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POLIMERY

Enhanced aging resistance of poly(ε-caprolactone)/brewers' spent grain composites

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Abstract: The presented paper investigated the influence of brewers' spent grain (BSG) extrusion parameters on the photo-oxidative resistance of poly(ε-caprolactone)-based wood polymer composites. Filler samples characterized by the higher melanoidin content were more efficient in hindering of polymer degradation, inhibiting the decomposition of the polymer amorphous phase. As a result, deterioration of mechanical performance was limited, which was expressed by the higher values of aging factor for samples containing BSG extruded at higher temperatures.

Keywords: brewers' spent grain, poly(ε-caprolactone), wood-polymer composites, filler modification, aging resistance.

Odporność starzeniowa kompozytów poli(ε-kaprolakton)/młóto browarniane

Streszczenie: W prezentowanej pracy zbadano wpływ parametrów wytłaczania młóta browarnianego na odporność fotooksydacyjną kompozytów polimerowo-drzewnych na osnowie poli(ε-kaprolaktonu). Próbki napełniaczy o wyższej zawartości melanoidyn skuteczniej spowalniały degradację polimeru, hamując dekompozycję fazy amorficznej polimeru. W efekcie, obserwowano wyższe wartości współczynnika starzenia dla próbek zawierających młóto browarniane wytłaczane w wyższej temperaturze, co oznacza ograniczone zmniejszenie właściwości mechanicznych.

Słowa kluczowe: młóto browarniane, poli(ε-kaprolakton), kompozyty polimerowo-drzewne, modyfikacja napełniacza, odporność starzeniowa.

Wood-polymer composites (WPCs) are a class of composites consisting of one or more lignocellulosic fillers and one or a mixture of polymeric materials. Thanks to applying plant-based fillers, these materials may be characterized by, *e.g.*, lower density, higher stiffness, renewable nature, biodegradability, and reduced costs [1]. Moreover, due to lower hardness compared to mineral fillers, WPCs may be processed with reduced machine wear and damage of processing equipment comparing. From an economic and, most of all, environmental point of view, the most beneficial is incorporating waste-based fillers, which are not used in other applications [2–4]. Such an approach enables a noticeable reduction of the environmental impacts of polymer composites, which was indicated by multiple works dealing with the

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waste-based fillers for wood-polymer composites [5–7]. Sommerhuber *et al.* [8] investigated the manufacturing of HDPE/wood polymer composites from virgin and secondary raw materials. Considering six out of seven analyzed environmental parameters (except for the formation potential of tropospheric ozone photochemical oxidants, where no changes were noted), the application of recycled materials was significantly more beneficial than conventional production. Over 65% reduction in global warming potential, eutrophication potential, and acidification potential of land and water were noted for 30% filler loading. However, the most significant decrease was noted for abiotic depletion potential for fossil resources – over 83%. Moreover, the authors linked the material's physical properties with ecological parameters, which led to the conclusion that the more recycled filler was used, the lower potential environmental impacts were.

Therefore, it seems to be very interesting to manufacture polymer biocomposites using brewers' spent grain (BSG), which is the major by-product of the brewing industry generated in the mashing process [9]. According to the statistics [10], European producers manufacture over 41 billion liters of beer each year, generating over 2.5 million tons of BSG, which could be incorporated into polymer matrices. Assuming the average filler share of 50 wt% in WPCs, the current demand on lignocellulosic fillers is around 2.2 million tons annually, so it can be seen that even partial utilization of BSG could be a significant contribution to the WPCs market. However, to obtain WPCs with desired performance, introduced fillers need to show particular properties, among which very important is proper particle size (affecting mechanical performance, barrier properties, biodegradation rate, or appearance of final composite) [11]. Currently applied size reduction methods of fillers are mainly based on processes with periodic character and use various types of mills [12]. More perspective solutions, definitely more cost-effective, should be based on continuous processes, such as extrusion, applied in the presented study.

Our previous work [13] reported the extrusion as an auspicious method for size reduction of BSG and potentially other lignocellulosic fillers. Moreover, except for the reduction of particle size, the temperature and shear forces acting on the material beneficially affected the antioxidant activity of BSG, providing fillers' additional features. Such an effect was attributed to the Maillard reactions leading to the generation of melanoidins. These compounds are often responsible for an extended shelf-life of multiple food products and are commonly treated as natural preservatives [14], which suggests that they may potentially inhibit the oxidative degradation of polymers, especially combined with phenolics present in BSG, which also show antioxidant activity [15]. Our previous works [16, 17] proved such an effect, where melanoidin-rich coffee silverskin was applied as multifunctional waste filler for high-density polyethylene (HDPE) composites. The introduction of this material noticeably elongated the oxidation induction time of HDPE determined by the differential scanning calorimetry (DSC) from initial 20.0 minutes to 54.8, 83.9, and 131.9 minutes, respectively for 1, 2, and 5 wt% filler content.

There are a few reports on the BSG utilization as a filler for polymer composites, which investigated the aging of composites. Revert *et al.* [18] introduced it into polypropylene matrix. Despite insufficient interfacial interactions and unfavorable mechanical performance, the BSG positively impacted the thermo-oxidative stability of the matrix, shifting the oxidation onset temperature even by 23°C. Such an effect was associated with the antioxidant activity of phenolics present in BSG.

Therefore, the presented work aimed to investigate the impact of the BSG modification process stimulating its antioxidant activity on the photo-oxidative aging of poly(ε-caprolactone)-based composites. The presented work should noticeably contribute to the current state of knowledge related to polymer/BSG composites. Hardly any works dealing with this type of composites investigated the modification of filler or the impact of BSG on the oxidative stability of composites.

EXPERIMENTAL PART

Materials

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.

As a matrix for polymer composites, the poly(ε-caprolactone) Capa 6800 from Perstorp (Sweden) was applied. It was characterized by the M_W of 80,000 g/mol and *MFI* of 3 g/10 min (160°C, 2.16 kg).

Thermo-mechanical treatment of brewers' spent grain

BSG was thermo-mechanically modified via extrusion grinding using EHP 2×20 Sline co-rotating twin-screw extruder from Zamak Mercator (Poland), according to patent application [19] and research works, where more details were presented [13, 20]. In the previous works, we presented results for the following ranges of extrusion parameters:

- output – 1, 3, or 5 kg/h,
- screw speed – 75, 150, 225, 300, or 375 rpm,
- barrel temperature – 30, 60, 120, 180, or 240°C.

In the presented work, we applied only selected sample series depicted in Table 1. According to the previous results [13, 20], the temperature of treatment showed the most significant influence on the properties of modified BSG. Samples 120/1/150 and 180/3/150 were analyzed because they were characterized by the most extreme color parameters, which could be related to the antioxi-

T a b l e 1. Parameters applied during thermo-mechanical treatment of analyzed BSG samples

Temperature, °C	Output, kg/h	Screw speed, rpm
120	3	225
180	3	225
240	3	225
120	1	150
180	3	150

dant activity of BSG [21]. For comparison, unmodified BSG was also analyzed.

After grinding, thermo-mechanically treated BSG was left to cool down to room temperature. As presented in our previous work [22], the average particle size of the following BSG samples: 120/2/225, 180/3/225, 240/3/225, 120/1/150, and 180/3/150 was 223, 164, 157, 185, and 204 μm.

Preparation of polymer composites

Polymer composites based on the poly(ε-caprolactone) (PCL) matrix were prepared using EHP 2×20 Sline co-rotating twin-screw extruder from Zamak Mercator (Poland) at 100°C and a rotor speed of 100 rpm. To determine the impact of BSG modification on the performance of composites, filler content in each sample was fixed at 30 wt%. At least 1 kg of each type of material was extruded. Next, composites were subjected to compression molding at 100°C and 4.9 MPa. Samples were molded for 2 minutes and then kept under pressure at room temperature for another 5 minutes to ensure proper solidification. Ready-to-test samples were obtained for tensile tests (sample 1BA according to ISO 527 standard) and dynamic mechanical analysis (40×10×2 mm^3). Composites were coded as PCLX/Y/Z, where X was the temperature of BSG treatment, Y the applied throughput, and Z the screw speed. For comparison, the sample of unfilled PCL was also prepared and was named PCL.

Photo-oxidative aging of polymer composites

Composite samples were subjected to photo-oxidative aging due to ultraviolet radiation (UV-A) according to EN 927-6:2007 standard. During the test, samples for tensile tests were irradiated for 100 and 200 h. Samples were irradiated with UV-A 340 lamps, $\lambda = 360$ nm, which accounts for energy of ~330 kJ/mol. Aging was performed in the air atmosphere at a constant temperature of 23°C.

Characterization techniques

The tensile strength and elongation at break were estimated following ISO 527 standard for dumbbell samples type 1BA. Tensile tests were performed on a Zwick/Roell Z020 (Germany) apparatus with a cell load capacity of 20 kN at a constant speed of 20 mm/min (for tensile strength and elongation at break) and 1 mm/min (for Young's modulus).

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 in the temperature range of -80 to 170°C under a nitrogen atmosphere at a heating rate of 15°C/min. The results were used to calculate the crystallinity degree (X_{cr}) of the composites using Equation (1):

$$X_{cr} = \frac{\Delta H_m}{(1-\varphi) \cdot \Delta H_{m100\%}} \cdot 100\% \tag{1}$$

where:

ΔH_m – melting enthalpy of a sample, J/g

$\Delta H_{m100\%}$ – melting enthalpy of 100% crystalline PCL, J/g, $\Delta H_{m100\%} = 139.5$ J/g [23]

φ – filler weight fraction, %.

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

The color parameters of thermo-mechanically treated BSG samples were determined according to the CIE Standard through $L^*a^*b^*$ coordinates [24]. The analysis was performed using the optical HunterLab Miniscan MS/S-4000S spectrophotometer, placed additionally in a specially designed light trap chamber. Table 2 summarizes the color parameters determined during analysis. Calculations of the browning index were based on the work of Dadali *et al.* [25].

Moreover, to visualize the samples color changes, obtained parameters were converted to the commonly used Adobe RGB color space defined by the three chroma-

T a b l e 2. Parameters determined during color analysis of modified BSG

Parameter	Description/calculation method
Lightness (L^*)	$L^* = 0$ – black; $L^* = 100$ – white
Green/red component (a^*)	$a^* < 0$ – green; $a^* > 0$ – red
Blue/yellow component (b^*)	$b^* < 0$ – blue; $b^* > 0$ – yellow
Chroma	Chroma = $(a^{*2} + b^{*2})^{0.5}$
Hue	$\text{Hue} = \tan^{-1}\left(\frac{b^*}{a^*}\right)$
Browning index (BI)	$BI = \frac{100 \cdot \left[\left(\frac{a^* + 1.75L^*}{5.645L^* + a^* - 0.3012b^*}\right) - 0.31\right]}{0.17}$

ticities of the red, green, and blue additive primaries [26]. The conversion was based on the mathematical operations and was described in detail in our previous work [13].

RESULTS AND DISCUSSION

The impact of photo-oxidative aging on the performance of prepared composites

Fig. 1 presents the impact of photo-oxidative aging on the mechanical properties of prepared composites and unfilled PCL. The incorporation of BSG filler significantly limited the mechanical performance of neat PCL, which was associated with the reduced homogeneity of the material. The tensile strength was reduced from the initial 15.6 MPa to 9.9–11.1 MPa, suggesting the insufficient interfacial interactions between matrix and filler noted in other works [27, 28]. Noticeably the highest ductility was reported for the 180/3/150 sample, suggesting the plasticizing effect of filler [29]. For all the composite samples, a substantial rise of Young's modulus was observed, related to the reduced mobility of PCL macromolecular chains and increased stiffness. Generally, the performance was affected by the type of introduced filler, which was attributed to differences in the chemical structure, probably affected during filler thermo-mechanical treatment.

It can be seen that the main changes during the aging of PCL are associated with the significant reduction of its ductility and stiffening of material. It was noted by other researchers as well [30]. Such an effect could be attributed to the decomposition of the PCL amorphous phase, characterized by the lower density and higher oxygen permeability [31]. Therefore, the amorphous part could be easily degraded by UV radiation.

Nevertheless, the tensile strength was not reduced, which is in line with the results of other researchers. According to Bajsić *et al.* [32], the UV light may induce cross-linking of the PCL structure, resulting in material stiffening. Tsuji *et al.* [33] reported even the increase in tensile strength of PCL

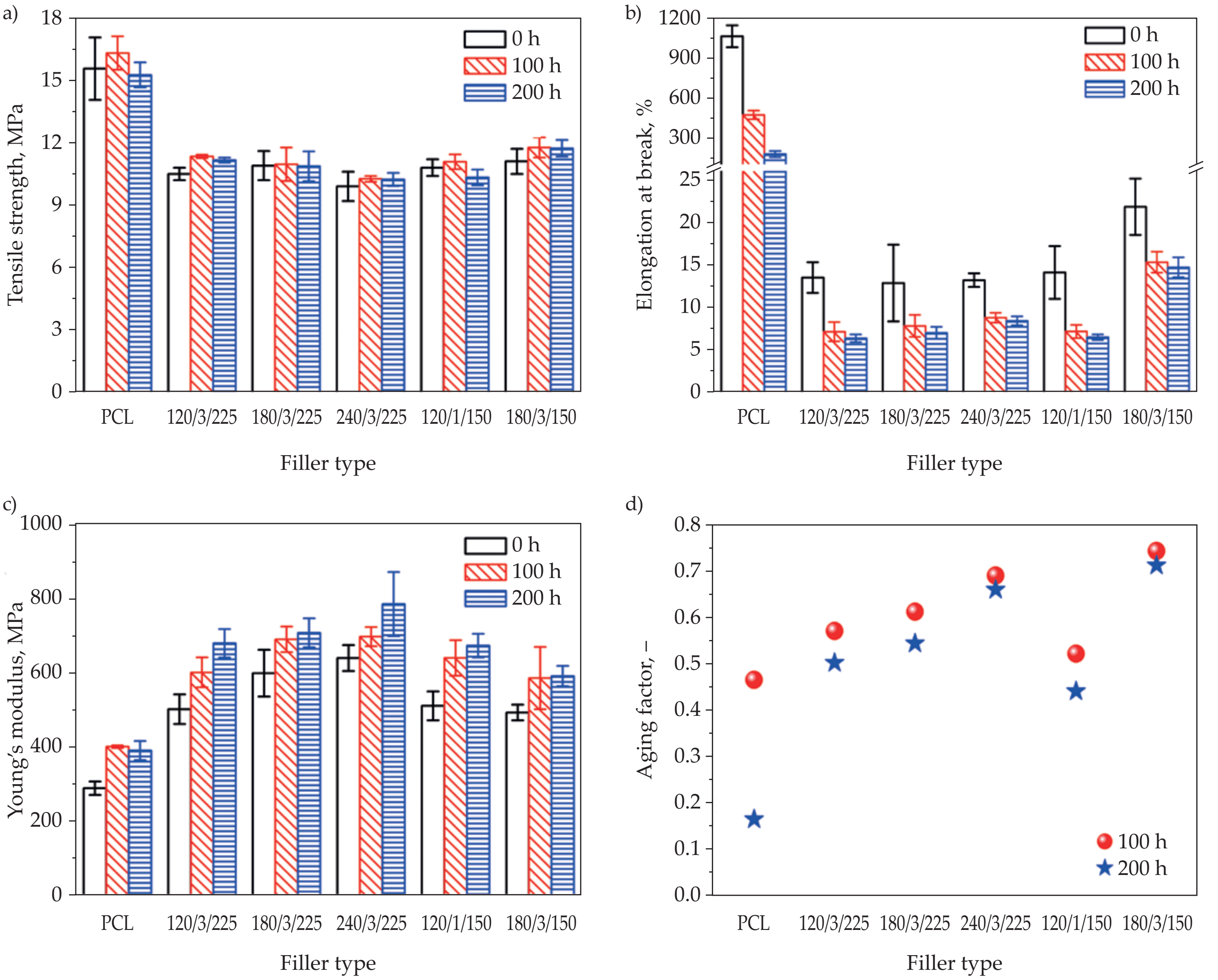

Fig. 1. Influence of UV exposure time of the composites on: a) tensile strength, b) elongation at break, c) Young's modulus, d) aging factor

after UV irradiation for 100 and 200 h despite the significant drop in the average molecular weight, which pointed to the decomposition of the material.

The introduction of brewers' spent grain into the PCL matrix did not influence the character of changes induced by UV radiation. Nevertheless, quantitative differences may be observed, especially considering elongation at break. The irradiation for 100 and 200 h caused the 55 and 83% reduction of this parameter for the neat matrix. Obviously, such an effect is associated with an excellent ductility of unfilled PCL. Nevertheless, for composites, the elongation was decreased by 30–49% and 33–51%, respectively, for 100 and 200 h of exposure. The most significant drop of elongation was noted for composites containing BSG modified at 120°C, while the most substantial effect was observed for 180/3/150 filler. The deterioration was lower for the increasing temperature of BSG treatment. Such an effect may point to the antioxidant activity of filler resulting from the generation of melanoidins in Maillard reactions occurring during thermo-mechanical modification. López-Rubio *et al.* [34] observed that adding another natural antioxidant – β-carotene – may effectively inhibit the deterioration in PCL ductility after UV exposure.

The opposite trend was observed for Young's modulus. The rise of BSG treatment temperature reduced the stiffness increase, which indicated a lower extent of cross-linking resulting from the recombination of PCL macromolecules broken due to the UV irradiation [34]. Such an effect indicated that the BSG modified at higher temperatures was more efficient in inhibiting PCL UV decomposition.

Fig. 1d presents the values of aging factor (*K*) calculated for prepared samples using the following Equation (2) suggested by Marzec *et al.* [35]:

$$K = \frac{(T_s \cdot \varepsilon_b)_{\text{after aging}}}{(T_s \cdot \varepsilon_b)_{\text{before aging}}} \tag{2}$$

where:

T_s – tensile strength, MPa

ε_b – elongation at break, %.

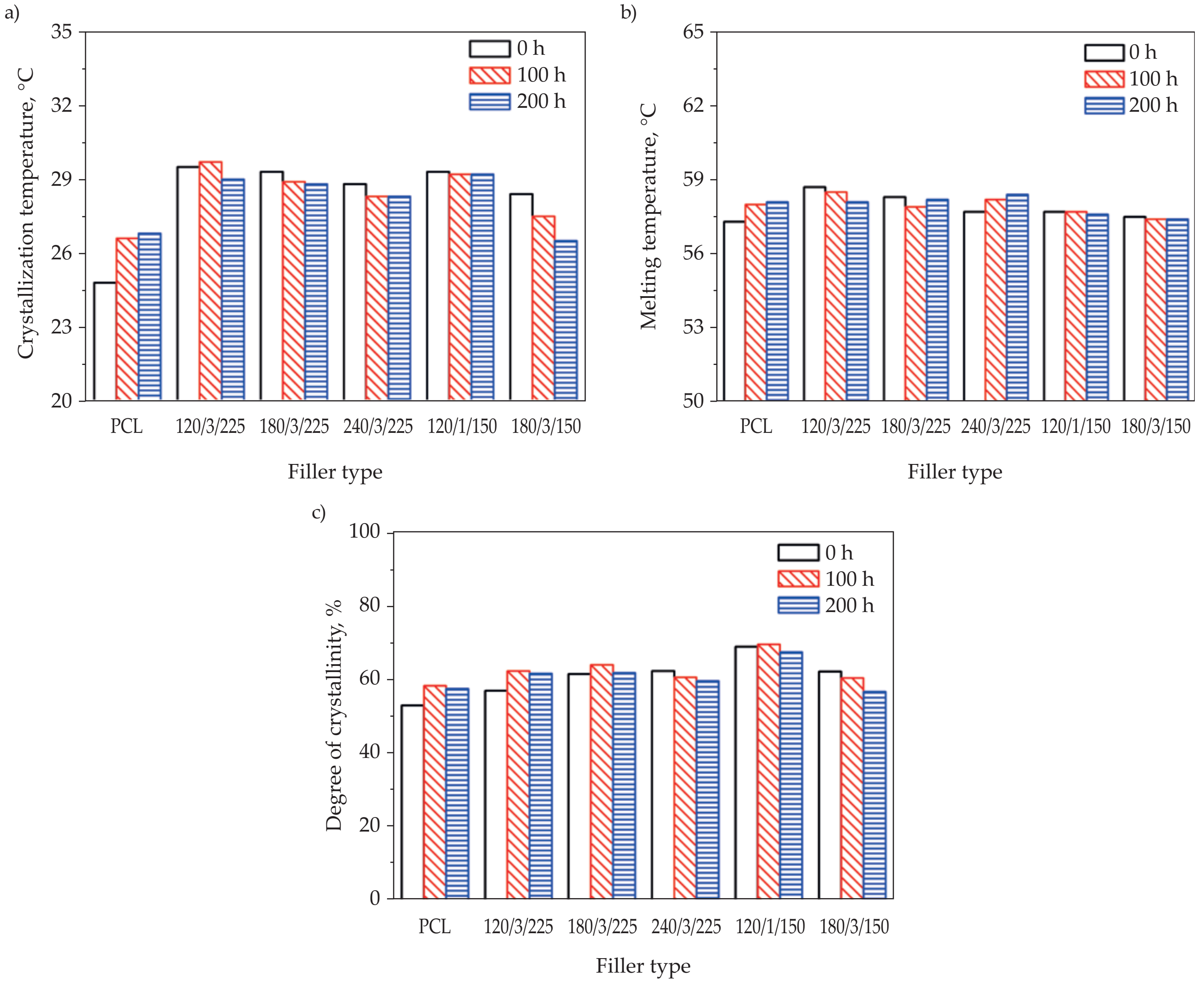

Fig. 2. Influence of UV exposure time of the composites on: a) crystallization temperature, b) melting temperature, c) degree of crystallinity

Calculated values confirmed the beneficial influence of applied fillers on the photo-oxidative stability of PCL composites. Clearly, the increase of the BSG treatment temperature enhanced the resistance of composite materials. The lowest stability was noted for the 120/1/150 sample, attributed to the most gradual drop in elongation at break. Interestingly, the application of 180/3/150 filler was found to be more effective in hindering the unfavorable changes caused by the photo-oxidative aging than 240/3/225 material. Values exceeding 0.70 were noted, similarly to the effect of natural antioxidants like quercetin or curcumin incorporated into epoxidized natural rubber/poly(lactic acid) blends [36]. Such an effect points to the antioxidant activity resulting from the thermo-mechanical modification of BSG.

The above-mentioned changes in the mechanical performance of PCL and its composites after UV exposure are associated with the changes in their thermal properties. Fig. 2 shows the impact of photo-oxidative aging on the melting and crystallization temperatures and degree of crystallinity. Observed changes confirmed that the UV degradation of poly(ε-caprolactone) occurs mainly in the amorphous phase, affecting crystallization behavior. The UV-light exposure usually led to polymeric matrix chain-scission effects, which provided higher mobility of PCL chains during solidification and the ability to create crystalline domains [37]. The increase in T_c was noted from the initial 24.8 to 26.8°C. Similarly, 2°C was observed by Bajsić *et al.* [32] and França *et al.* [30]. This effect pointed to the increased crystallization rate after UV exposure and was confirmed by the increased degree of crystallinity, as suggested by other works [31].

Clearly, the T_c was higher for composites, which could be attributed to the nucleating ability of fillers [38]. Nevertheless, photo-oxidative aging caused its drop for composites instead. Such an effect could be associated with the antioxidant activity of modified BSG and reduced decomposition of the amorphous part of the PCL phase. For composites containing BSG modified at higher temperatures, the degree of crystallinity was maintained or even reduced after UV exposure, which is in line with the observed changes in mechanical performance, *e.g.*, smaller drop in elongation at break. Bajsić *et al.* [32] also reported that the degree of crystallinity of PCL-based composites remained unchanged after UV treatment.

The story behind the inhibited photo-oxidation of PCL/BSG composites

The results mentioned above indicated that thermo-mechanical treatment of BSG resulted in the inhibition of PCL/BSG composites photo-oxidation, pointing to the antioxidant activity of introduced fillers. Such an effect could be attributed to the Maillard reactions occurring during BSG modifications, which result in the generation of melanoidins, a group of complex compounds characterized by noticeable antioxidant activity [13]. This effect is commonly used in food chemistry and technology, where melanoidins are responsible for the extended shelf-life of various products [14]. From the chemical point of view, Maillard reactions occur between amine groups of amino acids and carbonyl groups of sugars, and they are accelerated by elevated temperature [39].

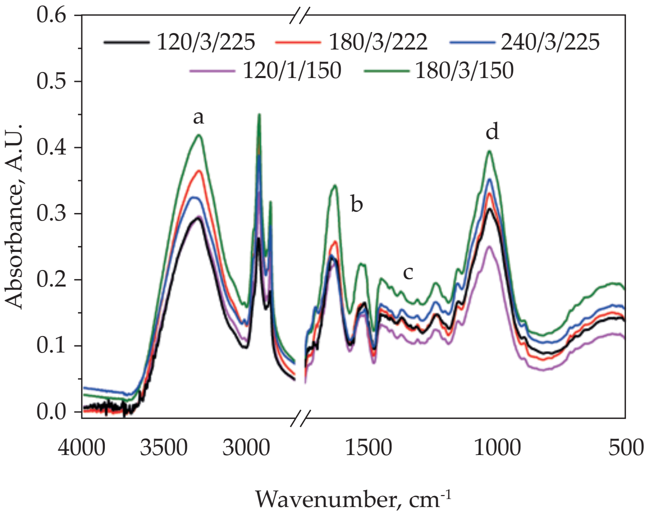

Fig. 3. FTIR spectra of modified BSG samples

To confirm these chemical changes resulting from thermo-mechanical modification of BSG, Fig. 3 presents the FTIR spectra of applied fillers. As we stated in our previous work [13], the spectra of modified BSG samples do not differ qualitatively. Nevertheless, shifts and changes in the magnitudes of particular peaks point to the changes in chemical structure. Signal (a) was attributed to the vibrations of O-H and N-H bonds present in the lignocellulose fraction of BSG and proteins, respectively [40]. Increasing its intensity points to the generation of Maillard reaction products characterized by a significant antioxidant activity. Oracz and Zyzelewicz [41] observed a similar effect during the roasting of cocoa beans and reported a positive correlation between the number of hydroxyl groups and antioxidant activity. The highest absorbance was observed for samples processed at the highest temperatures, especially at 180°C, attributed to the temperature-enhanced yield of Maillard reactions [42]. Other significant peaks (b) were observed in the range of 1520–1640 cm^{-1}. Their presence was related to the amide I and amide II vibrations, mainly attributed to stretching vibrations of C=O and C-N bonds and in-plane bending of N-H bonds [43]. The highest intensity was noted for sample 180/3/150, pointing to the greatest extent of Maillard reactions. Other research works [40, 41] revealed the positive correlation between the magnitude of the peak observed around 1630 cm^{-1} and the antioxidant activity of plant-based materials. In the case of modified BSG, such activity could be associated with the presence of melanoidins, which are well known for their antioxidant properties [39].

Multiple low-intensity signals (c) in the range of 1240–1450 cm^{-1} were attributed to the stretching of C-N and C-O bonds and the bending of the C-H and O-H

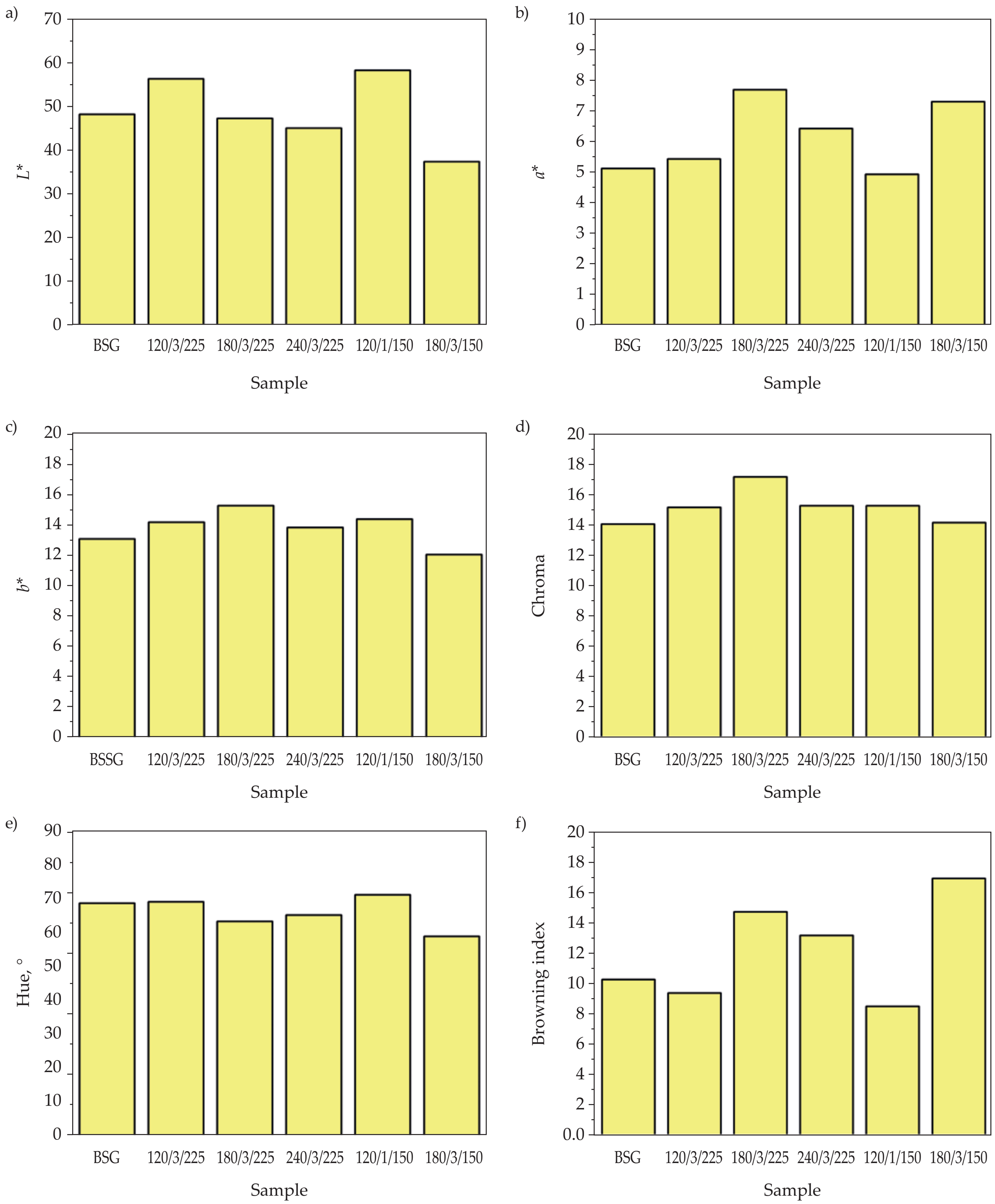

Fig. 4. Values of modified BSG samples: a) lightness, b) *a parameter, c) *b** parameter, d) chroma, e) hue, f) browning index**

bonds [44]. It may point to the enhanced Maillard reactions and caramelization occurring during thermo-mechanical treatment. Strong bands (d) at 1030 cm^{-1} were associated with the stretching vibrations of C=O and C-O bonds. The increase in their intensity with the extrusion temperature may result from the oxidation of polysaccharides during thermo-mechanical treatment.

The observed changes in the FTIR spectra pointed to the partial degradation and oxidation of BSG material during extrusion and suggested the generation of melanoidins in Maillard reactions between amino acids (BSG is characterized by the protein content of ~20% [9]) and reducing sugars.

Fig. 4 shows the results of the color analysis of prepared BSG samples, partially presented in previous work [13]. Considering the final application of modified BSG in polymer composites, color is an important parameter because it affects the appearance of the composite. It is often an essential property for the final recipients of the products made with these composites, *e.g.*, furniture. Moreover, it can be important for the oxidative resistance of wood-polymer composites since the color of the composite is enormously dependent on the color of filler. As mentioned above, during thermo-mechanical treatment, Maillard reactions can occur, leading to the generation of melanoidins. Except for the noticeable antioxidant activity, these compounds are characterized by a dark brown color. Therefore, their content is often estimated based on the so-called browning factor obtained by UV-VIS spectroscopic measurements of properly prepared extracts [20]. In the presented work, the browning index was calculated using L^*, a^*, and b^* color parameters.

Fig. 4 shows that thermo-mechanical treatment mainly affected the lightness of the material, whose decrease pointed to the increasing extent of Maillard reactions and generation of melanoidins [45]. Caramelization reactions could also occur, but due to the relatively low content of simple sugars related to the characteristics of the mashing process, it is somewhat limited compared to Maillard reactions [46]. The most extensive changes in lightness were noted for samples modified at 180°C. Increasing the temperature up to 240°C caused only minor changes. Such an effect could be attributed to the decomposition of reducing sugars and the protein denaturation, hence the lower extent of Maillard reactions.

Considering other color parameters, they were not affected as strongly as lightness by changes in the extrusion parameters. Parameters a^* and b^* in the range of 0–20 (with higher b^*) are usually characterized of brown colors, which was confirmed in the presented case [47]. Due to the influence of multiple factors on color perception, *e.g.*, lightness, the changes in a^* and b^* parameters are often not directly proportional to the visible color changes [48].

Nevertheless, a^* and b^* values may be used to determine other color parameters such as chroma, hue, or browning index. Observed chroma and hue values are also typical for brown colors [49]. However, due to the low color saturation of modified BSG, chroma values were relatively similar and rather low. Considering the hue, the brown colors are characterized with angles in the range of 30–70° [48]. The higher values are typical for more yellow-like colors [50]. Therefore, the decrease in hue angle for analyzed samples could be correlated with the increasing browning index and represented by the "deeper" brown color.

As mentioned above, the content of melanoidins is often estimated based on the browning index [9]. However, this parameter was calculated from color measurements in the presented case, not determined by spectroscopic analysis of proper extracts. It can be seen that it is significantly higher for elevated temperatures of thermo-mechanical treatment. Such an effect is in line with the differences in FTIR spectra between fillers and the aging behavior of particular composite samples.

CONCLUSIONS

The presented paper aimed to investigate the impact of thermo-mechanical treatment of brewers' spent grain in co-rotating twin-screw extruder on the photo-oxidative UV resistance of poly(ε-caprolactone)-based wood polymer composites. To assess it, the changes in mechanical performance and thermal properties were investigated. Moreover, the properties of modified fillers governing the resistance of final composites were analyzed.

Presented modification process, combining simultaneous grinding of filler and its thermo-mechanical modification, should be considered as very promising. By changes in process parameters, the structure and appearance of modified BSG could be adjusted, which, as presented, may significantly impact the performance and stability of wood-polymer composites. Beneficially, during the presented extrusion process, these properties could be easily adjusted. Under more demanding conditions, higher temperature and shear forces, favorable changes in BSG structure were related to the caramelization and mostly Maillard reactions. Such changes enhanced the antioxidant activity of fillers and led to the higher resistance of composites to oxidation expressed by the less pronounced deterioration of the mechanical performance, as proven by the calculated aging factor. The lower extent of degradation was attributed to the hindered decomposition of the amorphous phase of PCL. To sum up, modified BSG could be considered a potential substitute for conventionally applied fillers for WPC, such as wood flour, which could increase the stability of composites.

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