

## **Sustainable upcycling of brewers' spent grain by thermo-mechanical treatment in twin-screw extruder**

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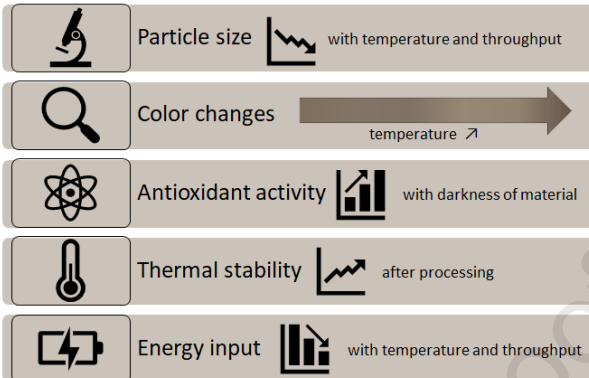
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Extrusion grinding

Temperature

Shear forces



Journal Pre-proof

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3

## 4 **Abstract**

5 Thermo-mechanical treatment of brewers' spent grain (a by-product of beer manufacturing)  
6 was successfully performed via the extrusion process. The impact of temperature (from 30 to  
7 180 °C), throughput (from 1 to 5 kg/h) and screw speed (from 75 to 375 rpm) on particle size,  
8 color, chemical structure, antioxidant activity and thermal stability of resulting material, as  
9 well as correlations between particular properties, were investigated. The color of treated  
10 brewers' spent grain was strongly influenced by particle size and the extent of Maillard  
11 reactions occurring during extrusion, responsible for the browning of material. Moreover,  
12 products of these reactions, melanoidins, enhanced the antioxidant activity of brewers' spent  
13 grain, which after extrusion at 180 °C was increased by even 100%. Thermo-mechanical  
14 treatment of brewers' spent grain at 120 and 180 °C increased its thermal stability  
15 investigated by thermogravimetric analysis. It was also observed that temperature treatment  
16 above 100 °C also led to the reduction in friction inside the extruder barrel and reduced by at  
17 least 20% specific mechanical energy required to brewers' spent grain modification, which  
18 positively affects the economic aspect of the process. The results confirm that a proper  
19 adjustment of extrusion parameters allows easy tailoring of the appearance (color, particle  
20 size distribution) and performance properties (thermal stability, antioxidant activity) of  
21 brewers' spent grain, which significantly extend applications of this cellulosic-rich waste in  
22 wood polymer composites technology.

## 23 **Keywords**

24 Brewers' spent grain; upcycling; thermo-mechanical treatment; extrusion; color and  
25 performance properties; chemical structure



## 26 1. Introduction

27 Wood polymer composites (WPCs) are a class of composites consisting of one or  
28 more lignocellulosic fillers and one or a mixture of polymeric materials. Thanks to the  
29 application of lignocellulosic fillers, these materials may be characterized, e.g., with lower  
30 density, higher stiffness, renewable nature, biodegradability, and reduced costs (Zajchowski  
31 and Ryszkowska, 2009). Moreover, due to lower hardness, the application of lignocellulosic  
32 filler reduces machine wear and damage of processing equipment comparing to, e.g., mineral  
33 fillers, commonly used in polymer composites.

34 In order to obtain WPCs with desired parameters, used fillers need to show particular  
35 properties. Fillers' properties affect the performance of the resulting WPCs. However, one of  
36 the most important is the particle size distribution. It was repeatedly proven that smaller  
37 particles often show higher specific surface areas, which together enhance the mechanical  
38 performance of composites (Fu et al., 2008). Moreover, the small particle size of filler may  
39 enhance the barrier properties of the composite, which can have an influence on, e.g., the rate  
40 of biodegradation (Kargarzadeh et al., 2017, 2018). Currently applied methods of size  
41 reduction of fillers are mostly based on processes with periodic character and use of various  
42 types of mills (Bridgeman et al., 2007; Silva et al., 2011). More perspective solutions, which  
43 are more cost-effective, should be based on continuous processes, such as extrusion, which  
44 was applied in the presented study.

45 Another parameter, essential for the applications of WPCs, affecting their aesthetic  
46 aspect is their color. Commonly used natural fillers may vary in color because of different  
47 type and source of raw material (e.g., different types of wood or other lignocellulosic fillers),  
48 but also because of the applied treatment, most often associated with size reduction. During  
49 grinding or milling of fillers, shear forces and sometimes also the temperature is applied to the  
50 material, which is inducing color changes of material.

51 Generally, changes in color during grinding of fillers are associated with two factors:  
52 final particle size and chemical reactions occurring inside the material during processing. The  
53 changes in the roughness of the surface, hence light scattering and particle size of fillers,  
54 significantly affect the light transmittance, which was confirmed for diverse natural materials  
55 (Bolade et al., 2009; Sun et al., 2016).

56 Chemical reactions resulting in the changes in color are generally referred to as non-  
57 enzymatic browning reactions. This group consists mainly of caramelization and Maillard  
58 reactions. The first reaction is a complex process of sugar pyrolysis, including, e.g.,  
59 dehydration, condensation, fragmentation, isomerization, or polymerization reactions of  
60 sugars, resulting in the generation of caramelans ( $C_{24}H_{36}O_{18}$ ), caramelens ( $C_{36}H_{50}O_{25}$ ) and  
61 caramelins ( $C_{125}H_{188}O_{80}$ ) (Villamiel et al., 2006). During caramelization, volatile compounds  
62 are also formed, which are responsible for characteristic caramel flavor. Maillard reactions,  
63 which involve chemical reactions between amino groups of amino acids and carbonyl groups  
64 of sugars, can take place at lower temperatures than caramelization. They involve reactions of  
65 reducing sugars with amino acids and result in the hard to characterize complex mixture of  
66 compounds responsible for the final color and flavor of resulting material, which is very  
67 important in polysaccharide-based food products, such as cookies, biscuits, bread, etc.  
68 (Maillard, 1912). Generally, a group of resulting products, responsible for the color change, is  
69 referred to as melanoidins – higher molecular weight oligomeric and polymeric substances  
70 (Martins et al., 2000). The general scheme of Maillard reactions, which show their  
71 complexity, is presented in Fig. S1. It is also crucial that melanoidins are commonly known in  
72 food chemistry and technology for their antioxidant activity, which enhances the storage  
73 stability of various food products (Pastoriza and Rufián-Henares, 2014; Rivero-Pérez et al.,  
74 2002). Therefore, based on the literature data, it can be assumed that they could also enhance  
75 the stability of WPCs (Moraczewski et al., 2019).



76 From an economical and ecological point of view, the most beneficial is the  
77 incorporation of fillers, which are considered as by-products or wastes resulting from the  
78 processing of renewable raw materials. Therefore, it seems very interesting for the  
79 manufacturing of polymer biocomposites to use the brewers' spent grain (BSG), which is the  
80 major by-product of the brewing industry, generated in the mashing process (Hejna et al.,  
81 2015). BSG shows relatively similar composition to various waste fillers applied during the  
82 preparation of WPCs, e.g., pulp resulting from the paper industry or wood flour. However, it  
83 contains significantly higher amounts of proteins, which can participate in Maillard reactions,  
84 enhancing the antioxidant activity of filler (Rufián-Henares and Morales, 2007). BSG stands  
85 for ~85% of the total by-products of beer manufacturing, and according to literature data,  
86 accounts for around 31% of the initial malt weight (Mussatto et al., 2006). According to The  
87 Brewers of Europe Beer Statistics Report from 2018 (The Brewers of Europe, 2018),  
88 European producers manufacture over 41 billion liters of beer each year, which results in the  
89 generation of over 2.5 million tonnes of BSG. Market Research Store reports that global  
90 production of WPCs is increasingly growing, from almost 3.5 million tonnes in 2015 to over  
91 4.3 million tonnes in 2017, and is expected to reach over 6.0 million tonnes in 2020 (Market  
92 Research Store, 2018). Therefore, research associated with the development of this group of  
93 materials is very perspective. Assuming with average filler share of 50 wt.% in WPCs, the  
94 current demand on lignocellulosic fillers is around 2.2 million tonnes annually, so it can be  
95 seen that utilization of BSG produced only in Poland could be a significant contribution to  
96 WPCs market.

97 The main limitation related to the application of BSG in polymer composites is related  
98 to two factors: relatively high humidity and large particle size of this cellulosic-rich waste.  
99 The dried form of BSG is present in the market. Therefore this research work is focused on  
100 solving the issues related to the particle size of BSG and the characteristics of ground BSG.



101 So far, BSG has not been very often investigated as a filler for WPCs. In previous  
102 works, BSG was successfully applied as filler into rigid polyurethane foams (Formela et al.,  
103 2017; Hejna et al., 2017), natural rubber (Zedler et al., 2018, 2020), and poly( $\epsilon$ -caprolactone)  
104 (Hejna et al., 2015). Obtained results indicated that proteins present in BSG acted as  
105 plasticizers and reduced the adhesion to polymer matrices. Therefore, suitable treatment of  
106 BSG prior application in WPCs should be investigated in order to understand how the  
107 changes in the chemical structure of BSG affect their impact on compatibility with polymer  
108 matrices. Authors investigating polymer/BSG composites (Berthet et al., 2015; Cunha et al.,  
109 2014; Revert et al., 2017) studied the microscopic structure, mechanical, and thermal  
110 properties of obtained WPCs, which indicated insufficient interfacial adhesion between matrix  
111 and filler. The only modification of filler was alkali treatment applied by Berthet et al. (2015).  
112 However, they were not able to prepare WPCs due to the aggregation of the fibers. Therefore,  
113 the effect of treatment could not be evaluated. Moreover, the impact of melanoidins,  
114 potentially enhancing the resistance of composites towards oxidation, has not been  
115 investigated yet.

116 In this paper, sustainable upcycling of brewers` spent grain by thermo-mechanical  
117 treatment in the twin-screw extruder was developed. The twin-screw extruder was selected  
118 due to: i) high mixing and shearing efficiency of processed material; ii) common application  
119 in the industry (more straightforward implementation of laboratory results at industrial scale),  
120 and iii) continuity of process (high throughput and good repeatability of results). Recently,  
121 extrusion techniques found application in the treatment of biomass and lignocellulosic wastes  
122 (Duque et al., 2017; Leonard et al., 2019; Offiah et al., 2018). However, there is a lack of  
123 published information about the application of this technique for utilization or up-cycling of  
124 brewers` spent grain. Therefore, in this research work, the impact of extrusion conditions  
125 (temperature, throughput, screw speed) on the specific mechanical energy required to BSG



126 particles size reduction, particle size distribution, chemical structure, color properties, thermal  
127 stability and antioxidant activity of treated BSG were investigated in order to evaluate the  
128 possibility of its application in wood polymer composites technology.

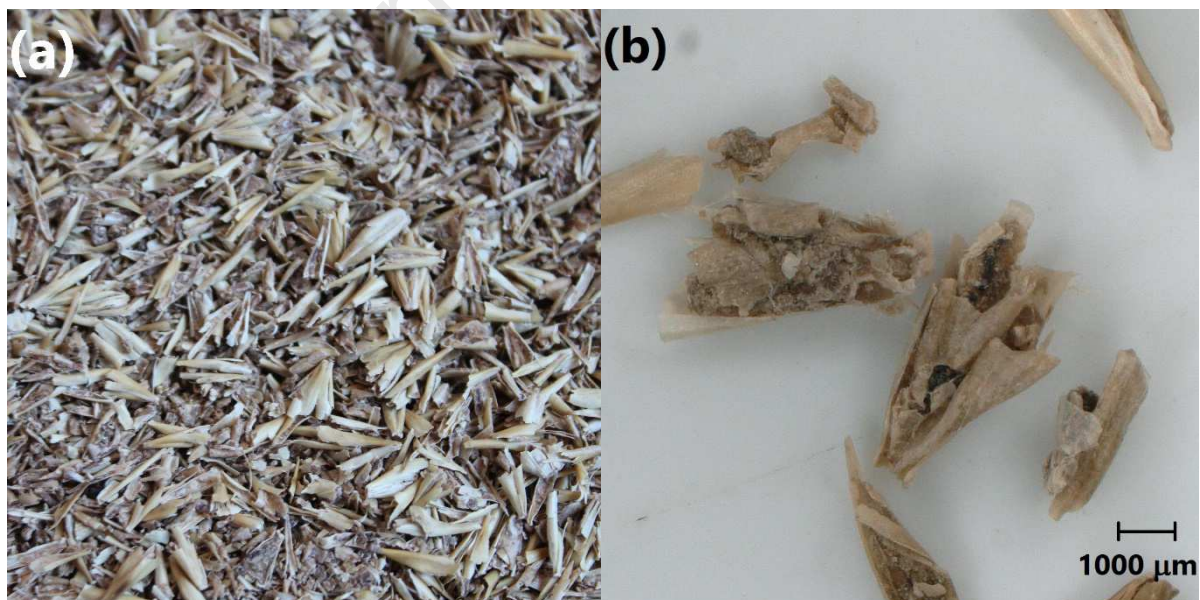
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## 130 2. Experimental

### 131 2.1. Materials

132 Brewers' spent grain used in the presented study was obtained from Energetyka  
133 Złoczew sp. z o.o. (Poland). It was waste from the production of light lager and consisted  
134 solely of barley malts. The supplier already dried obtained BSG. In Fig. 1, there is shown the  
135 appearance of used BSG.

136 Synthetic 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical ( $\geq 95\%$ , solid crystal) and  
137 70% water solution of ethanol were used during the determination of the antioxidant activity  
138 of modified BSG. Both compounds were acquired from Sigma Aldrich (Poland) and used as  
139 received.



140

141 **Figure 1.** Macroscopic (a) and microscopic (b) appearance of applied BSG before extrusion grinding.

142

143



144

## 145 2.2. Extrusion grinding of BSG

146 Extrusion grinding of BSG was performed with EHP 2x20 Sline co-rotating twin-  
147 screw extruder from Zamak Mercator (Poland), following patent application (Hejna and  
148 Formela, 2019). The extruder has eleven heating/cooling zones with a screw diameter of 20  
149 mm and an L/d ratio of 40. The screw configuration is shown in Fig. S2. BSG was dosed into  
150 the extruder by a volumetric feeder with a constant throughput of 1, 3, or 5 kg/h. Screw speed  
151 varied from 75 to 225, from 150 to 300 and from 225 to 375 rpm, respectively, for increasing  
152 throughput. Barrel temperature in all zones was set at 30, 60, 120, or 180 °C. For each set of  
153 parameters, extrusion was carried out for at least 60 minutes after stabilization of the motor  
154 load of the extruder, which indicated stabilization of the process. After grinding, samples of  
155 BSG were left in order to cool down to room temperature. Samples were coded as X/Y/Z,  
156 where X stands for the processing temperature, Y for the throughput, and Z for the screw  
157 speed.

158

## 159 2.3. Characterization techniques

160 The characterization of the particle size distribution of investigated BSG fillers was  
161 evaluated using a laser particle sizer Fritsch ANALYSETTE 22 apparatus operated in the  
162 range of 0.08 - 2000 µm.

163 The chemical structure of studied samples was determined using Fourier transform  
164 infrared spectroscopy (FTIR) analysis performed by a Nicolet Spectrometer IR200 from  
165 Thermo Scientific (USA). The device had an ATR attachment with a diamond crystal.  
166 Measurements were performed with 1 cm<sup>-1</sup> resolution in the range from 4000 to 400 cm<sup>-1</sup> and  
167 64 scans. For each sample, at least three spectra were recorded.



168 The color of treated BSG was evaluated according to the Commission Internationale  
 169 de l'Eclairage (CIE) through  $L^*a^*b^*$  coordinates (International Commission on Illumination,  
 170 1978). In this system,  $L^*$  is the color lightness ( $L^*=0$  for black and  $L^*=100$  for white),  $a^*$  is  
 171 the green(-) / red(+) axis, and  $b^*$  is the blue(-) / yellow(+) axis. Thirty tests of each sample  
 172 were done and used for the determination of arithmetic mean values. The color was  
 173 determined by optical spectroscopy using HunterLab Miniscan MS/S-4000S  
 174 spectrophotometer, placed additionally in a specially designed light trap chamber. The total  
 175 color difference parameter ( $\Delta E^*$ ) was calculated according to the following formulation (1)  
 176 (Bociaga and Trzaskalska, 2016):

$$177 \quad \Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (1)$$

178 Moreover, obtained values of  $a^*$  and  $b^*$  may be used to calculate other parameters  
 179 used to describe colors, such as chroma and hue, defined by the following equations (2 and 3):

$$180 \quad C_{ab}^* = (a^{*2} + b^{*2})^{\frac{1}{2}} \quad (2)$$

$$181 \quad h_{ab} = \tan^{-1} \left( \frac{b^*}{a^*} \right) \quad (3)$$

182 Determined color parameters were also converted to the commonly used Adobe RGB  
 183 color space defined by the three chromaticities of the red, green, and blue additive primaries  
 184 (Hunt, 2004). The first step was the conversion from CIELab to normalized CIEXYZ space  
 185 according to the following equations (4-8) (Lopez et al., 2005):

$$186 \quad X = X_w f^{-1} \left( \frac{L^*+16}{116} + \frac{a^*}{500} \right) \quad (4)$$

$$187 \quad Y = Y_w f^{-1} \left( \frac{L^*+16}{116} \right) \quad (5)$$

$$188 \quad Z = Z_w f^{-1} \left( \frac{L^*+16}{116} - \frac{b^*}{200} \right) \quad (6)$$

189 where:

$$190 \quad f^{-1}(t) = \begin{cases} t^3 & t > \delta \\ 3\delta^2 \left( t - \frac{4}{29} \right) & \text{otherwise} \end{cases} \quad (7)$$

191 and

$$192 \quad \delta = \frac{6}{29} \quad (8)$$

193 and

194  $X_w$ ,  $Y_w$  and  $Z_w$  are the values for the reference white point, which for Illuminant D65 equal  
195 0.950450, 1.000000 and 1.088754, respectively, according to ITU-R Recommendation  
196 BT.709.

197 Next, conversion from CIEXYZ color space to linear RGB ( $v$ ) was made according to  
198 the following formulas (9-20):

$$199 \quad \begin{bmatrix} r \\ g \\ b \end{bmatrix} = [M]^{-1} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \quad (9)$$

200 where:

$$201 \quad [M] = \begin{bmatrix} S_r X_r & S_g X_g & S_b X_b \\ S_r Y_r & S_g Y_g & S_b Y_b \\ S_r Z_r & S_g Z_g & S_b Z_b \end{bmatrix} \quad (10)$$

202 where:

$$203 \quad X_r = \frac{x_r}{y_r} \quad (11)$$

$$204 \quad Y_r = 1 \quad (12)$$

$$205 \quad Z_r = \frac{(1-x_r-y_r)}{y_r} \quad (13)$$

$$206 \quad X_g = \frac{x_g}{y_g} \quad (14)$$

$$207 \quad Y_g = 1 \quad (15)$$

$$208 \quad Z_g = \frac{(1-x_g-y_g)}{y_g} \quad (16)$$

$$209 \quad X_b = \frac{x_b}{y_b} \quad (17)$$

$$210 \quad Y_b = 1 \quad (18)$$

211 
$$Z_b = \frac{(1-x_b-y_b)}{y_b} \quad (19)$$

212 
$$\begin{bmatrix} S_r \\ S_g \\ S_b \end{bmatrix} = \begin{bmatrix} X_r & X_g & X_b \\ Y_r & Y_g & Y_b \\ Z_r & Z_g & Z_b \end{bmatrix}^{-1} \begin{bmatrix} X_w \\ Y_w \\ Z_w \end{bmatrix} \quad (20)$$

213 and:

214  $(x_r, y_r)$ ,  $(x_g, y_g)$ , and  $(x_b, y_b)$  are chromaticity coordinates of RGB system, which in the case of  
 215 Adobe RGB are (0.64, 0.33), (0.21, 0.71) and (0.15, 0.06), while  $X_w$ ,  $Y_w$  and  $Z_w$  are the values  
 216 for the reference white point, as mentioned above (Adobe Systems Incorporated, 2005).

217 Conversion from linear RGB ( $v$ ) to nonlinear RGB ( $V$ ) was made using gamma  
 218 companding according to the following equation (21):

219 
$$V = v^{\frac{1}{\gamma}} \quad (21)$$

220 where  $\gamma$  stands for gamma value characteristic for a color system, in the case of Adobe RGB  
 221 equals 2.2.

222 Obtained RGB values were in the nominal range [0.0, 1.0]. In order to present them in  
 223 the most commonly used range of [0, 255], components were multiplied by 255.

224 Samples of extruded BSG for the determination of antioxidant activity were prepared  
 225 by the extraction of proper compounds in the following manner. Samples with a mass of 1 g  
 226 were weighed on analytical balance with an accuracy of 0.001 g and then mixed with 9 cm<sup>3</sup> of  
 227 70% solution of ethanol. The mixtures were shaken vigorously and allowed to stand at room  
 228 temperature in the dark for 20 hours. All extracts were centrifuged in a centrifuge Hettich  
 229 Rotina 380 for 3 minutes at 3500 rpm. Subsequently, the antioxidant activity of supernatants  
 230 was determined with a modified method described by Brand-Williams et al. (1995) using  
 231 synthetic DPPH radical – 2,2-diphenyl-1-picrylhydrazyl. Three specimens were analyzed for  
 232 each sample. For each analysis, 1 ml of analyzed extract was mixed with 5 ml of the 0.5 mM  
 233 DPPH solution. The absorbance of the mixtures ( $A_i$ ) was measured at 517 nm after 15

234 minutes of incubation at room temperature. The negative control ( $A_0$ ) was prepared for 1 ml  
235 of 70% ethanol. The percent DPPH scavenging effect was calculated by using the following  
236 equation (22):

$$237 \quad I_{\%} = \frac{(A_0 - A_i)}{A_0} \cdot 100\% \quad (22)$$

238 The thermal analysis was performed using the TG 209 F3 apparatus from Netzsch  
239 (Germany). Samples of composites weighing approx. 10 mg were placed in a ceramic dish.  
240 The study was conducted in an inert gas atmosphere - nitrogen in the range from 30 to 900 °C  
241 with a temperature increase rate of 10 °C/min. Two specimens were analyzed for each sample.

242 In order to evaluate the effect of barrel temperature on the progress of ground tire  
243 rubber reclamation, the specific mechanical energy (SME, in kWh/kg) was determined. SME  
244 was calculated using equation (23):

$$245 \quad SME = \frac{N}{Q} \quad (23)$$

246 where  $N$  is the consumption of drive motor power (kW), and  $Q$  is throughput (kg/h). For  
247 calculations of the specific mechanical energy, the average motor load from at least 60  
248 minutes of extrusion was used.

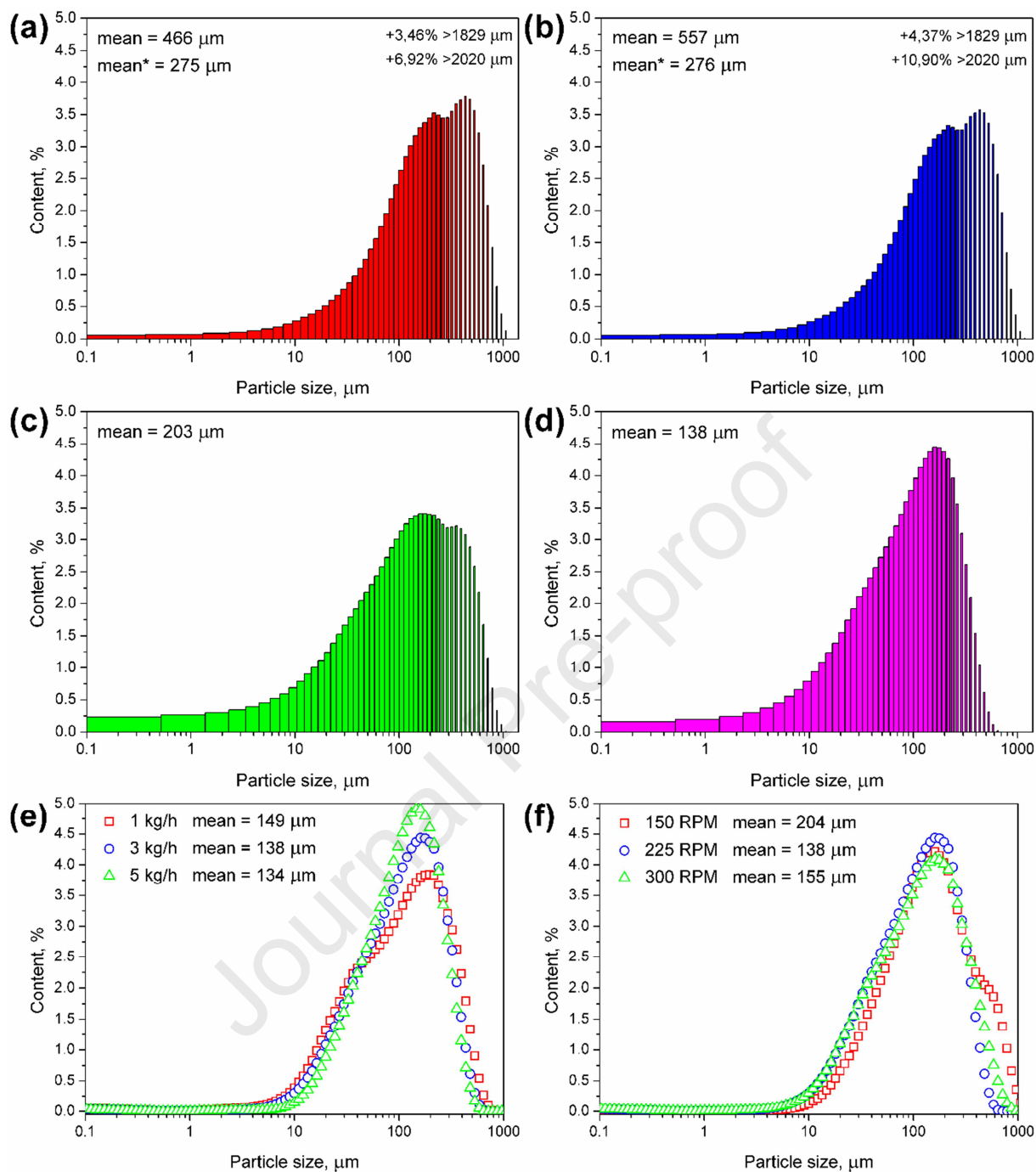
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### 250 **3. Results and discussion**

#### 251 *3.1. Particle size distribution*

252 Fig. 2 shows the particle size distribution of the selected filler samples in order to  
253 determine its dependence on the adjusted extrusion parameters. The impact of process  
254 temperature on the particle size of obtained samples (for throughput of 3 kg/h and a screw  
255 speed of 225 rpm) is presented in Fig. 2a-d. It can be seen that lower extrusion temperatures,  
256 below 100 °C, resulted in larger particle sizes, due to the agglomeration of treated BSG

257 related to higher moisture content. At lower temperatures (30 and 60 °C), moisture present in  
258 the BSG due to its hygroscopic nature (as other lignocellulosic materials) combined with the  
259 external forces causes granulation of particles. Such an effect is related to the enhanced  
260 hydrogen bonding between lignocellulosic particles caused by the presence of moisture  
261 (Sahputra et al., 2019). As a result, particles bigger than 1200 µm were present in extruded  
262 material, which is presented in Fig. 2a and 2b. Such an effect is often observed during  
263 extrusion cooking and used in the manufacturing of grain flakes and snacks (Dhanalakshmi et  
264 al., 2011). The appearance of these particles is presented in Fig. S3. The increase of the  
265 process temperature to 120 °C resulted in the reduction of average particle size, which is  
266 related to the lower share of particles bigger than 300 µm, and lack of agglomerates.  
267 Nevertheless, only for the temperature of 180 °C distribution of particle, diameters were  
268 noticeably more homogenous, comparing to lower temperatures. Such an effect was probably  
269 associated with the lower moisture content and partial decomposition of the extractives and  
270 other low molecular weight components of BSG (Mahmood et al., 2013).



271

272

273

274 **Figure 2.** The particle size distribution of samples extruded with a screw speed of 225 rpm and throughput of 3  
 275 kg/h at (a) 30 °C, (b) 60 °C, (c) 120 °C and (d) 180 °C, as well as the impact of (e) throughput and (f) screw  
 276 speed on particle size distribution.

277

278 Fig. 2e shown the impact of the extrusion throughput on the particle size distribution  
 279 of ground BSG (for process temperature of 180 °C and a screw speed of 225 rpm).  
 280 Throughput is associated with the degree of fill of extruder barrel, hence the level of shear

281 forces between the BSG particles and between particles and extruder barrel (Kao and Allison,  
282 1984). Suparno et al. (2010) developed a model based on experimental data, which indicates  
283 that shear forces are significantly increasing with the degree of fill of extruder barrel.  
284 However, an increase in throughput shows the opposite effect because it is associated with  
285 shorter residence time in the extruder and its more homogenous distribution (Altomare and  
286 Ghossi, 1986). In the presented case, it resulted in noticeably more homogenous particle size  
287 distribution and slightly smaller average particle size (Yeh et al., 1992). Such effect may be  
288 considered very beneficial from the potential application point of view (e.g., in wood polymer  
289 composites) because it enables the preparation of material showing superior properties with  
290 higher efficiency.

291 The plot in Fig. 2f presents the impact of screw speed on the particle size distribution  
292 of BSG ground at 180 °C and with a throughput of 3 kg/h. It can be seen that despite the  
293 similar distribution of particle size, differences between screw speed of 150 rpm and higher  
294 values were noted. Such an effect is associated with the increase of shear forces inside the  
295 extrusion barrel for higher screw speed values, which facilitate the disintegration of BSG  
296 particles. A similar effect was observed for the extrusion treatment of ground tire rubber  
297 particles by Formela et al. (2014). On the other hand, similar to throughput, an increase of  
298 screw speed shows opposite effects associated with the shortening of material's residence  
299 time in the extruder barrel. As a result, the increase of screw speed over 225 rpm for analyzed  
300 process parameters increased average particle size.

301

### 302 *3.2. Color properties*

303 The color parameters of prepared BSG samples are presented in Table 1. As mentioned  
304 above, in section 2.3. Measurements, the color of materials was evaluated using CIELab color  
305 space, and then parameters were converted to popular Adobe RGB space. Moreover, the total





306 color difference parameter ( $\Delta E^*$ ) related to the unprocessed reference sample is presented, as  
307 well as the color of obtained materials.

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308 **Table 1.** Color parameters of extruded BSG samples and antioxidant activity of selected samples.

| Temperature,<br>°C | Throughput,<br>kg/h | Screw<br>speed, rpm | Color parameters |      |       |              |       |       | Antioxidant<br>activity towards<br>DPPH, % |       |                   |                     |    |
|--------------------|---------------------|---------------------|------------------|------|-------|--------------|-------|-------|--|-------|-------------------|---------------------|----|
|                    |                     |                     | L*               | a*   | b*    | $\Delta E^*$ | R     | G     | B  | Color | C <sub>ab</sub> * | h <sub>ab</sub> , ° |    |
|                    |                     | Reference sample    | 48.17            | 5.11 | 13.04 | -            | 124.8 | 110.3 | 93.8                                       |       | 14.0              | 68.6                | 36 |
|                    |                     | 75                  | 49.87            | 4.66 | 12.14 | 1.97         | 128.3 | 114.6 | 99.1                                       |       | 13.0              | 69.0                | -  |
|                    | 1                   | 150                 | 56.50            | 4.71 | 13.43 | 8.35         | 145.8 | 130.9 | 112.8                                      |       | 14.2              | 70.7                | -  |
|                    |                     | 225                 | 56.81            | 4.88 | 13.91 | 8.69         | 147.0 | 131.6 | 112.8                                      |       | 14.7              | 70.7                | -  |
|                    |                     | 150                 | 51.98            | 4.87 | 13.09 | 3.82         | 134.2 | 119.6 | 102.6                                      |       | 14.0              | 69.6                | -  |
| 30                 | 3                   | 225                 | 50.97            | 4.61 | 12.31 | 2.94         | 131.1 | 117.3 | 101.4                                      |       | 13.1              | 69.5                | 49 |
|                    |                     | 300                 | 52.55            | 4.73 | 13.21 | 4.40         | 135.6 | 121.1 | 103.7                                      |       | 14.0              | 70.3                | -  |
|                    |                     | 225                 | 50.37            | 4.80 | 12.45 | 2.30         | 129.8 | 115.8 | 99.8                                       |       | 13.3              | 68.9                | -  |
|                    | 5                   | 300                 | 50.95            | 4.61 | 12.42 | 2.89         | 131.1 | 117.3 | 101.2                                      |       | 13.3              | 69.6                | -  |
|                    |                     | 375                 | 53.44            | 5.03 | 13.70 | 5.32         | 138.3 | 123.1 | 105.1                                      |       | 14.6              | 69.8                | -  |
|                    |                     | 75                  | 50.64            | 4.44 | 12.23 | 2.68         | 130.0 | 116.6 | 100.7                                      |       | 13.0              | 70.0                | -  |
|                    | 1                   | 150                 | 51.50            | 4.70 | 13.27 | 3.36         | 132.9 | 118.5 | 101.2                                      |       | 14.1              | 70.5                | -  |
|                    |                     | 225                 | 52.89            | 4.65 | 13.50 | 4.76         | 136.5 | 122.0 | 104.1                                      |       | 14.3              | 71.0                | -  |
|                    |                     | 150                 | 50.18            | 4.81 | 12.60 | 2.08         | 129.4 | 115.3 | 99.1                                       |       | 13.5              | 69.1                | -  |
| 60                 | 3                   | 225                 | 49.60            | 4.60 | 11.83 | 1.94         | 127.4 | 114.0 | 98.9                                       |       | 12.7              | 68.8                | 49 |
|                    |                     | 300                 | 50.02            | 4.32 | 12.38 | 2.11         | 128.4 | 115.2 | 99.1                                       |       | 13.1              | 70.8                | -  |
|                    |                     | 225                 | 50.41            | 4.69 | 12.59 | 2.32         | 129.9 | 115.9 | 99.7                                       |       | 13.4              | 69.6                | -  |
|                    | 5                   | 300                 | 50.48            | 4.76 | 13.23 | 2.34         | 130.3 | 116.0 | 98.8                                       |       | 14.1              | 70.2                | -  |
|                    |                     | 375                 | 51.35            | 4.84 | 12.67 | 3.21         | 132.4 | 118.1 | 101.7                                      |       | 13.6              | 69.1                | -  |
|                    |                     | 75                  | 57.64            | 5.32 | 14.52 | 9.59         | 149.9 | 133.4 | 113.8                                      |       | 15.5              | 69.9                | -  |
|                    | 1                   | 150                 | 58.23            | 4.92 | 14.35 | 10.15        | 150.9 | 135.1 | 115.5                                      |       | 15.2              | 71.1                | 54 |
|                    |                     | 225                 | 56.55            | 5.15 | 14.33 | 8.48         | 146.8 | 130.7 | 111.5                                      |       | 15.2              | 70.2                | -  |
| 120                |                     | 150                 | 55.55            | 5.88 | 14.82 | 7.63         | 145.1 | 127.8 | 108.3                                      |       | 15.9              | 68.4                | -  |
|                    | 3                   | 225                 | 56.29            | 5.42 | 14.14 | 8.20         | 146.3 | 129.9 | 111.2                                      |       | 15.1              | 69.0                | 54 |
|                    |                     | 300                 | 57.28            | 5.23 | 14.32 | 9.20         | 148.7 | 132.5 | 113.3                                      |       | 15.3              | 69.9                | -  |

|     |   |     |       |      |       |       |       |       |       |  |      |      |    |
|-----|---|-----|-------|------|-------|-------|-------|-------|-------|--|------|------|----|
|     |   | 225 | 57.15 | 5.50 | 14.46 | 9.10  | 148.7 | 132.0 | 112.8 |  | 15.5 | 69.2 | -  |
|     | 5 | 300 | 55.63 | 5.47 | 14.34 | 7.58  | 144.7 | 128.2 | 109.3 |  | 15.4 | 69.1 | -  |
|     |   | 375 | 56.32 | 5.42 | 14.29 | 8.25  | 146.4 | 130.0 | 111.0 |  | 15.3 | 69.2 | -  |
|     |   | 75  | 45.26 | 7.91 | 15.18 | 4.57  | 121.1 | 101.7 | 84.0  |  | 17.1 | 62.5 | -  |
|     | 1 | 150 | 49.33 | 7.15 | 15.33 | 3.28  | 130.6 | 111.8 | 93.0  |  | 16.9 | 65.0 | -  |
|     |   | 225 | 50.30 | 6.82 | 15.34 | 3.57  | 132.8 | 114.3 | 95.2  |  | 16.8 | 66.0 | 63 |
|     |   | 150 | 37.38 | 7.29 | 12.02 | 11.05 | 100.4 | 84.1  | 71.3  |  | 14.1 | 58.8 | 73 |
| 180 | 3 | 225 | 47.23 | 7.68 | 15.23 | 3.50  | 125.8 | 106.4 | 88.3  |  | 17.1 | 63.2 | 71 |
|     |   | 300 | 49.74 | 7.18 | 15.42 | 3.53  | 131.7 | 112.7 | 93.8  |  | 17.0 | 65.0 | 71 |
|     |   | 225 | 42.43 | 7.57 | 13.59 | 6.27  | 113.3 | 95.3  | 80.0  |  | 15.6 | 60.9 | -  |
|     | 5 | 300 | 49.06 | 6.97 | 14.74 | 2.67  | 129.6 | 111.3 | 93.3  |  | 16.3 | 64.7 | 75 |
|     |   | 375 | 48.46 | 7.31 | 15.28 | 3.15  | 128.6 | 109.6 | 91.1  |  | 16.9 | 64.4 | -  |

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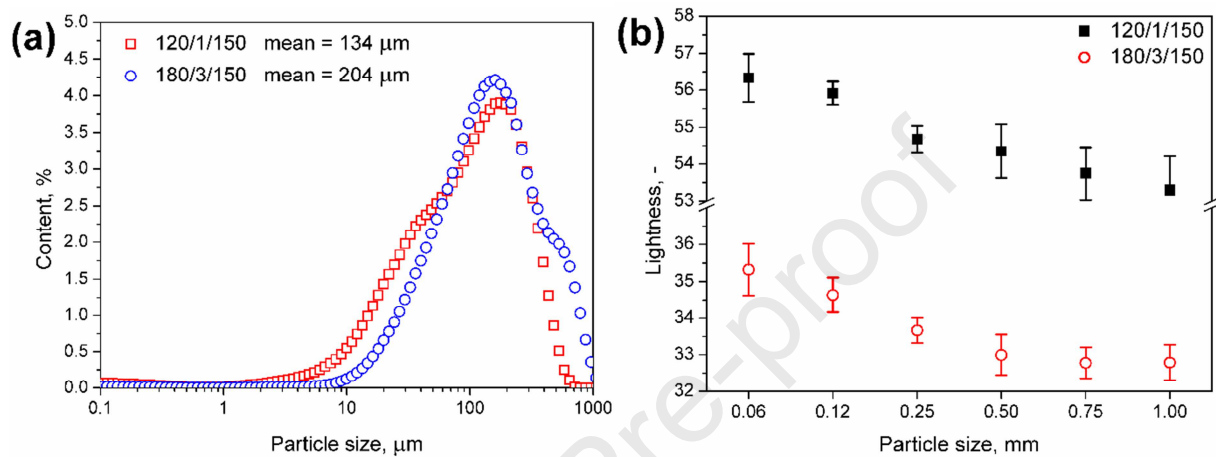
317 As mentioned above, CIELab color space defines color with three parameters,  $L^*$ ,  $a^*$ ,  
318 and  $b^*$ . According to equation (1), these parameters can be used to calculate the difference  
319 between the color of particular materials. According to standard ISO 2813:2001, the value of  
320  $\Delta E^*$  is associated with the human ability to distinguish colors and notice the color difference  
321 (Bociaga and Trzaskalska, 2016).

322 Although all of them are affected by the physical structure of the material, the one  
323 most significantly affected by the particle size is lightness (Ahmed et al., 2014, 2015, 2016).  
324 Generally, independently of  $a^*$  and  $b^*$  parameters, hence hue of material, smaller particles  
325 show higher lightness, which is associated with the increase of specific surface area that  
326 allows more reflection of light (Chen et al., 1999; Horvath and Halasz-Fekete, 2005). In Table  
327 S1, there are summarized results published by other researchers, which confirm the presented  
328 results.

329 A similar phenomenon can be observed in the presented study. Most of the materials  
330 prepared at lower temperatures (30 and 60 °C) had the highest values of average particle size  
331 among analyzed samples. As a result, they were characterized by similar color properties to  
332 the neat BSG. It was expressed by the values of  $\Delta E^*$  parameter lower than 3.5, which indicate  
333 invisible ( $\Delta E^* < 1.0$ ), small ( $\Delta E^*$  in the range of 1.0-2.0), or medium ( $\Delta E^*$  in the range of 2.0-  
334 3.5) color variations (Bociaga and Trzaskalska, 2016). Higher values, hence more significant  
335 color variations, were noted for samples extruded with higher screw speed, which reduced  
336 particle size and increased lightness of materials. Samples extruded at 120 °C show higher  
337 lightness comparing to lower extrusion temperatures, as a result of smaller particle size.  
338 Samples prepared at 180 °C were darker because of the chemical reactions occurring in the  
339 material and possible partial decomposition of polysaccharides present in BSG. Nevertheless,  
340 in Fig. 3, there is shown particle size distribution for the samples with the highest (120/1/150)  
341 and the lowest (180/3/150) lightness. It can be seen that except chemical reactions also



342 particle size and its distribution shows a noticeable impact on the lightness of the material.  
 343 Despite the better homogeneity of distribution for sample 180/3/150, the share of particles  
 344 with lower diameters was higher for 120/1/150 samples. Hence its average particle size was  
 345 lower. As a result, noticeable differences in lightness were observed, which, among other  
 346 factors, was caused by different particle size distribution.



347  
 348 **Figure 3.** Particle size distribution for (a) samples with the lowest and the highest lightness and (b) fractions of  
 349 these samples with various particle sizes.

350 For more detailed analysis, the samples mentioned above were fractionated using  
 351 sieves with diameters of 0.06, 0.12, 0.25, 0.50, 0.75, and 1.00 mm, and their color parameters  
 352 were determined. The obtained results are presented in Fig. 3b and confirm results published  
 353 by other researchers (Kim and Shin, 2014; Liu, 2009).

354 As mentioned above, two groups of reactions are responsible for color changes in  
 355 treated BSG: caramelization and Maillard reactions. In the presented case, caramelization  
 356 does not play a significant role because it involves mono- and disaccharides, which are hardly  
 357 present in brewers' spent grain (they are removed during mashing) and occurs at temperatures  
 358 of 160  $^{\circ}\text{C}$  or higher, except fructose (110  $^{\circ}\text{C}$ ) (Mussatto et al., 2006). Only minimal amounts  
 359 of lower molecular weight saccharides may be generated during extrusion due to the shear-  
 360 induced breakdown of glycosidic links (Ott, 1964). Therefore, for the investigated materials,  
 361 caramelization reactions were not so significant, especially when processing temperatures of

362 30 and 60°C were applied. More critical are Maillard reactions, because they can take place at  
363 lower temperatures than caramelization. They involve reactions of reducing sugars, which can  
364 be present in BSG in the amount of ~15 wt.% (Waters et al., 2012). Except for typical  
365 reducing sugars, also other BSG compounds, lignin may show some reducing potential due to  
366 the presence of aldehyde groups, hence the ability to take part in Maillard reactions (Maillard,  
367 1912). Moreover, BSG usually contains at least 15-20 wt.% of proteins, among which the  
368 most popular amino acids, which take part in Maillard reactions, are histidine, glutamic acid,  
369 lysine, and leucine (Lynch et al., 2016).

370 Products of Maillard reactions, e.g., melanoidins, are responsible for the change of  
371 BSG's color (Wang et al., 2011). One of the factors significantly affecting the final color  
372 change is reaction time, hence the residence time of material in the extruder. As proven by  
373 other researchers (Haugaard et al., 1951), the depth of color increases with the square of time.  
374 It is in line with the results of the presented study, which indicate that an increase of screw  
375 speed during treatment in extruder increased BSG's lightness (see Table 1). As mentioned  
376 above, also increasing throughput results in the shortening of residence time and exposition to  
377 elevated temperature (Yeh et al., 1992). Nevertheless, both screw speed and increased  
378 throughput may also show opposite effects, resulting in the enhancement of shear rate, hence  
379 shear forces acting on the material, which increases the temperature of the material and results  
380 in the darkening of material (Suprano et al., 2010). It can be seen that the increase in  
381 throughput caused a slight lowering of the lightness of BSG samples.

382 Except for lightness also other color properties, such as chroma or hue (presented in  
383 Table 1), are affected by the generation of melanoidins and resulting browning of BSG  
384 (Echavarria et al., 2013a). According to CIELab color space, typical brown color is  
385 characterized by a hue angle of ~50° (Berry, 1998). Therefore an increase of extrusion  
386 temperature enhances the browning of BSG related to the generation of melanoidins



387 (Maillard, 1912). Morales and van Boekel (1998) demonstrated a positive correlation between  
388 browning of casein/sugar solutions measured by spectrophotometer and chroma of generated  
389 melanoidins. Later, Wu et al. (2011) confirmed these findings for the malt drying process,  
390 during which chroma of malt was increasing with the content of melanoidins. Therefore, the  
391 observed increase of chroma value should be considered as a potential indicator of  
392 melanoidins' generation during extrusion grinding.

393 In the presented case, observed changes of color were not so strong because the  
394 absence of moisture during Maillard reactions tends to minimize browning, which can be  
395 noticed here, because of the relatively low moisture content of initial BSG (6.9 wt.%,  
396 according to TGA analysis). Nevertheless, the presented data indicate that the color of filler,  
397 which has a crucial impact on the appearance of the resulting composite (which is very  
398 important for the recipients of final products), depends on the processing conditions. In most  
399 cases, during the manufacturing of WPCs, filler pretreatment includes at least grinding aimed  
400 at achieving the desired particle size, which impacts the mechanical performance of the  
401 composite. Therefore, by adjustment of processing conditions, the desired color of the  
402 resulting filler can be achieved. As a result, it could significantly reduce or even eliminate the  
403 use of additional pigments or dyes, rarely composed only of natural compounds.

404

### 405 *3.3. Antioxidant activity*

406 For the manufacturing of WPCs, it can also be very interesting that melanoidins have  
407 been reported to show noticeable antioxidant activity. Hence, their presence, in combination  
408 with phenolic compounds (which can also be found in BSG), indicates that grinding may  
409 provide additional, antioxidant properties to BSG, simultaneously enhancing the durability of  
410 WPCs (Meneses et al., 2013). Such an effect was noted by other researchers for other natural  
411 fillers showing antioxidant activity (Sarasini et al., 2018). Iver et al. (2015) noted that the



412 value of elongation at break was maintained at the same level after ten extrusion cycles for  
413 low-density polyethylene composites filled with 4, 8, and 12 wt.% of grape waste, turmeric  
414 waste and coffee grounds, respectively. Therefore, it is very interesting to investigate the  
415 antioxidant properties of thermo-mechanically treated BSG, which could potentially enhance  
416 the performance of WPCs. According to literature data, relatively high activity was observed  
417 for melanoidins based on histidine, which, as mentioned above, which is a significant amino  
418 acid of BSG (Yilmaz and Toledo, 2005). Based on these literature reports, further research  
419 was aimed to examine the antioxidant properties of selected samples of extruded BSG. The  
420 results of the performed tests are presented in Table 1.

421 Relatively high activity of the reference sample may be associated with the presence  
422 of phenolic compounds in BSG, such as ferulic and *p*-coumaric acids (Mussatto et al., 2006).  
423 It can be seen that performed modifications via extrusion grinding resulted in noticeable  
424 enhancement of BSG's antioxidant activity. The highest inhibition effect was noted for  
425 samples with the lowest lightness, which most likely contained the highest amount of  
426 melanoidins. It can also be seen that despite relatively similar values of lightness, BSG  
427 extruded at 120 and, especially at 180 °C showed higher antioxidant activity, suggesting a  
428 more intensive generation of melanoidins. The increase of samples' chroma may confirm such  
429 an assumption. A similar correlation between DPPH radical scavenging activity and  $a^*$  and  
430  $b^*$ , hence also chroma values for melanoidins was observed by Echavarría et al. (2013b).

431  
432

#### 433 *3.4. Fourier-transform infrared spectroscopy analysis*

434 Fig. 4 shows the impact of the extrusion process and its parameters on the FTIR  
435 spectra of BSG. Generally, analyzed materials showed spectra typical for lignocellulose  
436 materials, such as wood flour, wheat bran, and others. All samples show typical signal (a)  
437 around  $3290-3300\text{ cm}^{-1}$ , associated with the stretching vibrations of hydroxyl groups present

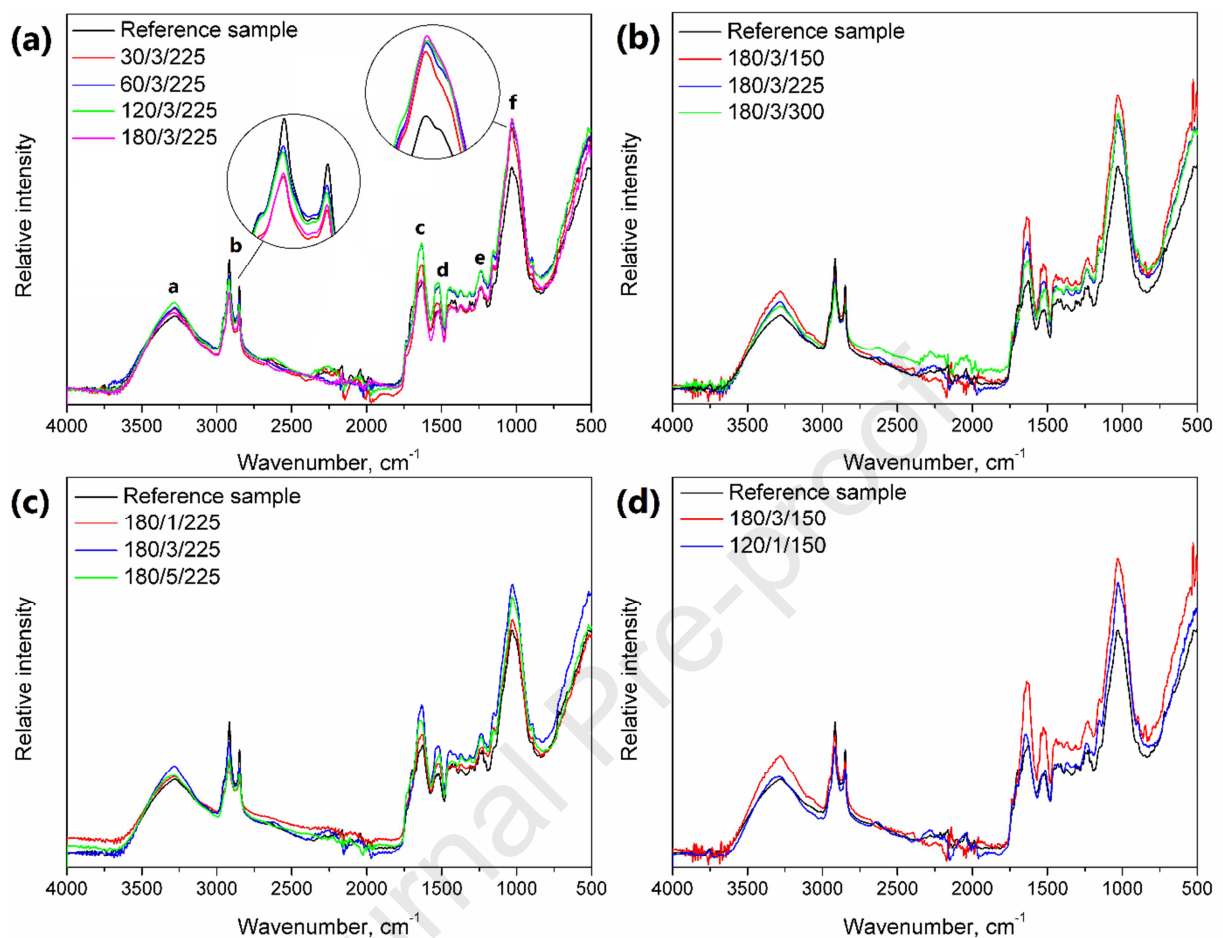




438 in the structure of polysaccharides, as well as the NH stretching vibrations related to the  
439 presence of proteins in BSG (Mohsin et al., 2018). It can be seen that the intensity of this  
440 signal is hardly affected by the extrusion of material. Fig. 4b indicated that the most  
441 significant influence was noted for the screw speed, which directly affects the residence time  
442 and level of shear forces acting on the material. The increase of these forces results in the  
443 greater extent of materials decomposition and oxidation during the extrusion. In the range of  
444 2850-2950  $\text{cm}^{-1}$ , there are observed absorption bands (b) attributed to the symmetric and  
445 asymmetric stretching vibrations of C-H bonds in methyl and methylene groups. The  
446 extrusion treatment decreased the intensity of these bands, and it was more noticeable for  
447 BSG modified at higher temperatures. Such an effect is associated with a greater extent of  
448 polysaccharides decomposition and oxidation. Peaks (c) in the range of 1620-1700  $\text{cm}^{-1}$  were  
449 related to the stretching vibrations of unconjugated C=O and C=C bonds in polysaccharides,  
450 but also to the amide I vibrations (stretching vibrations of C=O and C-N bonds in amide  
451 groups) (Barth, 2007). Their intensity was increased by the extrusion treatment, which points  
452 to oxidation of polysaccharides and the formation of melanoidins in Maillard reactions.  
453 Signals (d) in the range of 1515-1550  $\text{cm}^{-1}$  are due to amide II vibrations – the combination of  
454 NH bending and CN stretching vibrations of amide groups. These signals, similar to (c), were  
455 affected by extrusion treatment. The changes in processing parameters strongly influenced the  
456 intensity of signals (c) and (d). Nevertheless, there was no straightforward impact because of  
457 the contradictory effects of screw speed and throughput, related to the strength of shear forces  
458 and residence time of material in the extruder barrel. Bands (e) and (f) in the range of 1220-  
459 1240 and 1030  $\text{cm}^{-1}$  are associated with stretching vibrations of C-O and C=O bonds present  
460 in structures of polysaccharides (Hejna et al., 2020). The increase in their intensity confirms  
461 the oxidation of polysaccharides during grinding. Slight shifts of positions of signals



462 associated with vibrations of carbon-oxygen are related to the chemical reactions occurring in  
463 the system and resulting in new interactions.



466 **Figure 4.** FTIR spectra of extruded BSG depending on (a) temperature, (b) screw speed, and (c) throughput of  
467 the process, as well as (d) spectra of samples with the lowest and the highest lightness.

468 Generally, presented FTIR spectra confirm the partial decomposition of  
469 polysaccharides during extrusion treatment followed by their oxidation and occurring  
470 Maillard reactions leading to the generation of melanoidins responsible for the color change.  
471 In Fig. 4b, the impact of screw speed on the FTIR spectra is presented. It can be seen that  
472 lower screw speed, hence longer residence time of material in the extruder, increased the  
473 intensity of signals associated with the reactions mentioned above occurring in the material.  
474 The most significant effect was noted for signal (f), which was related to the thermo-oxidation  
475 of material during treatment. FTIR spectra were also influenced by process throughput, hence  
476 the degree of fill, which affects the friction inside the barrel. Similar changes, compared to the

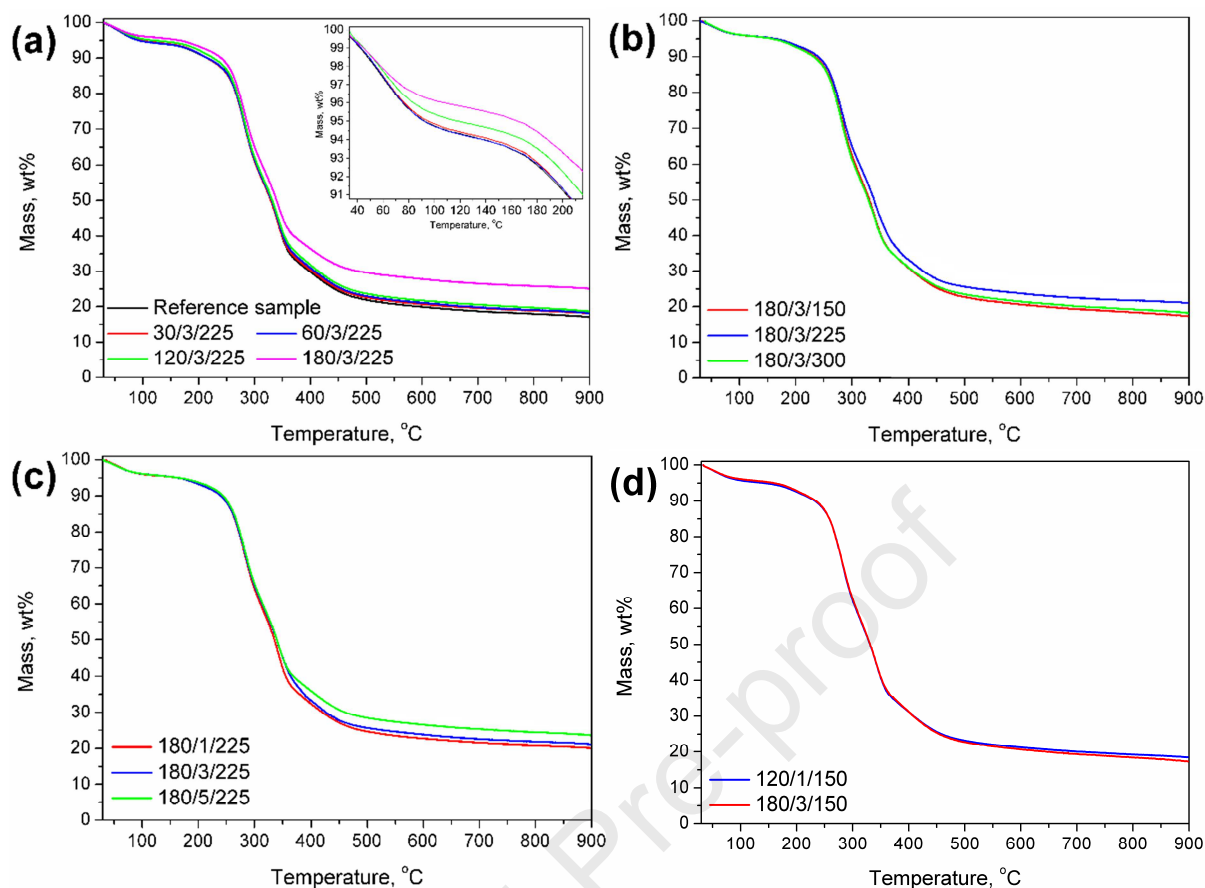
477 reference material, were noted. However, the effect was weaker than for the screw speed,  
478 which suggests that residence time is a more significant factor than shear forces. Moreover, in  
479 Fig. 4d there are shown spectra for the lightest (120/1/150) and for the darkest sample  
480 (180/3/150), which indicates color changes were strictly associated with changes in the  
481 chemical composition of BSG.

### 482 *3.5. Thermal stability*

483

484 The results of the thermogravimetric analysis performed for samples of extruded BSG  
485 are presented in Fig. 5 and summarized in Table 2. It can be noticed that the extrusion process  
486 caused some changes in the thermal stability of the material. The reduction of moisture  
487 content was noted, which was measured as the magnitude of mass loss from 30 to 160 °C. It  
488 probably also included the decomposition of some extractives. However, it is here presented  
489 only for comparison purposes. The lowest content of moisture was noted for sample  
490 180/3/225. It was mainly affected by the temperature of extrusion rather than throughput and  
491 screw speed, which, as mentioned before, show opposite effects associated with shear forces  
492 and residence time. The impact of extrusion temperature on the moisture content can be seen  
493 in Fig. 5a. In general, the presence of moisture in the modified BSG samples was associated  
494 with the hygroscopic character of natural fillers, which was confirmed by other researchers  
495 (Almeida et al., 2018; George et al., 2001). However, the reduction of moisture content was  
496 noted after treatment, which indicates changes in the polarity of the BSG surface.  
497 Nevertheless, even samples extruded at higher temperatures contained over 4.5 wt.% of  
498 moisture, which is still too much for the manufacturing of WPCs. Such values implicate the  
499 drying of filler before the manufacturing of composites, which is commonly applied practice.





500

501

502 **Figure 5.** Thermogravimetric curves of extruded BSG depending on (a) temperature, (b) screw speed, and (c)  
 503 throughput of the process, as well as (d) spectra of samples with the lowest and the highest lightness.

504 Generally, extrusion of BSG and increase of extrusion temperature enhanced BSG's  
 505 thermal stability, which can be expressed by the rise of temperature associated with 5 wt.%  
 506 mass loss during analysis ( $T_{5\%}$ ). Such an effect can be associated with the reduction in the  
 507 content of low molecular weight compounds, which may take part in Maillard reactions or can  
 508 be degraded during processing at higher temperatures. Most of the weight loss of BSG occurs  
 509 between 160 and 500 °C. In this range, there can be noticed two peaks on DTG curves, which  
 510 are related to the decomposition of hemicelluloses and cellulose, ~281 and ~341 °C,  
 511 respectively, which is in line with the results presented by other researchers (Vanreppelen et  
 512 al., 2014). Independently of extrusion parameters, char yield at a temperature of 900 °C was  
 513 very similar in the range of 18-19 wt.%, which is typical for BSG (Mahmood et al., 2013).

514 **Table 2.** Results of thermogravimetric analysis of extruded BSG samples.

| Temperature, °C  | Throughput, kg/h | Screw speed, rpm | Moisture content, wt. % | T <sub>1%</sub> , °C | T <sub>5%</sub> , °C | T <sub>50%</sub> , °C | T <sub>max1</sub> , °C | T <sub>max2</sub> , °C |       |
|------------------|------------------|------------------|-------------------------|----------------------|----------------------|-----------------------|------------------------|------------------------|-------|
| Reference sample |                  |                  | 6.90                    | 43.7                 | 91.7                 | 332.6                 | 281.1                  | 346.8                  |       |
| 30               | 3                | 225              | 6.05                    | 43.0                 | 95.4                 | 329.1                 | 281.2                  | 341.4                  |       |
| 60               |                  |                  | 6.20                    | 42.8                 | 92.3                 | 329.9                 | 281.3                  | 342.0                  |       |
| 120              |                  |                  | 5.50                    | 44.6                 | 117.1                | 332.1                 | 280.7                  | 342.3                  |       |
| 180              |                  |                  | 4.65                    | 45.1                 | 159.3                | 340.0                 | 282.0                  | 340.2                  |       |
|                  |                  |                  | 4.70                    | 45.5                 | 162.9                | 332.4                 | 279.5                  | 341.3                  |       |
| 180              | 3                | 225              | 4.65                    | 45.1                 | 159.3                | 340.0                 | 282.0                  | 340.2                  |       |
|                  |                  | 300              | 4.85                    | 46.8                 | 152.7                | 332.3                 | 281.0                  | 342.0                  |       |
|                  |                  | 1                | 4.85                    | 46.1                 | 157.2                | 335.0                 | 281.4                  | 344.1                  |       |
| 180              | 3                | 225              | 4.65                    | 45.1                 | 159.3                | 340.0                 | 282.0                  | 340.2                  |       |
|                  |                  |                  | 5                       | 4.65                 | 45.2                 | 162.2                 | 340.0                  | 281.2                  | 341.8 |
| 120              |                  |                  | 1                       | 150                  | 5.10                 | 44.7                  | 139.2                  | 332.3                  | 280.7 |
| 180              | 3                | 150              | 4.70                    | 45.5                 | 162.9                | 332.4                 | 279.5                  | 341.3                  |       |

515

516

517 *3.6. Energy consumption*

518 From the industrial point of view, an essential aspect of all processes included in the  
519 production cycle is energy consumption, which has a direct impact on the cost-efficiency of  
520 production. Grinding processes are considered as very energy-intensive. Therefore their  
521 investigations and optimization are significant (Li et al., 2012). On the other hand, twin-screw  
522 extrusion is considered a mechanical treatment method characterized by low energy demand  
523 (Rol et al., 2017). In Table 3, there are presented values of SME calculated according to  
524 equation (20) presented in 2.3. Measurements section. It can be seen that the amount of  
525 energy required to process BSG generally decreases with higher screw speed, which is  
526 directly associated with the residence time of material in the extruder barrel (Kelly et al.,  
527 2006). For higher temperatures, this effect was not so evident and strong, due to the above  
528 mentioned opposite effects of screw speed.

529

530 **Table 3.** Values of specific mechanical energy required for extrusion grinding of BSG under various conditions.

| Temperature, °C | Throughput, kg/h | Screw speed, rpm | Motor load, % | SME, kWh/kg |
|-----------------|------------------|------------------|---------------|-------------|
| 30              | 1                | 75               | 55.5          | 0.872       |
|                 |                  | 150              | 21.0          | 0.660       |
|                 |                  | 225              | 13.5          | 0.636       |
|                 | 3                | 150              | 72.0          | 0.754       |
|                 |                  | 225              | 41.5          | 0.652       |
|                 |                  | 300              | 27.0          | 0.565       |
|                 | 5                | 225              | 76.5          | 0.721       |
|                 |                  | 300              | 52.5          | 0.662       |
|                 |                  | 375              | 37.0          | 0.581       |
| 60              | 1                | 75               | 42.0          | 0.660       |
|                 |                  | 150              | 18.0          | 0.565       |
|                 |                  | 225              | 11.5          | 0.542       |
|                 | 3                | 150              | 59.5          | 0.623       |
|                 |                  | 225              | 35.0          | 0.550       |
|                 |                  | 300              | 24.0          | 0.503       |
|                 | 5                | 225              | 64.0          | 0.603       |
|                 |                  | 300              | 45.0          | 0.565       |
|                 |                  | 375              | 34.5          | 0.542       |
| 120             | 1                | 75               | 23.5          | 0.369       |
|                 |                  | 150              | 11.5          | 0.361       |
|                 |                  | 225              | 8.5           | 0.400       |
|                 | 3                | 150              | 36.5          | 0.382       |
|                 |                  | 225              | 19.5          | 0.306       |
|                 |                  | 300              | 14.5          | 0.304       |
|                 | 5                | 225              | 34.5          | 0.325       |
|                 |                  | 300              | 23.5          | 0.295       |
|                 |                  | 375              | 19.5          | 0.306       |
| 180             | 1                | 75               | 26.0          | 0.408       |
|                 |                  | 150              | 12.0          | 0.377       |
|                 |                  | 225              | 8.5           | 0.400       |
|                 | 3                | 150              | 38.0          | 0.398       |
|                 |                  | 225              | 19.0          | 0.298       |
|                 |                  | 300              | 14.0          | 0.293       |
|                 | 5                | 225              | 29.5          | 0.278       |
|                 |                  | 300              | 20.5          | 0.258       |
|                 |                  | 375              | 17.0          | 0.267       |

531  
 532 At 30 and 60 °C, SME was slightly increasing with throughput, which was associated  
 533 with an increase in friction between the extruder barrel and processed material (Rasid and

534 Wood, 2003). At higher temperatures, friction was probably reduced due to the presence of a  
 535 slight amount of water generated during Maillard reactions. It cannot be neglected that for  
 536 materials processed with higher temperature values, i.e., 120 and 180 °C, low molecular  
 537 weight products migrating from organic particles as well as decomposition products provide  
 538 to the reduction of internal friction, which results in lowered SME values during extrusion.

539 **Table 4.** Dependence of SME on various extrusion parameters.

| Dependence of SME vs |         |                |                 |        |                |                |        |                |
|----------------------|---------|----------------|-----------------|--------|----------------|----------------|--------|----------------|
| Screw speed (R)      |         |                | Temperature (T) |        |                | Throughput (Y) |        |                |
| T, °C                | Y, kg/h | R <sup>2</sup> | Y, kg/h         | R, rpm | R <sup>2</sup> | T, °C          | R, rpm | R <sup>2</sup> |
| 30                   | 1       | 0.825          | 1               | 75     | 0.788          | 30             | 225    | 0.865          |
| 30                   | 3       | 0.998          | 1               | 150    | 0.828          | 60             | 225    | 0.847          |
| 30                   | 5       | 0.992          | 1               | 225    | 0.848          | 120            | 225    | 0.569          |
| 60                   | 1       | 0.890          | 3               | 150    | 0.830          | 180            | 225    | 0.869          |
| 60                   | 3       | 0.985          | 3               | 225    | 0.876          |                |        |                |
| 60                   | 5       | 0.980          | 3               | 300    | 0.886          |                |        |                |
| 120                  | 1       | 0.566          | 5               | 225    | 0.919          |                |        |                |
| 120                  | 3       | 0.769          | 5               | 300    | 0.912          |                |        |                |
| 120                  | 5       | 0.392          | 5               | 375    | 0.916          |                |        |                |
| 180                  | 1       | 0.062          |                 |        |                |                |        |                |
| 180                  | 3       | 0.786          |                 |        |                |                |        |                |
| 180                  | 5       | 0.302          |                 |        |                |                |        |                |

540  
 541 Table 4 presents the values of correlation coefficients ( $R^2$ ) for dependences of SME  
 542 vs. screw speed, temperature, and throughput. It can be seen that the best correlation can be  
 543 observed for the temperature dependence of SME, which is in line with data presented by  
 544 other researchers (Abeykoon et al., 2009, 2014). Lower values of  $R^2$ , observed mainly for the  
 545 dependence of SME vs. screw speed at higher temperatures, are associated with very similar  
 546 values of SME (see Table 3).

#### 548 4. Conclusions

549 The structure and properties of brewers' spent grain subjected to extrusion grinding  
 550 were investigated in order to determine its potential for application as filler for wood polymer

551 composites. BSG was extruded in various conditions to analyze the impact of process  
552 temperature, throughput, and screw speed, which affect the magnitude of shear forces acting  
553 on material and material residence time in the extruder barrel. The most significant influence  
554 was observed for temperature since both throughput and screw speed show opposite effects.

555 In the case of particle size, very important for the manufacturing of WPCs, the rise of  
556 temperature led to more than two-fold size reduction, from 466 and 557  $\mu\text{m}$  for 30 and 60  $^{\circ}\text{C}$   
557 to 203 and 138  $\mu\text{m}$ , respectively for 120 and 180  $^{\circ}\text{C}$ . In the case of lower temperatures,  
558 unfavorable granulation of BSG was observed, which on the other side could be desired, i.e.,  
559 in the food industry. The influence of screw speed, and especially throughput, was not so  
560 significant.

561 Together with changes in chemical structure, particle size noticeably affected the color  
562 of the resulting material, which is crucial for the end-products users. The highest values of  
563 lightness, exceeding 55, were noted for samples extruded at 120  $^{\circ}\text{C}$ , so this parameter was  
564 increased by almost 15% despite occurring browning reactions (whose intensity was moderate  
565 at this temperature). Further rise of temperature resulted in the intensification of Maillard  
566 browning reactions and significant changes in BSG's color. These changes were confirmed by  
567 FTIR analysis and rising antioxidant activity of material, which was associated with the  
568 presence of melanoidins, generated during processing. After extrusion at 180  $^{\circ}\text{C}$ , antioxidant  
569 activity was even doubled compared to the reference sample and 35% higher than after  
570 processing at 120  $^{\circ}\text{C}$ .

571 Higher processing temperatures also resulted in the enhancement of the thermal  
572 stability of BSG samples, which was related to the reduction of moisture content and possible  
573 partial decomposition and evaporation of its products. This phenomenon also favorably  
574 affected the specific mechanical energy required for extrusion of BSG, by reduction of  
575 internal friction inside the extruder barrel. For the temperatures of 120 and 180  $^{\circ}\text{C}$ , SME was





576 in the range of 0.25-0.41 kWh/kg, comparing to 0.50-0.66 for 60 °C, and 0.56-0.87 for 30 °C.  
577 Such an effect may noticeably affect the economic aspect of BSG extrusion.

578 Generally, it was proven that extrusion of BSG might be considered an effective  
579 method for the preparation of fillers for WPC manufacturing, whose properties may be  
580 engineered by proper adjustment of extrusion parameters. Nevertheless, to enhance the  
581 industrial potential of the investigated process, the following issues should be addressed:

- 582 • emissions of volatile organic compounds should be analyzed, both in qualitative and  
583 quantitative terms, to determine the safety of the process considering health aspects,
- 584 • total energy use, related not only to the specific mechanical energy needed for screws  
585 rotation but also to heating the extrusion barrel, should be determined for different  
586 parameters of the process so that the economic calculations could be made,
- 587 • for similar reasons, the amount of water used during extrusion should be calculated and  
588 included in the economic calculations,
- 589 • the influence of BSG melanoidins generated during treatment on the resistance of various  
590 polymer matrices towards oxidation should be evaluated,
- 591 • the possibility of incorporation of additional modifiers enhancing the compatibility of  
592 modified BSG with polymer matrices should be evaluated.

593 These issues should be investigated in further works related to the thermo-mechanical  
594 treatment of brewers' spent grain via the extrusion process.

595 Moreover, the presented results indicate that except for the application in the  
596 manufacturing of polymer composites, modified brewers' spent grain may also be applied,  
597 e.g., as a functional food ingredient. According to the characteristics of the mashing process  
598 (source of BSG) and literature data, BSG contains very significant amounts of dietary fiber,  
599 which is very beneficial from the nutritional point of view. The increase of melanoidins  
600 content resulting from the extrusion treatment significantly increases the antioxidant activity

601 of BSG. Therefore, it could be used as a substitute for conventional flour, simultaneously  
602 reducing the caloric value of food products and enhancing their shelf life.

603

#### 604 **Acknowledgments**

605 This work was supported by the National Science Centre (NCN, Poland) in the frame  
606 of SONATINA 2 project 2018/28/C/ST8/00187 - *Structure and properties of lignocellulosic*  
607 *fillers modified in situ during reactive extrusion.*

608

#### 609 **Conflict of interest**

610 On behalf of all authors, the corresponding author states that there is no conflict of  
611 interest.

612

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- Upcycling of brewers' spent grain (BSG) by treatment of twin-screw extruder
- Evaluation of temperature, throughput and rotational speed on properties of BSG
- Adjustment of extrusion parameters leads to desired appearance and properties of BSG
- Treated BSG was characterized by higher thermal stability and antioxidant activity
- Extrusion of BSG allows extend its applications in wood polymer composites technology

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