

APPLICATION OF COCOA BEAN SHELL EXTRACTS IN THE PRODUCTION OF CORN SNACK PRODUCTS

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Summary

Extruded snacks products are group of products that are consumed by all age groups in significant amounts. Although these products are mainly made from raw materials rich in starch (corn grits, wheat grits, etc.), recently nutritional values is improved by adding various supplements which contain components like polyphenols, food fibers, vitamins, etc. The aim of this study was to examine the possibility of application of extracts from cocoa shell, which is by-product in the processing of cocoa beans, in production of corn snack products. The expansion ratio, bulk density, color, hardness and fracturability, total polyphenol content and antioxidant activity were tested for the obtained extrudates, thereby determining the quality of the obtained products. It has been found that there is a reduction in the expansion ratio and increase in bulk density, as well as increased hardness and reduced fracturability of tested extrudates with the addition of extracts from cocoa shell. Also samples with the addition of extracts were darker. Addition of cocoa shell extracts resulted in increased polyphenol content and antioxidant activity.

Keywords: cocoa bean shell extracts, corn grits, snack products, physical properties, total polyphenol content

Introduction

Extrusion is a process without which today's food industry is unthinkable, and due to its multiple applications, it is indispensable process in food production. It is mechanical and thermal process during which food raw material, which is rich in starch and proteins, and that is mostly corn or wheat grits, goes under different technological operations, like heating, mixing and compression. Finally, material passes through special shaped nozzle, forms and dries with expansion to the finished product which is called extrudate. Extrusion products are increasingly enriched, in order to increase their nutritional value, by using different additives that contain valuable components such as polyphenol, dietary fibers, vitamins etc. (Jozinović et al., 2019; Ačkar et al., 2018; Jozinović, 2015). One of the valuable by-product is cocoa bean shell, which remains as a by-product of cocoa bean processing, and since it represents about 10% of the bean, it is produced in a relatively large quantity. It is commonly used as a fuel (energy source), adsorbent or less frequently as the animal feed because it contains theobromine (Barišić et al., 2020; Jozinović et al., 2019). However, due to its chemical composition, cocoa bean shell has a great potential for use in the production of new food products, since it contains a large amount of dietary fibers (50-60 %), proteins (11-18 %) and polyphenols

(from 1.8 to 5.8 %) (Okiyama et al., 2017; Nsor-Aindana et al., 2012). In the case of polyphenols, catechins, epicatechins and procyanidins are the most important components. Also, a higher content of polyphenols was recorded in non-fermented and unroasted beans, as opposed to fermented and roasted cocoa beans. Polyphenols migrate from cocoa beans into the shell during the various cocoa beans processing operations, such as fermentation, roasting and alkalization (Panak Balentinić et al., 2018). The extraction of these valuable components from the cocoa bean shell has been a subject of many researches (Jokić et al., 2019), and one of the newer extraction methods is certainly application of high voltage electrical discharge (HVED) (Li et al., 2019; Boussetta and Vorobiev, 2014). The method is based on an electrical discharge during which a series of physical and chemical reactions take place in the water, which ultimately lead to the destruction of the cell structure and the extraction of the target compounds. There are two phases of the process in the aqueous medium: the phase that occurs before the destruction, so-called *streamer*, and discharge phase. By applying a very high voltage between the two electrodes, electrons that have enough energy to stimulate physical and chemical processes in water are accelerated. At the moment when discharge reaches the electrode, shock

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waves, cavitation bubbles (main bubble and numerous small bubbles) and turbulence in the liquid occur. Mass transfer increases turbulence, while shock waves and burst of cavitation bubbles are responsible for fragmentation (Lončarić et al., 2020; Boussetta and Vorobiev, 2014).

The aim of this study was to produce water extracts of cocoa bean shell by using HVED extraction as an innovative technique and to examine the possibility of their application in the production of corn snack products with the aim of obtaining nutritionally more valuable extrudates.

Materials and methods

Materials used in this research were:

- Corn grits, kindly provided by the „Đakovo Mill” of the Žito Ltd. Osijek, Croatia, suitable for production of expanded snack products;
- Cocoa bean shell, kindly provided by Kandit Ltd. Osijek, Croatia.

Water extracts of cocoa bean shell used in the mixtures for extrusion were prepared by using the high voltage electric discharge (HVED) technique as an innovative technology. Namely, the extracts used in this study are part of our previous study, which examined the possibility of extraction of bioactive components from cocoa bean shell using the HVED procedure (Jokić et al., 2019). In that paper, HVED extraction under different conditions of extraction time (30, 60 and 90 min), frequency (40, 70 and 100 Hz) and cocoa shell:water ratio (1:10, 1:30 and 1:50) was investigated, by application of the Box-Behnken design of the experiment, where 17 extraction experiments were performed. Based on the results obtained for total polyphenols content, antioxidant activity (% DPPH), as well as a share of individual bioactive components for this study were selected extracts obtained in the listed survey during run no. 4 and run no. 10:

- 1) Extract 4 (water:cocoa bean shell = 1:30; HVED frequency 100 Hz; time 30 min);
- 2) Extract 10 (water:cocoa bean shell = 1:50; HVED frequency 100 Hz; time 60 min).

These extracts were chosen because they had the highest content of two dominant methylxanthines, theobromine and caffeine, namely Extract 4 (5246.36 mg/kg of theobromine; 752.32 mg/kg of caffeine) and Extract 10 (6031.51 mg/kg of theobromine; 849.88 mg/kg of caffeine). Furthermore, Extract 4 had the highest content of catechin (284.33 mg/kg) and a high content of epicatechin (270.13 mg/kg), while Extract 10 with a total polyphenol content of 92.39 mg GAE/g

and an antioxidative activity of 45.45% DPPH proved to be one of the best (Jokić et al., 2019). The obtained extracts were used as a substitute for water in the preparation of corn grits for extrusion, whereby the extracts being added in the amount necessary to adjust the moisture of the mixture to 15%. A control sample was prepared with the addition of distilled water in corn grits. The mixtures were prepared on the base of 1 kg d. m., by using laboratory mixer (Kenwood KMM020, JVC Kenwood, Uithoorn, Netherlands), and left overnight in the plastic bags at temperature of 4 °C, in order to distribute moisture evenly. Extrusion was conducted in a laboratory single-screw extruder (Brabender GmbH, Model 19/20DN, Duisburg, Germany) under the following conditions:

- screw with compression ratio: 4:1;
- round die head with 4mm nozzle diameter;
- screw speed: 100 rpm;
- dosing speed: 20 rpm;
- temperature profiles (in dosing/compression/ejection zone): 135/170/170 °C and 155/185/185 °C.

The extrudates were air-dried overnight at room temperature, and after that expansion ratio, bulk density, color, hardness and fracturability, as well as total polyphenol content and antioxidative activity were determined.

Expansion ratio

On expanded dry samples the diameter (in millimetres) by calliper was measured. Five parallel measurements were performed for each sample, and the expansion ratio was calculated, which represents the value of the ratio of the diameter of the extrudate and the diameter of the extruder nozzle (4 mm) (Brnčić et al., 2008). The results were expressed as mean with standard deviation of measurements and shown graphically.

Bulk density

The bulk density was determined by Alvarez-Martinez et al. (1988), and the mass, diameter, and length of the extrudate were measured in five parallel measurements. The results were expressed as mean with standard deviation of measurements and shown graphically.

Color

For the color determination of non-extruded corn grits and extruded (milled) products it was used Chroma Meter CR-400 (Konica Minolta, Japan) with granular

materials attached according to Jozinović et al. (2016). Before the color measurement in CIE-Lab system (L^* - whiteness/darkness); a^* - redness/greenness; b^* - yellowness/blueness) the device was calibrated using a white standard calibration plate. For each sample five measurements were performed and the total colour change (ΔE) was calculated by Equation 1:

$$\Delta E \sqrt{(L - L_0)^2 + (b - b_0)^2 + (a - a_0)^2} \quad (1)$$

where the parameters with subscript „0“ indicates the color value for control non-extruded sample of corn grits. Results are shown graphically as a mean value and standard deviation.

Texture analysis

Extrudate texture was determined using texture analyzer TA.XT2 Plus (Stable Micro Systems, Godalming, United Kingdom), by the method for hardness (N) and fracturability measurement (mm) using the Warner–Bratzler shear blade with guillotine probe (Ačkar et al., 2018). The results were expressed as the mean value and the standard deviation of 10 replications and shown graphically.

Total polyphenol content

The total polyphenol content was determined by colorimetric method according to Wang and Ryu (2013). The absorbance of developed blue color was measured at 725 nm, using 80% methanol as a blank, and test was performed in two parallel measurements. Obtained results were expressed in mg of gallic acid equivalents (GAE) per 100 g of dry matter.

Antioxidant activity by DPPH method

Determination of antioxidant activity was conducted by Wang and Ryu (2013) method. The absorbance was measured at 517 nm, and the inhibition percentage of DPPH radicals was calculated by the Equation 2:

$$\% \text{ inhibition} = \frac{A_0 - A_s}{A_0} \times 100 \quad (2)$$

where it is:

A_0 – absorbance of control,

A_s – absorbance of sample.

Results and discussion

The aim of this study was to examine the possibility of applying aqueous extracts of cocoa bean shell prepared using HVED technique as an innovative extraction method in the production of corn snack products. After extrusion, the physical properties, antioxidant activity and total polyphenol content in obtained extrudates were determined.

Texture is a sensory characteristic, that is crucial in determining the quality of the snack products, and depends on a number of factors, among which the most prominent are expansion ratio, bulk density, hardness and fracturability of the extrudate. The expansion ratio is important for the physical properties of extrudates and plays an important role in the acceptance of products by the customers (Obradović et al., 2015). The addition of the Extract 4 of cocoa bean shell, as well as the Extract 10, during extrusion at a temperature profile 135/170/170 °C, resulted in a significant reduction in the expansion ratio of extrudates compared to the control corn extrudate produced with water (without extract) (Fig. 1). A possible reason for the decrease in the expansion ratio when applying extracts instead of water is that the extracts contain various soluble components from cocoa bean shell, including soluble dietary fiber, which negatively affects the expansion of pure corn grits (Jozinović, 2015). Namely, cocoa shell contains high fiber content, about 57%, with cellulose as dominant polysaccharide and lower amount of pectin and hemicellulose (Redgwell et al., 2003). The obtained results are in accordance with our previous study, in which extruded products enriched with different by-products with a high content of fiber were investigated (Ačkar et al., 2018), and where the addition of brewer's spent grain, sugar beet pulp and an apple pomace caused significant reduction in the expansion ratio. The addition of whole grains or wild legumes rich in fiber to the extrusion mixture also shows a decrease in the expansion ratio (Pastor-Cavada et al., 2011). At the temperature profile 155/185/185 °C the expansion ratio was slightly lower in relation to the lower extrusion temperature profile, and it was found that the addition of extracts resulted in a slight increase in the expansion ratio in relation to the control sample.

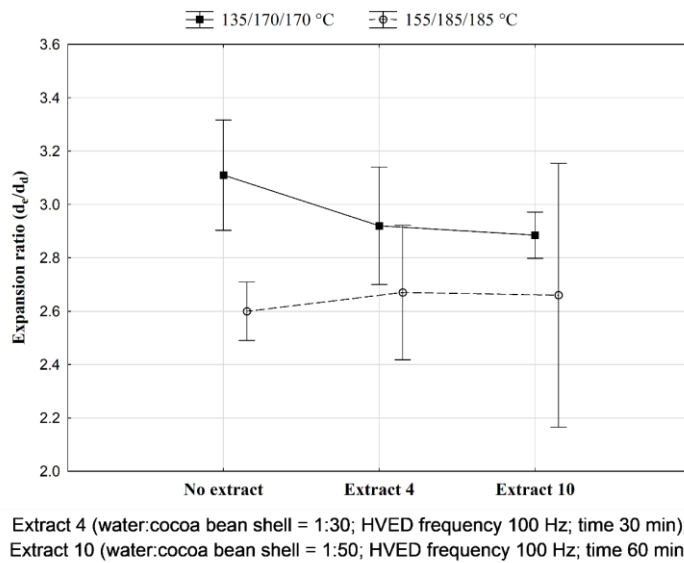


Fig. 1. The effect of the cocoa shell extracts addition on the expansion ratio of the extruded corn grits at different extrusion temperatures

The bulk density is important as a parameter for physical assessment of the quality of produced extrudates. It gives information on how much mass occupies a certain volume, and it is desirable to have as little value. At the temperature profile 135/170/170 °C there was an increase of bulk density with the addition of Extract 4 compared to the bulk density of extrudates without extract addition, while extrudates with the addition of Extract 10 had higher bulk density in relation to corn grits extrudate with water (without

extract), but lower than extrudates produced with Extract 4 (Fig. 2). The increase of bulk density in extrudates with extracts is consistent with research by other authors, where the materials with high protein content (Adamafio, 2013) or dietary fibers caused an increase of bulk density (Bishart et al., 2013; Stojceska and Ainsworth, 2008). At the temperature profile 155/185/185 °C there was a slight decrease of products' bulk density with extracts addition in relation to corn grits extrudates without extract.

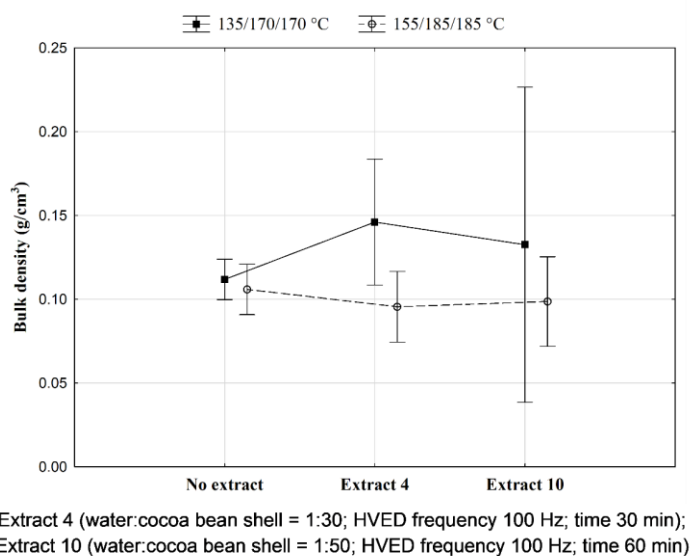


Fig. 2. The effect of the cocoa shell extracts addition and extrusion temperatures on bulk density of extrudates

The addition of cocoa bean shell extracts at the temperature profile 135/170/170 °C reduced the total color change in relation to control sample which was extruded with water (without extracts) (Fig. 3). At the temperature profile 155/185/185 °C higher values of the total color change were

recorded in relation to the lower temperature profile. Furthermore, at a higher extrusion temperature profile with the addition of Extract 4 there was a higher change in color, while the addition of Extract 10 there was no significant change in color compared to the control sample.

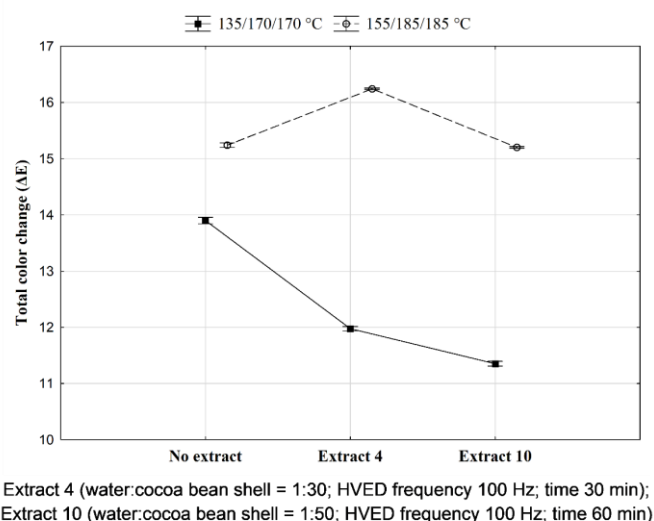


Fig. 3. Total color change of the extrudates with the addition of cocoa shell extracts at different extrusion temperatures

Texture was determined by the parameters for hardness and fracturability, and it is directly related to expansion and bulk density (Anton et al., 2009; Stojceska et al., 2009). At the temperature profile 135/170/170 °C there was an increase of the products' hardness with the addition of both extracts, which is not desirable (Fig. 4). Changes in texture are the result

of loss of moisture, formation or decomposition of emulsions and gels, hydrolysis of polymeric carbohydrates and coagulation and/or hydrolysis of proteins (Akdogan et al., 1997). At the temperature profile 155/185/185 °C there was no significant change in products' hardness in relation to control sample.

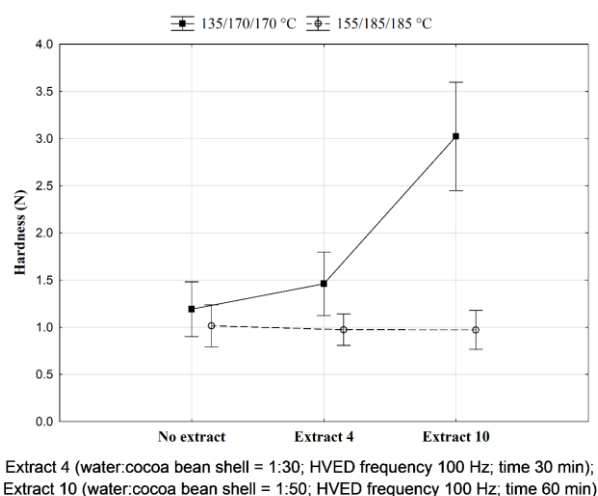


Fig. 4. The effect of the cocoa shell extracts addition and the extrusion temperatures on hardness of extrudates

With the addition of Extract 4 to the extrusion mixture, the fracturability of extrudates did not significantly change at both temperature profiles. On the other hand, with the addition of Extract 10, there was a significant decrease in fracturability at the temperature profile 135/170/170 °C, while at the temperature profile 155/185/185 °C there was an

increase of fracturability (Fig. 5). Increasing the amount of fibers in the extrusion mixture also increases the hardness of the extrudates. In accordance with the increase in hardness, the fracturability of extrudates decreases with the addition of Extract 4, while with Extract 10 at higher temperatures this was not the case.

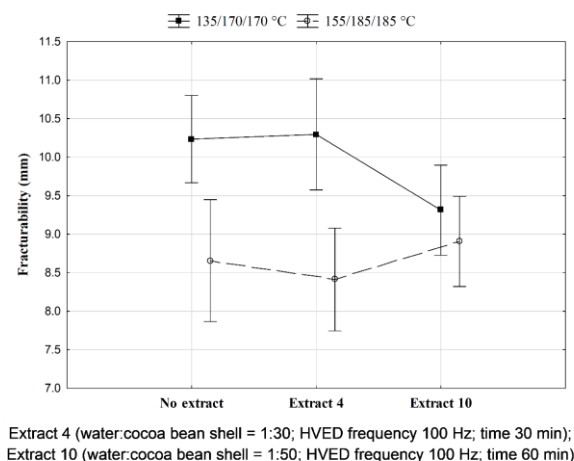


Fig. 5. The effect of cocoa shell extracts addition and extrusion temperatures on fracturability of extrudates

At both temperature profiles of extrusion there was a significant increase of total polyphenol content with the addition of cocoa bean shell extracts (Fig. 6), from which it can be concluded that cocoa shell is rich in polyphenolic compounds, which was confirmed for the used extracts in our previous study (Jokić et al., 2019). Since, the total polyphenol content in Extract 10 (92.39 mg GAE/g extract) was significantly higher than in Extract 4 (72.39 mg GAE/g extract) (Jokić et al., 2019), so the increase of total polyphenol content in extrudates was in line with this (Fig. 6). Other studies have also shown that cocoa shell is rich in polyphenolic

compounds, so Vriesmann et al. (2011) in their study recorded high polyphenol content in cocoa shell, but did not investigate in detail which those compounds are. On the other hand, Nsor-Atiandana et al. (2012) stated that about 60% of total polyphenols in cocoa shell are epicatechin and catechin. Amin and Chew (2006) found that the total phenolic content of cocoa shell was 112.9 ± 0.6 mg GAE/g extract, extracted with 70% ethanol, while the extract with 80% ethanol gave total phenolic content of 23.36 ± 1.59 mg GAE/g extract, indicating that the total polyphenol content depends on the extraction technique used.

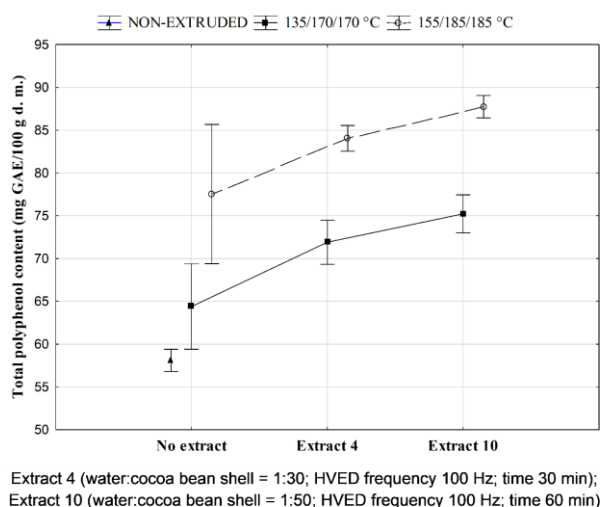


Fig. 6. Total polyphenol content in non-extruded corn grits and extruded products with addition of cocoa shell extracts extruded at different temperatures

Since the addition of cocoa shell extracts had an effect on total polyphenol content in the obtained extrudates, an increase in antioxidant activity was also expected, as the polyphenols are carriers of antioxidant activity. The addition of Extract 4 to the mixture for extrusion at both temperature profiles resulted in a slight increase of antioxidant activity (Fig. 7), while the addition of Extract 10 at temperature profile 155/185/185 °C caused significant increase of antioxidant activity. The higher increase of antioxidant activity with the addition of

Extract 10 regardless to the temperature profile is consistent with the higher antioxidant activity of this extract (45.45% DPPH) in relation to Extract 4 (40.37% DPPH) (Jokić et al., 2019). It can be concluded that the antioxidant activity increased with the addition of both cocoa shell extracts, with a significant increase at the temperature profile 155/185/185 °C, which confirms that cocoa shell is rich in antioxidants, and this is consistent with researches of other authors (Jokić et al., 2019; Karim et al., 2014).

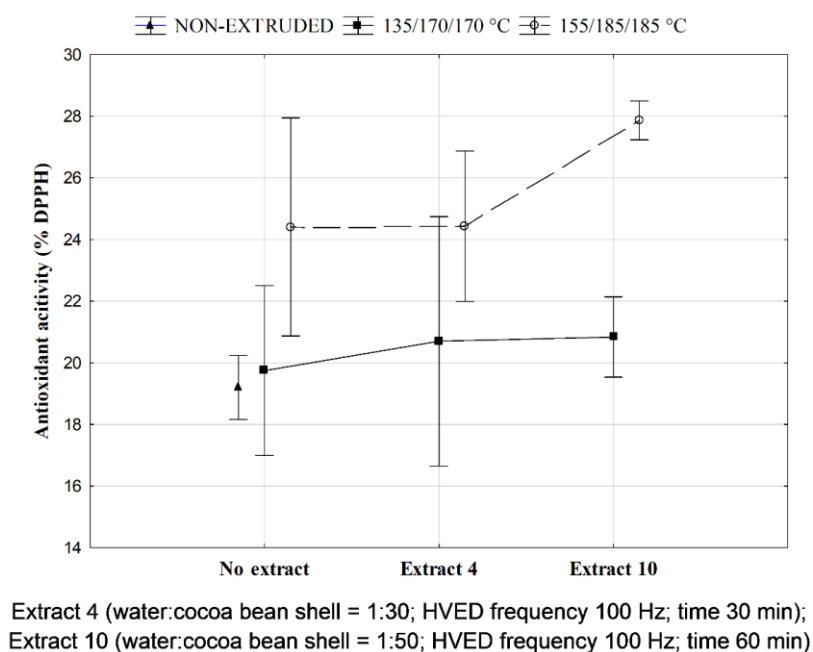


Fig. 7. Antioxidant activity of non-extruded corn grits and extruded products with addition of cocoa shell extracts extruded at different temperatures

Conclusions

Based on the obtained results in this study, it can be concluded that the addition of cocoa bean shell extracts to the extrusion mixtures resulted in a decrease of expansion ratio and an increase of bulk density of extrudates at lower extrusion temperature profile, while at higher extrusion temperatures there was an increase in expansion ratio and bulk density. With the addition of cocoa shell extracts at lower extrusion temperatures there was no significant change in the color of the extrudate, while at higher temperatures the change in color was more pronounced. At lower extrusion temperature profile there was an increase in hardness and a decrease in fracturability of extrudates with the addition of cocoa shell extracts, compared to the control sample, while at higher temperatures there was no significant change

in hardness, while fracturability increased slightly. The addition of cocoa shell extracts increased total polyphenol content and antioxidant activity of extrudates at both extrusion temperature profiles, which means that cocoa shell is rich in polyphenolic compounds. From all the above, it can be concluded that the addition of cocoa bean shell extracts leads to changes in the physical properties of extrudates, which may affect the acceptability of those products by consumers, but at the same time the addition of cocoa shell extracts significantly improves their antioxidant activity.

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