

Brief Report

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

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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(ϵ -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(ϵ -caprolactone); biocomposites; cellulose filler; filler modification; diisocyanates; biodegradation; seawater



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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 thermo-plastic 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(ϵ -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(ϵ -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 μ 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.

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.

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 cm⁻¹ resolution in the range from 4000 to 400 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 ~1 µL 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 mm. The average Ra value was calculated from five measurements on five different spots on the sample's surface (25 measurements in total).



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.

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 ³	0.0
Salinity	PSU	5.59	Chlorophyll a	mg/m ³	7.2
N-NH ₄	mg/m ³	6.4	Chlorophyll b	mg/m ³	0.49
N-NO ₃	mg/m ³	18.1	Chlorophyll c	mg/m ³	0.51
P-PO ₄	mg/m ³	20.1	Photoprotective carotenoids	mg/m ³	1.56
Si-SiO ₄	mg/m ³	531	Photosynthetic carotenoids	mg/m ³	1.17
Dissolved oxygen	g/m ³	12.5	Phytoplankton	mg/m ³	97.2

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 ± 0.2 mg samples in the temperature range of -80 to 170 °C, under a nitrogen atmosphere, at a heating rate of 15 °C/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 °C and 800 °C at a heating rate of 15 °C/min

under a nitrogen flow using a TG 209 F1 Netzsch (Selb, Germany) apparatus. Samples of 10.0 ± 0.1 mg and ceramic pans were applied.

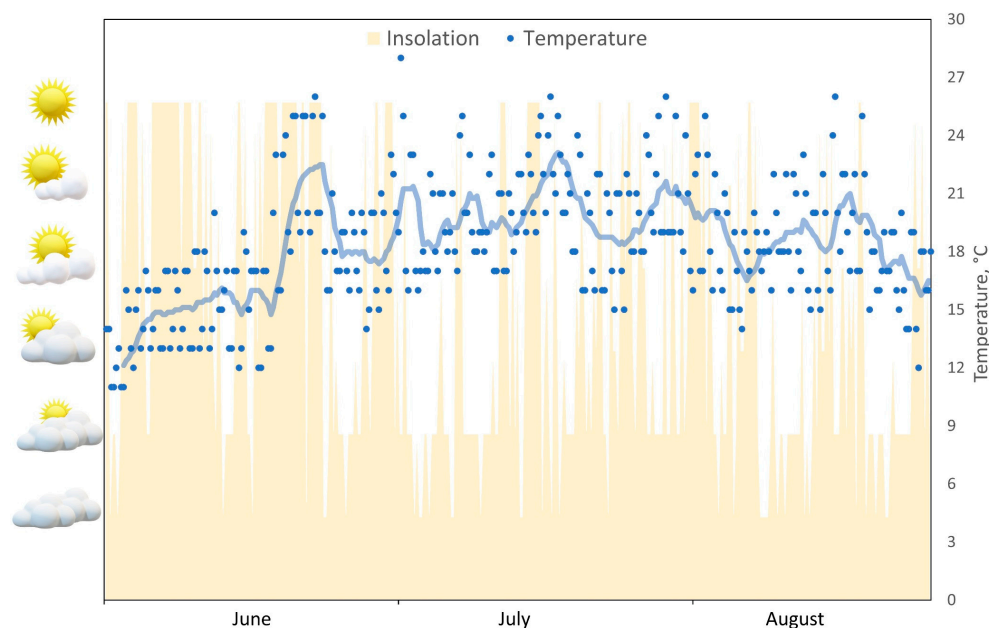





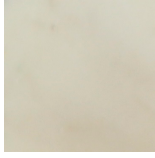








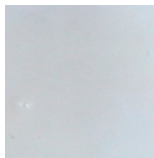





Figure 2. The temperature and insolation over the analyzed period.

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].

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 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 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 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 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].

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						

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 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.

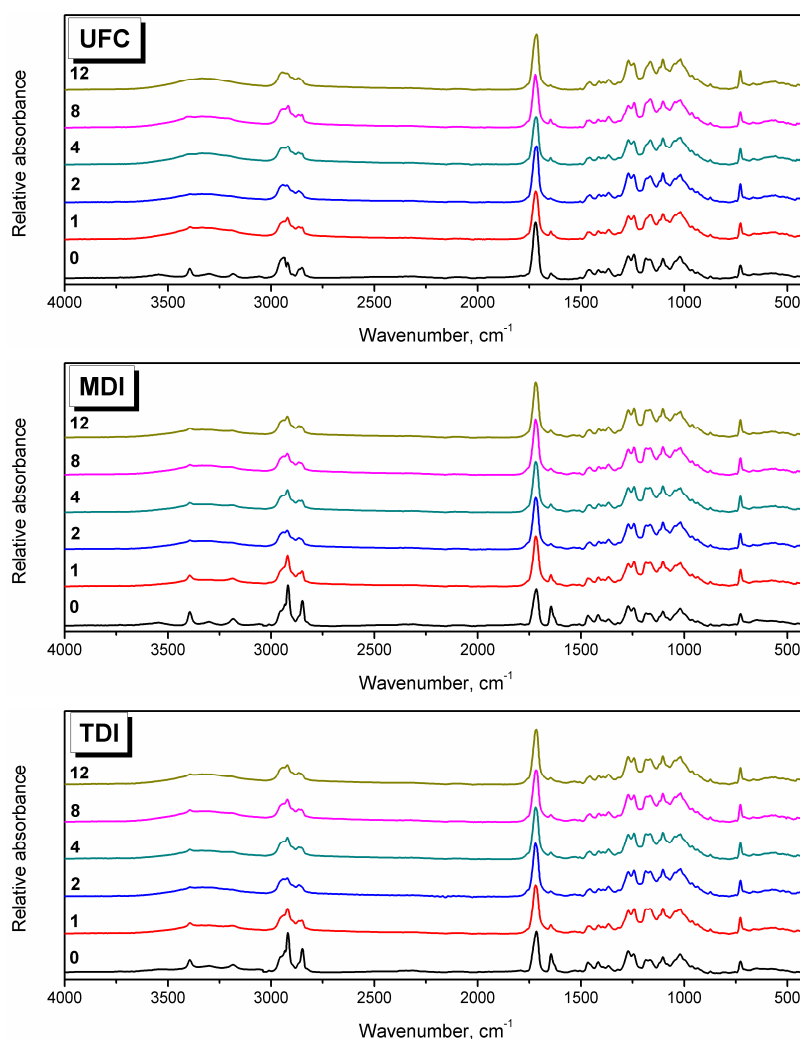


Figure 3. The impact of seawater degradation (from 0 to 12 weeks) on the FTIR spectra of prepared composites.

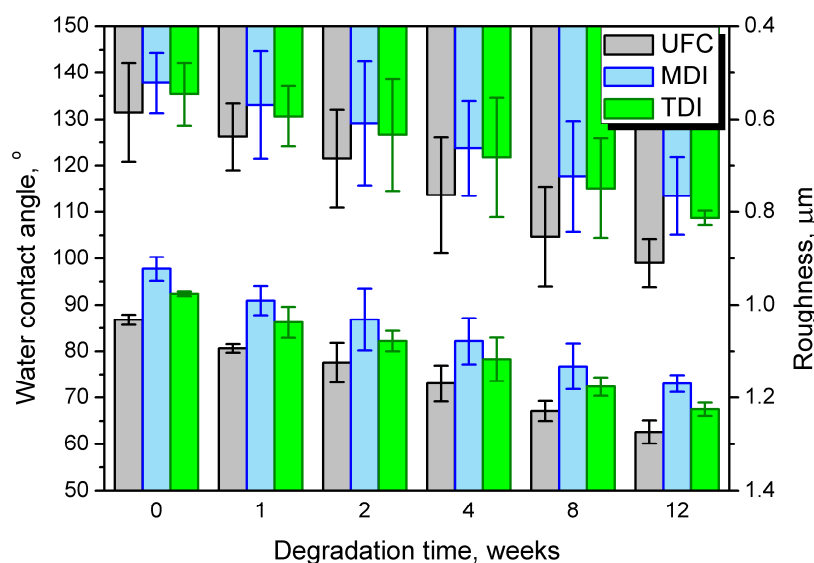


Figure 4. Changes in the water contact angle (bottom columns) and surface roughness (top columns) of prepared composites over the biodegradation course (from 0 to 12 weeks).

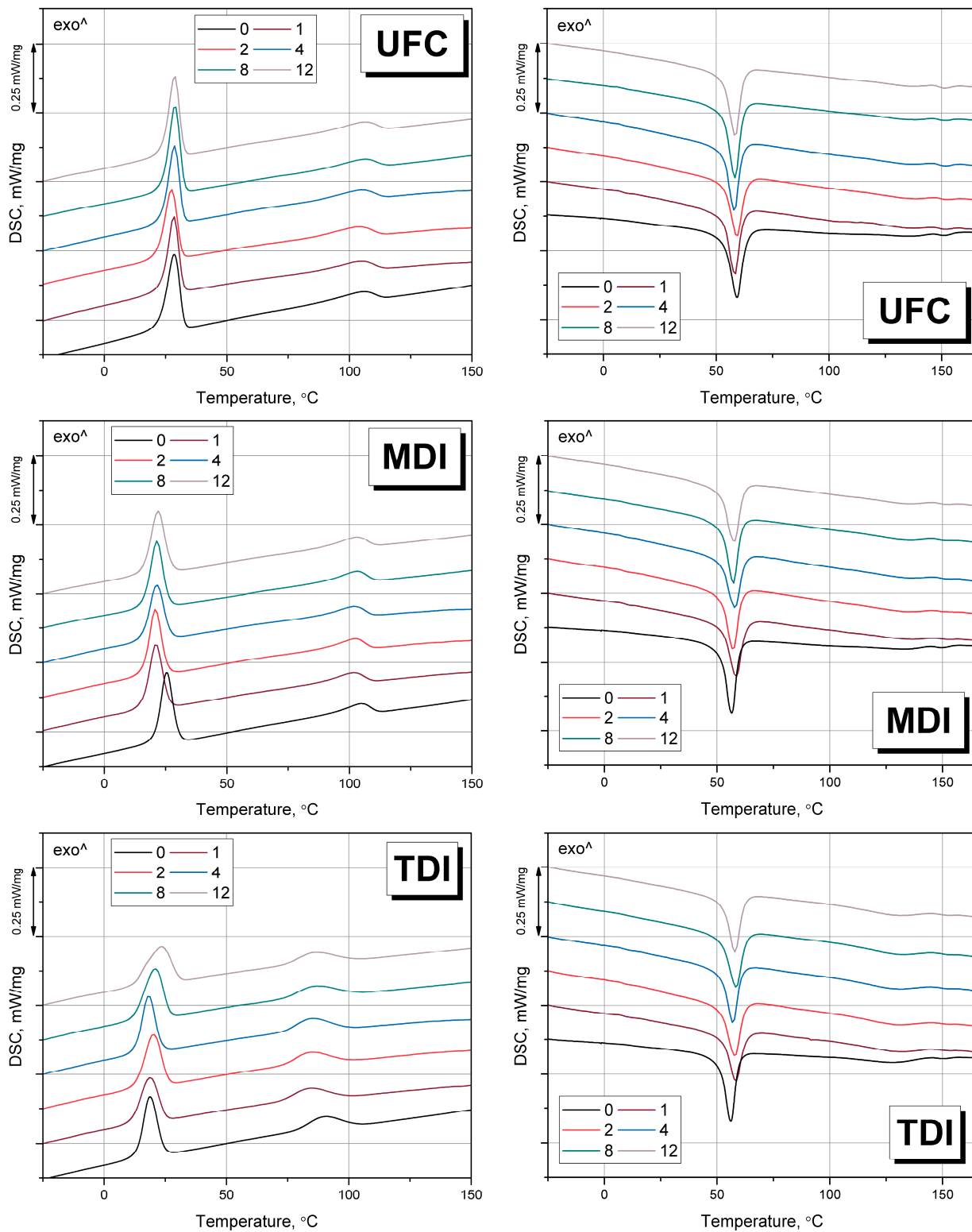


Figure 5. Cooling (left) and the second heating (right) thermograms of prepared composites before and after seawater degradation (from 0 to 12 weeks).



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	ΔH _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

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 chemocrystallization [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.

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.

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

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

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