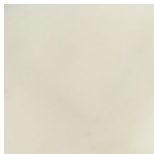



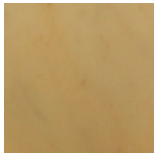





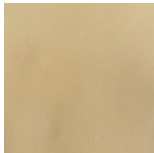


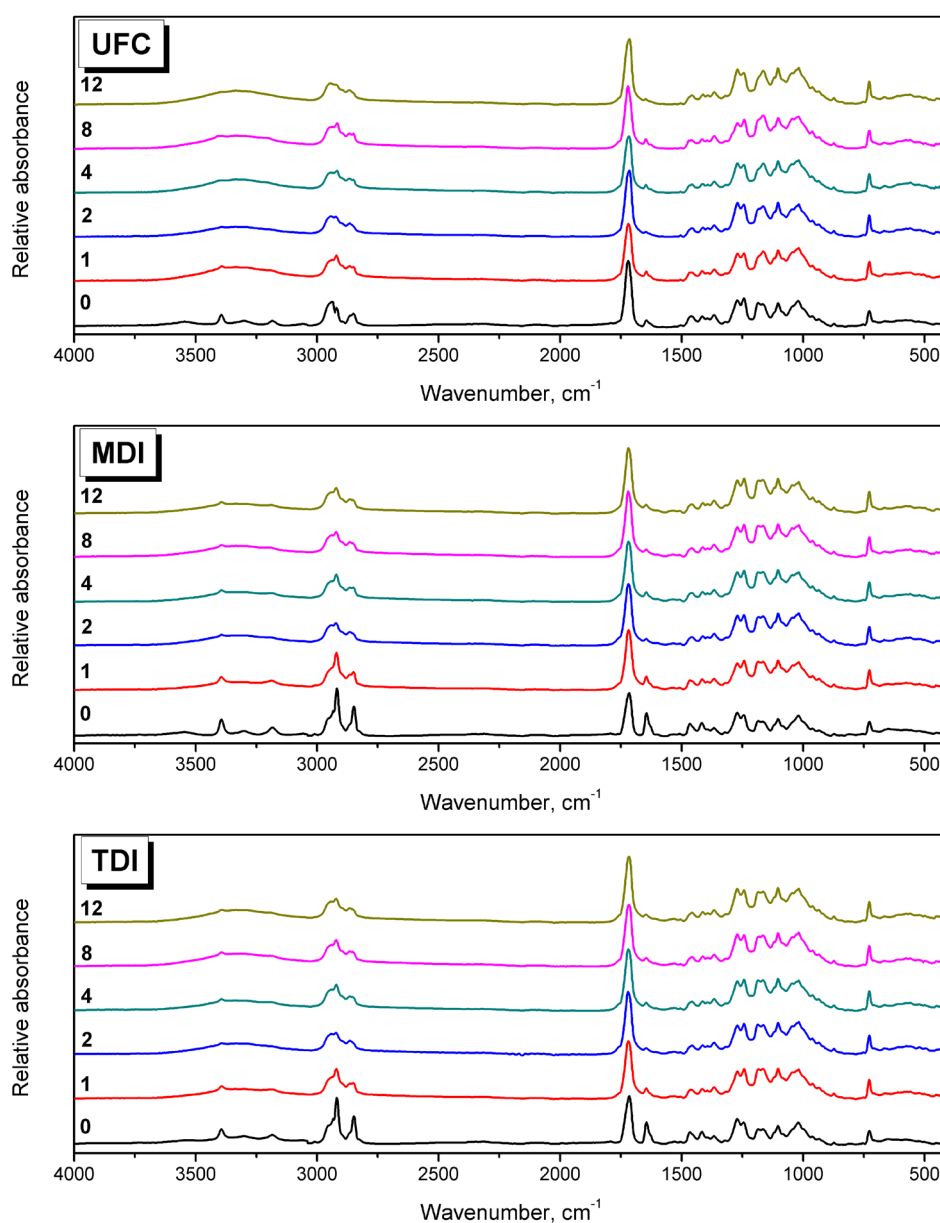
Sample	Degradation Time, Weeks					
	0	1	2	4	8	12
UFC						
MDI						
TDI						

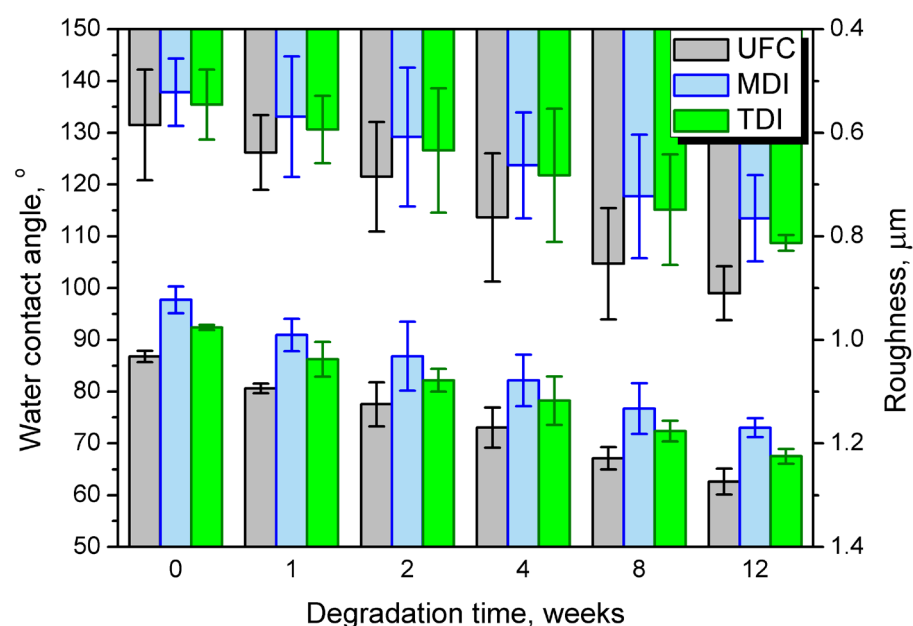
Figure 3 presents the impact of seawater degradation on the FTIR spectra of prepared composites. Prior to degradation, all of the analyzed composites showed the spectra appearance typical for Mater-Bi-based materials [60,61]. Qualitatively, seawater degradation hardly affected the spectra appearance. However, changes in the magnitude of particular peaks have been observed pointing to the structural changes in composites. The intensity of signal between 3000 and 3600  $\text{cm}^{-1}$ , associated with the stretching vibrations of O-H and N-H bonds, has been noticeably increased with the degradation time. It can be attributed to the hydrolysis of ester groups in PCL and PBAT phases, which has been reported as the primary mechanism of decomposition [62,63]. Accordingly, the magnitude of the 1720  $\text{cm}^{-1}$  peak, attributed to the vibrations of C=O bonds in the ester groups of PBAT and PCL, was increased [64]. The decrease of the 2847 and 2917  $\text{cm}^{-1}$  signals' strength, related to the stretching C-H vibrations, has been associated with the surface erosion of samples and probably with the decreasing molecular weight of polymers included in the matrices of composites. Moreover, the peak observed at 1644  $\text{cm}^{-1}$ , related to the N-H deformation and C-N stretching vibration [65], was disappearing as a result of degradation, which may be attributed to the impact of urethane photooxidation related to the composites yellowing and corresponding conversion of urethanes to quinone-imide structures [66].



**Figure 3.** The impact of seawater degradation (from 0 to 12 weeks) on the FTIR spectra of prepared composites.

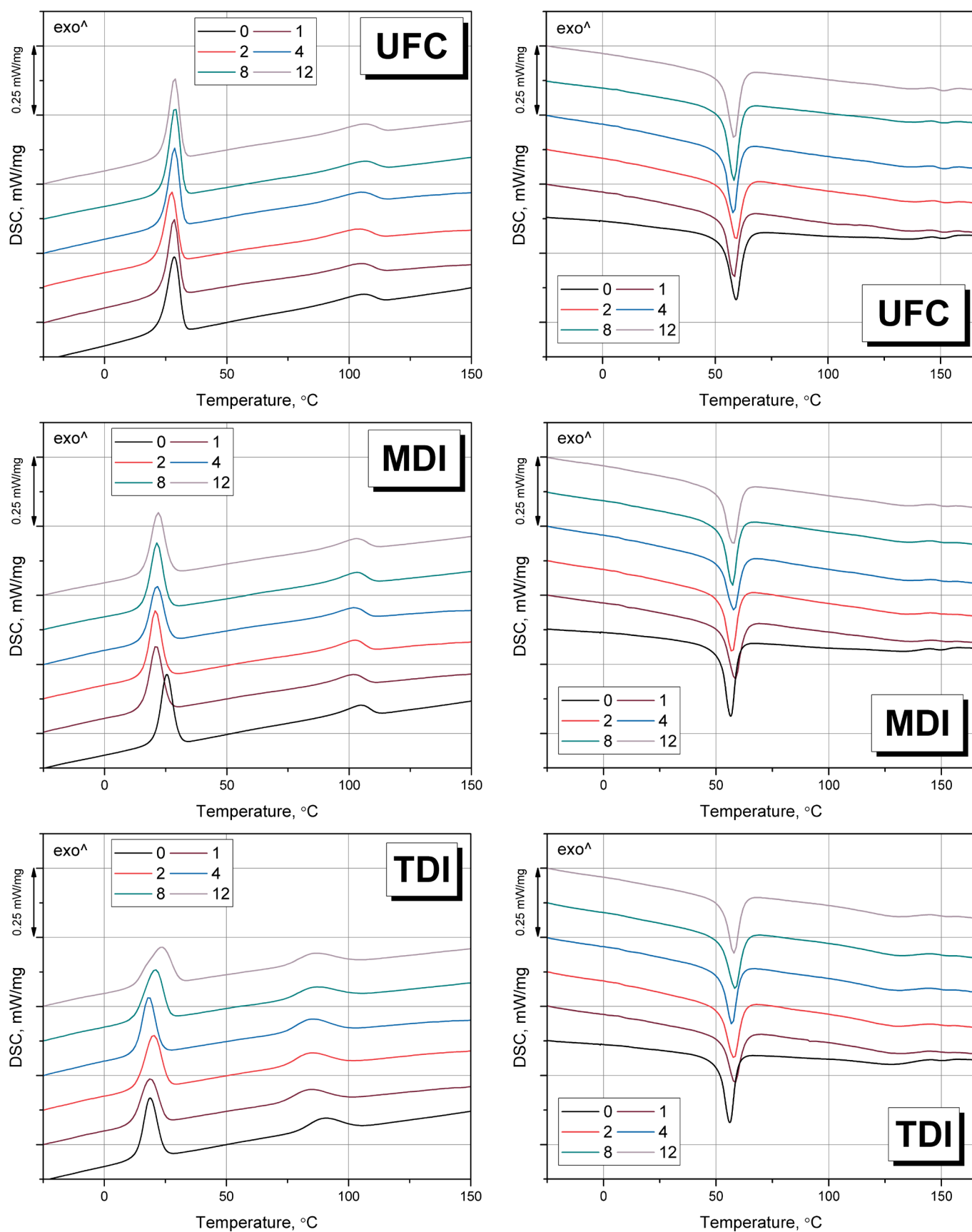
Changes in the surface polarity of the prepared composites, caused by the seawater degradation and expressed by the variations of water contact angle, are presented in Figure 4. It can be seen that a noticeable increase in hydrophilicity was noted for all samples. As mentioned above, such an effect was associated with the primary decomposition mechanism of PCL and PBAT—ester group hydrolysis. Similar effects have been observed by other researchers [67]. Irrespectively of the degradation time, the diisocyanate-modified composites showed noticeably higher water contact angle values, pointing to the higher hydrophobicity, attributed to the reduced polarity of introduced fillers, as reported in our previous works [49,50]. The changes in the surface wettability were also positively correlated with the increasing surface roughness related to the surface erosion of the composites. According to the literature data [68], the impact of roughness on contact angle depends on the surface characteristics. The character of both hydrophilic and hydrophobic surfaces deepened with the increasing roughness [69]. In the presented case, the unmodified composites showed hydrophilic character, while diisocyanate modifications shifted

it towards hydrophobicity. Nevertheless, the impact of roughness was similar for all samples.



**Figure 4.** Changes in the water contact angle (bottom columns) and surface roughness (top columns) of prepared composites over the biodegradation course (from 0 to 12 weeks).

Figure 5 and Table 3 present cooling and heating thermograms and the results of DSC analysis of prepared composites before and after seawater immersion. On the cooling curves, two separate peaks related to the crystallization of PCL and PBAT phases of composites were noted. For the UFC sample, only minor changes in the crystallization temperatures ( $T_c$ ) and peaks height were noted, pointing to only slight changes in the crystallization rate after biodegradation. On the other hand, noticeable changes were noted for MDI- and TDI-modified samples. For MDI modification, a drop of both  $T_c$  values was noted, which suggests the reduced nucleating activity of fillers expressed by the lower value of melting enthalpy resulting in reduced melting peaks height [70]. For TDI modifications, the crystallization peak of PBAT was noted at significantly lower temperatures, which may be attributed to the different polarity of the modified filler and hindered crystallization of this phase. On the other hand, the PCL peak was slightly shifted to higher temperatures, which may indicate an increased crystallization rate. The difference could be attributed to the more hydrophobic character of PCL. Literature data reports values of water contact angle for PCL in the range of 110–120° [71–73], while for PBAT in the range of 70–75° [74–76]. Considering the melting behavior, the TDI-modified composite acted similarly to the MDI sample.



**Figure 5.** Cooling (left) and the second heating (right) thermograms of prepared composites before and after seawater degradation (from 0 to 12 weeks).

All the effects were observed, despite the literature reports indicating the increase of PCL and PBAT crystallinity after hydrolysis or water degradation, which is associated with faster decomposition of the amorphous phase, and so-called chemicrystallization [77,78]. It was probably related to the increasing hydrophilicity of the polymer matrix and higher polarity difference between the matrix and rather hydrophobic filler (due to diisocyanate modification). However, after 8 and 12 weeks, a slight shift of melting temperature ( $T_m$ ) of PCL was noted for all samples, suggesting increased crystallinity due to the decomposition of the amorphous phase.

**Table 3.** Results of DSC analysis of prepared composite samples before and after seawater degradation.

Sample	Biodegradation Time, Weeks	$T_{cPCL}$ , °C	$T_{cPBAT}$ , °C	$T_{mPCL}$ , °C	$\Delta H_m$ , J/g	$T_{mPBAT}$ , °C
UFC	0	28.5	106.0	59.2	16.31	135.2
	1	28.4	104.9	58.3	13.86	137.6
	2	27.4	104.1	59.2	13.99	138.0
	4	28.6	105.2	58.1	13.87	137.2
	8	28.8	106.4	58.3	14.56	138.0
	12	28.6	106.6	58.4	15.13	137.9
MDI	0	25.5	104.9	56.5	14.92	133.9
	1	21.0	101.9	58.5	13.91	136.5
	2	20.9	102.6	57.1	13.16	134.6
	4	21.3	102.0	57.9	12.96	135.9
	8	21.4	103.3	57.2	14.05	136.0
	12	21.9	103.2	57.6	14.74	136.1
TDI	0	18.7	91.2	56.1	13.73	127.2
	1	19.0	85.2	58.3	12.30	133.1
	2	20.2	85.5	57.8	13.58	131.3
	4	18.2	85.8	57.1	12.32	131.2
	8	20.8	86.8	58.5	13.38	132.1
	12	23.4	87.0	57.9	13.46	131.4

**Author Contributions:** Conceptualization, A.H.; methodology, P.K. and O.M.; validation, A.H. and M.B.; formal analysis, M.B.; investigation, A.H., P.K., O.M. and M.B.; resources, A.H.; writing—original draft preparation, A.H.; writing—review and editing, P.K., O.M. and M.B.; visualization, A.H. and O.M.; supervision, A.H.; project administration, A.H.; funding acquisition, A.H. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the National Science Centre (NCN, Poland) in the frame of SONATINA 2 project 2018/28/C/ST8/00187-Structure and properties of lignocellulosic fillers modified in situ during reactive extrusion. The study was co-funded under project with grants for education allocated by the Ministry of Science and Higher Education in Poland executed under the subject of No. 0613/SBAD/4820.

**Data Availability Statement:** Data are available in Insights into seawater biodegradation of sustainable Mater-Bi/poly( $\epsilon$ -caprolactone)-based biocomposites filled with diisocyanate-modified cellulose particles.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Geyer, R. A Brief History of Plastics. In *Mare Plasticum—The Plastic Sea*; Springer International Publishing: Cham, Switzerland, 2020; pp. 31–47.
2. George, A.; Shah, P.A.; Shrivastav, P.S. Natural Biodegradable Polymers Based Nano-Formulations for Drug Delivery: A Review. *Int. J. Pharm.* **2019**, *561*, 244–264. <https://doi.org/10.1016/j.ijpharm.2019.03.011>.

3. Asghari, F.; Samiei, M.; Adibkia, K.; Akbarzadeh, A.; Davaran, S. Biodegradable and Biocompatible Polymers for Tissue Engineering Application: A Review. *Artif. Cells Nanomed. Biotechnol.* **2017**, *45*, 185–192. <https://doi.org/10.3109/21691401.2016.1146731>.
4. Zarrintaj, P.; Jouyandeh, M.; Ganjali, M.R.; Hadavand, B.S.; Mozafari, M.; Sheiko, S.S.; Vatankhah-Varnoosfaderani, M.; Gutierrez, T.J.; Saeb, M.R. Thermo-Sensitive Polymers in Medicine: A Review. *Eur. Polym. J.* **2019**, *117*, 402–423. <https://doi.org/10.1016/j.eurpolymj.2019.05.024>.
5. Makvandi, P.; Iftekhhar, S.; Pizzetti, F.; Zarepour, A.; Zare, E.N.; Ashrafizadeh, M.; Agarwal, T.; Padil, V.V.T.; Mohammadinejad, R.; Sillanpaa, M.; et al. Functionalization of Polymers and Nanomaterials for Water Treatment, Food Packaging, Textile and Biomedical Applications: A Review. *Environ. Chem. Lett.* **2021**, *19*, 583–611. <https://doi.org/10.1007/s10311-020-01089-4>.
6. Nogueira, G.F.; de Oliveira, R.A.; Velasco, J.I.; Fakhouri, F.M. Methods of Incorporating Plant-Derived Bioactive Compounds into Films Made with Agro-Based Polymers for Application as Food Packaging: A Brief Review. *Polymers* **2020**, *12*, 2518. <https://doi.org/10.3390/polym12112518>.
7. Baschetti, M.G.; Minelli, M. Test Methods for the Characterization of Gas and Vapor Permeability in Polymers for Food Packaging Application: A Review. *Polym. Test.* **2020**, *89*, 106606. <https://doi.org/10.1016/j.polymertesting.2020.106606>.
8. Czarnecka-Komorowska, D.; Wiszumirska, K. Sustainability Design of Plastic Packaging for the Circular Economy. *Polimery* **2020**, *65*, 8–17. <https://doi.org/10.14314/polimery.2020.1.2>.
9. Abdelhamid, M.E.; O'Mullane, A.P.; Snook, G.A. Storing Energy in Plastics: A Review on Conducting Polymers & Their Role in Electrochemical Energy Storage. *RSC Adv.* **2015**, *5*, 11611–11626. <https://doi.org/10.1039/C4RA15947K>.
10. Basnayaka, P.A.; Ram, M.K. A Review of Supercapacitor Energy Storage Using Nanohybrid Conducting Polymers and Carbon Electrode Materials. In *Conducting Polymer Hybrids*; Springer: Cham, Switzerland, 2017; pp. 165–192.
11. Shi, Y.; Peng, L.; Ding, Y.; Zhao, Y.; Yu, G. Nanostructured Conductive Polymers for Advanced Energy Storage. *Chem. Soc. Rev.* **2015**, *44*, 6684–6696. <https://doi.org/10.1039/C5CS00362H>.
12. Bassyouni, M.; Abdel-Aziz, M.H.; Zoromba, M.Sh.; Abdel-Hamid, S.M.S.; Drioli, E. A Review of Polymeric Nanocomposite Membranes for Water Purification. *J. Ind. Eng. Chem.* **2019**, *73*, 19–46. <https://doi.org/10.1016/j.jiec.2019.01.045>.
13. Dongre, R.S.; Sadasivuni, K.K.; Deshmukh, K.; Mehta, A.; Basu, S.; Meshram, J.S.; Al-Maadeed, M.A.A.; Karim, A. Natural Polymer Based Composite Membranes for Water Purification: A Review. *Polym.-Plast. Technol. Mater.* **2019**, *58*, 1295–1310. <https://doi.org/10.1080/25740881.2018.1563116>.
14. Elrasheedy, A.; Nady, N.; Bassyouni, M.; El-Shazly, A. Metal Organic Framework Based Polymer Mixed Matrix Membranes: Review on Applications in Water Purification. *Membranes* **2019**, *9*, 88. <https://doi.org/10.3390/membranes9070088>.
15. Wiese, M.; Thiede, S.; Herrmann, C. Rapid Manufacturing of Automotive Polymer Series Parts: A Systematic Review of Processes, Materials and Challenges. *Addit. Manuf.* **2020**, *36*, 101582. <https://doi.org/10.1016/j.addma.2020.101582>.
16. Sarfraz, M.S.; Hong, H.; Kim, S.S. Recent Developments in the Manufacturing Technologies of Composite Components and Their Cost-Effectiveness in the Automotive Industry: A Review Study. *Compos. Struct.* **2021**, *266*, 113864. <https://doi.org/10.1016/j.compstruct.2021.113864>.
17. Kosmela, P.; Hejna, A.; Suchorzewski, J.; Piszczczyk, L.; Haponiuk, J.T. Study on the Structure-Property Dependences of Rigid PUR-PIR Foams Obtained from Marine Biomass-Based Biopolyol. *Materials* **2020**, *13*, 1257. <https://doi.org/10.3390/ma13051257>.
18. Antov, P.; Savov, V.; Trichkov, N.; Křišťák, L.; Réh, R.; Papadopoulos, A.N.; Taghiyari, H.R.; Pizzi, A.; Kunecová, D.; Pachikova, M. Properties of High-Density Fiberboard Bonded with Urea-Formaldehyde Resin and Ammonium Lignosulfonate as a Bio-Based Additive. *Polymers* **2021**, *13*, 2775. <https://doi.org/10.3390/polym13162775>.
19. Bekhta, P.; Noshchenko, G.; Réh, R.; Kristak, L.; Sedláčik, J.; Antov, P.; Mirski, R.; Savov, V. Properties of Eco-Friendly Particleboards Bonded with Lignosulfonate-Urea-Formaldehyde Adhesives and PMDI as a Crosslinker. *Materials* **2021**, *14*, 4875. <https://doi.org/10.3390/ma14174875>.
20. Dhineshbabu, N.R.; Mahadevi, N.; Assein, D. Electronic Applications of Multi-Walled Carbon Nanotubes in Polymers: A Short Review. *Mater. Today Proc.* **2020**, *33*, 382–386. <https://doi.org/10.1016/j.matpr.2020.04.221>.
21. Cao, Y.; Uhrich, K.E. Biodegradable and Biocompatible Polymers for Electronic Applications: A Review. *J. Bioact. Compat. Polym.* **2019**, *34*, 3–15. <https://doi.org/10.1177/0883911518818075>.
22. Shakil, U.A.; Hassan, S.B.A.; Yahya, M.Y.; Nurhadiyanto, D. A Review of Properties and Fabrication Techniques of Fiber Reinforced Polymer Nanocomposites Subjected to Simulated Accidental Ballistic Impact. *Thin-Walled Struct.* **2021**, *158*, 107150. <https://doi.org/10.1016/j.tws.2020.107150>.
23. Nurazzi, N.M.; Asyraf, M.R.M.; Khalina, A.; Abdullah, N.; Aisyah, H.A.; Rafiqah, S.A.; Sabaruddin, F.A.; Kamarudin, S.H.; Norrrahim, M.N.F.; Ilyas, R.A.; et al. A Review on Natural Fiber Reinforced Polymer Composite for Bullet Proof and Ballistic Applications. *Polymers* **2021**, *13*, 646. <https://doi.org/10.3390/polym13040646>.
24. Browning, S.; Beymer-Farris, B.; Seay, J.R. Addressing the Challenges Associated with Plastic Waste Disposal and Management in Developing Countries. *Curr. Opin. Chem. Eng.* **2021**, *32*, 100682. <https://doi.org/10.1016/j.coche.2021.100682>.
25. Korol, J.; Hejna, A.; Burchart-Korol, D.; Wachowicz, J. Comparative Analysis of Carbon, Ecological, and Water Footprints of Polypropylene-Based Composites Filled with Cotton, Jute and Kenaf Fibers. *Materials* **2020**, *13*, 3541. <https://doi.org/10.3390/ma13163541>.
26. Korol, J.; Hejna, A.; Burchart-Korol, D.; Chmielnicki, B.; Wypiór, K. Water Footprint Assessment of Selected Polymers, Polymer Blends, Composites, and Biocomposites for Industrial Application. *Polymers* **2019**, *11*, 1791. <https://doi.org/10.3390/polym11111791>.

27. Rujnić-Sokele, M.; Pilipović, A. Challenges and Opportunities of Biodegradable Plastics: A Mini Review. *Waste Manag. Res. J. Sustain. Circ. Econ.* **2017**, *35*, 132–140. <https://doi.org/10.1177/0734242X16683272>.
28. Thakur, S.; Chaudhary, J.; Sharma, B.; Verma, A.; Tamulevicius, S.; Thakur, V.K. Sustainability of Bioplastics: Opportunities and Challenges. *Curr. Opin. Green Sustain. Chem.* **2018**, *13*, 68–75. <https://doi.org/10.1016/j.cogsc.2018.04.013>.
29. Zhou, Q.; Zhang, H.; Fu, C.; Zhou, Y.; Dai, Z.; Li, Y.; Tu, C.; Luo, Y. The Distribution and Morphology of Microplastics in Coastal Soils Adjacent to the Bohai Sea and the Yellow Sea. *Geoderma* **2018**, *322*, 201–208. <https://doi.org/10.1016/j.geoderma.2018.02.015>.
30. Cressey, D. Bottles, Bags, Ropes and Toothbrushes: The Struggle to Track Ocean Plastics. *Nature* **2016**, *536*, 263–265. <https://doi.org/10.1038/536263a>.
31. Digka, N.; Tsangaris, C.; Torre, M.; Anastasopoulou, A.; Zeri, C. Microplastics in Mussels and Fish from the Northern Ionian Sea. *Mar. Pollut. Bull.* **2018**, *135*, 30–40. <https://doi.org/10.1016/j.marpolbul.2018.06.063>.
32. Fossi, M.C.; Marsili, L.; Baini, M.; Giannetti, M.; Coppola, D.; Guerranti, C.; Caliani, I.; Minutoli, R.; Lauriano, G.; Finoia, M.G.; et al. Fin Whales and Microplastics: The Mediterranean Sea and the Sea of Cortez Scenarios. *Environ. Pollut.* **2016**, *209*, 68–78. <https://doi.org/10.1016/j.envpol.2015.11.022>.
33. Cincinelli, A.; Scopetani, C.; Chelazzi, D.; Martellini, T.; Pogojeva, M.; Slobodnik, J. Microplastics in the Black Sea Sediments. *Sci. Total Environ.* **2021**, *760*, 143898. <https://doi.org/10.1016/j.scitotenv.2020.143898>.
34. Gewert, B.; Plassmann, M.M.; MacLeod, M. Pathways for Degradation of Plastic Polymers Floating in the Marine Environment. *Environ. Sci. Process. Impacts* **2015**, *17*, 1513–1521. <https://doi.org/10.1039/C5EM00207A>.
35. Ruggero, F.; Gori, R.; Lubello, C. Methodologies to Assess Biodegradation of Bioplastics during Aerobic Composting and Anaerobic Digestion: A Review. *Waste Manag. Res.* **2019**, *37*, 959–975. <https://doi.org/10.1177/0734242X19854127>.
36. la Mantia, F.; Ascione, L.; Mistretta, M.; Rapisarda, M.; Rizzarelli, P. Comparative Investigation on the Soil Burial Degradation Behaviour of Polymer Films for Agriculture before and after Photo-Oxidation. *Polymers* **2020**, *12*, 753. <https://doi.org/10.3390/polym12040753>.
37. Vasile, C.; Pamfil, D.; Râpă, M.; Darie-Niță, 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. B Eng.* **2018**, *142*, 251–262. <https://doi.org/10.1016/j.compositesb.2018.01.026>.
38. Scaffaro, R.; Morreale, M.; lo Re, G.; la Mantia, F.P. Degradation of Mater-Bi®/Wood Flour Biocomposites in Active Sewage Sludge. *Polym. Degrad. Stab.* **2009**, *94*, 1220–1229. <https://doi.org/10.1016/j.polymdegradstab.2009.04.028>.
39. Puglia, D.; Tomassucci, A.; Kenny, J.M. Processing, Properties and Stability of Biodegradable Composites Based on Mater-Bi® and Cellulose Fibres. *Polym. Adv. Technol.* **2003**, *14*, 749–756. <https://doi.org/10.1002/pat.390>.
40. Alvarez, V.A.; Ruseckaite, R.A.; Vázquez, A. Degradation of Sisal Fibre/Mater Bi-Y Biocomposites Buried in Soil. *Polym. Degrad. Stab.* **2006**, *91*, 3156–3162. <https://doi.org/10.1016/j.polymdegradstab.2006.07.011>.
41. Kim, M.-N.; Lee, A.-R.; Yoon, J.-S.; Chin, I.-J. Biodegradation of Poly(3-Hydroxybutyrate), Sky-Green® and Mater-Bi® by Fungi Isolated from Soils. *Eur. Polym. J.* **2000**, *36*, 1677–1685. [https://doi.org/10.1016/S0014-3057\(99\)00219-0](https://doi.org/10.1016/S0014-3057(99)00219-0).
42. Re, G.L.; Morreale, M.; Scaffaro, R.; La Mantia, F.P. Biodegradation Paths of Mater-Bi®/Kenaf Biodegradable Composites. *J. Appl. Polym. Sci.* **2013**, *129*, 3198–3208. <https://doi.org/10.1002/app.39027>.
43. Bastioli, C.; Bellotti, V.; Giudice, L.; Gilli, G. Mater-Bi: Properties and Biodegradability. *J. Environ. Polym. Degrad.* **1993**, *1*, 181–191. <https://doi.org/10.1007/BF01458026>.
44. Knitter, M.; Czarnecka-Komorowska, D.; Czaja-Jagielska, N.; Szymanowska-Powałowska, D. Manufacturing and Properties of Biodegradable Composites Based on Thermoplastic Starch/Polyethylene-Vinyl Alcohol and Silver Particles. In *Advances in Manufacturing II: Volume 4—Mechanical Engineering*; Springer International Publishing: Cham, Switzerland, 2019; pp. 610–624.
45. Hejna, A.; Barczewski, M.; Kosmela, P.; Mysiukiewicz, O.; Aniśko, J.; Sulima, P.; Andrzej Przyborowski, J.; Reza Saeb, M. The Impact of Thermomechanical and Chemical Treatment of Waste Brewers' Spent Grain and Soil Biodegradation of Sustainable Mater-Bi-Based Biocomposites. *Waste Manag.* **2022**, *154*, 260–271. <https://doi.org/10.1016/j.wasman.2022.10.007>.
46. Hejna, A.; Przybysz-Romatowska, M.; Kosmela, P.; Zedler, Ł.; Korol, J.; Formela, K. Recent Advances in Compatibilization Strategies of Wood-Polymer Composites by Isocyanates. *Wood Sci. Technol.* **2020**, *54*, 1091–1119. <https://doi.org/10.1007/s00226-020-01203-3>.
47. Yatigala, N.S.; Bajwa, D.S.; Bajwa, S.G. Compatibilization Improves Physico-Mechanical Properties of Biodegradable Biobased Polymer Composites. *Compos. Part A Appl. Sci. Manuf.* **2018**, *107*, 315–325. <https://doi.org/10.1016/j.compositesa.2018.01.011>.
48. Shamsuri, A.A.; Jamil, S.N.A.M. Application of Quaternary Ammonium Compounds as Compatibilizers for Polymer Blends and Polymer Composites—A Concise Review. *Appl. Sci.* **2021**, *11*, 3167. <https://doi.org/10.3390/app11073167>.
49. Hejna, A.; Marć, M.; Korol, J. Modification of Cellulosic Filler with Diisocyanates—Volatile Organic Compounds Emission Assessment and Stability of Chemical Structure over Time. *Nord. Pulp Pap. Res. J.* **2021**, *36*, 353–372. <https://doi.org/10.1515/npprj-2020-0104>.
50. Hejna, A.; Marć, M.; Skórczewska, K.; Szulc, J.; Korol, J.; Formela, K. Insights into Modification of Lignocellulosic Fillers with Isophorone Diisocyanate: Structure, Thermal Stability and Volatile Organic Compounds Emission Assessment. *Eur. J. Wood Wood Prod.* **2021**, *79*, 75–90. <https://doi.org/10.1007/s00107-020-01604-y>.
51. Vilar, W.D. *Química e Tecnologia dos Poliuretanos*, 2nd ed.; Vilar Consultoria Técnica Ltd.: Rio de Janeiro, Brazil, 1998.
52. Instytut Oceanologii PAN w Sopocie System Satbałtyk. Available online: <http://www.satbałtyk.pl> (accessed on 1 March 2023).
53. Instytut Oceanografii, U.G. Prognoza Ekohydrodynamiczna. Available online: <http://model.ocean.univ.gda.pl/php/frame.php?area=ZatokaGdanska> (accessed on 1 March 2023).

54. França, D.C.; Morais, D.D.; Bezerra, E.B.; Araújo, E.M.; Wellen, R.M.R. Photodegradation Mechanisms on Poly( $\epsilon$ -Caprolactone) (PCL). *Mater. Res.* **2018**, *21*, e20170837. <https://doi.org/10.1590/1980-5373-mr-2017-0837>.
55. Martins-Franchetti, S.M.; Campos, A.; Egerton, T.A.; White, J.R. Structural and Morphological Changes in Poly(Caprolactone)/Poly(Vinyl Chloride) Blends Caused by UV Irradiation. *J. Mater. Sci.* **2008**, *43*, 1063–1069. <https://doi.org/10.1007/s10853-007-2210-9>.
56. Davies, P.; Evrard, G. Accelerated Ageing of Polyurethanes for Marine Applications. *Polym. Degrad. Stab.* **2007**, *92*, 1455–1464. <https://doi.org/10.1016/j.polymdegradstab.2007.05.016>.
57. Rosu, D.; Rosu, L.; Cascaval, C.N. IR-Change and Yellowing of Polyurethane as a Result of UV Irradiation. *Polym. Degrad. Stab.* **2009**, *94*, 591–596. <https://doi.org/10.1016/j.polymdegradstab.2009.01.013>.
58. Ren, L.; Tang, Z.; Geng, J.; Xing, Z.; Qiang, T. Improvement for Yellowing Resistance of Aromatic PU Film by Fluoro Alcohol Termination and Branching Modification. *Prog. Org. Coat.* **2021**, *155*, 106227. <https://doi.org/10.1016/j.porgcoat.2021.106227>.
59. Lu, B.; Wang, G.-X.; Huang, D.; Ren, Z.-L.; Wang, X.-W.; Wang, P.-L.; Zhen, Z.-C.; Zhang, W.; Ji, J.-H. Comparison of PCL Degradation in Different Aquatic Environments: Effects of Bacteria and Inorganic Salts. *Polym. Degrad. Stab.* **2018**, *150*, 133–139. <https://doi.org/10.1016/j.polymdegradstab.2018.02.002>.
60. Ruggero, F.; Carretti, E.; Gori, R.; Lotti, T.; Lubello, C. Monitoring of Degradation of Starch-Based Biopolymer Film under Different Composting Conditions, Using TGA, FTIR and SEM Analysis. *Chemosphere* **2020**, *246*, 125770. <https://doi.org/10.1016/j.chemosphere.2019.125770>.
61. Borchani, K.E.; Carrot, C.; Jaziri, M. Biocomposites of Alfa Fibers Dispersed in the Mater-Bi® Type Bioplastic: Morphology, Mechanical and Thermal Properties. *Compos. Part A Appl. Sci. Manuf.* **2015**, *78*, 371–379. <https://doi.org/10.1016/j.compositesa.2015.08.023>.
62. Wang, H.; Wei, D.; Zheng, A.; Xiao, H. Soil Burial Biodegradation of Antimicrobial Biodegradable PBAT Films. *Polym. Degrad. Stab.* **2015**, *116*, 14–22. <https://doi.org/10.1016/j.polymdegradstab.2015.03.007>.
63. França, D.C.; Bezerra, E.B.; de Souza Morais, D.D.; Araújo, E.M.; Wellen, R.M.R. Hydrolytic and Thermal Degradation of PCL and PCL/Bentonite Compounds. *Mater. Res.* **2016**, *19*, 618–627. <https://doi.org/10.1590/1980-5373-MR-2015-0797>.
64. França, D.C.; Almeida, T.G.; Abels, G.; Canedo, E.L.; Carvalho, L.H.; Wellen, R.M.R.; Haag, K.; Koschek, K. Tailoring PBAT/PLA/Babassu Films for Suitability of Agriculture Mulch Application. *J. Nat. Fibers* **2019**, *16*, 933–943. <https://doi.org/10.1080/15440478.2018.1441092>.
65. Ji, Y.; Yang, X.; Ji, Z.; Zhu, L.; Ma, N.; Chen, D.; Jia, X.; Tang, J.; Cao, Y. DFT-Calculated IR Spectrum Amide I, II, and III Band Contributions of N-Methylacetamide Fine Components. *ACS Omega* **2020**, *5*, 8572–8578. <https://doi.org/10.1021/acsomega.9b04421>.
66. Seo, J.; Jang, E.-S.; Song, J.-H.; Choi, S.; Khan, S.B.; Han, H. Preparation and Properties of Poly(Urethane Acrylate) Films for Ultraviolet-Curable Coatings. *J. Appl. Polym. Sci.* **2010**, *118*, 2454–2460. <https://doi.org/10.1002/app.32344>.
67. Nashchekina, Y.; Chabina, A.; Moskalyuk, O.; Voronkina, I.; Evstigneeva, P.; Vaganov, G.; Nashchekin, A.; Yudin, V.; Mikhailova, N. Effect of Functionalization of the Polycaprolactone Film Surface on the Mechanical and Biological Properties of the Film Itself. *Polymers* **2022**, *14*, 4654. <https://doi.org/10.3390/polym14214654>.
68. Wenzel, R.N. Surface Roughness and Contact Angle. *J. Phys. Colloid Chem.* **1949**, *53*, 1466–1467. <https://doi.org/10.1021/j150474a015>.
69. Li, C.; Zhang, J.; Han, J.; Yao, B. A Numerical Solution to the Effects of Surface Roughness on Water–Coal Contact Angle. *Sci. Rep.* **2021**, *11*, 459. <https://doi.org/10.1038/s41598-020-80729-9>.
70. Muthuraj, R.; Misra, M.; Mohanty, A.K. Hydrolytic Degradation of Biodegradable Polyesters under Simulated Environmental Conditions. *J. Appl. Polym. Sci.* **2015**, *132*, 42189. <https://doi.org/10.1002/app.42189>.
71. Ivanova, A.A.; Syromotina, D.S.; Shkarina, S.N.; Shkarin, R.; Cecilia, A.; Weinhardt, V.; Baumbach, T.; Saveleva, M.S.; Gorin, D.A.; Douglas, T.E.L.; et al. Effect of Low-Temperature Plasma Treatment of Electrospun Polycaprolactone Fibrous Scaffolds on Calcium Carbonate Mineralisation. *RSC Adv.* **2018**, *8*, 39106–39114. <https://doi.org/10.1039/C8RA07386D>.
72. Srikanth, M.; Asmatulu, R.; Cluff, K.; Yao, L. Material Characterization and Bioanalysis of Hybrid Scaffolds of Carbon Nanomaterial and Polymer Nanofibers. *ACS Omega* **2019**, *4*, 5044–5051. <https://doi.org/10.1021/acsomega.9b00197>.
73. Janvikul, W.; Uppanan, P.; Thavornnyutikarn, B.; Kosorn, W.; Kaewkong, P. Effects of Surface Topography, Hydrophilicity and Chemistry of Surface-Treated PCL Scaffolds on Chondrocyte Infiltration and ECM Production. *Procedia Eng.* **2013**, *59*, 158–165. <https://doi.org/10.1016/j.proeng.2013.05.106>.
74. Moustafa, H.; Guizani, C.; Dupont, C.; Martin, V.; Jeguirim, M.; Dufresne, A. Utilization of Torrefied Coffee Grounds as Reinforcing Agent To Produce High-Quality Biodegradable PBAT Composites for Food Packaging Applications. *ACS Sustain. Chem. Eng.* **2017**, *5*, 1906–1916. <https://doi.org/10.1021/acssuschemeng.6b02633>.
75. Rasyida, A.; Fukushima, K.; Yang, M.-C. Structure and Properties of Organically Modified Poly(Butylene Adipate-Co-Terephthalate) Based Nanocomposites. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, *223*, 012023. <https://doi.org/10.1088/1757-899X/223/1/012023>.
76. Can, B.N.; Ozkoc, G. PBAT/Thermoplastic Starch Blends: “Effects of Oxidized Starch and Compatibilizer Content”. In *AIP Conference Proceedings, Proceedings of the 32nd International Conference of the Polymer Processing Society, Lyon, France, 25–29 July 2016*; AIP Publishing LLC: Melville, NY, USA, 2017; p. 070004.

- 
77. Bartnikowski, M.; Dargaville, T.R.; Ivanovski, S.; Hutmacher, D.W. Degradation Mechanisms of Polycaprolactone in the Context of Chemistry, Geometry and Environment. *Prog. Polym. Sci.* **2019**, *96*, 1–20. <https://doi.org/10.1016/j.progpolymsci.2019.05.004>.
  78. Kijchavengkul, T.; Auras, R.; Rubino, M.; Selke, S.; Ngouajio, M.; Fernandez, R.T. Biodegradation and Hydrolysis Rate of Aliphatic Aromatic Polyester. *Polym. Degrad. Stab.* **2010**, *95*, 2641–2647. <https://doi.org/10.1016/j.polymdegradstab.2010.07.018>.

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.