



# The impact of thermomechanical and chemical treatment of waste Brewers' spent grain and soil biodegradation of sustainable Mater-Bi-Based biocomposites

Aleksander Hejna<sup>a,b,\*</sup>, Mateusz Barczewski<sup>a</sup>, Paulina Kosmela<sup>b</sup>, Olga Mysiuikiewicz<sup>a</sup>, Joanna Aniśko<sup>a</sup>, Paweł Sulima<sup>c</sup>, Jerzy Andrzej Przyborowski<sup>c</sup>, Mohammad Reza Saeb<sup>b</sup>

<sup>a</sup> Institute of Materials Technology, Poznan University of Technology, Piotrowo 3, 61-138 Poznań, Poland

<sup>b</sup> Department of Polymer Technology, Gdańsk University of Technology, Narutowicza 11/12 80-233, Gdańsk, Poland

<sup>c</sup> Department of Genetics, Plant Breeding and Bioresource Engineering, University of Warmia and Mazury in Olsztyn, Plac Łódzki 3, 10-724 Olsztyn, Poland

## ARTICLE INFO

### Keywords:

Mater-Bi  
Brewers' spent grain  
Biocomposites  
Biodegradation  
Filler modification

## ABSTRACT

Due to the massive plastic pollution, development of sustainable and biodegradable polymer materials is crucial to reduce environmental burdens and support climate neutrality. Application of lignocellulosic wastes as fillers for polymer composites was broadly reported, but analysis of biodegradation behavior of resulting biocomposites was rarely examined. Herein, sustainable Mater-Bi-based biocomposites filled with thermomechanically- and chemically-modified brewers' spent grain (BSG) were prepared and subjected to 12-week soil burial test simulating their biodegradation in natural environment. BSG stabilizing effect on polymer matrix affected by the content of melanoidins and antioxidant phytochemicals, along with the impact of diisocyanate applied to strengthen the interfacial adhesion. Biocomposites showed 25–35 wt% mass loss over 12 weeks resulting from swelling of BSG filler and sample microcracking, which increased surface roughness by 247–448 %. The degree of decomposition was partially reduced by BSG modifications pointing to the stabilizing effect of melanoidins and phytochemicals, and enhanced interfacial adhesion. Soil burial-induced structural changes enhanced biocomposites' thermal stability determined by thermogravimetric analysis shifting decomposition onset by 14.4–32.0 °C due to the biodegradation of lower molecular weight starch macromolecules confirmed by differential scanning calorimetry. For unfilled Mater-Bi, it caused an average 32 % reduction in complex viscosity and storage modulus captured by oscillatory rheological measurements. Nonetheless, the inverse effect was noted for biocomposites where modulus increased even by one order of magnitude due to the swelling of BSG particles and amorphous phase decomposition. Presented results indicate that BSG promotes soil degradation of Mater-Bi and its rate can be engineered by biofiller treatment elaboration.

## 1. Introduction

Considering the environmental concerns worldwide, and lessons learned from circular economy concept, it is very beneficial to introduce biodegradable, renewable, recycled, or waste-based raw materials as fillers and modifiers in plastics (Barczewski et al., 2019). Both routes are realized during preparation of polymer composites, where biobased or biodegradable polymers are often applied as matrices, while lignocellulosic plant-based materials are incorporated as biofillers (Bortolatto et al., 2022). Among these materials, starch is very auspicious due to its

abundance and low cost (Bernardo et al., 2022). Nevertheless, to become an efficient candidate to be used as bioplastic, the native starch should undergo modification to decrease its melting point, originally exceeding degradation temperature (Zdanowicz, 2020). The resulting thermoplastic starch (TPS) has gained much attention as a potential substitute for conventional polymers, mainly polyolefins, but it still suffered from serious limitations like fragility or low water resistance (Hejna et al., 2019). Therefore, to maintain its environmentally-friendly character and enhance its performance, it can be blended with biobased or biodegradable polymers such as poly(lactic acid) (PLA),

\* Corresponding author at: Department of Polymer Technology, Chemical Faculty, G. Narutowicza Str. 11/12, Gdansk University of Technology, G. 80-233 Gdansk, Poland.

E-mail address: [aleksander.hejna@put.poznan.pl](mailto:aleksander.hejna@put.poznan.pl) (A. Hejna).

<https://doi.org/10.1016/j.wasman.2022.10.007>

Received 25 June 2022; Received in revised form 16 September 2022; Accepted 7 October 2022

Available online 21 October 2022

0956-053X/© 2022 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

polyhydroxyalkanoates (PHAs), poly( $\epsilon$ -caprolactone) (PCL) or polybutylene adipate terephthalate (PBAT) (Manoel et al., 2022; Przybytek et al., 2018). The blending of TPS with these polymers significantly affects the cost of the material, but it can be reduced by the above-mentioned incorporation of lignocellulosic plant-based materials. They are conventionally applied as fillers for polymer matrix in the manufacturing of wood-polymer composites, which is related to their composition, mainly high contents of celluloses and lignin (Antov et al., 2021; Salasinska et al., 2018).

Among the potential waste-based lignocellulose fillers for wood-polymer composites (WPCs) is brewers' spent grain (BSG) – a by-product of the beer production (Hejna, 2021). It is mainly composed of cellulose, hemicellulose, and lignin – the main components of various plant-based wastes (Mathias et al., 2015). Moreover, BSG contains significant portions of proteins (even up to 30 wt%) and lipids (often over 10 wt%), which makes it a very auspicious material, because of potential possibilities for modifications or providing additional interactions with polymer matrices (Lynch et al., 2016). Considering its economic and industrial potentials, BSG looks very promising. However, its disadvantage is relatively high moisture content, exceeding even 75 %. It stands for over 85 % of all brewing by-products, and considering global beer production is generated in amounts reaching almost 12 million tonnes (Hejna et al., 2021b). Its generation, similar to beer production, is spread globally. Therefore, BSG may serve as raw material for manufacturing polymer composites almost all over the world.

Multiple natural-based materials, including wastes like brewers' spent grain, contain phytochemicals or other compounds, whose presence may be beneficial for the plastics' performance. Among such compounds, it is worth mentioning various natural-based antioxidants and antimicrobials like terpenes, terpenoids, phenolic acids, hydroxycinnamic acids, flavonoids, and others (Ahangarpour et al., 2019; Chang et al., 2019). During their primary life cycle, plant-based materials are often subjected to thermal, mechanical, or combined treatments. As a result, they may contain significant portions of melanoidins, which also show antioxidant and antimicrobial potential (Delgado-Andrade et al., 2005). They are generated through Maillard reactions occurring between the amino groups and reducing sugars (van Boekel, 2006). Both melanoidins and the phytochemicals mentioned above are often responsible for the extended shelf-life of multiple food products. They are commonly treated as natural preservatives (Bouarab Chibane et al., 2019) or anti-aging agents in cosmetics (Cherubim et al., 2020), suggesting that they may potentially inhibit the oxidative degradation of polymers. Such an effect was confirmed by researchers introducing various plant extracts (Battezzore et al., 2014; Moraczewski et al., 2019), or even single phytochemicals like thymol (Lukic et al., 2020), quercetin (Masek and Latos-Brozio, 2018), limonene (Arrieta et al., 2013), and the most popular  $\alpha$ -tocopherol (Byun et al., 2010), into polymer matrices. In our previous work dealing with poly( $\epsilon$ -caprolactone)-based composites, modified brewers' spent grain characterized by the different melanoidin content was introduced as filler, beneficially impacting oxidative resistance of materials (Hejna et al., 2022).

An important issue associated with the oxidative stability of polymeric materials is their performance stability and durability, as well as the post-consumer disposal. Considering biodegradable polymers, the beneficial scenarios would include their material recycling and reuse after processing, composting, or, even more beneficially, biodegradation in the natural environment. Currently, considering the environmental aspects like human health, ecosystem quality, or use of resources, the material recycling, including separation, washing, grinding, and reprocessing into regranulate, is a very beneficial option (Piemonte et al., 2013). On the other hand, the forces acting on the material during the process affect the mechanical performance of the resulting regranulate, which may limit its potential applications (Piemonte et al., 2013). However, irrespectively of the recycling type, for its realization to be economically feasible, the share of a particular material in plastic waste should exceed some level, which has not been reached yet for

biodegradable polymers, according to Maga et al. (Maga et al., 2019). In such a case, or when recycling is unavailable, composting or biodegradation would be the most suitable and beneficial option (Cosate de Andrade et al., 2016). On the other hand, lately more emphasis has been put on anaerobic digestion, which poses as interesting alternative due to lack of limitations related to aerobic approach and possibility of energy production (Cucina et al., 2022; Gadaleta et al., 2022). Nevertheless, biodegradation in the natural environment would be beneficial alternative because it does not require complex installations like composting and could be realized everywhere and without hardly any interference (Sintim et al., 2020). Considering the influence of phytochemicals or melanoidins applied as polymer modifiers or contained in plant-based fillers, they may substantially impact polymers' biodegradation. It may be associated with their above-mentioned antioxidant and antimicrobial activity (Prakash et al., 2020). Therefore, their presence may impede the polymers' decomposition, which should be examined because the biodegradation inhibition may overcome the beneficial stabilization effects. Moreover, their impact on the polymer structure prior to the biodegradation may be essential. Interestingly, Jeon and Kim (Jeon and Kim, 2013) reported that excessive exposure of PLA to UV irradiation inhibits its further biodegradation because the material turns into a white brittle solid, which is difficult to be digested by microorganisms. Such an effect could be attributed to the increased crystallinity of the material. A similar effect was reported by Stloukal et al. (Stloukal et al., 2012) for PLA composting. The composting rate was similar for non-irradiated material and samples subjected to 50 h irradiation. At the same time, 10 h treatment caused a significant increase in composting rate. These results point to the need for polymers' modification to reduce the excessive changes caused by UV irradiation, which could significantly hinder the possibility of their biodegradation in the environment.

Herein, we take a close-up image of biodegradation of Mater-Bi-based composites containing thermomechanically modified brewers' spent grain waste, based on long shot photograph taken in a previous episode of our survey (Hejna et al., 2022). Previously, we confirmed the beneficial antioxidant activity of BSG in Mater-Bi-based composites leading to polymer stabilization. In particular, we modified samples containing fillers with isophorone diisocyanate to enhance the filler-polymer interfacial adhesion; followed by monitoring its impact on the course and rate of biodegradation. The analysis and quantification of success in biodegradation of Mater-Bi-based composites was carried out by monitoring the mass loss of biocomposites, as well as the changes in their chemical structure, morphology, mechanical, rheological and thermal properties.

## 2. Experimental

### 2.1. Materials

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

Brewers' spent grain was obtained from Energetyka Złoczew sp. z o. o. (Poland). According to the supplier, it originated from the production of light lager and consisted solely of barley malts. The supplier already dried applied BSG. The chemical composition of BSG was analyzed in the Department of Genetics, Plant Breeding and Bioresource Engineering at the University of Warmia and Mazury in Olsztyn in accordance with the methodology described by Stolarski et al. (Stolarski et al., 2020). Composition of applied waste filler was presented in Table S1.

Isophorone diisocyanate (IPDI) acquired from Sigma Aldrich (Poland) was applied as a chemical modifier of BSG fillers. Its purity was 99 %, and it was characterized by a density of 1.06 g/cm<sup>3</sup>.

## 2.2. Modifications of brewers' spent grain

Prior to the incorporation into the polymer matrix, BSG was subjected to thermomechanical and chemical treatment. The thermomechanical modification was described in detail in previous works (Hejna et al., 2021b, 2021a). Samples applied in the presented work were modified using an EHP 2x20 Sline co-rotating twin-screw extruder from Zamak Mercator (Poland), using a throughput of 3 kg/h, screw speed of 225 rpm, and barrel temperature of 180 or 240 °C.

Moreover, to evaluate the impact of isocyanate modification, the BSG fillers were modified with 5 wt% of IPDI using GMF 106/2 Brabender (Germany) batch mixer at room temperature (varied from 21.1 to 23.1 °C) and rotor speed of 100 rpm. The proper amount of filler was placed in an internal mixer with a calculated amount of diisocyanate, respectively to the mass of filler. Mixing was performed for 5 min, and then samples were put in zipper storage bags. Isocyanate content was based on the results presented in our previous paper (Hejna and Kosmela, 2020).

## 2.3. Preparation of polymer composites

Composites were prepared using GMF 106/2 Brabender (Germany) batch mixer at 140 °C and rotor speed of 100 rpm. The processing time equaled 6 min, including the 1-minute phase of matrix plasticization and 5 min of melt blending with selected filler. 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 X/Y, where X stands for the BSG thermomechanical treatment temperature and Y for IPDI content applied during modification. Unfilled Mater-Bi was processed similarly for comparison.

## 2.4. Biodegradation of prepared composites

Biodegradation of composites was conducted in simulated soil burial conditions. Samples were placed in the plastic container on the layer of potting soil and covered with another layer. Universal potting soil containing high peat with H3-H8 decomposition degree, compost, lime, NPK fertilizer and phosphorous-silicon fertilizer was applied. Salinity of applied soil was below 3.0 g KCl/l, and its pH (CaCl<sub>2</sub>) was in the range of 5.0–6.5. Specimens have been placed in separate compartments. Three compartments were used for each sample. To evaluate the potential plant growth inhibition effects resulting from the thermomechanical and chemical modifications of filler included in prepared biocomposites, in each compartment were placed four sunflower sprout seeds (*Helianthus annuus*) from W. Legutko Przedsiębiorstwo Hodowlano-Nasienne Sp. z o. o. (Poland) acquired in Leroy Merlin store (Poland). Plastic containers were placed on the balcony facing east. The soil was watered every day to keep it moist. The soil biodegradation test lasted for twelve weeks (from 31.05.2021 to 23.08.2021). Figures S1 and S2 show the temperature, insolation, humidity, and total precipitation over the analyzed period according to the local weather information. All the parameters were noted every-six hours. Precipitation values were accumulated from the previous six hours. Insolation was expressed in a 0–5 scale, where: 0 – very cloudy, 1 – cloudy, 2 – partly sunny/moderately cloudy, 3 – little cloudiness, 4 – mostly sunny, 5 – sunny/cloudless.

After 2, 4, 8, and 12 weeks, samples were retrieved, cleaned from the soil, and dried at room temperature before characterization. Moreover, the sunflower sprouts were retrieved, and after cleaning their roots from the soil, residues were weighted to evaluate the impact of the samples' composition on their growth.

## 2.5. Characterization techniques

To evaluate the biodegradation rate, the samples' weight retention

( $W_R$ ) was calculated according to the equation (1):

$$W_R = \frac{m_t}{m_i} \bullet 100\% \quad (1)$$

where:  $m_t$  – the mass of the sample after given biodegradation time, g;  $m_i$  – the initial mass of the sample, g.

Accordingly, to evaluate the impact of composites' composition on the growth of sunflower sprouts, the mass gain ( $M_G$ ) of plants was calculated according to the equation (2):

$$M_G = \frac{m_t}{m_i} \bullet 100\% \quad (2)$$

where:  $m_t$  – the mass of sprout after the given time, g;  $m_i$  – the initial mass of sprout seed, taken to be 0.08 g, an average from one hundred seeds.

For comparison, sunflower sprouts planted in compartments without composites' samples were also weighted.

The scanning electron microscope (SEM) Tescan MIRA3 (Czech Republic) was used to analyze the degradation-induced changes in samples' surfaces. The accelerating voltage of 12 kV and a working distance of 16 mm was applied. A thin carbon coating of approximately 20 nm was deposited on samples using the Jeol JEE 4B vacuum evaporator.

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. (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).

Color coordinates in the CIELab space were determined for the samples using an NR145 colorimeter from Envi Sense (Poland) operating in a 45°/0° geometry. The color change during the biodegradation  $\Delta E$  was calculated according to the equation (3).

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (3)$$

where:  $\Delta L$ ,  $\Delta a$ , and  $\Delta b$  are differences of the  $L^*$ ,  $a^*$ , and  $b^*$  parameters determined for the as-received and aged samples, respectively.

Shore hardness type D was estimated using Zwick 3131 durometer from Zwick Roell (Germany) following PN-ISO 868. Each evaluation was prepared for five test specimens.

The thermal properties of the samples were measured by differential scanning calorimetry (DSC) carried out on a DSC 204 F1 Phoenix apparatus from Netzsch (Germany). Measurements were performed on 5 ± 0.2 mg samples placed in Aluminum crucibles with pierced lids in the temperature range of –80 to 170 °C under a nitrogen atmosphere at a heating/cooling rate of 15 °C/min.

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 (Germany) apparatus. Samples of 10.0 ± 0.1 mg and ceramic pans were applied.

Rheological investigations were carried out using an Anton Paar (Austria) MCR 301 rotational rheometer, with 25 mm diameter parallel plates and a 0.5 mm gap under the oscillatory mode. The experiments were conducted at 170 °C. The strain sweep experiments were conducted before performing the dynamic oscillatory measurements in the frequency sweep mode. The strain sweep experiments of all the samples were performed at 170 °C with a constant angular frequency of 10 rad/s in the varying strain window of 0.01–100 %. The preliminary investigations allow determining the value of 0.05 % strain as applicable for frequency sweep experiments and located for all samples in the linear viscoelastic (LVE) region. The angular frequency used during the studies was in the range of 0.05–500 rad/s.

### 3. Results and discussion

#### 3.1. Soil burial biodegradation of prepared composites

Fig. 1 presents the results of performed soil burial biodegradation including weight retention of prepared composite samples and unfilled Mater-Bi and the impact of buried materials' composition on the mass gain of sunflower sprouts. At the same time, Figure S3 shows the changing appearance of growing sprouts over time. Moreover, a control sample without buried materials was analyzed.

The mass loss of the neat matrix was lower compared to the results shown in other works dealing with NF803 grade (Briassoulis, 2007, 2006). However, these works dealt with thin, 30–60  $\mu\text{m}$  films obtained by extrusion blow molding, noticeably thinner than samples analyzed in the presented paper. Moreover, compared to extrusion blow molding, applied compression molding results in higher packing and crystallinity of polymer material, which affects the biodegradation rate (Mejia et al., 2021). On the other hand, Aldas et al. (Aldas et al., 2021) investigated

compression molded films based on a similar Mater-Bi NF866 grade. They reported  $\sim 25\%$  mass loss after 12 weeks but during the composting process instead of soil burial. During soil burial, the decomposition rate of PBAT, the main phase of applied Mater-Bi material, is meager, especially compared to TPS (Wang et al., 2015). Therefore, values of weight retention of neat Mater-Bi reported in the presented work seem viable.

Composite materials containing different types of modified BSG showed significantly reduced weight retention, indicating faster biodegradation. Such an effect could be associated with the introduction of lignocellulose fillers. According to literature data, decomposition of Mater-Bi materials during soil burial biodegradation is lower than cellulose, which is one of the main components of BSG (Barbale et al., 2021). Sample 180/0 showed 35% mass loss after 12 weeks, which should be considered very beneficial from the environmental point of view. The introduction of brewers' spent grain thermomechanically modified at 240 °C resulted in a slightly lower mass loss of 31%, which could be associated with more demanding conditions of thermomechanical treatment and a greater extent of Maillard and caramelization reactions. These reactions include complex transitions of lower-molecular weight compounds like proteins and sugars into oligomeric or polymeric fractions – melanoidins, caramelans, caramelens, and caramelins (Göncüoğlu Taş and Gökmen, 2017). As a result, the degradation of higher-molecular weight fractions occurred slower, affecting composites' weight retention.

Modifying BSG fillers with isophorone diisocyanate also affected the composites' biodegradation rate. Enhanced interfacial adhesion, associated with the additional chemical interactions between matrix and filler, delayed the degradation and disintegration of the materials. A similar effect was noted for Mater-Bi-based materials by Aldas et al. (Aldas et al., 2021).

Considering sprouts' growth, without buried samples, sprout mass gain was increasing more rapidly, which was attributed to the lack of restrictions for roots' development in containers. Clearly, the presence of any polymer materials slowed the mass gain of sunflower sprouts. Comparing the unfilled Mater-Bi material with its composites, slightly lower values of mass gain were noted, which can be confirmed by the size of growing plants presented in Figure S3. Such an effect may be attributed to the more pronounced degradation of composite samples, expressed by their lower weight retention compared to unfilled material (see Fig. 1). As mentioned above, decomposition occurred more rapidly for composite samples due to the presence of lignocellulose materials, whose degradation might provide nutrients for sprouts' growth. Moreover, it can be observed that after 12 weeks, the mass gain was lower than after 8 weeks, which could be attributed to the characteristics of sunflower sprouts and their prolonged exposure to the sunlight (see Figure S1). The typical growing time of sunflower sprouts is around 2 weeks, after they are ready for consumption (Koike et al., 2009). Figure S3 shows that after 12 weeks, they are dried, despite the systematic watering. Therefore, sunflower sprouts should not be considered a viable option for analyzing longer biodegradation times.

Comparing the particular composite samples, differences caused by the temperature of thermomechanical modification and by chemical modification with isocyanate can be seen. For samples modified at 180 °C, sprout mass gain was higher than 240 °C, which could be associated with milder treatment conditions and lower extent of the above-mentioned Maillard and caramelization reactions. As a result, the accessibility of simpler compounds was reduced, which, combined with slower composites' decomposition, limited the nutritional value of residue. Chemical modification with isophorone diisocyanate also slightly reduced sprout mass gain, which could be associated with potential toxic effects of isocyanates and plant growth-inhibiting effect of ureas generated during decomposition (sen Gupta et al., 1991; Yang et al., 2021). On the other hand, the interfacial adhesion between filler and matrix was enhanced, which lowered the composites' biodegradation rate (see Fig. 1).

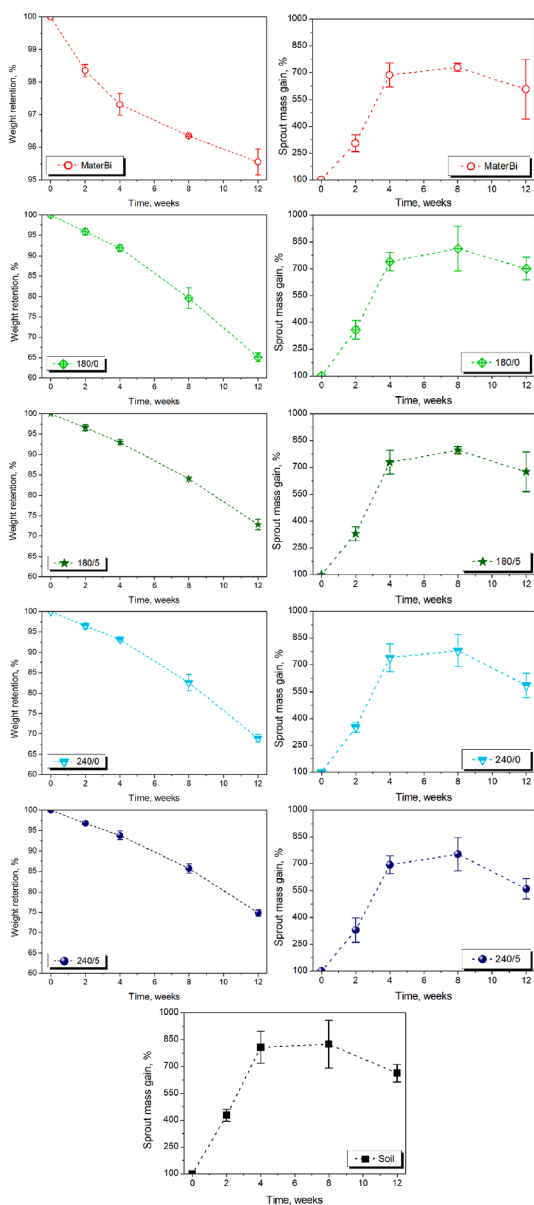


Fig. 1. The weight retention of prepared composite samples and unfilled Mater-Bi and their impact on the mass gain of sunflower sprouts during soil burial biodegradation.

### 3.2. Physical changes in prepared biocomposites during soil burial biodegradation

The appearance of the studied samples subjected to soil burial is presented in Fig. 2. The results of the colorimetric measurements and surface roughness  $R_a$  are collected in Table 1. It can be observed that during the soil burial, both unfilled Mater-Bi and its composite change colors. The unfilled sample becomes generally lighter, as indicated by an increase of the  $L^*$  value, but darker stains can also be seen. Along with the aging time, more and more dark spots appear on the Mater-Bi's surface, and the specimen's color becomes more uneven, indicating the activity of several different microorganisms (Hon and Shiraiishi, 2001). The composite samples show different behavior. After two weeks of soil burial, light-colored filler particles can be noticed on the studied surfaces. This results from swelling of the lignocellulosic particles in the presence of water. Further biodegradation up to eight weeks leads to whitening of the composites, which is a commonly observed behavior in polymeric composites with natural fibers and results from the attack of microorganisms (Luthra et al., 2020). When the composite samples are buried in soil for 12 weeks, their surface becomes darker, but it does not mean that the biodegradation process was stopped, but rather that different types of microorganisms dominate in the soil. Interestingly, no correlation between the composites' appearance and the filler type can

be found – regardless of the pre-processing of BSG and the isocyanate treatment, the surface of the samples are colonized by similar types of bacteria and fungi. Such an effect can be considered beneficial because it indicates that despite the enhancement of photooxidative stability resulting from the thermomechanical treatment of BSG (Hejna et al., 2022) or mechanical performance caused by the application of isocyanates (Hejna and Kosmela, 2020) the biodegradation was not stopped. Therefore, even modified materials could be efficiently decomposed in the natural environment.

The changes in the samples' roughness also indicate the progress of biodegradation. The  $R_a$  values measured for the Mater-Bi samples do not change substantially and remain in the range of 0.43–0.78  $\mu\text{m}$ . The observed differences may result from the manufacturing process, where the samples were compression molded in Teflon fabric-lined molds, whose surfaces were not controlled. The behavior of the composite samples is different. In their case, the initial roughness values increase notably during the biodegradation, which results from both swelling of the filler particles in the presence of water and the surface erosion. As it was shown by Olewnik-Kruszkowska et al. (Olewnik-Kruszkowska et al., 2020), the biofilm present on the soil-buried samples tends to deposit in the crevices and cracks on the surface. During the initial biodegradation stage, the composites' filler particles swell, resulting in the creation of microcracks and an increase in roughness. The microorganisms can then

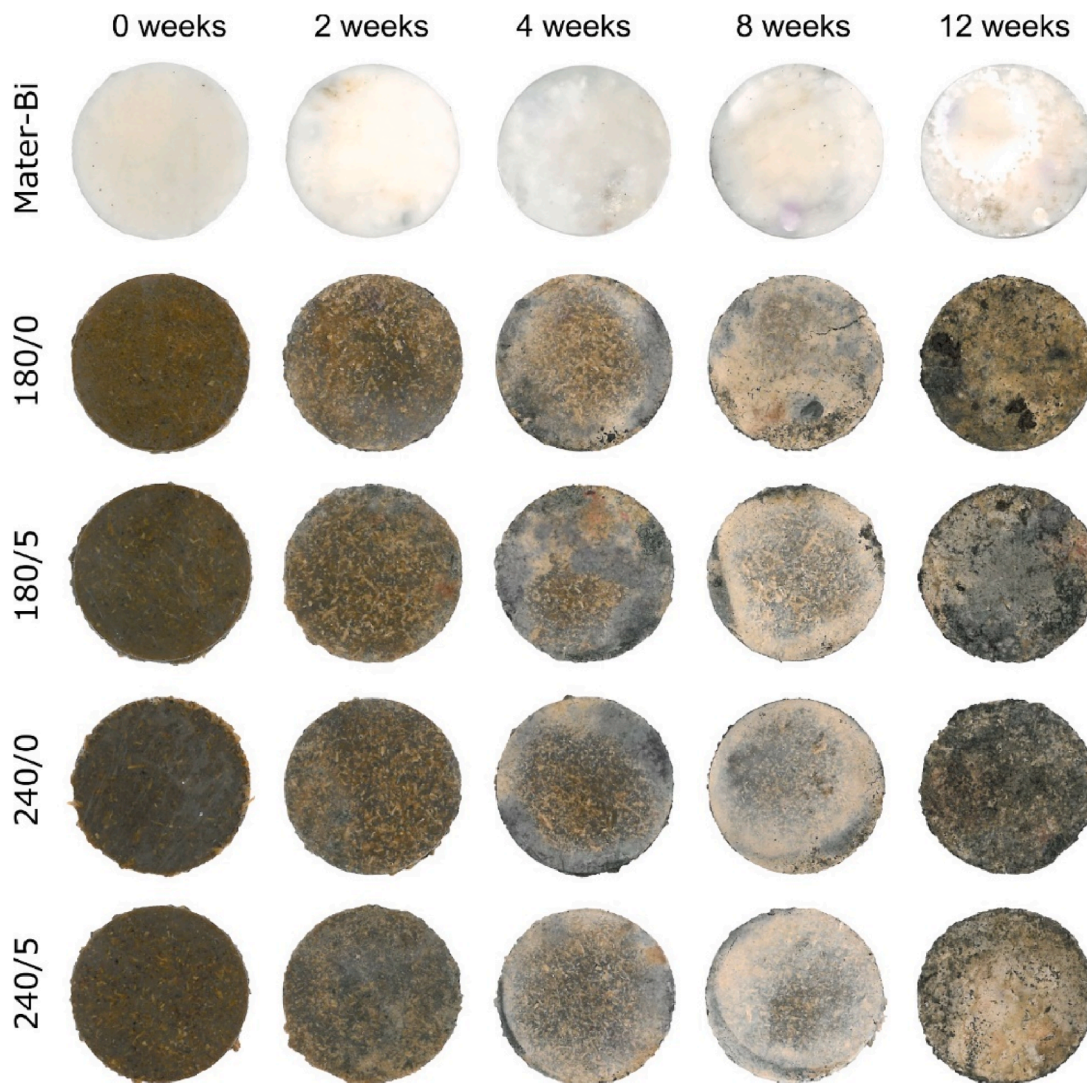


Fig. 2. The appearance of the as-received and aged samples showing color changes and increase of surface roughness induced by biodegradation.

**Table 1**

The values of L\*, a\*, and b\* color coordinates, the  $\Delta E$  color change, and Ra surface roughness of the samples subjected to soil burial.

		0 weeks	2 weeks	4 weeks	8 weeks	12 weeks
Mater-Bi	L*	76.91 ± 0.575	86.45 ± 0.294	81.03 ± 0.539	80.94 ± 0.273	87.26 ± 0.987
	a*	−0.03 ± 0.079	−0.47 ± 0.049	0.42 ± 0.041	0.30 ± 0.068	1.14 ± 0.122
	b*	8.87 ± 0.140	8.33 ± 0.325	7.72 ± 0.359	9.35 ± 0.243	6.86 ± 0.666
	$\Delta E$	–	9.56	4.30	4.07	10.61
	Ra, $\mu\text{m}$	0.43 ± 0.029	0.78 ± 0.065	0.66 ± 0.040	0.48 ± 0.069	0.68 ± 0.101
	180/0	L*	37.88 ± 1.384	46.41 ± 1.503	55.18 ± 0.674	62.22 ± 0.330
a*		10.26 ± 0.738	9.09 ± 0.573	8.91 ± 0.075	7.14 ± 0.100	8.44 ± 0.279
b*		16.24 ± 1.349	15.65 ± 0.590	16.89 ± 0.284	13.30 ± 0.275	17.12 ± 0.343
$\Delta E$		–	8.48	17.26	24.32	12.18
Ra, $\mu\text{m}$		0.75 ± 0.086	1.86 ± 0.381	2.96 ± 0.182	2.96 ± 0.348	4.11 ± 0.264
180/5		L*	36.87 ± 0.696	45.03 ± 0.635	55.25 ± 1.750	63.57 ± 0.613
	a*	9.66 ± 0.150	9.26 ± 0.152	6.09 ± 0.810	16.45 ± 23.618	4.18 ± 0.234
	b*	15.27 ± 0.399	16.00 ± 0.313	8.44 ± 0.969	12.94 ± 0.399	10.13 ± 0.238
	$\Delta E$	–	8.20	19.92	27.65	16.01
	Ra, $\mu\text{m}$	1.11 ± 0.107	1.65 ± 0.205	2.43 ± 0.274	2.41 ± 0.255	3.86 ± 0.482
	240/0	L*	34.75 ± 0.863	42.30 ± 0.281	44.74 ± 0.862	61.99 ± 0.681
a*		8.72 ± 0.268	9.86 ± 0.084	8.08 ± 0.477	5.21 ± 0.194	5.68 ± 0.320
b*		12.18 ± 0.652	15.15 ± 0.509	13.82 ± 0.274	9.94 ± 0.440	11.77 ± 0.271
$\Delta E$		–	8.19	10.14	27.55	8.15
Ra, $\mu\text{m}$		1.21 ± 0.227	2.10 ± 0.167	2.00 ± 0.157	3.17 ± 0.432	6.06 ± 0.427
240/5		L*	36.34 ± 0.104	45.82 ± 0.739	51.90 ± 0.296	65.03 ± 0.859
	a*	10.04 ± 0.190	5.55 ± 0.348	6.59 ± 0.158	4.14 ± 0.387	7.07 ± 0.134
	b*	13.62 ± 0.164	11.00 ± 0.424	12.01 ± 0.278	11.46 ± 0.452	13.96 ± 0.268
	$\Delta E$	–	10.81	16.02	29.37	25.97
	Ra, $\mu\text{m}$	0.99 ± 0.100	2.61 ± 0.245	1.74 ± 0.162	2.76 ± 0.517	3.81 ± 0.480

colonize these crevices, facilitating degradation and erosion of the surface, leading to a further increase of roughness. Interestingly, it can also be noticed that the Ra values measured for the isocyanate-treated samples are lower than those containing untreated BSG. Therefore it can be concluded that chemical modification of the filler, which improves adhesion between the composite phases, partially limits the surface erosion during biodegradation of the materials.

Fig. 3 shows SEM images of Mater-Bi brittle fractures and composite samples made after cryogenic exposure. In the case of the sample not filled with BSG, the prolonged exposure to burning in soil did not cause any noticeable changes in the structure of the pressed sample. Different behavior was noted for materials produced with the filler. There is a noticeable increase in the samples' thickness and the filler particles' swelling effect caused by long-term exposure to the conditions of increased humidity. It should be noted that, in the case of the isocyanate-modified sample, a change in the fractured surface character of the polymer matrix was noticed only after 12 weeks. For the series made using a filler subjected only to thermomechanical treatment, a more extensive fracture surface was noted after 4 (180/0) and 8 (240/0) weeks of aging. Such an effect indicates that thermomechanical treatment of BSG slightly inhibits the biodegradation of samples, pointing to the enhanced antioxidant and antimicrobial activity possibly resulting from increased melanoidin content.

Changes in the surface quality of the material samples subjected to the aging process are summarized in the form of SEM images in Fig. 4. In the case of composite samples containing the filler not exposed to isocyanates, an earlier appearance of surface defects in the form of cracks is observed than for the series with chemically modified fillers. After 12-week biodegradation in soil, all composite series can observe a significant surface quality deterioration. The numerous crumbled particles of polymer and filler are visible, resulting from the more intense course of degradation changes in the outer layers of samples and swelling of the lignocellulosic filler particles located near the surface and its defragmentation. Similar to brittle fractures, surfaces of samples indicated slower decomposition for samples containing BSG modified at 240 °C compared to 180 °C.

### 3.3. Changes in thermal and rheological performance of prepared biocomposites during soil burial biodegradation

Table 2 show the results of thermogravimetric analysis and their changes after biodegradation of prepared samples. Moreover, mass loss curves and differential thermogravimetric curves are presented in Figure S4. Literature works on the Mater-Bi NF grades' thermal decomposition reported only temperatures associated with the 5 wt% mass loss (Aldas et al., 2020; Elfehri Borchani et al., 2015). In the presented work, its value was 279.5 °C, which is in line with the literature reports (Aldas et al., 2020; Elfehri Borchani et al., 2015). For biocomposites, irrespectively of the applied filler, decomposition starts in the range of 250.1–257.9 °C, which is related to the decomposition of hemicellulose present in the BSG (Vanreppelen et al., 2014).

Mater-Bi applied as a polymer matrix showed three main stages of degradation, as reported in other works (Aldas et al., 2020; Elfehri Borchani et al., 2015). The first one, represented on the differential thermogravimetric curves by  $T_{\text{max}1}$  peak, is associated with the decomposition of glucose rings in amylose and amylopectin, components of starch macromolecules (Harini et al., 2018). The second component of the blend applied as a matrix, polybutylene adipate terephthalate, was represented by the  $T_{\text{max}3}$  peak, the most significant one, which is related to its prevailing content in applied Mater-Bi material (Aldas et al., 2021). As suggested by other works, the middle, smallest peak  $T_{\text{max}2}$  was attributed to the decomposition of additives added to Mater-Bi material (Aldas et al., 2020). The addition of BSG, irrespectively to applied treatments, did not change the three-stage character of thermal decomposition. However, the peaks  $T_{\text{max}1}$  and  $T_{\text{max}2}$  were shifted towards lower temperatures, which was attributed to the composition of applied fillers, especially the content of hemicellulose and cellulose. The presence of these two fractions implicates the two-step decomposition of thermomechanically treated BSG with local maximum rates around 281 and 342 °C, respectively (Hejna et al., 2021a).

For all samples, the biodegradation process significantly affected the course of thermal decomposition. TGA and DTG curves presented in Figure S4 point to the small decomposition step between 70 and 150 °C for the Mater-Bi matrix and between 50 and 130 °C for composites. It could be associated with the evaporation of moisture resulting from the water absorption by starch components during biodegradation [NO\_PRINTED\_FORM]. However, the temperature related to 5 wt% and 10 wt% mass loss was increased after biodegradation, which could be related to the partial degradation of starch components and enhanced stability. As a result, the shift of  $T_{\text{max}1}$  peak towards higher temperatures indicates the delayed degradation of starch. Such an effect is in line with the samples' weight retention values presented in Fig. 1. Considering that during biodegradation, lower molecular weight macromolecules, which often show lower thermal stability, are decomposed faster, the effect of enhanced thermal stability of the residual part of the material seems viable (Cesur, 2018). Due to the changes in the course of TPS phase degradation, peak  $T_{\text{max}2}$  disappeared for most samples, which was related to its overlapping with other signals. The course of

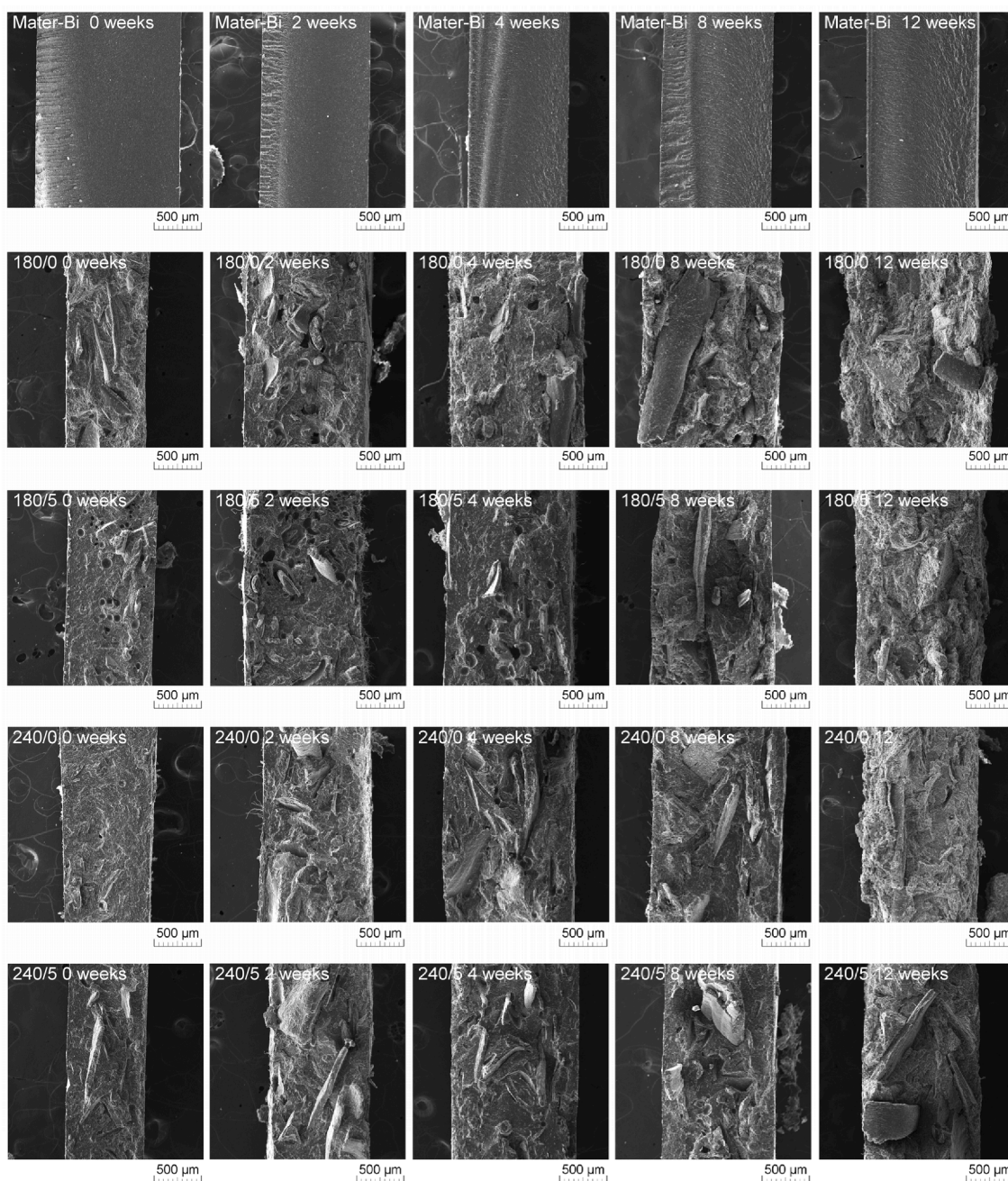


Fig. 3. SEM images of sample brittle fractures after different times of biodegradation test in soil.

decomposition of prepared samples at the latter stages (part of TGA curves below  $\sim 70$  wt% for Mater-Bi and  $\sim 50$  wt% for composites) was hardly affected by biodegradation during soil burial. It indicates that the PBAT phase of the material was almost unaffected by applied conditions, which is in line with the samples' mass loss (Fig. 1). A similar effect was noted by Wang et al. (Wang et al., 2015), who investigated soil burial of PBAT and its blends with TPS.

Fig. 5 shows the DSC curves obtained during the cooling and second heating of Mater-Bi and its composites. All the studied samples – both the unfilled polymeric blend and its composites – present similar behavior. The first thermal event visible on the heating curve around  $-30$  °C is the glass transition of PBAT, which is one of the components of Mater-Bi. It melts around  $130$  °C, as indicated by a shallow endothermic peak. Then, at around  $150$  °C, the melting of thermoplastic starch takes place (Aldas et al., 2020). The cooling curve presents only one thermal event – crystallization of PBAT around  $96$  °C (Elfehri Borchani et al.,

2015).

Even though the shape of the DSC thermograms is similar for all the studied materials, biodegradation influences them differently. In the case of the unfilled Mater-Bi, soil burial shifts the PBAT melting and crystallization peaks towards higher temperatures. This results from decreasing the polymer's molecular weight and shortening the polymeric chains, which can crystallize more easily and form more perfect crystals. A similar melting point shift can be observed in the case of thermoplastic starch in the unfilled Mater-Bi sample, which indicates that different phases contained in this blend undergo biodegradation similarly.

The composite samples also change their thermal properties due to the soil burial. In their case, the PBAT melting peak becomes increasingly shallow and, for the specimens aged 12 weeks, is almost invisible. Similar behavior can be observed in the case of the composites' polybutylene adipate terephthalate crystallization peak, which also shifts to

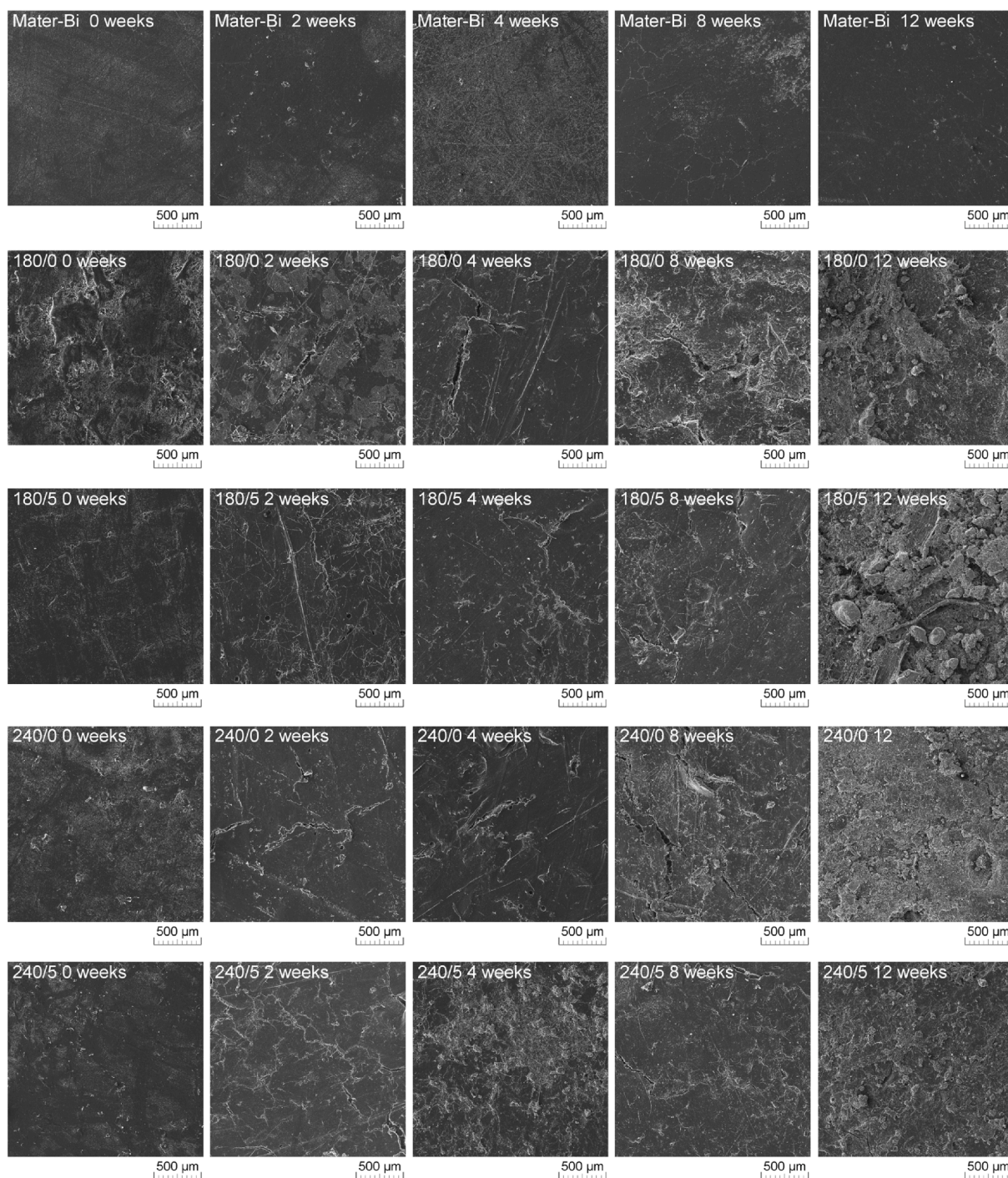


Fig. 4. SEM images of sample surfaces after different times of biodegradation test in soil.

higher temperatures. Unlike for unfilled Mater-Bi, soil burial not only leads to the changes in the molecular weight of the polymers contained by the materials but also reduces its percentage in the sample, so the DSC signal of the phase transition becomes weaker. This is in agreement with the mass loss measurements and proves that the addition of brewer's spent grain promotes biodegradation of Mater-Bi in soil. It also needs to be said that similar results were obtained for different types of composites – therefore, BGS chemical modification with isocyanate, which was performed to improve the adhesion between the phases, does not limit the biodegradability of the composites.

Fig. 6 compares the complex viscosity and storage modulus curves of Mater-Bi and its' composites with BSG subjected to thermomechanical

and thermochemical modifications before and after being buried in the soil. When analyzing the course of changes in  $G'(\omega)$  curves for unfilled ones using the BSG Mater-Bi series, a limitation of the dependence of the angular frequency effect on changes in the storage modulus in the range of about 1 rad/s is observed. This is due to hindering of rigid dispersed in biodegradable polymeric matrix starch inclusions that create a physical network resulting in the occurrence of a rheological percolation threshold (Hassanabadi et al., 2014).

Moreover, only in the case of non-filled with BSG series storage modulus and viscosity decrease with extending exposure to soil. For composite series, the tendency was reciprocal, and limitation in dependency of the storage modulus occurred at much lower angular



**Table 2**

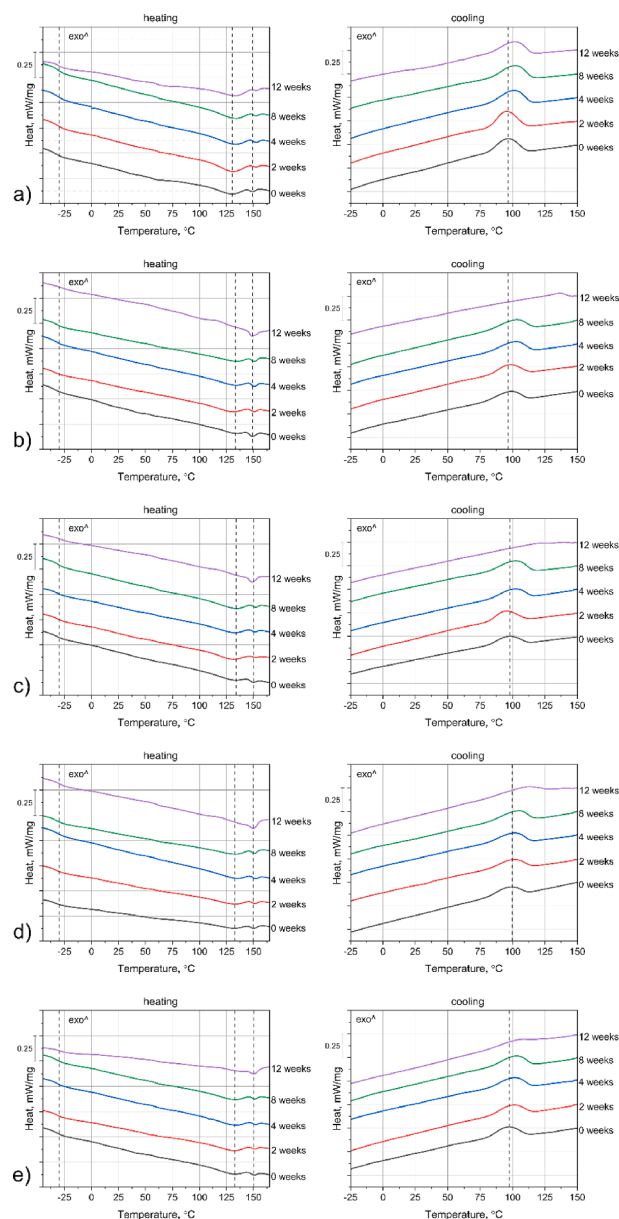
The results of TGA analysis for prepared composites.

Sample	Aging time, weeks	T <sub>5%</sub> , °C	T <sub>10%</sub> , °C	T <sub>50%</sub> , °C	T <sub>max1</sub> , °C	T <sub>max2</sub> , °C	T <sub>max3</sub> , °C
Mater-Bi	0	279.5	310.6	399.9	319.6	362.1	412.1
	2	306.2	321.2	399.1	324.9	358.1	409.0
	4	310.3	324.9	400.6	331.1	359.4	410.6
	8	310.5	325.6	400.6	330.2	357.9	412.8
	12	307.9	323.4	400.1	329.2	–	410.9
180/0	0	250.1	291.2	395.2	314.6	356.8	412.1
	2	267.8	299.6	394.9	327.4	360.4	408.3
	4	278.5	308.0	401.1	329.0	357.8	410.7
	8	282.3	312.9	401.6	–	356.4	410.2
	12	282.1	310.6	401.8	–	–	410.8
180/5	0	255.2	295.0	394.7	317.2	355.5	409.7
	2	279.1	305.9	396.4	324.0	360.4	408.0
	4	273.1	303.1	399.1	310.9	360.9	411.4
	8	273.7	299.5	397.7	328.3	364.5	410.3
	12	269.6	302.6	398.1	331.8	358.3	408.2
240/0	0	255.7	290.8	392.8	312.3	359.7	409.8
	2	274.7	302.3	397.2	320.6	359.5	408.3
	4	277.5	305.3	399.0	319.2	356.5	409.9
	8	278.7	303.8	398.2	327.3	360.0	410.0
	12	285.4	311.5	401.7	336.9	361.6	410.6
240/5	0	257.9	296.5	394.8	322.3	351.9	409.8
	2	279.4	306.9	397.3	325.9	357.4	407.8
	4	269.5	300	396.3	321.6	363.6	409.0
	8	278.9	302.8	379.2	317.8	358.5	407.4
	12	282.0	309.5	400.6	328.8	362.0	410.8

frequencies. This effect was understandable considering the increased amount of filler in composites and the size of the incorporated BSG particles. In the case of polymer composites, it can be assumed that two phenomena occur, which lead to different rheological effects due to exposure to soil. The observed increase in the viscosity of composites should be attributed to the swelling of the filler in the matrix and increasing its volumetric fraction, rather than the limitations in the degradation process, which result in a reduction of viscosity and  $G'$ . The fact that exposition of PCL-based materials, including commercial Mater-Bi and their composites with natural fillers, to a long-term humid environment, including burning in soil, by both soil and water environment, results in lowering of its molecular weight is well described in the literature (Bastioli et al., 1993). The molecular parameters of thermoplastic polymers are strictly connected with their rheological properties (Cross, 1969). Usually, degradative behavior with various origins strongly influences especially rheological properties of polymers measured in the range of low shear rates. Therefore the application of oscillatory rheometry as a qualitative tool for evaluating degradation-originated changes in polymeric structure is reasonable.

#### 4. Conclusions

The presented paper aimed to investigate the effect of thermo-mechanical and chemical treatments of waste plant-based filler – brewers' spent grain – on the biodegradation of Mater-Bi-based biocomposites. Subjecting of samples to the 12-week soil burial experiment enabled evaluation the potential stabilizing effect of BSG filler on polymer matrix resulting from the content of melanoidins and other antioxidant phytochemicals, as well as the impact of introduced compatibilizer applied to strengthen the interfacial adhesion. Results of the performed experiment revealed that applied thermomechanical and chemical treatments of waste BSG filler showed noticeable impact on the course and rate of soil burial biodegradation of Mater-Bi based biocomposites. Differences in the weight retention, structure and properties' changes between materials containing different types of fillers confirmed enhanced stability induced by the increase of BSG thermo-mechanical treatment temperature, which can be attributed to enhanced generation of melanoidins. Also chemical modification of BSG with



**Fig. 5.** The DSC curves obtained during the second heating and cooling of Mater-Bi and its composites aged for different periods of time.

diisocyanate showed beneficial impact of interfacial adhesion within the biocomposites. Nevertheless, despite the beneficial impact of applied modifications, the biodegradation of analyzed materials was not detained, but only inhibited. Therefore, described treatments could be efficiently applied in the development of sustainable materials with the engineered biodegradation rate driven by the applied filler treatment and its extent. Presented results may provide auspicious insights into development of biodegradable polymer composites. Composition of plant-based fillers, mainly content of antioxidant and antimicrobial phytochemicals but also melanoidins resulting from applied treatments affect the composites' biodegradation rate. Therefore, presented research results could be extended in future works dealing with biodegradation of polymer composites.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

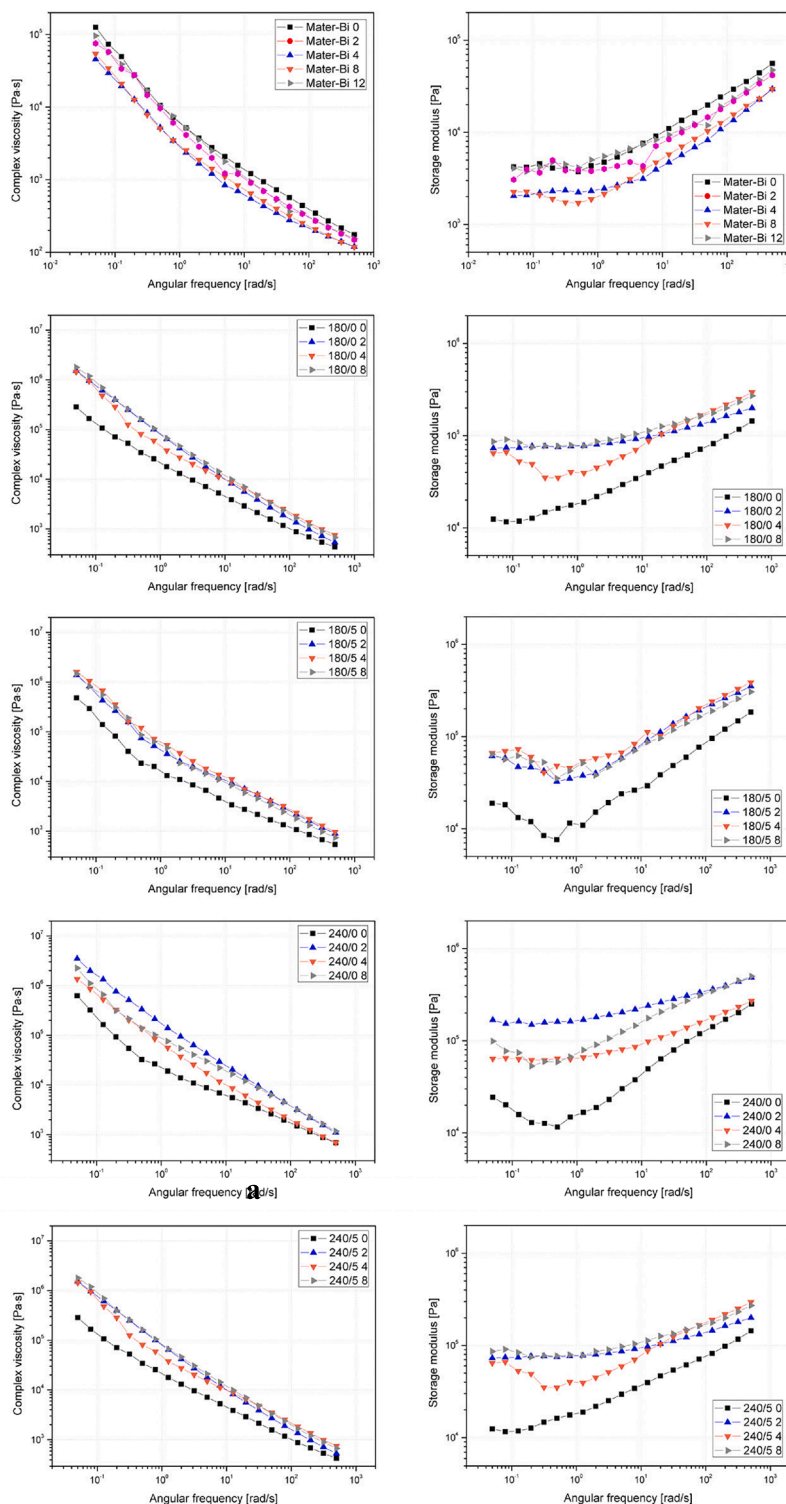


Fig. 6. Results of oscillatory rheometer, complex viscosity ( $\eta^*$ ), and storage modulus ( $G'$ ) vs angular frequency ( $\omega$ ).

the work reported in this paper.

**Data availability**

Data will be made available on request.

**Acknowledgments**

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 analysis of chemical composition of applied BSG presented in this paper were financed by the University of Warmia and Mazury in Olsztyn, Faculty of Agriculture and Forestry, Department of

Genetics, Plant Breeding and Bioresource Engineering (grant No. 30.610.007-110).

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.wasman.2022.10.007>.

## References

- Ahangarpour, A., Sayahi, M., Sayahi, M., 2019. The antidiabetic and antioxidant properties of some phenolic phytochemicals: A review study. *Diabetes & Metabolic Syndrome: Clinical Research & Reviews* 13, 854–857. <https://doi.org/10.1016/j.dsx.2018.11.051>.
- Aldas, M., Ferri, J.M., Lopez-Martinez, J., Samper, M.D., Arrieta, M.P., 2020. Effect of pine resin derivatives on the structural, thermal, and mechanical properties of Mater-Bi type bioplastic. *J Appl Polym Sci* 137, 48236. <https://doi.org/10.1002/app.48236>.
- Aldas, M., Pavon, C., Ferri, J.M., Arrieta, M.P., López-Martínez, J., 2021. Films Based on Mater-Bi® Compatibilized with Pine Resin Derivatives: Optical, Barrier, and Disintegration Properties. *Polymers (Basel)* 13, 1506. <https://doi.org/10.3390/polym13091506>.
- Antov, P., Krišt'ák, L., Réh, R., Savov, V., Papadopoulos, A.N., 2021. Eco-Friendly Fiberboard Panels from Recycled Fibers Bonded with Calcium Lignosulfonate. *Polymers (Basel)* 13, 639. <https://doi.org/10.3390/polym13040639>.
- Arrieta, M.P., López, J., Ferrández, S., Peltzer, M.A., 2013. Characterization of PLA-limonene blends for food packaging applications. *Polym Test* 32, 760–768. <https://doi.org/10.1016/j.polymertesting.2013.03.016>.
- Barbale, M., Chinaglia, S., Gazzilli, A., Pischedda, A., Pognani, M., Tosin, M., Degli-Innocenti, F., 2021. Hazard profiling of compostable shopping bags. Towards an ecological risk assessment of littering. *Polym Degrad Stab* 188, 109592. <https://doi.org/10.1016/j.polymdegradstab.2021.109592>.
- Barczewski, M., Sałasińska, K., Szulc, J., 2019. Application of sunflower husk, hazelnut shell and walnut shell as waste agricultural fillers for epoxy-based composites: A study into mechanical behavior related to structural and rheological properties. *Polym Test* 75, 1–11. <https://doi.org/10.1016/j.polymertesting.2019.01.017>.
- Bastoli, C., Bellotti, V., Giudice, L., Gilli, G., 1993. Mater-Bi: Properties and biodegradability. *J Environ Polym Degrad* 1, 181–191. <https://doi.org/10.1007/BF01458026>.
- Battegazzore, D., Bocchini, S., Alongi, J., Frache, A., 2014. Plasticizers, antioxidants and reinforcement fillers from hazelnut skin and cocoa by-products: Extraction and use in PLA and pp. *Polym Degrad Stab* 108, 297–306. <https://doi.org/10.1016/j.polymdegradstab.2014.03.003>.
- Bernardo, C.N., Kling, I.C.S., Ferreira, W.H., Andrade, C.T., Simao, R.A., 2022. Starch films containing starch nanoparticles as produced in a single step green route. *Ind Crops Prod* 177, 114481. <https://doi.org/10.1016/j.indcrop.2021.114481>.
- Bortolato, R., Bittencourt, P.R.S., Yamashita, F., 2022. Biodegradable starch / polyvinyl alcohol composites produced by thermoplastic injection containing cellulose extracted from soybean hulls (*Glycine max* L.). *Ind Crops. Prod* 176, 114383. <https://doi.org/10.1016/j.indcrop.2021.114383>.
- Bouarab Chibane, L., Degraeve, P., Ferhout, H., Bouajila, J., Oulahal, N., 2019. Plant antimicrobial polyphenols as potential natural food preservatives. *J Sci Food Agric* 99, 1457–1474. <https://doi.org/10.1002/jsfa.9357>.
- Briassoulis, D., 2006. Mechanical behaviour of biodegradable agricultural films under real field conditions. *Polym Degrad Stab* 91, 1256–1272. <https://doi.org/10.1016/j.polymdegradstab.2005.09.016>.
- Briassoulis, D., 2007. Analysis of the mechanical and degradation performances of optimised agricultural biodegradable films. *Polym Degrad Stab* 92, 1115–1132. <https://doi.org/10.1016/j.polymdegradstab.2007.01.024>.
- Byun, Y., Kim, Y.T., Whiteside, S., 2010. Characterization of an antioxidant poly(lactic acid) (PLA) film prepared with  $\alpha$ -tocopherol, BHT and polyethylene glycol using film cast extruder. *J Food Eng* 100, 239–244. <https://doi.org/10.1016/j.jfoodeng.2010.04.005>.
- Cesur, S., 2018. The Effects of Additives on the Biodegradation of Polycaprolactone Composites. *J Polym Environ* 26, 1425–1444. <https://doi.org/10.1007/s10924-017-1029-y>.
- Chang, S.K., Alasalvar, C., Shahidi, F., 2019. Superfruits: Phytochemicals, antioxidant efficacies, and health effects – A comprehensive review. *Crit Rev Food Sci Nutr* 59, 1580–1604. <https://doi.org/10.1080/10408398.2017.1422111>.
- Cherubim, D.J., Martins, C.V., Fariña, L., Lucca, R.A., 2020. Polyphenols as natural antioxidants in cosmetics applications. *J Cosmet Dermatol* 19, 33–37. <https://doi.org/10.1111/jocd.13093>.
- Cosate de Andrade, M.F., Souza, P.M.S., Cavalett, O., Morales, A.R., 2016. Life Cycle Assessment of Poly(Lactic Acid) (PLA): Comparison Between Chemical Recycling, Mechanical Recycling and Composting. *J Polym Environ* 24, 372–384. <https://doi.org/10.1007/s10924-016-0787-2>.
- Cross, M.M., 1969. Polymer rheology: Influence of molecular weight and polydispersity. *J Appl Polym Sci* 13, 765–774. <https://doi.org/10.1002/app.1969.070130415>.
- Cucina, M., Soggia, G., de Nisi, P., Giordano, A., Adani, F., 2022. Assessing the anaerobic degradability and the potential recovery of biomethane from different biodegradable bioplastics in a full-scale approach. *Bioresour Technol* 354, 127224. <https://doi.org/10.1016/j.biortech.2022.127224>.
- Delgado-Andrade, C., Rufián-Henares, J.A., Morales, F.J., 2005. Assessing the Antioxidant Activity of Melanoidins from Coffee Brews by Different Antioxidant Methods. *J Agric Food Chem* 53, 7832–7836. <https://doi.org/10.1021/jf0512353>.
- Mathias, T.R. dos S., Alexandre, V.M.F., Cammarota, M.C., de Mello, P.P.M., Sêrvulo, E.F. C., 2015. Characterization and determination of brewer's solid wastes composition. *Journal of the Institute of Brewing* 121, 400–404. <https://doi.org/10.1002/jib.229>.
- Elfeghi Borchani, K., Carrot, C., Jaziri, M., 2015. Biocomposites of Alfa fibers dispersed in the Mater-Bi® type bioplastic: Morphology, mechanical and thermal properties. *Compos Part A Appl Sci Manuf* 78, 371–379. <https://doi.org/10.1016/j.compositesa.2015.08.023>.
- Gadaleta, G., de Gisi, S., Picuno, C., Heerenklage, J., Cafiero, L., Oliviero, M., Notarnicola, M., Kuchta, K., Sorrentino, A., 2022. The influence of bio-plastics for food packaging on combined anaerobic digestion and composting treatment of organic municipal waste. *Waste Manage.* 144, 87–97. <https://doi.org/10.1016/j.wasman.2022.03.014>.
- Göncüoğlu Taş, N., Gökmen, V., 2017. Maillard reaction and caramelization during hazelnut roasting: A multiresponse kinetic study. *Food Chem* 221, 1911–1922. <https://doi.org/10.1016/j.foodchem.2016.11.159>.
- Harini, K., Chandra Mohan, C., Ramya, K., Karthikeyan, S., Sukumar, M., 2018. Effect of Punica granatum peel extracts on antimicrobial properties in Walnut shell cellulose reinforced Bio-thermoplastic starch films from cashew nut shells. *Carbohydr Polym* 184, 231–242. <https://doi.org/10.1016/j.carbpol.2017.12.072>.
- Hassanabadi, H.M., Wilhelm, M., Rodrigue, D., 2014. A rheological criterion to determine the percolation threshold in polymer nano-composites. *Rheol Acta* 53, 869–882. <https://doi.org/10.1007/s00397-014-0804-0>.
- Hejna, A., 2021. More than just a beer—the potential applications of by-products from beer manufacturing in polymer technology. *Emergent Mater.* <https://doi.org/10.1007/s42247-021-00304-4>.
- Hejna, A., Lenza, J., Formela, K., Korol, J., 2019. Studies on the Combined Impact of Starch Source and Multiple Processing on Selected Properties of Thermoplastic Starch/Ethylene-Vinyl Acetate Blends. *J Polym Environ* 27, 1112–1126. <https://doi.org/10.1007/s10924-019-01406-1>.
- Hejna, A., Barczewski, M., Skórczewska, K., Szulc, J., Chmielnicki, B., Korol, J., Formela, K., 2021a. Sustainable upcycling of brewers' spent grain by thermo-mechanical treatment in twin-screw extruder. *J Clean Prod* 285, 124839. <https://doi.org/10.1016/j.jclepro.2020.124839>.
- Hejna, A., Marć, M., Kowalkowska-Zedler, D., Pladzyk, A., Barczewski, M., 2021b. Insights into the Thermo-Mechanical Treatment of Brewers' Spent Grain as a Potential Filler for Polymer Composites. *Polymers (Basel)* 13, 879. <https://doi.org/10.3390/polym13060879>.
- Hejna, A., Formela, K., Barczewski, M., Kuang, T., Saeb, M.R., 2022. Enhanced aging resistance of poly( $\epsilon$ -caprolactone)/brewers' spent grain composites. *Polimery* 67, 3–12. <https://doi.org/10.14314/polimery.2022.1.1>.
- Hejna, A., Kosmela, P., 2020. Insights into compatibilization of poly( $\epsilon$ -caprolactone)-based biocomposites with diisocyanates as modifiers of cellulose fillers. *Mindanao Journal of Science and Technology* 18, 221–241.
- Hon, D.-N.-S., Shiraishi, N., 2001. Wood and cellulosic chemistry. *Marcel Dekker*.
- Jeon, H.J., Kim, M.N., 2013. Biodegradation of poly(L-lactide) (PLA) exposed to UV irradiation by a mesophilic bacterium. *Int Biodeterior Biodegradation* 85, 289–293. <https://doi.org/10.1016/j.ibiod.2013.08.013>.
- Koike, S.T., Fake, C.E., Correll, J.C., 2009. Anthracnose of Sunflower Sprouts Caused by *Colletotrichum acetatum* in California. *Plant Dis* 93, 1351–1351. <https://doi.org/10.1094/PDIS-93-12-1351A>.
- Lukic, I., Vulic, J., Ivanovic, J., 2020. Antioxidant activity of PLA/PCL films loaded with thymol and/or carvacrol using scCO<sub>2</sub> for active food packaging. *Food Packag Shelf Life* 26, 100578. <https://doi.org/10.1016/j.fpsl.2020.100578>.
- Luthra, P., Vimal, K.K., Goel, V., Singh, R., Kapur, G.S., 2020. Biodegradation studies of polypropylene/natural fiber composites. *SN Appl Sci* 2. <https://doi.org/10.1007/s42452-020-2287-1>.
- Lynch, K.M., Steffen, E.J., Arendt, E.K., 2016. Brewers' spent grain: a review with an emphasis on food and health. *J. Inst. Brew.* 122, 553–568. <https://doi.org/10.1002/jib.363>.
- Maga, D., Hiebel, M., Thonemann, N., 2019. Life cycle assessment of recycling options for polylactic acid. *Resour Conserv Recycl* 149, 86–96. <https://doi.org/10.1016/j.resconrec.2019.05.018>.
- Manoel, A.F., Claro, P.I.C., Galvani, F., Mattoso, L.H.C., Marconini, J.M., Mantovani, G. L., 2022. Poly( $\epsilon$ -caprolactone) blended with thermoplastic waxy starch matrix reinforced with cellulose nanocrystals from Macauba (*Acrocomia* spp.) *Rachis. Ind Crops. Prod* 177, 114446. <https://doi.org/10.1016/j.indcrop.2021.114446>.
- Masek, A., Latos-Brozio, M., 2018. The Effect of Substances of Plant Origin on the Thermal and Thermo-Oxidative Ageing of Aliphatic Polyesters (PLA, PHA). *Polymers (Basel)* 10, 1252. <https://doi.org/10.3390/polym10111252>.
- Mejia, E., Cherupurakal, N., Mourad, A.-H.I., al Hassanieh, S., Rabia, M., 2021. Effect of Processing Techniques on the Microstructure and Mechanical Performance of High-Density Polyethylene. *Polymers (Basel)* 13, 3346. <https://doi.org/10.3390/polym13193346>.
- Moraczewski, K., Stepczyńska, M., Malinowski, R., Karasiewicz, T., Jagodziński, B., Rytlewski, P., 2019. The Effect of Accelerated Aging on Poly(lactide) Containing Plant Extracts. *Polymers (Basel)* 11, 575. <https://doi.org/10.3390/polym11040575>.
- Olewnik-Kruszkowska, E., Burkowska-But, A., Tarach, I., Walczak, M., Jakubowska, E., 2020. Biodegradation of polylactide-based composites with an addition of a compatibilizing agent in different environments. *Int Biodeterior Biodegradation* 147. <https://doi.org/10.1016/j.ibiod.2019.104840>.
- Piemonte, V., Sabatini, S., Gironi, F., 2013. Chemical Recycling of PLA: A Great Opportunity Towards the Sustainable Development? *J Polym Environ* 21, 640–647. <https://doi.org/10.1007/s10924-013-0608-9>.

- Prakash, B., Kumar, A., Singh, P.P., Songachan, L.S., 2020. Antimicrobial and antioxidant properties of phytochemicals, in: *Functional and Preservative Properties of Phytochemicals*. Elsevier, pp. 1–45. <https://doi.org/10.1016/B978-0-12-818593-3.00001-4>.
- Przybytek, A., Sienkiewicz, M., Kucińska-Lipka, J., Janik, H., 2018. Preparation and characterization of biodegradable and compostable PLA/TPS/ESO compositions. *Ind Crops Prod* 122, 375–383. <https://doi.org/10.1016/j.indcrop.2018.06.016>.
- Salasinska, K., Barczewski, M., Górny, R., Kloziński, A., 2018. Evaluation of highly filled epoxy composites modified with walnut shell waste filler. *Polym. Bull.* 75, 2511–2528. <https://doi.org/10.1007/s00289-017-2163-3>.
- sen Gupta, R., Sarkar, A., Kureishy, T.W., 1991. Biodegradation and anticholinesterase activity of methyl isocyanate in the aquatic environment of Bhopal. *Water Res* 25, 179–183. [https://doi.org/10.1016/0043-1354\(91\)90027-N](https://doi.org/10.1016/0043-1354(91)90027-N).
- Sintim, H.Y., Bary, A.I., Hayes, D.G., Wadsworth, L.C., Anunciado, M.B., English, M.E., Bandopadhyay, S., Schaeffer, S.M., DeBruyn, J.M., Miles, C.A., Reganold, J.P., Flury, M., 2020. In situ degradation of biodegradable plastic mulch films in compost and agricultural soils. *Sci. Total Environ.* 727, 138668 <https://doi.org/10.1016/j.scitotenv.2020.138668>.
- Stloukal, P., Verney, V., Commereuc, S., Rychly, J., Matisova-Rychlá, L., Pis, V., Koutny, M., 2012. Assessment of the interrelation between photooxidation and biodegradation of selected polyesters after artificial weathering. *Chemosphere* 88, 1214–1219. <https://doi.org/10.1016/j.chemosphere.2012.03.072>.
- Stolarski, M.J., Warmiński, K., Krzyżaniak, M., Tyśkiewicz, K., Olba-Zięty, E., Graban, Ł., Lajszner, W., Zaluski, D., Wiejak, R., Kamiński, P., Rój, E., 2020. How does extraction of biologically active substances with supercritical carbon dioxide affect lignocellulosic biomass properties? *Wood Sci Technol* 54, 519–546. <https://doi.org/10.1007/s00226-020-01182-5>.
- van Boekel, M.A.J.S., 2006. Formation of flavour compounds in the Maillard reaction. *Biotechnol Adv* 24, 230–233. <https://doi.org/10.1016/j.biotechadv.2005.11.004>.
- Vanreppelen, K., Vanderheyden, S., Kuppens, T., Schreurs, S., Yperman, J., Carleer, R., 2014. Activated carbon from pyrolysis of brewer's spent grain: Production and adsorption properties. *Waste Management & Research: The Journal for a Sustainable Circular Economy* 32, 634–645. <https://doi.org/10.1177/0734242X14538306>.
- Wang, H., Wei, D., Zheng, A., Xiao, H., 2015. Soil burial biodegradation of antimicrobial biodegradable PBAT films. *Polym Degrad Stab* 116, 14–22. <https://doi.org/10.1016/j.polymdegradstab.2015.03.007>.
- Yang, Z., Zhu, L., Tian, H., Wang, J., Yin, J., Duan, L., Tan, W., 2021. Design, synthesis and biological activities of novel urea derivatives with superior plant growth-inhibiting activity. *Plant Growth Regul* 93, 243–252. <https://doi.org/10.1007/s10725-020-00682-5>.
- Zdanowicz, M., 2020. Starch treatment with deep eutectic solvents, ionic liquids and glycerol. A comparative study. *Carbohydr Polym* 229, 115574. <https://doi.org/10.1016/j.carbpol.2019.115574>.