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Biopolymer Based on Brewing Waste and Extruded Maize: Characterization and Application

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The brewing industry produces more than 100 billion litres a year worldwide and consequently more than 20 million ton of solid waste. This waste is mostly destined for animal feed; however, it ends up being a form of disposal of low added value. On the other hand, furniture and decorations items of a bar can use such waste for its confection, which adds value to the waste and mentions the own beer. This work aimed to develop and characterize a biopolymer obtained from the brewing residue (milled malt after mashing process) and extruded maize to be used as a raw material for furniture and in architectural wall coverings. The proportions of components, time and temperature of the drying process and malt milling were variated in nine treatments. The wood chipboard was used as a control as well. Tensile strength, young's modulus, and elongation at break were analysed, water absorption index (WAI) and water solubility index (WSI) were determined, and the colour was evaluated. After the material was characterised, the better mixtures were applied to make a board used in furniture and wall coverings. The sensorial analysis (visual) was made with 117 non trained panellists to evaluate the new material's acceptance to replace wood-based boards. The main results showed that lower drying temperature, as well as the higher amount of extruded maize, could increase the resistance of the material. There is no significant evidence that particle size affects the material's resistance; on the other hand, it was essential to increase the material acceptability, the smaller was particle size, the better was the acceptance as a substitute of wood-based boards. It was possible to conclude that the material has high acceptance and adequate physical properties to be used in some furniture and covering walls. It is an excellent alternative to increase the value of this industrial waste.

1. Introduction

Plastics are unique materials that fulfil a wide range of functions in society but harm the environment by consuming resources (Wang and Wang, 2017). According to Rutiaga et al. (2005), conventional plastics are obtained from synthetic polymers derived from petroleum and, for this reason, constitute an environmental problem because their high stability can result in more than 100 years of degradation. The higher the global plastic production level, the greater the CO_2 and greenhouse gas (GHG) emissions. In this context, there are several initiatives to minimise this problem, such as the one undertaken by the United Nations (UN), which has sought to motivate the implementation of ecologically correct methods in all countries of the world (Oktavilia et al., 2020).

Technologies have been applied to reuse agro-industrial by-products and, thereby, reduce their disposal, adding value, and minimising environmental impacts (Saraiva et al., 2019). Cereal-based by-products can be applied in the production of bio-based materials, for example, bio-based polyethene (bio-PE), bio-based polyethene terephthalate (bio-PET), bio-based polyurethane (bio-PUR), polylactic acid (PLA), modified starch, cellulose derivatives and polyhydroxyalkanoates (PHA). These compounds have high added value and

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transversal application in the industry, following a circular economy approach and minimal or zero waste generation (Skendi et al., 2020).
Beer is a beverage widely consumed worldwide, made from water, malt, hops and yeast as primary ingredients. The leading global countries in beer production are China, the United States and Brazil. According to the Statistics Portal, beer production has increased in recent years, from 130 billion litres in 1998 to 191 billion litres in 2019 (STATISTA, 2020). Consequently, the waste generated by the brewing industry also increased. The production of beer is characterised by a process that generates many residues (among them, malt cake, brewer's yeast and trub), which have characteristics that make it possible, in many cases, to be reused in other industrial processes (Marsarioli, 2019). In the last few decades, there has been a large increase in the number of micro-breweries globally, adding value to the product. However, the waste from these small factories generally does not have a correct destination, since as they are not large volumes in each factory, there is usually no economic interest in this waste, so solutions for the disposal of this waste on a smaller scale can be useful to reduce the environmental impact of this growing industrial sector and at the same time add value to manufacturers (Monteiro et al., 2019).
The efficient management of these by-products aims to limit environmental pollution caused by their elimination and make these by-products useful. Disposing of waste in an environmentally sustainable manner is a critical challenge, with the development of viable processes for using or valorising brewery waste (Rachwal et al., 2020). Some works have been using beer residues mixed with synthetic or natural resins to produce biodegradable materials. However, these resins have a considerable environmental impact as well as a high cost. On the other hand, corn is a source of starch, natural, cheap, renewable, and biodegradable, is an attractive combination of availability and price. Thus, it is an excellent candidate to produce biodegradable materials.
However, to obtain a material using starch, it is necessary to employ techniques to destroy the original semicrystalline structure of its granules, which can be done by a combination of mechanical and thermal energy. The resulting material is biodegradable and fully decomposable into non-toxic waste (Schlemmer et al., 2014). Thus, maize must undergo an extrusion process for its pre-gelatinisation and thus act as a binding agent in the material. From different sources, starch can be mixed, kept intact, used in various resins as filler or melted to mix compounds. According to Justin et al. (2017), the extruded maize is made in a highly efficient and low-cost material and energy consumptions.
Thermoplastic starch or plasticised starch offers an exciting alternative to synthetic polymers in specific applications (Vroman and Tighzert, 2009). Significant research is carried out to develop a new class of totally biodegradable "green" composites called biocomposites (Netravali and Chabba, 2003). Starch can be used as a biodegradable polymeric compound. Degradation occurs by hydrolysis in the acetal bond by enzymes. Amylases attack the α-1,4 bond while glycosidases attack the α-1,6 bond. Degradation products are non-toxic (Vroman and Tighzert, 2009).
The traditional industrial production model (extraction, production, consumption and waste) has proved unsustainable in the context of the current market, of technology, of the quest for conscious production. The new way of thinking about production fits the circular economy concept, which proposes a behavioural change in the way of consuming and using natural resources and waste. Important actions in this circular economy scenario are the change in product design and consumption, in the process of raw materials and waste exploitation and the conflicting action between environmental sustainability and economic growth (Cosenza, 2020).
The production of materials with the addition of industrial residues and reducing the environmental impacts caused by the plastic industry and its chain can contribute significantly and add value and reduce these industries' environmental impact. Therefore, this work aimed to develop and characterize a material produced with beer residue and extruded maize.

2. Material and methods

2.1 Materials

To obtain ground and standardised beer residue, the used malt residue was supplied by a small local brewery (Maringá, PR, Brazil). After the mashing process of a pure malt lager, the resulting residue was immediately dried in an oven at 70 °C with air circulation for 48 hours, the grinding was done in a hammer mill and separated into three different granulometry (3.5-6, 6-14, 14-28 mash) and later stored in polypropylene bags until the moment of use.
Corn grits, used to obtain the milled corn extrudate, were provided by Nutrimilho (Maringá, PR, Brazil) and extruded according to Monteiro et al. (2016) using IMBRA RX50 single screw equipment (INBRAMAQ, Ribeirão Preto, SP, Brazil) with 50 mm diameter and 200 mm length. The die plate had two holes of 3 mm diameter, and extrusion parameters were 20 A of motor amperage, a feed rate of 12 $g.s^{-1}$ and a screw speed

of 90 rpm. After the extrusion, the extrudates were ground, and the 60-80 mesh fraction was separated and later stored in polypropylene bags until use.

2.2 Material production process

To prepare the biomaterial, beer residues were mixed with the extruded ground corn in the proportions and granulometry shown in Table 1. Experimental design of material production, with 25 g of distilled water was added and homogenised manually until a uniform mixture was obtained. Subsequently, the mixture was added in a metallic tray 15 cm in diameter and pressed by a hydraulic press at 7 ton, and it results in a 40 kg/cm^2 pressure for 300 seconds. The materials were then transferred to greenhouses at the respective temperatures provided in the experimental design (next section) for 24 hours. Finally, the samples were conditioned in a dryer for 48 hours before analysis.

2.2.1 Experimental design

The proportions of components, the temperature of the drying process and particle size of waste malt milled were variated in eight treatments. It was made a central point in triplicate. Table 1 shows the experimental design of material production.

Table 1: Experimental design of the material production process

Treatment	Malt waste (g)	Extruded maize (g)	Dry temperature (ºC)	Particle size of malt waste (mash)
T1	55	45	45	14-28
T2	55	45	45	3,5 – 6
T3	55	45	105	14-28
T4	55	45	105	3,5 – 6
T5	85	15	45	14-28
T6	85	15	45	3,5 – 6
T7	85	15	105	14-28
T8	85	15	105	3,5 – 6
T9	70	30	75	6 – 14

2.3 Material characterization

For the material characterisation, the sample was cut into specimens with 10 x 100 mm dimensions.

2.3.1 Density

Specimen’s thickness was determined using a digital micrometre (0.001 mm resolution, Mitutoyo, Japan). Five points of each specimen area were evaluated, and the volume was calculated using the average thickness with specimen dimension. The mass of specimens was evaluated in an analytical balance.

2.3.2 Tensile strength

The mechanical resistance was analysed using a Universal testing machine (model DL1000, EMIC, São José dos Pinhais, Brazil). Each sample was loaded by 100 kgf at 1 mm*s^{-1}, with probe angled at 135° and analysed according to ASTM D1037-12 (ASTM, 2012), with some modifications.

2.3.3 Water absorption index (WAI)

The Water Absorption Index of the samples was evaluated according to Ayrilmis et al. (2009) with modifications made by Monteiro (2019). To evaluate WAI, the specimens were dipped in water, fast dried, and weighed (initial weight), immersed in distilled water (30:1 water/sample w/w) for 24 h at 25 °C, fast dried again and weight (final weight). The WAI is calculating by the division of final weight by initial weight. The tests were conducted in triplicate.

2.3.4 Colour

Colour was evaluated using a Minolta Chroma Meter CR-400 colourimeter with D65 illuminate as the reference, with readings in three-point each sample for each treatment. Results were expressed by the CIELAB system, with values of L*, a* and b* whose L* values. The nine treatments were evaluated.

2.3.5 Acceptance

The materials' acceptability test was made in a virtual environment by 117 untrained testers (37 male and 80 females from 18 to 48 years old, mean 28 years old). The samples were photographed in a 56 Megapixels camera to make the appearance evaluation. All eight samples and three repetitions of the central point were presented, coded with random numbers. To evaluate appearance's overall acceptability, the 11-point structured hedonic scale was used, where 0 represented the minimum score 'disliked extremely' and 10, the maximum score 'liked extremely'. The Research Ethics Committee approved these tests of the State University of Maringa (CAAE 18718013.3.0000.0104).

2.3.6. Statistical analysis

All data were treated statistically from the analysis of variance (ANOVA) with subsequent analysis of the Tukey tests' means at 5 % probability and correlation test. The statistical tests were made using software Sisvar 5.6 (Ferreira, 2011).

3. Results and discussion

Table 2 presents the results obtained for density, mechanical resistance, and water resistance (WAI). The results obtained for density and mechanical resistance show a significant correlation (Pearson, p-value=0.00) between them (r=0.76). In this way, it is possible to affirm that the increase in density contributed positively to the increase in resistance. However, it was not the only aspect that defined the resistance.

Table 2: Physical properties of the material

Treatment	Particle size of malt waste (mash)	Density (g.mL)	Mechanical resistance (Kgf)	WAI
T1	14-28	0.89^{ab}	21.95^{b}	2.69^{a}
T2	3,5 – 6	0.94^{a}	27.32^{a}	un
T3	14-28	0.85^{b}	14.05^{c}	1.64^{c}
T4	3,5 – 6	0.72^{d}	10.15^{d}	un
T5	14-28	0.82^{bc}	5.37^{e}	2.97^{a}
T6	3,5 – 6	0.78^{c}	10.75^{d}	un
T7	14-28	0.83^{bc}	6.37^{e}	2.18^{b}
T8	3,5 – 6	0.65^{e}	4.14^{e}	un
$T9_1$	6 – 14	0.79^{c}	10.81^{d}	un
$T9_2$	6 – 14	0.82^{bc}	10.13^{d}	un
$T9_3$	6 – 14	0.83^{bc}	10.67^{d}	un

Means with different letters in the same column are significantly different ($P \leq 0.05$).
un – undetermined (the sample was completely dissolved)

Based on the statistical analysis of the data, it was possible to identify that the granulometry of the raw material was not an important factor for increasing the resistance of the material, which differ from the work of Mikalouski et al. (2014) which reported an influence of the granulometry in the expansion index of the samples. On the other hand, the increase in extruded maize in the mixture has contributed positively to the increase in the material's resistance.

Water absorption was not evaluated for seven samples because they were completely dissolved. For the other four samples, the values are too high indicating that the material is not suitable for water-resistant functions. Compared with the results found by Monteiro et al. (2019), the results are lower. Low water resistance is a disadvantage compared to more resistant materials; however, this can be easily solved using a sealant to be applied to the material after its production, if it requires waterproof resistance.

Table 3 presents the results of the material appearance analysis. The colour tests showed that the malt residue's granulometry had little influence on colour. On the other hand, the increase of the proportion of extruded corn in the mixture, as expected, increased the intensity of yellow in the sample. The drying temperature was the factor that most interfered in the sample's staining, especially the samples that dried at 105 °C, as can also be seen in Figure 1. Figure 1 shows the appearance of the materials obtained in the eight treatments, as well as the repetitions at the central point (T9).

Figure 1: Appearance of material

It was not possible to establish a relationship between the samples' instrumental colour parameters and sensorial acceptance. By the sensorial acceptance of appearance, the materials produced with finer granulometry (14/28) had significantly higher acceptance then the thicker granulometry (3.5 – 6). The drying temperature also exerted influence in the evaluation of appearance.

Table 3: Appearance of material

Treatment	Colour			Sensorial acceptance
	L	a	b	
T1	50.34 (1.74)	2.36 (0.26)	24.78 (0.19)	7.16^{ab}
T2	53.03 (2.71)	0.73 (0.23)	26.24 (1.86)	4.99^{c}
T3	41.17 (0.94)	5.90 (0.76)	22.65 (0.32)	7.39^{a}
T4	39.33 (0.78)	6.78 (0.59)	22.48 (1.56)	6.35^{b}
T5	53.39 (1.55)	3.01 (0.46)	24.84 (0.07)	7.25^{ab}
T6	53.58 (1.79)	1.29 (0.17)	24.34 (1.54)	5.89^{b}
T7	41.25 (1.57)	6.72 (0.35)	23.49 (1.01)	7.83^{a}
T8	40.92 (2.60)	7.47 (0.60)	25.41 (1.13)	7.01^{ab}
$T9_1$	52.75 (1.06)	1.28 (0.42)	24.41 (1.96)	5.76^{bc}
$T9_2$	53.88 (1.76)	0.85 (0.33)	24.29 (0.87)	6.02^{b}
$T9_3$	55.46 (1.55)	1.14 (0.11)	25.00 (1.55)	6.23^{b}

Means with different letters in the same column are significantly different ($P \leq 0.05$).

Although the T2 treatment had the best mechanical resistance, this treatment resulted in the worst acceptance of appearance. However, the T1 sample, the second-best in mechanical resistance was also one of the best samples in the appearance attribution. Thus, T1 and T3 samples' resistance can be considered adequate simultaneously as these treatments provide good sensory acceptance of appearance.

The resistance of the materials produced in the T1, T2 and T3 treatments were significantly lower than those found by Monteiro et al. (2019) up to 80.9 Kgf in the samples and 61.9 in the Medium Density Fiberboard (MDF). However, the resistance is sufficient for the elaboration of some furniture and utensils that do not require high mechanical resistance and application in wall coatings.

The low variability presented in the treatments $T9_1$ to $T9_3$ indicated the material's high reproducibility, and even in the sensorial acceptance analysis, the values were within the same confidence interval.

4. Conclusions

Based on the results presented, the treatments with 55 % malt residue and 45 % extruded corn with more acceptable grain size (14/28) showed good performance both in resistance and in sensorial acceptance in appearance attribute. Thus, the sample T1 presented the best process parameters within the studied range, resulting in a material with desirable characteristics. Although the material has a lower resistance than materials in which the waste is mixed with resins, this resistance is sufficient for several applications. The great advantage is represented by the much lower environmental impact than materials with resins as binding agents.

So, this work showed that it is possible to produce a low-cost material, totally biodegradable, and could be applied, in further research, to the construction of various utensils and architectural coatings.

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