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An Evaluation of the Quality and Microstructure of Biodegradable Composites as Contribution towards Better Management of Food Industry Wastes

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Received: 13 February 2019; Accepted: 9 March 2019; Published: 12 March 2019

Abstract: Biowastes from the food industry can be applied as a usable material after appropriate treatment (i.e., agglomeration). Biowastes are materials that could have better properties if they are mixed. Brewery and oilseed wastes were compressed and evaluated by their quality and microstructure. This article presents the influence of food wastes' type on their biodegradable composite properties. Rapeseed cake and brewer's threshing were used separately and mixed in three different proportions: 30:70, 50:50, 70:30. The data were obtained by mechanical testing on the Instron machine with different pressure forces of 30,000 N and 50,000 N. Strength and elasticity parameters, expansion after the test and in 24 h were estimated. The characteristics such as density, relaxation and compaction after the agglomeration process of biomass allows the selection of the best material and method for optimal composite quality. The results show an upward trend in composite density with decreasing content of brewery waste in a sample. Rapeseed cake can be considered as the material more susceptible to the compaction process. In addition to material properties and its lower density, the reason may be due to the granulometric composition of particles, density and particle size which was confirmed by SEM structure observations. Images of composites were analyzed on the basis of morphological plant tissue structures.

Keywords: agglomeration; food wastes; composites; relaxation; expansion; microstructure

1. Introduction

The actions implemented in the industrial branches should aim to preserve the concept of sustainable development in all of its aspects, namely ecological, economic and social. The continuous improvement of environmental efficiency requires the utilization of by-products generated as a result of the production process. The implementation of these assumptions should precisely define the activities limiting the emission of harmful substances to the atmosphere and water, effective management of energy and raw materials consumption, as well as searching for new solutions in waste management [1].

According to Dulcet [2], the management of brewing threshing poses a significant problem for breweries, in particular in summer when more beer is produced, and reduces the sustainability of the process. The threshing can be pelletized and used as a source of energy, it can be added to fodder or used as a substrate for biogas production [3]. Konrad at al. estimate the energetic value of brewery mash indicating the important role of humidity that decreases its calorific value. Consequently, specific conditions for combustion have to be fulfilled.

The authors also point out that ashes remaining after combustion appear applicable as agricultural fertilizers due to their high content of phosphates [4].

Several aspects of fuel pellet production, and property improvements including torrefaction and the addition of another binder are reviewed by Priyabrata Pradhan et al. [5]. Sperandio et al., in turn suggest the production of pellets and biochar for energetic purposes as a way of utilizing brewer spent grain [6]. The mechanism of brewer's spent grain pyrolysis was investigated in the paper by Borel et al. indicating the possibility of bio-oil production and various chemicals [7].Mostafa et al., in turn, report the effects of pelletization conditions on pellet properties as well as the Energy consumption during the technological operations [8]. This paper is important from the viewpoint of a possibility to estimate energetic efficiency of pellet production [9].

Several Authors propose various other applications of such waste, e.g., Guna at al. propose the application of sugarcane bagasse as a raw material substituting gypsum for the production of biodegradable ceiling tiles [10]. Also, Treinyte et al. propose other type of brewer's waste utilization, namely in composition with biodegradable polymer using the waste to produce encapsulating material for mineral fertilizers [11]. Neither work is devoted to the mixture of various types of food industry wastes, and the resulting properties of mixtures, and mixture derived products. The present study is attempting to partly fill this gap.

Rapeseed cake, a by-product of rapeseed processing, is produced in large quantities and is also difficult to manage. Pressed residues from the production of vegetable oil account for a large part of processed rapeseed, and they are not always effectively utilized [12]. Rapeseed, a biological material characterized by a high energy value and a high protein content, is not easily combustible [13,14].

Brewer's threshing and rapeseed cake can be combined to produce biodegradable composites [15] that may serve as an example of a contribution to sustainability. In our previous work, we analyzed the agglomeration of rapeseed cake without the addition of other components and with organic solvent residues [16,17]. The above materials can be processed and used as a source of energy.

Food wastes are biological materials that can be used as natural composites in industrial applications. The combination of two or more phases with various properties and structures improve composite characteristics and produces materials of a higher quality. Mutually insoluble solid phases can be combined by pressing, i.e., pressure agglomeration [18]. The energetic use of raw materials in the form of pellets or briquettes can be energetically unjustified when during their production, the energy expenditure will be much higher than the energy that may be obtained during their combustion. This situation might also be accompanied by an economic unprofitability. The solution might be the use of an intermediate stage. Biological wastes can be compacted and used for material purposes, e.g., single-use containers. They will find buyers who will cover the costs of their production. After their consumption, they could probably be transformed into pellets or briquettes and finally used for energy purposes. In these cases, however, when they do not find themselves in the process of energy conversion, they are biodegradable. It can be also introduced into the integrated management system described by Eriksson et al. [19] as another step in the promotion of renewable energy and waste utilization.

The agglomeration of food waste, energy crops and fodder crops such as cereal grains and legumes has been studied extensively [20–22], but our knowledge of this process remains limited. The properties of waste material used as biocomposites have also been insufficiently researched. Biocomposites are anisotropic media with a complex composition that is difficult to describe. The density, strength and durability of composites are also difficult to predict [23].

A material's susceptibility to compaction is determined by numerous factors [24], including the chemical properties of composite ingredients. According to some authors, the quality of agglomerated material is influenced by their molecular structure, namely their cellulose and lignin content. Cellulose contributes to hardness, and lignin is responsible for the cohesiveness of composites. Moisture affects the structural plasticity of lignin [25]. Lipid fractions are characterized by a higher energy value, but they can lower the agglomerated material's hardness when added to the mixture in large quantities. In a study investigating the effect of agglomerated material's composition on the strength of the final product, Kulig and Laskowski [26,27] observed that the replacement of lipids with the corresponding amounts of fiber increased hardness by approximately 95%. In experiments analyzing the compaction of wheat and rapeseed mixtures, the above authors reported a negative correlation between the rapeseed content of the mix and the agglomerate's kinetic strength.

In addition to the chemical composition of ingredients, the properties of composites are also influenced by density, moisture content, structure, porosity, particle size, granulometric composition, heat of combustion and energy value [28,29]. According to several authors, the optimal moisture content and smaller particle size of agglomerated materials enhance the quality of the final product [30–33].

The aim of this work is to investigate the pressing conditions and composition of the pressed mixture on the short-term behavior of the obtained products. This behavior determines the stability of the shape of produced composites.

This stability determines the suitability of waste material (rapeseed cake, brewer's spent grain) to be used for the production of utility materials such as ecological saucers, flower pots and so on. Therefore, the susceptibility of materials to the compaction process as a function of their composition, which is the most important stage in their production, was examined. Density, and relaxation behavior were determined as dependent on the percentage of components used, the particle size of the input material and the parameters used for the compaction process (force). A microscopic examination using the SEM technique was used to determine the microstructure of the material. The observed shape of the particles was qualitatively related to the durability of pellets.

2. Materials and Methods

2.1. Materials

The experimental material comprised brewer's threshing—barley husks, a malting by-product, and rapeseed cake. Spent grain was dried in a laboratory drier at 60 °C and ground in a hammer mill with a 5 mm mesh size. Rapeseed cake was produced by cold expression in a single screw press with an 8 mm outlet nozzle at the speed of 50 rpm. The resulting material did not require additional processing.

2.2. Moisture Content and Density

The moisture content of the analyzed material was determined on a drying scale at a temperature of 105 °C until the achievement of constant weight (standard PN-02/8-50092). Material density after agglomeration was determined by measuring the diameter and thickness of the resulting composites with the use of a micrometer screw gauge (with ±0.01 mm readability) directly after agglomeration and after 24 h. The results were used to determine composite expansion (%). The evaluated composites were characterized by significant porosity, but this attribute was not taken into account in the analysis.

2.3. Granulometric Composition and Fineness Modulus

The granulometric composition of the analyzed material was determined in a laboratory mesh shaker with mesh sizes of 4.75, 3.35, 2.36, 1.6, 1.18, 0.85, 0.6, 0.425, 0.3, 0.212, 0.15, 0.1 mm and an analytical balance with $\pm 10^{-3}$ g readability. The average particle size (fineness modulus) of the separated fractions was determined according to Polish Standard PN-R-64798_1989 for both materials applying the formula (Equation (1)) used by Kulig & Skonecki [30]:

$$d_s = \frac{\sum_{i=1}^{i=n} h_i \cdot P_i}{100} \quad (1)$$

where: d_s—average particle size, mm; h_i—average size of mesh openings in two adjacent sieves, mm; P_i—particles retained on a given mesh sieves, %; n—number of mesh sieves.

2.4. Agglomeration Process

Brewer's threshing and rapeseed cake were used to prepare pure samples (100% spent grain and 100% rapeseed cake) and composites with mixture ratios of 70:30, 50:50 and 30:70. Samples of 150 ± 5 mg of the analyzed materials were compressed in the Instron 8802 fatigue testing system equipped with a cylindrical piston with the diameter of 8 mm at compression force of 30 kN and 50 kN, which was equivalent to the pressure of 596.83 MPa and 994.72 MPa. Compression force was increased at the speed of 20 $kN \cdot min^{-1}$, relaxation time (under constant load) was 1.5 min, ambient temperature was 20°C (193.15 K) and relative air humidity was 33%. Every sample was tested in four replications.

Maximum relaxation strength of compressed material was measured by crosshead sensors in the fatigue testing device and registered in the Bluehill2 application. Relaxation strength is the reduction of stress in material subjected to constant strain over a longer period of time at constant temperature. Relaxation strength was determined in a creep test.

2.5. Microstructure Analysis

The surface and fractures of the analyzed samples were observed under the FEI Quanta 200 ESEM scanning electron microscope. Due to the low electrical conductivity of the studied materials, the observations were conducted in the low vacuum mode to avoid complex preparations such as gold plating. The resulting images combine the signals generated by the secondary electron (SE) detector and the back-scattered electron (BSE) detector. Images were viewed at 50-400x magnification.

2.6. Statistical Analysis

A Statistica 13.1 software was used to generate statistical analyses. Statistical inference was performed based on parametric tests. Results were analyzed with the use of ANOVA (post hoc Tukey HSD test of variance analysis).

3. Results and Discussion

Table 1 shows which factors (material, force, particle size) had a statistically significant effect on the dependent variable. Analysis of variance showed the importance of the type of material used for the density of pellets ($p < 0.0001$), expansion of pellets ($p < 0.0001$), and was not significant for relaxation strength ($p < 0.7976$) and particle content ($p < 0.6629$) (Table 1). The strength of relaxation was influenced significantly by the force of agglomeration ($p < 0.0001$). The insignificant influence of the applied force on the density of agglomerates ($p < 0.2841$; $p < 0.1250$) indicates that there is no need to apply more force and therefore higher energy consumption for the agglomeration process. The results of the analysis of variance allow for the conclusion of a statistically insignificant influence on the diversity of the value of the content of the material type.

Table 1. Variance analysis for composite density directly after agglomeration and after 24 h, relaxation strength of agglomerates, expansion of tested agglomerates depending on pressure force and material composition and variance analysis for particle content depending on particle size and material composition.

Source	Density Just after, $g \cdot cm^{-3}$	Density after 24 h, $g \cdot cm^{-3}$	Relaxation Strength, N	Expansion after 24 h, %	Source	Particle Content, %
	p value	*p* value	*p* value	*p* value		*p* value
Material: A	< 0.0001	< 0.0001	0.7976	0.0011	Material: A	0.6629
Force: B	0.2841	0.1250	< 0.0001	0.5203	Particle size: B	< 0.0001
Interaction: A × B	0.5830	0.4681	0.3315	0.7639	Interaction: A × B	< 0.0001

Table 2 presents the results of the average density values whose description can be found in the Sections 3.2 and 3.3.

Table 2. Average values of composite density directly after agglomeration and after 24 h, average relaxation strength of agglomerates, average expansion of tested agglomerates, subject to the applied pressure force and material composition.

Material	Force, kN	Density Just after, g·cm^{-3}	Density after 24 h, g·cm^{-3}	Relaxation Strength, N	Expansion after 24 h, %
100R	30	1.37 [a]	1.33 [a]	84.0 [a]	3.29 [a,b]
100R	50	1.43 [a]	1.39 [a]	121.5 [b]	2.88 [b]
70R30M	30	1.23 [b]	1.14 [b]	74.2 [a]	8.14 [a,b]
70R30M	50	1.23 [b]	1.16 [b]	137.0 [b]	6.13 [a,b]
50R50M	30	1.16 [b,c]	1.11 [b]	84.4 [a]	4.53 [a,b]
50R50M	50	1.16 [b,c]	1.10 [b,c]	129.0 [b]	5.91 [a,b]
30R70M	30	1.09 [c]	1.00 [d]	82.7 [a]	8.20 [a,b]
30R70M	50	1.10 [c]	1.02 [c,d]	136.9 [b]	7.86 [a,b]
100M	30	1.07 [c]	0.98 [d]	82.1 [a]	9.50 [a]
100M	50	1.08 [c]	1.00 [d]	136.6 [b]	8.13 [a,b]

[a,b,c,d] Mean values with identical letters do not differ statistically significantly at $p < 0.05$.

3.1. Granulometric Composition and Fineness Modulus

The results of the mesh sieves analysis are presented in Figure 1. Table 3 presents the results of the statistical analysis. Statistical analysis did not show differences between the materials, which was caused by the large heterogeneity of the material tested. An analysis of variance confirms the strong influence of particle size on their percentage distribution for a given type of material.

The fineness modulus was determined at a mean value of 0.14 for brewer's spent grain and 0.20 for rapeseed cake, which is statistically insignificant. Smaller particles are much more susceptible to mixing with particles of different material, and the resulting composite is more homogenous [34].

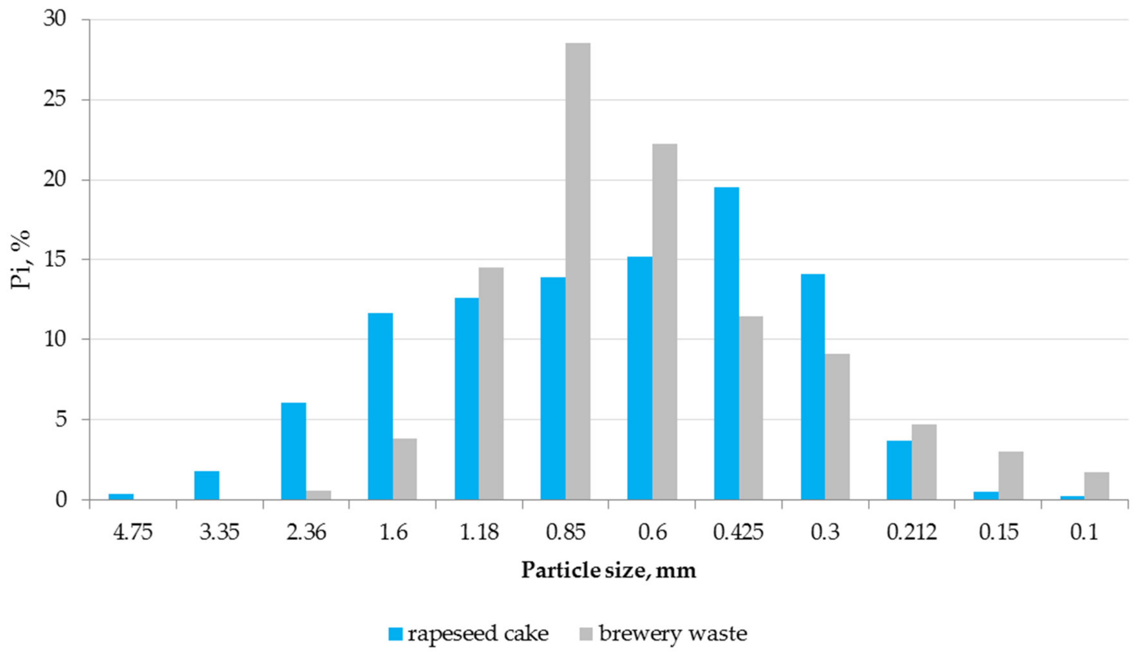

Figure 1. Particle content in separated fractions (%).

Table 3. Average values of particle content in separated fractions according to type of material.

Particle Size, mm	Average Particle Content of Brewery Waste, %	Average Particle Content of Rapeseed Cake, %
4.75	0.05 [a]	0.39 [a]
3.35	0.08 [a]	1.84 [a]
2.36	0.58 [a]	6.08 [a,b,c]
1.6	3.87 [a,b]	11.69 [c,d]
1.18	14.51 [d,e]	12.66 [c,d]
0.85	28.52 [g]	13.92 [d,e]
0.6	22.21 [f,g]	15.2 [d,e]
0.425	11.49 [c,d]	19.56 [e,f]
0.3	9.11 [b,c,d]	14.12 [d,e]
0.212	4.69 [a,b]	3.73 [a,b]
0.15	3.05 [a,b]	0.54 [a]
0.1	1.75 [a]	0.29 [a]

[a,b,c,d,e,f,g] Mean values with identical letters do not differ statistically significantly at $p < 0.05$.

3.2. Moisture Content and Material Density before and after Agglomeration

The moisture content of brewer's spent grain was determined at 12.6% and rapeseed cake at 12.4%. Bulk density before agglomeration was determined at 0.254 kg·m^{-3} for brewer's spent grain, and it was nearly twice as high for rapeseed cake at 0.471 kg·m^{-3}. The density of the analyzed composites measured directly after agglomeration and after 24 h is presented in Table 2.

Directly after agglomeration, the highest density was noted in 100% rapeseed cake and the noted values differed significantly from the remaining measurements. The density of successive samples decreased with a drop in rapeseed cake content, but the observed differences were not significant. The applied compression forces did not lead to significant variations in sample density.

The density of part of the samples decreased 24 h after agglomeration in comparison with the values reported directly after the process but some samples did not show a statistically significant difference. The density of rapeseed cake increased approximately three-fold and the density of brewer's grain cake increased roughly four-fold in comparison with their respective bulk density values before agglomeration. The noted decrease in density 24 h after agglomeration is indicative of the analyzed materials' tendency to relax. Composites achieve their final density 24 h after the process [31]. The low density of brewer's grain cake could be attributed to the shape and size of particles and greater susceptibility to compression. The above could suggest that larger particles are more elastic, less susceptible to compaction and contribute to the formation of more porous agglomerates. Product quality can be improved by using materials with a lower fineness modulus. The reduction in particle size from 3.2 to 0.8 mm improves pellet density [22].

3.3. Relaxation Strength and Expansion of Agglomerated Material

The relaxation strength of the analyzed samples and the expansion of the tested samples 24 h after agglomeration is presented in Table 2. No significant differences in relaxation strength were observed between samples subjected to compression force of 30 kN and 50 kN. The higher the compression force, the greater the reaction force as elastic materials partially return to their initial dimensions, more so if greater compression force is applied.

Significant differences in expansion were reported between 100% rapeseed cake at compressive force of 50 kN and 100% brewer's grain cake at compressive force of 30 kN. The above results could indicate that higher rapeseed cake content lowers pellet expansion. Rapeseed cake has greater compressibility. The remaining indicators did not differ significantly.

3.4. Microstructure

The last stage of the study involved a microstructure analysis of three types of agglomerates—100% rapeseed pellets, composite pellets containing 50% rapeseed cake, 50% brewer's spent grain and 100% brewer's grain pellets.

All of the studied materials were characterized by a significantly non-homogenous structure. The above can be attributed to a higher compilation of the primary structure of biological (plant) materials in comparison with the structure of materials composed of inanimate matter. Primary structures (tissues and organs) of biological materials are nearly completely damaged during technological processes that produce waste (rapeseed cake, brewer's spent grain) or during pressure agglomeration.

Rapeseed cake (Figure 2) is generally composed of two fractions. The first fraction contains particles with a relatively large surface area and small thickness. Those samples have clearly marked edges and fractures that testify to their hardness and brittleness. The discussed fraction is probably composed of fragments of seed coats that are very hard upon maturation. The seed coat of rapeseed comprises several layers of dead slightly elongated cells that are closely packed to produce a tight, hard and thick coat. Seed coat cells are characterized by different cell wall thickness, which produces a layered structure [35,36]. The second fraction is distributed between the particles of the first fraction. It is composed of smaller (<200 μm) particles that closely adhere to one another, which suggests the presence of fat and protein compounds. Rapeseed cake is an abundant source of fat and protein [13]. Those compounds probably contribute to the agglomerate's cohesiveness. The corresponding samples have relatively smooth edges, and large segments of broken material are not observed despite numerous fractures.

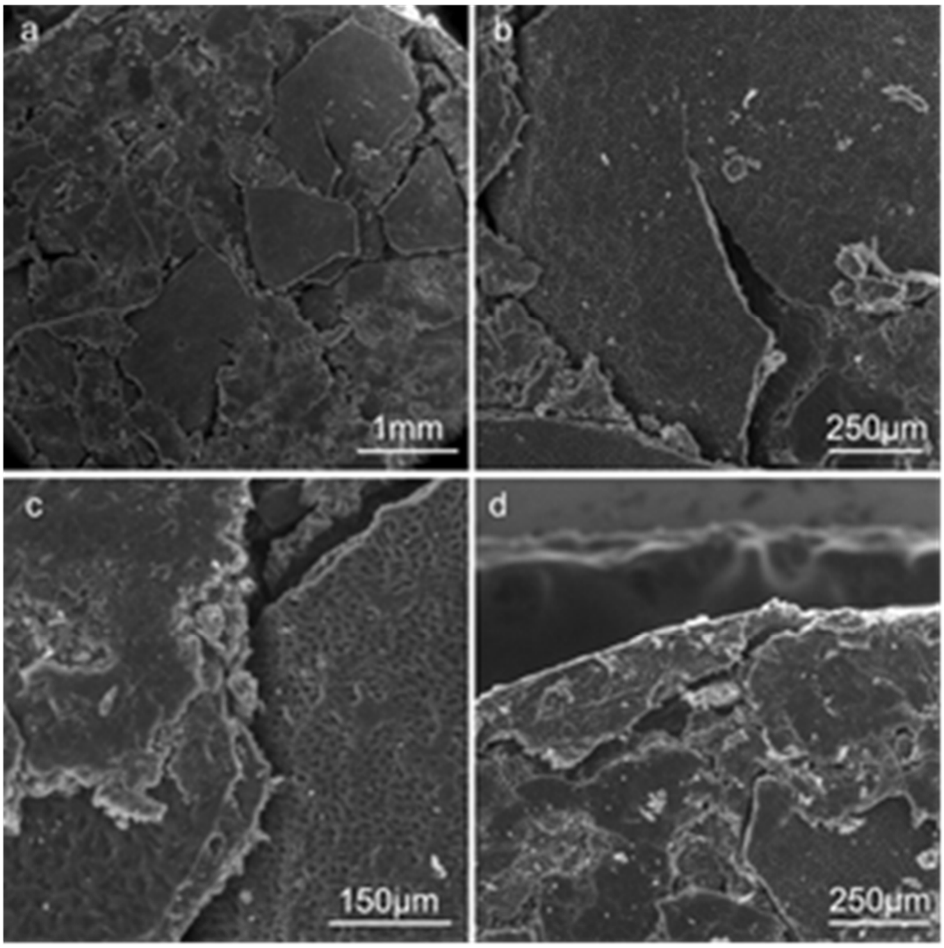

Figure 2. SEM microstructure images of 100% rapeseed pellets.

The surface structure of 100% brewer's grain pellets, characterized by a high fiber content [2], is presented in Figure 3. Those pellets are composed of differently sized particles, including larger, elongated particles that are perpendicular to the applied compression force and smaller particles in between them. A similar structure was described by Bledzki et al. [37]. The particles differ significantly in the structure. Some particles, both longer and shorter, have a fibrous structure, which suggests that they originated from the same barley grain or germ tissue. Other particles are covered by small spherical protrusions that represent characteristic formations on external cells of the seed coat [38,39]. The resulting material is less cohesive, it has a looser structure and its particles are not densely packed. Such pellets have an uneven surface and edges, and they chip easily.

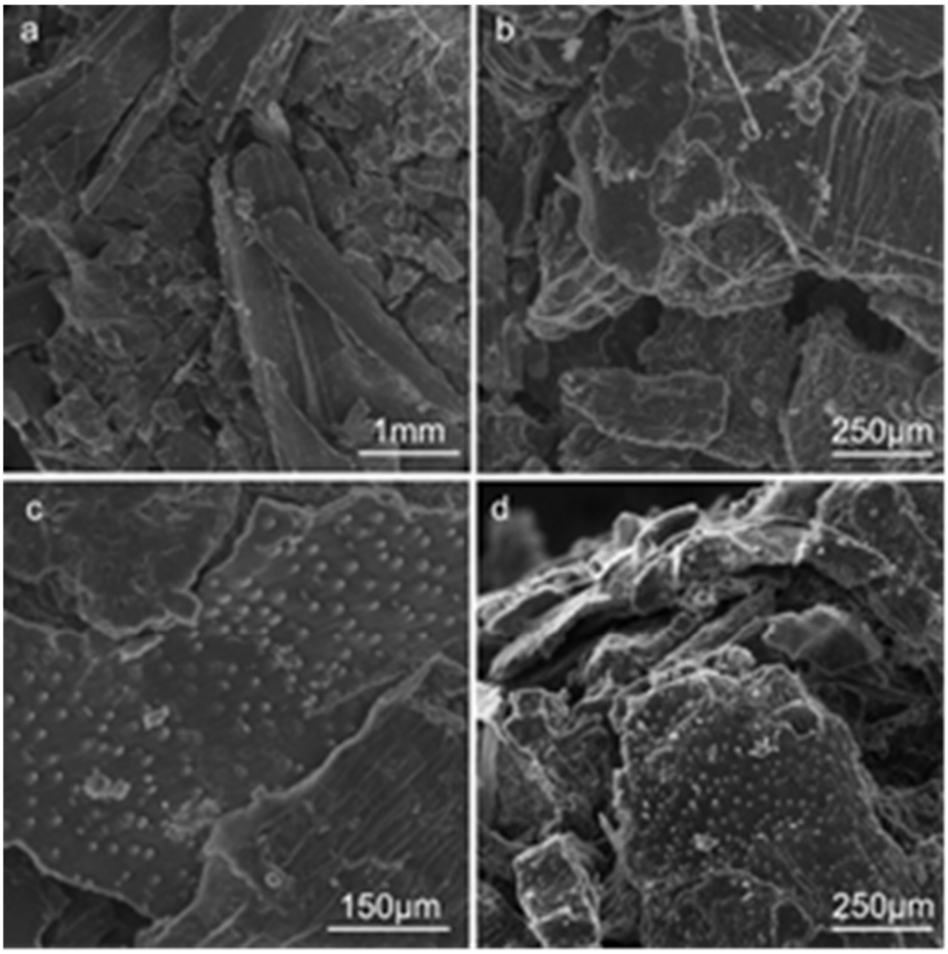

Figure 3. SEM microstructure images of 100% brewer's grain pellets.

Pellets combining brewer's spent grain and rapeseed cake (Figure 4) are characterized by the most uniform and smooth surface in the group of the analyzed agglomerates. Fine particles from rapeseed and barley seeds contribute to a high degree of pellet cohesiveness. Large fragments of brittle rapeseed and barley seed coats chip off, in particular long the edges.

According to Grochowicz et al. [33], materials whose particle size does not exceed 1.6 mm is characterized by the highest cohesiveness and susceptibility to compaction. The analyzed materials contained mostly small particles, the presence of larger particles contributed to fractures and chipping, which increased pellet brittleness and led to a higher energy expenditure during compaction. The results of SEM analyses were connected with fineness modulus values—pellets made of more diverse particles were less compressed. Our results corroborate the findings of Luo et al. [40]. Materials composed of finer particles are characterized by a greater density, and the compaction of fine particles also eliminates empty spaces in the material.

Functional properties of the composed materials will be the subject of further studies as well as the future publications.

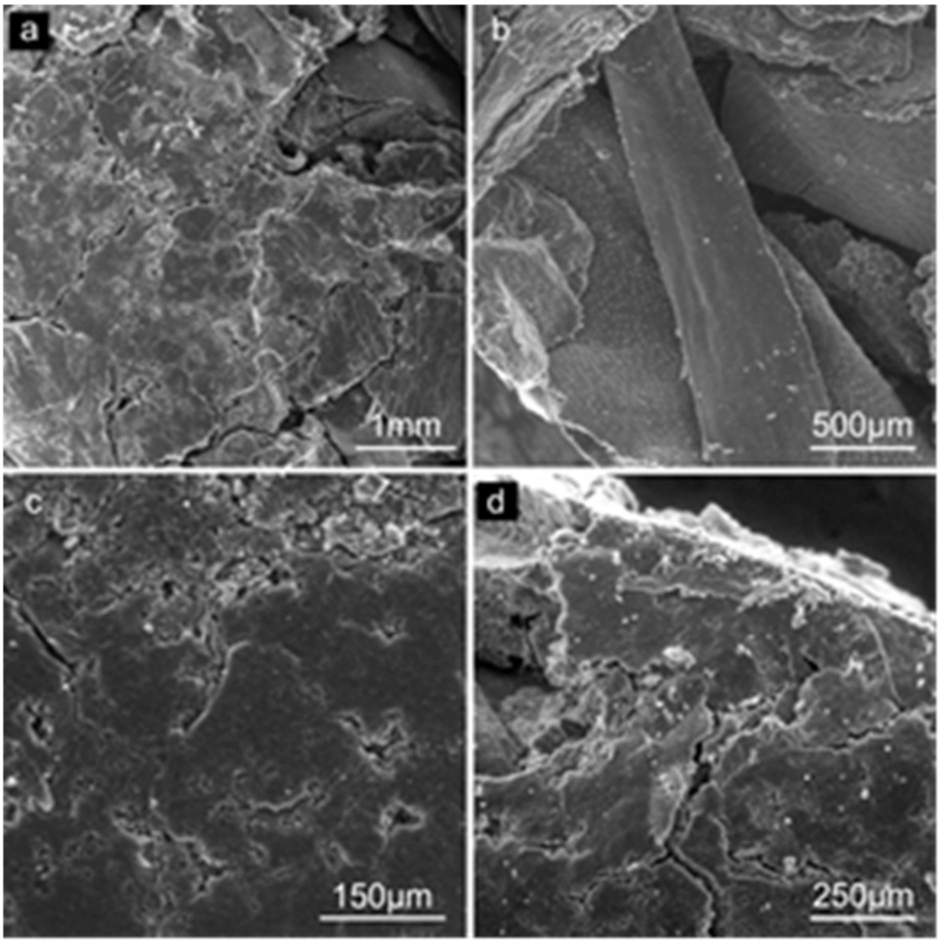

Figure 4. SEM microstructure images of pellets comprising 50% rapeseed cake and 50% brewer's spent grain.

4. Conclusions

The following conclusions can be drawn from the present study:

- The density of agglomerates increases with an increase in the rapeseed content of the analyzed samples, which indicates that rapeseed is more susceptible to compaction. An increase in the density of agglomerated material in comparison with its bulk density before compaction also confirms the above observation.
- The higher the compression force applied to samples of compacted material, the greater the reaction force—elastic materials partially return to their initial dimensions, more so if greater compression force is applied. The mixing ratio of composite pellets did not affect this parameter.
- The expansion of samples subjected to compression forces of 30 kN and 50 kN was significantly higher in most pellets with a higher content of brewer's spent grain. The above can be attributed to the specific properties, lower density, particle shape of brewer's spent grain.
- SEM images provide valuable information about the structure of the analyzed material that significantly affects pellet compression. Density influenced the cohesive strength of pellet particles shown in SEM images. Microscopic images were also analyzed based on the morphological structure of plant tissues in the examined biodegradable wastes.
- The type of grinding process should be adapted to the quality of the grinded material.
- Compounding of various types of food processing residues offers a possibility for utilization of the waste in several paths of applications. The first one is the formation of composed materials that can be used in various applications. Further study in this direction is necessary.
- The other path of mixed waste utilization consists in application for the production of fuels. This path requires careful choice of the mixture composition, possibly with addition of some other

components like wooden sawdust, eventually some content of waxes obtained from depolymerization of polyolefine wastes, as indicated by Król et al. [41].

- The new applications of the mentioned waste contribute to the sustainable development of agriculture and the food industry.

These results may, to a certain extent, improve the waste management system and at the same time allow the implementation of assumptions consistent with the sustainable development policy.

Author Contributions: Conceptualization, P.Z. and I.F.; J.S.; Methodology, K.T. and O.O.; Validation, A.W. and A.Ś.; Investigation, K.T. and O.O.; A.W.; Writing—Original Draft Preparation, P.Z. and I.F.; J.S.; A.Ś, Funding Acquisition, A.Ś. and P.Z.

Funding: This research received no external funding.

Acknowledgments: The authors would like to thank Grupa Żywiec S.A. for supplying brewery wastes and the Department of Agricultural and Forestry Machinery of the Warsaw University of Life Sciences for providing measuring equipment for the needs of this study. The Authors wish to express their deep gratitude to Lublin University of Technology for financial support given to the present publication (Antoni Świć), Warsaw University of Life Sciences (Paulina Zdanowska). The research was carried out under financial support obtained from the research subsidy of the Faculty of Engineering Management (WIZ) of Bialystok University of Technology (Olga Orynycz, Andrzej Wasiak).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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