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USE OF POLYMERS IN THE DEVELOPMENT OF EDIBLE PACKAGING MATERIALS FOR FOOD SUPPLEMENTS

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Abstract

Environmental pollution due to packaging waste requires solutions. Food supplements packaging is usually disposable and is obtained from materials difficult to sort and recycle. For this purpose, new materials were developed; entirely obtained from biopolymers, that can be used as packaging material for food supplements that require solubilisation before consumption. Thus, were developed eight films, with different compositions of agar, sodium alginate, and glycerol. The films were tested in order to evaluate physical and optical properties (thickness, retraction ratio, colour, transmittance or opacity), mechanical (tensile strength, elasticity), but also for the evaluation of humidity or rehydration capacity. The sample obtained from higher amounts of alginate and glycerol showed the best results and was completely solubilized in a very short time, in water, at a temperature of 35°C. For the safety of use and consumption, the films were microbiologically tested. No bacteria, yeasts or moulds developed on the culture media. All substances used are accepted in quantum statis doses. According to the results obtained, biopolymers have properties that can be successfully exploited in order to obtain zero-waste, eco-friendly, biodegradable and compostable packaging.

Key words*: hydrocolloids, environment, food, material.*

INTRODUCTION

The problems caused by the SARS-CoV-2 pandemic around the world have led scientists to turn their attention, research and resources to finding solutions in order to stop the Coronavirus effects. Thus, they focused on avoiding hunger and restarting the food industry, currently avoiding the problems caused by pollution. This issue needs to be rethought, given that many problems have been out of control including pollution due to the food industry which has long-term negative effects on the environment and public health.

In May 2020, the European Commission launched *From Farm to Fork* strategy to create a fair, healthy and environmentally friendly food system (*). *The European Green Deal* has outlined the principles by which Europe wants to become the first climate-neutral continent by 2050 (**). The benefits of this program favor the inclusion, the improvement of the health and quality of life of consumers, as well as the protection of the environment, especially due to the fact that EU is the largest importer and explorer of agri-food products in the world. The main objectives are to reduce the ecological and climate footprint and to strengthen the resilience of the food system. The current challenge is to develop sustainable food. But the manufacture, processing, packaging, transport, storage and marketing of food contribute significantly to air, soil, and water pollution, generating greenhouse gas emissions, with a massive contribution to the decline of biodiversity (Qasim et al., 2020; Shen et al., 2020). Food packaging plays a key role in the sustainability of food systems (Licciardello, 2017; Pauer et al., 2019). At this time, it is desired to reduce the use of hazardous chemicals, both as part of the food product and its packaging (Diggle & Walker, 2020). The aim of EU is to review legislation on food contact materials and support the development of innovative and sustainable packaging developed from environmentally friendly, reusable or recyclable materials, while helping to reduce food waste (Adam et al., 2020).

Biodegradable, fully edible materials obtained from biopolymers are a successful alternative to conventional materials (Haider et al., 2019). Based on renewable resources, these materials have found applicability in various industries,

from medical (special prostheses or wound dressings) to the industrial field (components for 3D printers). Food industry is one of the pioneering industries in this field, processing and capitalizing on these biopolymers for over 100 years (Yadav et al., 2018; Prameela et al., 2018).
Current tests indicate the use of biopolymers for the development of materials for food packaging (Ramesh Kumar et al., 2020); which generate zero waste due to the ability to be completely ingested or solubilized with the product contained.
The present study aimed to identify optimal compositions in order to obtain a material based on biopolymers, plasticized with glycerol and water. Based on agar and sodium alginate, it can be used for packaging food supplements and can be consumed with the product, by immersing in water with higher temperatures. Thus, once consumed with the product contained, the material used for packaging generates zero waste. When it is not desired to ingest it, it can be eliminated, being completely biodegradable and compostable.

MATERIALS AND METHODS

Films' development

The materials used to obtain the films were agar, sodium alginate from brown algae, glycerol and water. The hydrocolloids and plasticizer were purchased from Sigma Aldrich Company. The films were obtained using the casting method, described by Puscaselu et al., 2019. Thus, the film-forming solution was obtained by energetic homogenization and stirring at 90°C for 20 minutes, followed by pouring on the silicone surface used for drying. The solution obtained was maintained at room temperature (20 ± 2°C) until complete drying. Eight different types of materials were obtained, with different characteristics, depending on the composition used (Table 1).
Samples **B1**, **B3**, **B4** contain high amounts of agar in the composition, respectively 75%, 62.5% and 50%. Equal amounts of hydrocolloids were used to obtain the **B5** sample, while **B2**, **B6**, and **B7** were developed with higher amounts of sodium alginate (75%, 50%, 62.5%). The composition of sample **B8** was 25% glycerol, 40.875% agar and 34.125% sodium alginate. The volume of water used was 150 ml for all samples tested.

Table 1. Composition of the developed films

Sample*	m_{agar}, g	$m_{alginate}$, g	$m_{glycerol}$, g
B1	3	-	1
B2	-	3	1
B3	2.5	1	0.5
B4	2	1.5	0.5
B5	1.75	1.75	0.5
B6	1.5	2	0.5
B7	1	2.5	0.5
B8	1.635	1.365	1

*The volume of distilled water was 150 ml

Evaluation of physical properties

In order to evaluate the thickness (*T*) and the retraction ratio (*R*), initial and final thickness measurements were performed using the Mitutoyo digital micrometre. The noted results represented the arithmetic average of at least five measurements, made in different areas of the film surface.
The retraction ratio was calculated using the following formula:

$$R, (\%) = \frac{the\ thickness\ of\ the\ film-forming\ solution - final\ film\ thickness}{the\ thickness\ of\ the\ film-forming\ solution} * 100$$

To evaluate the general appearance, the adhesiveness of the film to the foil used for drying, fineness, gloss, homogeneity, presence of pores and cracks that can be observed by visual examination, regularity of edges, taste and smell were determined.

Optical properties

The color of the obtained films was evaluated using the CR-400 Konika Minolta colorimeter, using the CIE L*a*b* system, which determines the color in terms of the reflectivity spectrum of the material, but also the sensitivity of the human eye to the visible spectrum. For a correct evaluation, 5 readings were made in different areas of the film surface, and the noted values represent their arithmetic average.
Transmittance (*Tr*) and opacity (*O*) were tested using the Ocean - Optics HR 4000 CG-UV-NIR spectrophotometer. For this purpose, 10 readings were made at a wavelength of 600 nm to evaluate the transmittance and 10 readings at a wavelength of 600 nm to determine the opacity.

The opacity was calculated according to the formula:

$$O\,(\%) = \frac{absorbance}{film\ thickness, (mm)} * 100$$

Mechanical properties

Tensile strength (*TS*) and elongation (*E*) were tested using the Texture Analyzer ESM 301, Mark-10. The test specimens were prepared according to STAS ASTM D882 (Standard Test Method for Tensile Properties of Thin Plastic Sheeting) (***), with 100 mm x 30 mm size.

The test was performed at room temperature of 23.5°C.

$$TS\,(MPa) = \frac{F}{A}$$

$$E\,(\%) = \frac{\Delta l}{l} * 100$$

Where: *TS* - tensile strength (MPa); *F* - maximum force applied (N); *A*- area (m^2); *E* - elongation (%); *Δl* - elongation (mm); *l* - initial length (mm).

Determination of solubility characteristics

The determination of the moisture content of the new materials was performed according to the standardized method STAS 90-88.

The solubility of the films is an indicator of their water resistance; the samples (3 x 3 cm) initially weighed were immersed in a container with 50 ml of distilled water (room temperature) where they were kept for 8 hours. Then, the samples were kept at 110°C for 24 hours and then reweighed. The result was obtained by using the following formula:

$$WS\,(\%) = \frac{W0 - W1}{W0} * 100$$

Where: W_0 - initial mass of the sample (g); W_1 - the mass of the reweighted sample (g).

To evaluate the humidity, the film samples (3 x 3 cm) were weighed, kept for 24 hours at 110°C and reweighed; the results were obtained by using the following formula:

$$MC\,(\%) = \frac{W0 - W1}{W0} * 100$$

Where: W_0 - sample weight before drying (g); W_1 - sample weight after drying (g).

The water activity index (**a_w**) provides information on the stability of products when it is influenced by their water content. The growth of microorganisms in the food can be inhibited by reducing the water content (dehydration) or by binding it to the food. In general, microorganisms are considered to reduce or even stop their activity at a_w index values below 0.7. The water activity index (a_w) was determined with AquaLab equipment. The tests were carried out at a temperature of 24.4 ± 0.9°C. The final value represents the average of five readings in different areas of the film surface.

The microstructure of the films was evaluated with the MarSurf CWM 100 microscope, owned by the Mahr Gruppe. With the Mountains Lab Premium 8.1 software, it was possible to evaluate the appearance of the samples, their homogeneity, the degree of solubilization of the constituent compounds, and the presence of pores or fissures.

Microbiological evaluation

Because the material obtained aims to be consumed with the product contained and is intended for all categories of consumers, the safety of ingestion is essential. Thus, for the determination of microbiological properties of the material, the films were tested in order to establish the presence of coliforms, enterobacteria, *Staphylococcus aureus*, *Escherichia coli*, as well as for yeasts and molds. For this purpose, Compact Dry plates with specific culture media (Nissui Pharma) were used. To perform the determinations, 1 g of film was homogenized with 9 ml of microbiologically inert solution (here physiological serum). From the solution thus obtained, 1 ml was poured onto the plate with culture medium. The plates were maintained at 37 degrees for 72 hours for yeasts and molds, and 36 hours for the other microorganisms tested.

RESULTS AND DISCUSSIONS

Although the films showed medium to high adhesion, all samples were easily removed from the silicone support used for drying process. Samples **B1** (75% agar/25% glycerol), **B5** (43.75% agar/43.75% alginate/12.5%

glycerol), **B6** (37.5% agar/50% alginate/12.5% glycerol), **B7** (25% agar/62.5% alginate/12.5% glycerol), **B8** (40.875% agar/34.125% alginate/25% glycerol) had glossy surface on the inside, the area in direct contact with the silicone support and slight roughness on the outside, in contact with the air. The surfaces of samples **B2** (75% alginate/25% glycerol) and **B3** (62.5% agar/25% alginate/12.5% glycerol) were glossy on both sides, unlike sample **B4** (50% agar/37.5% alginate/12.5 % glycerol), with a strong tendency to flake (Figure 3). Sample **B1** showed tendency to retract and break, it was brittle, difficult to handle, with low transparency and dark color. In order to be manipulated, it requires a higher amount of plasticizer or combination with other biopolymers. **B2** and **B3** showed homogeneous structures, were transparent, odorless, allowed multiple bending, with medium and low solubility, respectively, in the oral cavity. The high content of agar in the composition of samples **B1**, **B3**, **B4** and **B5** led to harder films, with low solubility and even very low in the oral cavity, and unpleasant sensation. This type of material, in this form, cannot be used for packaging food or supplements and be consumed with them, due to the fact that it can negatively influence their sensory characteristics. The presence of pores was evident in the case of films **B5**, **B6**, **B7**, and **B8**. Uneven distribution of the composition and, implicitly, non-uniformities of the structure, can be observed in films **B6** and **B8**.

According to Figures 1 and 2, samples **B1**, **B4** and **B5** have values of thickness over 70 µm and, implicitly, low values of the retraction ratio (less than 2%), unlike samples **B2**, **B6**, **B7** and **B8**, where the higher amount of sodium alginate led to the development of thinner films, lower than 56 µm, and higher retraction ratio values (27.65- 55.9%).

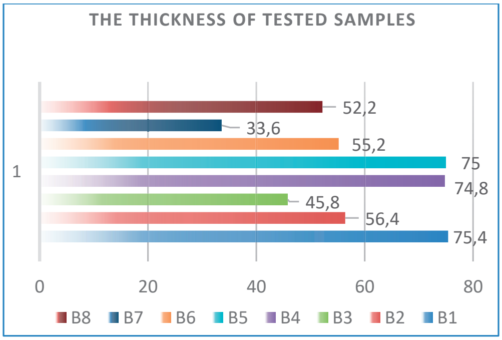

Figure 1. The thickness of tested samples, in µm

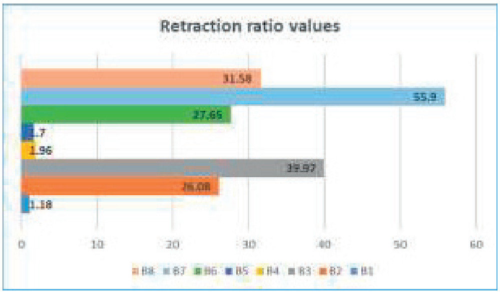

Figure 2. The retraction ratio of tested samples, %

Different results can be observed for **B3** sample, where, although the amount of agar is relatively high (62.5% of the content of substances used), the thickness is low (45.8 µm), and the retraction ratio has a value of about 40%.

According to the images generated after observation with MarSurf CWM 100 microscope (Figure 3), samples B2 and B3 presented the most homogeneous structures. The results confirm the ability of sodium alginate to create clear, transparent, and pleasant to touch films. Also, the high alginate content increases the solubility of the films. The data obtained is also reinforced by the results shown in Table 1.

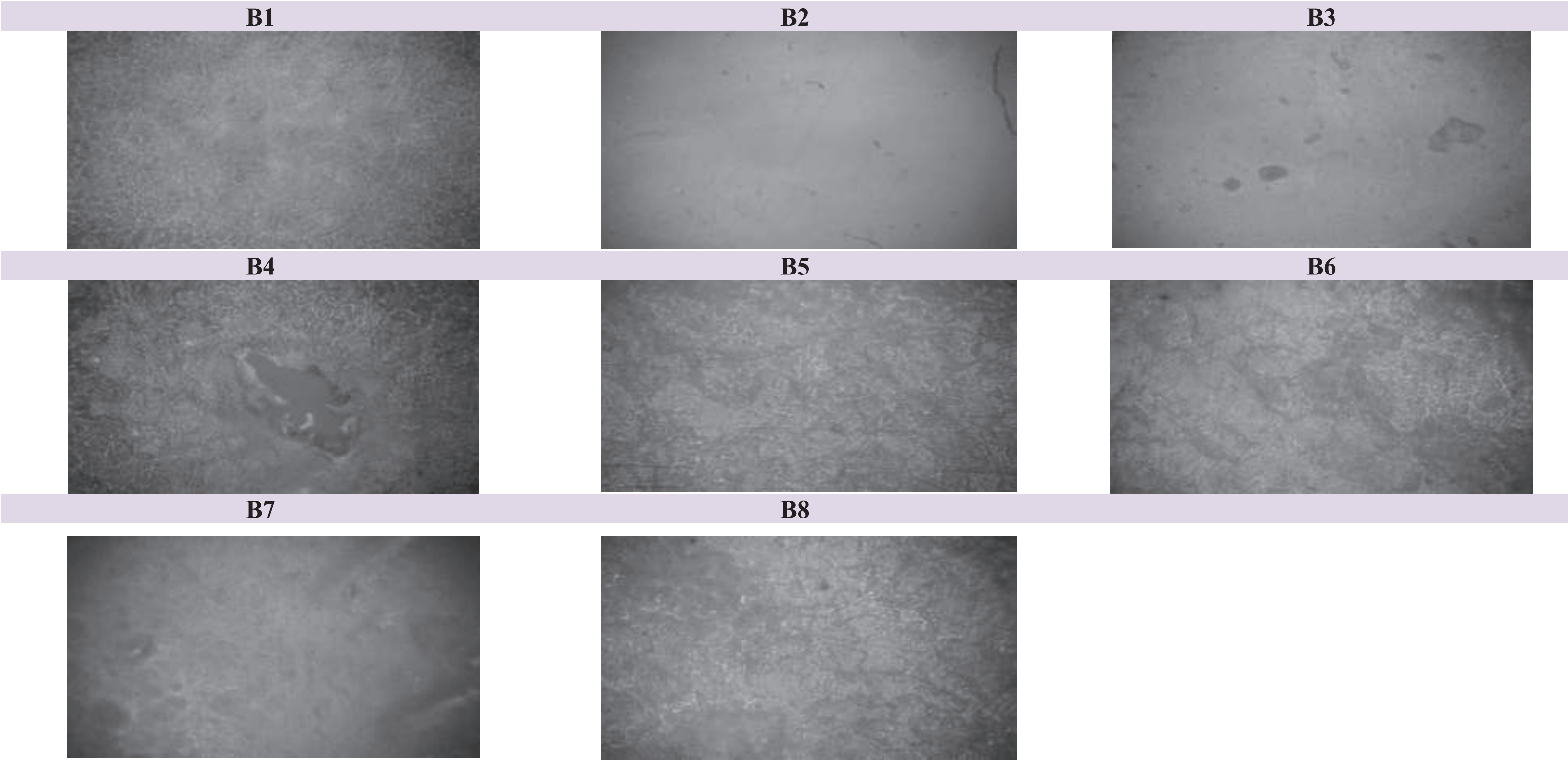

Figure 3. Microscope images of tested films

Thus, B2 sample could not be evaluated for water solubility, as it was completely solubilized in water. Sample B3, which also contains agar in the composition, maintained its integrity and did not absorb a large amount of water. It was easy to handle and did not present any difficulties in the next steps. However, for use as a package for powdered food supplements, which require solubilization before consumption, film B2 seems to be the ideal option.

According to microbiological determinations, none of the microorganisms developed on culture media. This can be related to the low values of the water activity index, a_w below 0.45, as can be seen in Table 2. The low values of the water activity index prevent the development and proliferation of microorganisms, as they will not find suitable environments for growth and multiplication. The results indicate the safety of consumption of these packages.

Table 2. Evaluation of water solubility and moisture content

	WS (%)	MC (%)	a_w
B1	42.75 ± 0.014	18.865 ± 0.003	0.447 ± 0.004
B2	**complete solubilization**	**16.329 ± 0.002**	**0.437 ± 0.003**
B3	33.57 ± 0.027	11.03 ± 0.023	0.441 ± 0.002
B4	34.963 ± 0.002	10.626 ±0.003	0.435 ± 0.004
B5	42.64 ± 0.03	9.615 ± 0.003	0.43 ± 0.001
B6	42.04 ± 0.038	14.117 ± 0.037	0.408 ± 0.013
B7	29.703 ± 0.002	14.332 ± 0.014	0.435 ± 0.003
B8	42.996 ± 0.406	14.505 ± 0.03	0.435 ± 0.007

The optical and mechanical properties are presented in Table 3 and Table 4. The transmittance (Tr) and lightness (L*) values increased with the increase in the amount of sodium alginate and glycerol, as well as the decrease in agar mass. Thus, the highest values of transmittance (81.10%) and lightness (92.03) were observed in sample **B2**, with 75% alginate and 25% glycerol. Samples with higher agar content in the composition showed low values of these parameters (**B1** and **B4**).

According to the results obtained, sample **B2** qualifies for use as packaging material for powdered food supplements. It was completely solubilized in water at temperatures of 20 ± 2°C.

Table 3. The optical properties of the developed films

	Tr (%)	O (%)	Color		
			L*	a*	b*
B1	6.63 ± 0.003	18.33 ± 0.982	87.44 ± 0.003	-4.59 ± 0.06	16.79 ± 0.001
B2	**81.1 ± 0.026**	**1.49 ± 0.06**	**92.03 ± 0.06**	**-5.62 ± 0.74**	**12.74 ± 0.15**
B3	67.17 ± 0.004	2.67 ± 0.003	90.87 ± 0.093	-5.40 ± 0.002	13.87 ± 0.054
B4	5.39 ± 0.003	12.22 ± 0.021	90.34 ± 0.001	-4.96 ± 0.036	16.09 ± 0.045
B5	19.34 ± 0.015	9.82 ± 0.015	91.11 ± 0.415	-5.30 ± 0.091	14.51 ± 0.15
B6	27.23 ± 0.003	10.28 ± 0.003	91.21 ± 0.042	-5.47 ± 0.013	14.08 ± 0.044
B7	63.79 ± 0.017	5.45 ± 0.001	91.61 ± 0.089	-5.63 ± 0.002	13.42 ± 0.97
B8	15.55 ± 0.003	15.56 ± 0.037	91.3 ± 0.056	-5.37 ± 0.69	13.91 ± 0.002

According to the obtained results, sample **B2** can be use as packaging for powdered food supplements (Figure 4). The high value of transmittance (81.10%) and low opacity (1.49%) indicate the need for packaging with an outer packaging. In this sense, paper bags or cardboard boxes can be used, thus avoiding environmental pollution and encouraging the use of recyclable materials.

Figure 4. Food supplements packed in B2 foil

B3, with the best characteristics of solubility and humidity, has very good values of transmittance (67.17%), opacity (2.67%) and lightness (90.87). Thus, the film can be used for packaging products with high humidity. The average value of transmittance makes the transfer of light radiation to be a conditioned one, fact that prevents lipid oxidation and has a positive effect for maintaining and even increasing the sensory properties and, implicitly, the shelf life for this type of product. The values of the parameters a* and b* in the CIE L*a*b* system are closely related to the lightness value. These are lower in the case of samples with a medium and even high content of sodium alginate in the composition and higher in the case of those with a high mass of agar.

The test of mechanical properties (Table 4) indicated the highest values of tensile strength for sample **B3** (2.78 MPa) and elongation for sample **B6** (65.60%).

Table 4. Results of the mechanical properties

	TS (MPa)	E (%)
B1	*	*
B2	**0.61 ± 0.003**	**17.80 ± 0.013**
B3	2.78 ± 0.001	34.40 ± 0.002
B4	0.11 ± 0.092	10.60 ± 0.367
B5	0.70 ± 0.002	12.20 ± 0.3
B6	1.04 ± 0.065	65.60 ± 0.037
B7	1.62 ± 0.002	39.00 ± 0.38
B8	0.84 ± 0.15	43.20 ± 0.04

*impossible to test, the specimen could not be dimensioned according to the standards used.

High values of elongation can be observed in the case of samples **B6** (65.60%) and **B8** (43.20%), with higher amounts of sodium alginate and glycerol in the composition. The composition of the **B2** sample - only sodium alginate and glycerol - facilitated the decrease in tensile strength, the value obtained after testing being 0.61 MPa.

Due to the shape, sample **B1** could not be tested for mechanical evaluation, because it was impossible to perform the test.

CONCLUSIONS

The purpose of these determinations was to develop, characterize and test a new material that can be used for packaging of low moisture content products, such as food supplements. The initiative is very useful, if we take into account the fact that the supplement industry is of great interest to the manufacturing companies. As proof are the figures regarding food supplements notifications; for example, IBA Romania (National Research and Development Institute for Food Bio resources Bucharest, Romania) notified over 920 food supplements in 2020 and over 1500 in 2019 (****).

The packaging used mainly for the delivery and sale of these products sold in small portions is usually multilayer, difficult to sort and recycle, highly pollutant to the environment. Taking into account the global and European programs that aim to identify alternative solutions, the newly developed and tested material is of great interest.

According to the results obtained, the sample **B7**, obtained from 62.5% agar, 25% sodium alginate and 12.5% glycerol presented the best results of physical and optical properties, but also high tensile strength and above average elongation. The sample without the addition of agar in the composition (**B1**) present the best solubility, but was impossible to be tested in order to establish the mechanical characteristics.

According to the microbiological results, all the materials obtained are safe for consumption. The films are free of the tested microorganisms, respectively coliform bacteria, *S. aureus*, *E. coli*, enterobacteria or yeasts and molds.

Future tests involve the use of films for the packaging of supplements, in order to establish the shelf life and possible changes that occur due to handling, transport, storage and marketing. To improve the sensory and nutritional characteristics and increase their shelf life, various natural substances can be added to the film-forming solution, such as fruit and vegetable powders, essential oils, dyes or flavorings.

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