

Valorisation of brewers' spent grain for manufacturing of wood polymer composites

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

From economical and, most of all, ecological point of view, the most beneficial is the incorporation of fillers, which are considered as by-products or wastes resulting from the processing of renewable raw materials. Therefore, it seems very interesting for the manufacturing of polymer biocomposites to use the brewers' spent grain (BSG), which is the major by-product of the brewing industry, generated in the mashing process (Hejna *et al.*, 2015). According to The Brewers of Europe Beer Statistics Report from 2018 (The Brewers of Europe, 2018), European producers manufacture over 41 billion litres of beer each year, which results in generation of over 2.5 million tonnes of BSG. Assuming the average filler share of 50 wt.% in WPCs, current demand on lignocellulosic fillers is around 2.2 million tonnes annually, so it can be seen that even partial utilization of BSG could be a major contribution to WPCs market.

Nevertheless, in order to obtain WPCs with desired parameters, introduced fillers need to show particular properties. Among them, one of the most important is particle size, which significantly affects mechanical performance, but also barrier properties, biodegradation rate or colour of modified filler (Sun *et al.*, 2016). Currently applied methods of size reduction of fillers are mostly based on processes with periodic character and use various types of mills (Silva *et al.*, 2011). More perspective solutions, which are definitely more cost-effective should be based on continuous processes, such as extrusion, which was applied in presented study.

The aim of presented study was to investigate the possibility of application of twin screw extrusion as a novel highly effective preliminary treatment method in waste organic fillers production. BSG resulting from the production of light lager was modified using co-rotating twin screw extruder, according to our patent application (Hejna and Formela, 2019). The influence of twin-screw extrusion grinding parameters (temperature: 30-180 °C, screw speed: 75-375 rpm and yield of the process: 1-5 kg/h) on the structure (particle size, chemical structure), colour and antioxidant properties, as well as thermal stability of BSG, which could be further potentially applied as lignocellulose filler in wood polymer composites was investigated. Also, specific mechanical energy required to reduce the particle size of BSG was calculated. Modified BSG was applied as filler for poly(ϵ -caprolactone) (PCL) and poly(lactic acid) (PLA) based wood polymer composites and compared to other, conventionally applied materials.

Table 1. Selected properties of modified BSG samples.

Temperature (°C)	Yield (kg/h)	Screw speed (rpm)	Average particle size (μ m)	Colour	Antioxidant activity towards DPPH (%)
Reference sample			-		36
30	3	225	466		49
60			557		49
120			203		54
180			138		71
180	3	150	204		73
		225	138		71
		300	155		71
180	1	225	149		63
	3		138		71
	5		134		75
120	1	150	134		54
180	3	150	204		73

In Table 1 there are presented properties of selected modified BSG samples. Particle size, hence also other properties of extruded BSG were significantly affected by extrusion parameters. At lower temperatures, agglomeration of particles was noted. It is often observed and desired during extrusion cooking and manufacturing of various cereals or snacks, however in case of WPCs is considered unfavourable. Therefore, considering particle size, temperatures of 120 and 180 °C were favoured, because they allowed to remove the moisture from material, which often causes generation of pores during processing of polymers and polymer composites, deteriorating their mechanical performance. Moreover, increase of process' yield resulted in decrease of particle size, which enables preparation of material showing superior properties with higher efficiency.

Changes in particle size affected also the colour of modified BSG, which is very important for its potential application in manufacturing of WPCs. It is commonly known that reduction of particle size influences light scattering and increases the lightness of material. Other factor affecting this parameter was temperature of the process, which directly affected the intensity of Maillard reactions occurring during extrusion. These reactions result in generation of melanoidins, compounds very important in food chemistry, which significantly impact the colour and antioxidant properties of the material. Generation of melanoidins, as well as the increase of its intensity was confirmed by spectroscopic analysis and browning of extruded BSG. After modification at higher temperatures, BSG showed thermal stability enabling its application as filler in the most commonly used polymer matrices. Moreover, increase of temperature and yield of the process allowed to reduce the amount of mechanical energy required for grinding and modification of BSG, which has to be considered very beneficial from the technological point of view.

Modified BSG was introduced into biodegradable polyesters in order to prepare polymer biocomposites. Incorporation of selected samples of modified filler resulted in the similar mechanical performance comparing to conventionally applied lignocellulosic fillers, such as various types of wood flour. Simultaneously, due to the enhanced antioxidant properties of extruded BSG, prepared biocomposites showed increased durability and stability of their performance after accelerated aging tests. This effect was correlated with the antioxidant activity of particular filler samples. Obtained results indicate that proper adjustment of properties of BSG by adaptation of extrusion parameters may result in manufacturing of wood polymer composites characterized by not only desired mechanical performance and appearance (colour), but also rate of decomposition.

Generally, it was proven that extrusion of BSG may be considered effective method for preparation of fillers for WPCs' manufacturing, whose properties may be engineered by proper adjustment of extrusion parameters. Moreover, modified BSG was found to be very efficient alternative for commercially applied lignocellulosic fillers used in manufacturing of WPCs thanks to its antioxidant properties obtained during modification process.

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