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THE MELT FLOWABILITY AND TENSILE PERFORMANCE OF POLY (ε-CAPROLACTONE)/BREWERS' SPENT GRAIN COMPOSITES AS A FUNCTION OF FILLER MODIFICATION

Abstract: *Nowadays, it is essential to reduce the environmental impact of products and technologies. Such an approach should be highlighted in all research activities. In the case of polymer composites, it can be realized by introducing by-products or waste materials as fillers. An auspicious example of such material is the brewers' spent grain, the major by-product of the beer production. Its chemical composition, relatively similar to conventional lignocellulose fillers, enables its application to manufacturing wood-polymer composites. However, to enhance its compatibility with polymer matrices, it could be modified. Therefore, in the presented paper, the impact of the extrusion grinding of brewers' spent grain on the processing and mechanical performance of polymer composites was evaluated.*

Keywords: *Poly(ε-caprolactone); brewers' spent grain; composites; filler modification; recycling*

Introduction

From an economical and ecological point of view, one of the most auspicious approaches towards manufacturing polymer composites is the incorporation of various by-products or waste materials as reinforcements [1]. Among the potential candidates for fillers, the very promising is brewers' spent grain (BSG) – the major by-product of the brewing industry [2]. According to the market reports [3], European beer production currently exceeds 42 billion liters annually, which generates over 2.5 million tonnes of BSG. In terms of chemical composition, brewers' spent grain is relatively similar to various lignocellulosic fillers used during composites production [4]. Nevertheless, to enhance the

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interfacial interactions, BSG should be modified prior to melt compounding. An important feature of BSG is the relatively high content of proteins, which may provide additional properties to polymer composites [5]. They may act as plasticizers of polymer matrices affecting the material's mechanical performance and its processing by increasing the melt flow index [2]. Moreover, proteins may also participate in Maillard reactions resulting in the generation of melanoidins. Nevertheless, incorporating BSG into polymer matrices also shows some limitations associated with relatively high humidity and large particle size [4]. Regarding the moisture content, BSG is present in the market in dried form, but at a significantly higher cost than the wet form. Moreover, in dried form, it still requires particle size reduction to be efficiently applied as a filler for composites. Therefore, in the presented research work, the influence of the BSG treatment via extrusion grinding on the melt flowability and tensile performance of PCL-based composites was investigated.

Materials and methods

Brewers' spent grain used in the presented study was acquired from Energetyka Złoczew sp. z o.o. (Poland) as a by-product from light lager production. The supplier already dried obtained BSG. Figure 1 presents the appearance of used BSG.

The poly (ε-caprolactone) (Capa 6800, M_w = 80000 g·mol^{-1}) was acquired from Perstorp (Malmö, Sweden). It was selected as a matrix because of its low processing temperature, reducing the energy consumption and decomposition of fillers.

Fig. 1. The appearance of applied BSG before extrusion grinding.

Applied modifications of BSG were described in our previous work [6]. Briefly, treatment of BSG was performed with EHP 2x20 Sline co-rotating twin-screw extruder from Zamak Mercator (Poland) with a screw diameter of 20 mm and an L/d ratio of 40, as presented in our patent application [7]. BSG was dosed into the extruder by a volumetric feeder with a constant throughput of 1-5 kg/h. Screw speed varied from 75 to 375 rpm, respectively, for increasing throughput. Barrel temperature in all zones was set at 120-240 °C. After grinding, samples of BSG were left in order to cool down to room temperature. Samples were coded as X/Y/Z, where X stands for the processing temperature, Y for the throughput, and Z for the screw speed. For the manufacturing of composites, the following BSG types were selected based on previous results: 120/3/225, 120/1/150, 180/3/225, 180/3/150 and 240/3/225 [6]. The average particle size of selected fillers was as follows: 223, 185, 164, 204, and 157 µm.

The preparation of composites was presented in previous work [7]. Briefly, they were prepared in an EHP 2 × 20 Sline co-rotating twin-screw extruder from Zamak Mercator (Poland) at 100 °C and a rotor speed of 100 rpm. Filler content in each sample was 20 wt.%, 30 wt.%, or 40 wt.%. Materials were molded into ready-to-test samples for tensile tests (sample 1BA according to ISO 527 standard). Obtained samples were coded as PCLX/Y, where X stands for the BSG symbol and Y for its content in composite. For comparison, the sample of unfilled PCL was also prepared and was named PCL.

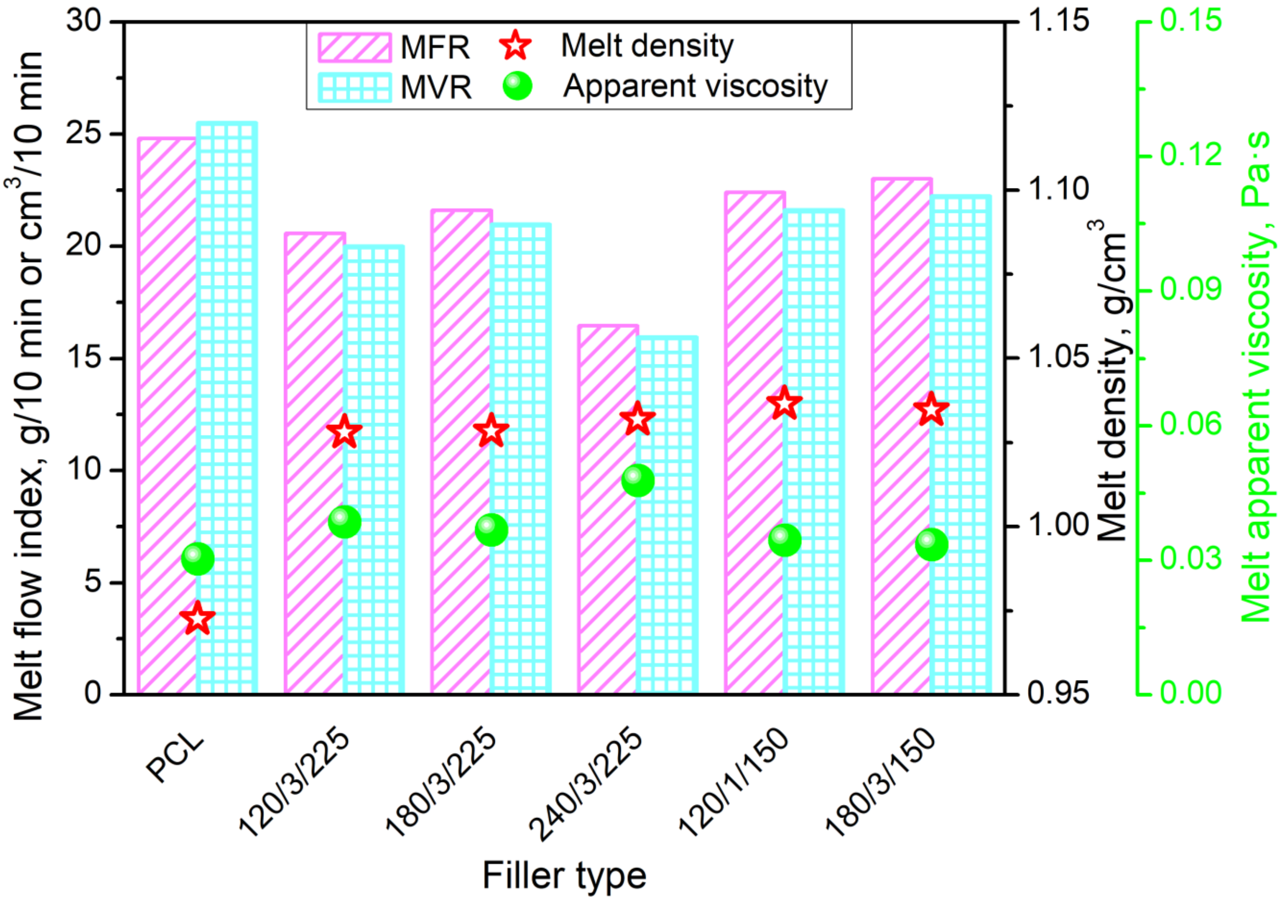
Melt flow index of composites was determined at 170 °C, with a load of 2.16 kg, according to ISO 1133, using Mflow plastometer from Zwick.

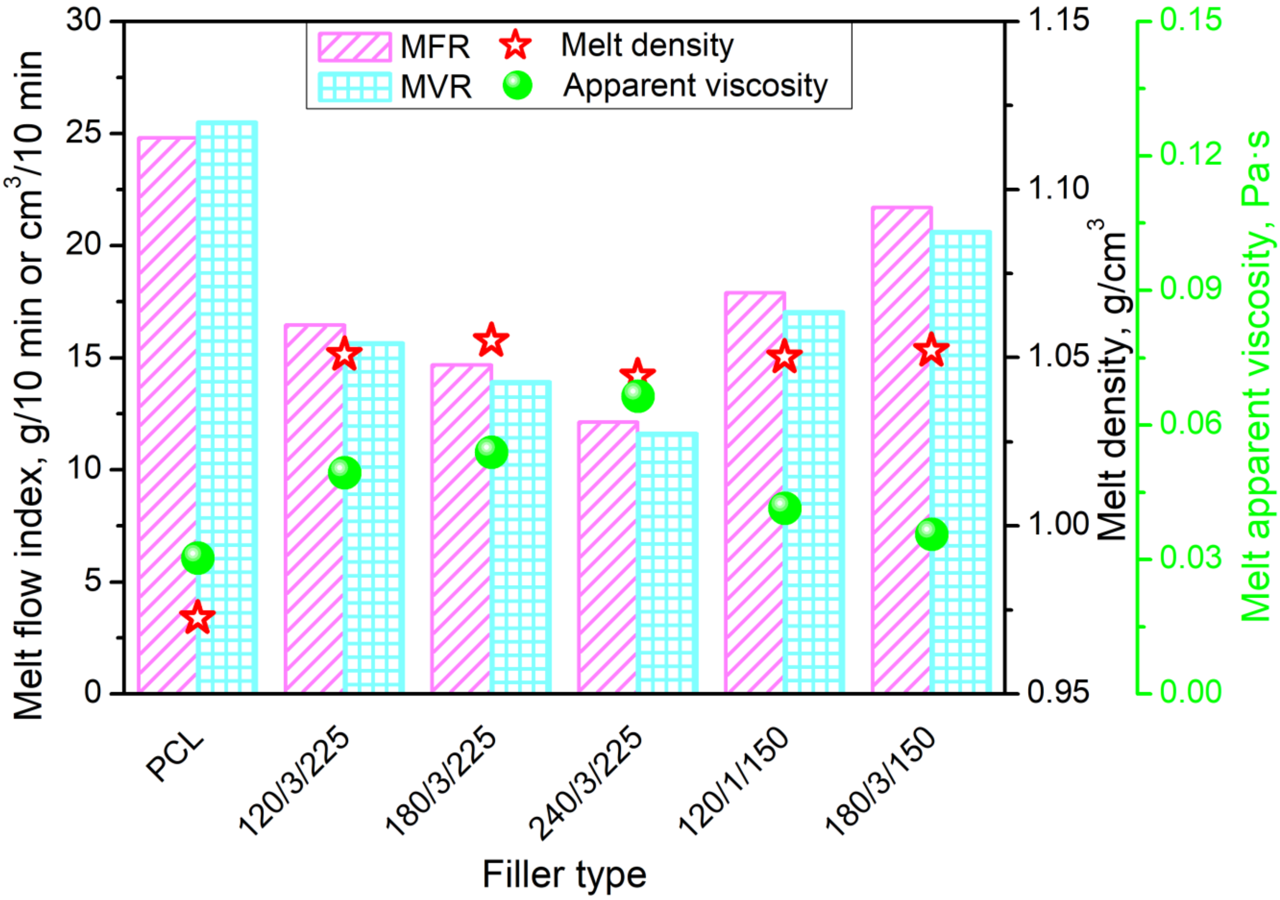
The tensile strength, elongation at break, and elastic modulus were estimated following the PN-EN ISO 527 standard, using the Instron 4465 H 1937 tensile testing machine with an elongation head and an extensometer. Sample type 1BA was used. Tensile tests were performed at a constant speed of 1 mm/min (for elastic modulus) and 20 mm/min (tensile strength and elongation at break). Five samples were analyzed for each specimen.

Results and discussion

Figure 2 presents the impact of type and content of modified BSG on the melt flow properties of prepared composites. For unfilled PCL matrix, values of MFR and

MVR equaled 24.81 g/10 min and 25.51 cm^3/10 min. As a result, the density of PCL melt was 0.973 g/cm^3. The incorporation of fillers resulted in a significant reduction in mass and volume melt flow index, as well as an increase in density. The values of density were similar for all types of fillers, pointing to the very similar filler loading. Moreover, it can be seen that the flowability of material is significantly affected by the applied BSG treatment. For 20 wt% loading of fillers, the drop of MFR and MVR was in the range of 7-34 and 13-38 %, respectively. The lowest values of flow index were noted for composite containing brewers' spent grain extruded at 240 °C, which was related to the highest melt apparent density – 0.0477 Pa·s. This value was almost 58% higher compared to the neat PCL. For higher contents of filler, a similar effect was noted. Despite the smallest average particle size of BSG modified at 240 °C, the melt viscosity was significantly higher than materials filled with other BSG types. Such an effect could be associated with the changes in the BSG surface chemical structure. As described in previous work [6], thermo-mechanical treatment of BSG results in the occurrence of caramelization and Maillard reactions due to the relatively high protein content of this brewing industry by-product [9]. Despite the low content of mono- and disaccharides in BSG, the lower molecular weight saccharides may be generated during extrusion due to the shear-induced breakdown of glycosidic links, especially at higher temperatures [10]. Therefore, at 240 °C, caramelization may occur significantly faster and to a greater extent compared to lower temperatures, especially considering the caramelization temperatures of simple sugars – exceeding 160 °C [4]. Considering the Maillard reactions, they occur at lower temperatures and involve amino groups of proteins and reducing sugars. At 240 °C, their yield was probably reduced due to the decomposition of reducing sugars, as well as the protein denaturation. Therefore, instead of melanoidins, which may act as plasticizers, the high-molecular-weight caramelans ($C_{24}H_{36}O_{18}$), caramelens ($C_{36}H_{50}O_{25}$), and caramelins ($C_{125}H_{188}O_{80}$) were rather produced. Moreover, the denaturation of proteins significantly increases their viscosity [11]. As a result, the flowability of composites was noticeably reduced when BSG treatment temperature was raised up to 240 °C.


MFR
MVR
Melt density
Apparent viscosity
Melt flow index, g/10 min or cm3/10 min
Melt density, g/cm3
Melt apparent viscosity, Pa·s
PCL
120/3/225
180/3/225
240/3/225
120/1/150
180/3/150
Filler type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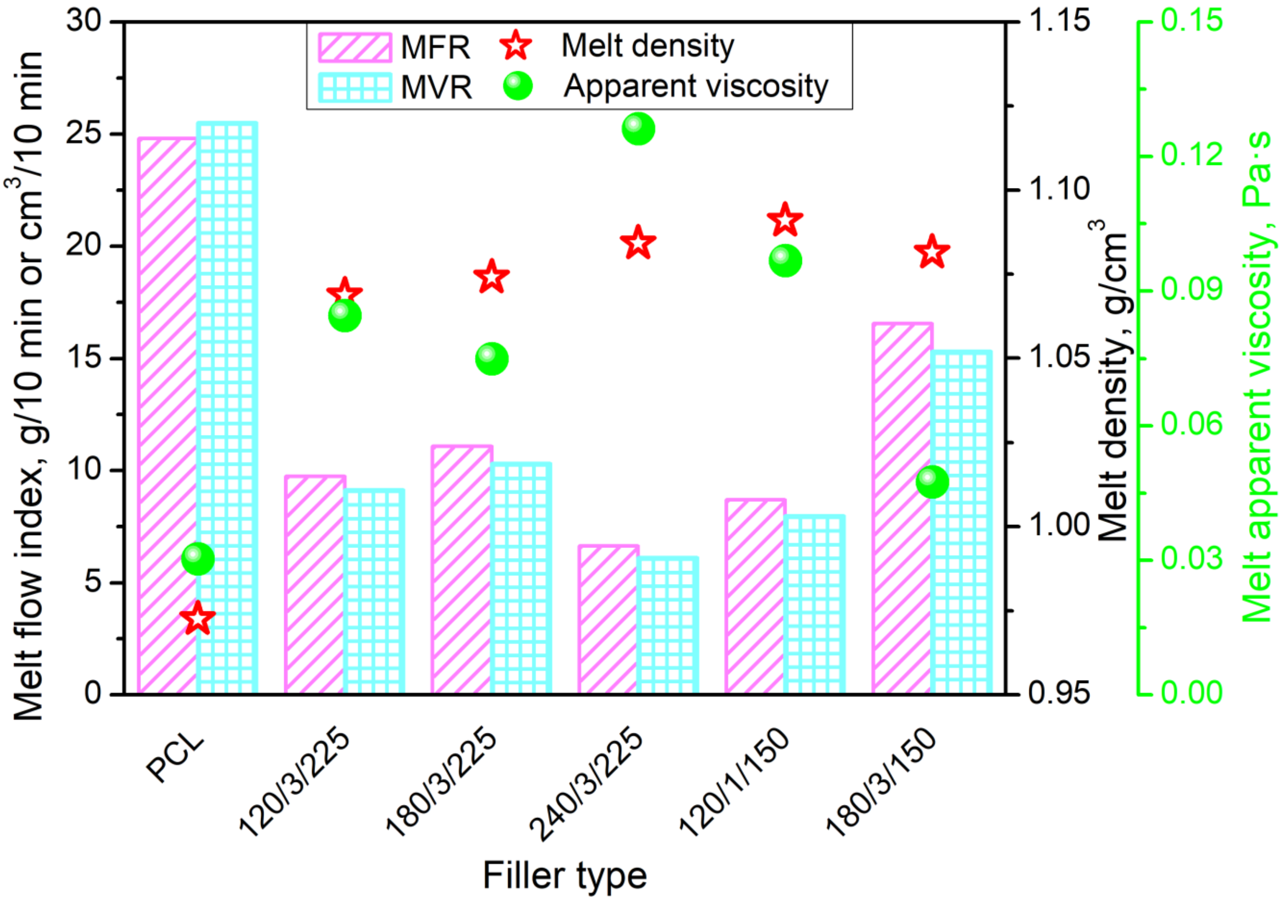

Fig. 2. Mass (MFR) and volume (MVR) flow rates, melt density, and melt apparent viscosity of PCL/BSG composites with 20, 30, and 40 wt% of fillers.

Considering the impact of the extrusion throughput and screw speed, for 120 °C, the effect was not very significant. Composites containing similar loadings of 120/3/225 and 120/1/150 fillers were characterized by similar values of flow index, as well as density and viscosity. On the other hand, for the treatment temperature of 180 °C, the impact of screw speed was very significant. The decrease of its value from 225 to 150 rpm resulted in the significant enhancement of composites' flowability. Such an effect was related to the changes in the chemical structure of BSG described in previous work [6]. The reduction of screw speed noticeably elongated the residence time of BSG in the extruder barrel, which enhanced the extent of Maillard reactions, also expressed by the color of filler. The noticeable browning of the material was noted, which points to the increase in melanoidin content. Obtained results suggest that their presence on the surface of modified brewers' spent grain may induce the plasticizing effect and enhance the material's flowability.

Table 1 presents the impact of filler type and content on the tensile performance of prepared composites. It can be seen that the incorporation of BSG filler significantly reduced the tensile strength of neat PCL. It was related to the high value of tensile strength for the neat matrix and was noted in other works [2,8,12]. At the same time, the substantial rise of Young's modulus was observed, which was related to the reduced mobility of PCL macromolecular chains and increased stiffness of composites.

The tensile performance of composites was noticeably affected by the type of applied filler. The plasticizing effect of 180/3/150 filler observed during the melt flow analysis was mirrored in composites' tensile performance. As a result, these samples showed the lowest values of Young's modulus and the highest values of elongation at break. For composite containing 20 wt% of 180/3/150 sample, the exceptionally high value of elongation at break was noted – almost 460%. It is significantly lower than for neat matrix, so the ductility and homogeneity of the material were disturbed. Nevertheless, compared to other fillers, it was significantly higher.

Table 2

Tensile properties of prepared composites

Filler type	Content, wt%	Tensile strength, MPa	Elongation at break, %	Young's modulus, MPa
-	-	34.6 ± 1.5	1061 ± 82	289 ± 18
120/3/225	20	11.1 ± 0.1	33.2 ± 9.7	469 ± 6
	30	10.5 ± 0.3	13.5 ± 1.8	502 ± 40
	40	9.8 ± 0.2	5.9 ± 0.2	615 ± 27
180/3/225	20	12.8 ± 0.3	33.5 ± 1.8	512 ± 11
	30	10.9 ± 0.7	12.9 ± 4.5	599 ± 63
	40	10.8 ± 0.3	6.1 ± 1.0	677 ± 44
240/3/225	20	11.8 ± 0.7	37.2 ± 9.7	536 ± 63
	30	9.9 ± 0.7	13.2 ± 0.8	640 ± 35
	40	9.1 ± 0.4	9.0 ± 0.4	735 ± 39
120/1/150	20	12.1 + 0.4	31.7 + 6.8	468 + 15
	30	10.8 + 0.4	14.1 + 3.1	511 + 39
	40	9.6 + 0.3	6.3 + 0.5	610 + 23
180/3/150	20	13.5 + 0.1	458.8 + 5.2	465 + 9
	30	11.1 + 0.6	38.5 + 8.9	493 + 21
	40	9.7 + 0.6	15.0 + 2.4	558 + 34

Generally, it can be seen that the modification of brewers' spent grain via extrusion grinding can be considered very auspicious. Depending on the applied conditions of BSG treatment, resulting composites can be characterized by a relatively broad range of potential properties. Therefore, by adjustment of the extrusion conditions, the performance of composites can be engineered.

Acknowledgments

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