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Lyophilized Protein Structures as an Alternative Biodegradable Material for Food Packaging

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Abstract: Considering the need for sustainable development in packaging production and environmental protection, a material based on lyophilized protein structures intended for frozen food packaging was produced and its selected thermophysical properties were characterized. Analyses of density, thermal conductivity and thermal diffusivity were performed and strength tests were carried out for lyophilized protein structures with the addition of xanthan gum and carboxymethyl cellulose. Packagings were made of new materials for their comparative assessment. Then, the surface temperature distribution during thawing of the deep-frozen product inside the packaging was tested. In terms of thermal insulation capacity, the best properties were obtained for sample B4 with a thermal conductivity of $\lambda = 0.06 \text{ W} \cdot (\text{mK})^{-1}$, thermal capacity $C = 0.29 \text{ (MJ} \cdot (\text{m}^3\text{K})^{-1})$ and thermal diffusivity $a = 0.21 \text{ (mm}^2 \cdot \text{s}^{-1})$. The density and hardness of the obtained lyophilized protein structures were significantly lower compared to foamed polystyrene used as a reference material. Thermal imaging analysis of the packaging showed the occurrence of local freezing. Lyophilized protein structures obtained from natural ingredients meet the needs of consumers and are environmentally friendly. These were made in accordance with the principles of sustainable development and can be an alternative material used for the production of frozen food packaging.

Keywords: packaging; biodegradable material; lyophilized protein structure

1. Introduction

Packaging is an important factor in maintaining food quality and commercial attractiveness, facilitating its transport at the same time. Nowadays, packaging, in addition to protecting, informing or marketing functions, should show additional functional properties and meet many different requirements. Innovations play a special role in modifying packaging functionality and improving its barrier, strength and aging resistance properties while avoiding the use of environmentally harmful materials. This contributes to the creation of a new generation of packagings that allow to maintain and even improve the quality of the packaged product, which is a very desirable feature, especially in the case of food packaging [1,2]. Legal regulations, legislative pressure from governments and non-governmental organizations dealing with environmental protection [3,4], as well as consumers themselves make food producers more and more interested in providing new pro-ecological and sustainable solutions in production. At the same time, packaging made in accordance with the principles of sustainable development must be safe for health, life and the environment [5–7].

One of the directions of development of food packaging technology that meets the requirements of sustainable development is obtaining fully composted and biodegradable materials with the addition of natural fillers [8]. An alternative that can reduce carbon footprint, pollution risks and greenhouse gas emissions caused by the use of conventional polymers is the use of biopolymers from agroindustrial sources that are renewable and low cost [9]. Recent studies have shown that starch can be used to obtain foams [10–12] retaining its biodegradable character when converted to a thermoplastic material. Research on the use of natural fillers such as: plantain flour, wood fiber, sugarcane bagasse, asparagus peel fiber [13,14], sunflower protein and cellulose fiber [15], plant protein, palm oil [16] and grape stalks [1] help to improve the physical, chemical, mechanical and technological properties of the material. For example, protein derivatives are the most attractive biopolymers for edible film formulations because they provide high nutritional value, superior mechanical properties and exhibit the oxygen barrier [17]. Carboxymethylcellulose based films are easily water soluble as it contains a hydrophobic polysaccharide backbone and many hydrophilic carboxyl groups [18]. Carboxymethylcellulose improves protein film mechanical properties by increasing thermal stability and the elasticity modulus [19]. Gelatin films blended with xanthan gum characterize a transparent film with excellent ultraviolet light resistance, low total soluble matter and moisture content, low water vapour permeability, improved mechanical properties and thermal stability [20]. Xanthan gum is cross-linker to be blended with various materials; it may dissolve directly in many highly acidic, alkaline, alcoholic systems containing different components. It is also compatible with commercially available thickeners such as sodium alginate, carboxymethylcellulose and starch [21].

Biodegradable packaging, due to the possibility of full compostability, does not pose a threat to the environment. On the contrary, it can enrich the soil with nutrients. Despite significant technological progress, there are no packaging that meets all the requirements. For each group of products, especially chilled and frozen ones, the most rational packaging is selected taking into account technical, economic and legal conditions [22–24].

This paper discusses the need for sustainable development in packaging production to protect the environment, and a material based on lyophilized protein structures for frozen food has been produced and its selected thermophysical properties have been characterized. Hence, the present work used xanthan gum and carboxymethylcellulose as a crosslinking agents to form a potentially new natural and biodegradable materials. For this purpose, prototype packagings were made from the obtained lyophilized structures. The thawing kinetics of food stored in these packagings and in packaging made of foamed polystyrene were compared.

2. Materials and Methods

2.1. Research Material

The research material was lyophilized protein structures prepared on the basis of foams obtained from powdered albumin with high foaming activity containing 84.3% protein (*Basso*), modified by addition of carboxymethylcellulose (*Agnex, Bialystok*) and xanthan gum (*Agnex, Bialystok*) in various percentage. Preparation of foams consisted of whipping albumin in distilled water for 5 minutes. Powdered carboxymethylcellulose and xanthan gum were added to the resulting foams and mixed for another 2–3 min. Four different foam variants with different percentages of individual components were prepared: 1-distilled water 88.0%, albumin 10.0% and carboxymethyl cellulose 2.0% (B1); 2-distilled water 88.0%, albumin 10.0% and xanthan gum 2.0% (B2); 3-distilled water 88.0%, albumin 6.0% and xanthan gum 6.0% (B3); 4-distilled water 88.0%, albumin 8.0% and xanthan gum 4.0% (B4). The obtained protein foams were transferred into 0.125 × 0.125 m plastic moulds. The samples prepared in this way were frozen in an air blast freezer at −30.0 °C. Then, after freezing, the sample was lyophilized for 72 h at a pressure of 20 Pa and an ice condensation temperature of −64 °C (ALPHA 2–4LD Plus freeze-dryer, Christ, Osterode am Harz, Germany) [25]. The obtained lyophilized protein structures with a thickness of 0.027 m are shown in Figure 1.

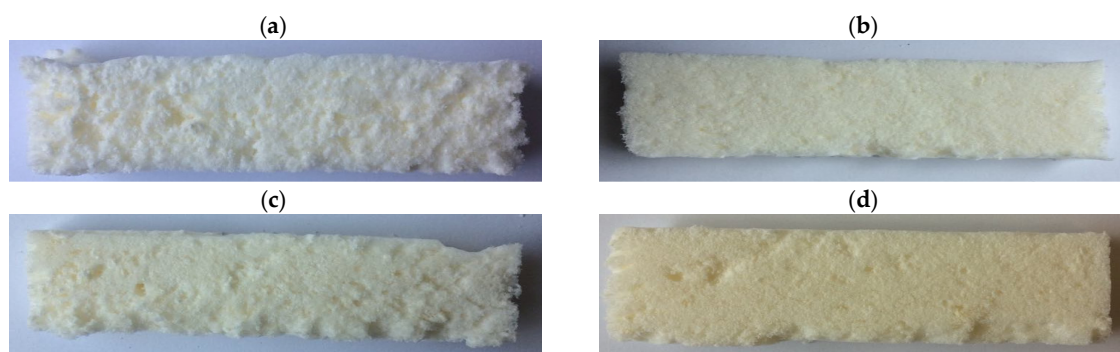


Figure 1. Cross-section of lyophilized protein structures: (a) B1, (b) B2, (c) B3, (d) B4.

2.2. Determination of Protein Structure Density

The density of the obtained samples (ρ) was calculated as the ratio of the mass of the samples to their volume. The volume of samples was determined using the formula for the cuboid volume (multiplying the dimensions: length, height and width).

2.3. Determination of the Strength of Protein Structures

For determination of the strength (hardness) of lyophilized protein structures, a fracture test was performed using a symmetrical knife with dimensions: blade thickness 0.003 m, blade angle 30° (texture analyzer LFRA 4500, Brookfield, Middleboro, MA, USA). Parameters of the device operation: knife speed $0.5 \text{ mm}\cdot\text{s}^{-1}$ and measurement accuracy 0.02 N. The dimensions of the tested samples were $0.10 \times 0.04 \text{ m}$. The test for each sample was performed in 3 replications [26].

2.4. Measurement of Thermophysical Properties of Protein Structures

Lyophilized samples were analyzed for thermophysical properties such as thermal conductivity, heat capacity and thermal diffusivity using a KD2 Pro meter (Decagon Devices, Pullman, WA, USA) with the SH-1 probe. The measurement was carried out in 8 replications under the same conditions [27].

2.5. Making a Packaging Prototype

The packaging was made of 6 even cuboid walls with dimensions of $0.115 \times 0.115 \text{ m}$ and thickness of 0.18 m. The walls were joined with a specialist adhesive approved for food contact (LOCTITE 454). Only samples B3 and B4 were used for packaging. The remaining samples were rejected due to the soft and fragile structure that made them impossible to test. The reference packaging was made of foamed polystyrene (XPS) (Figure 2).

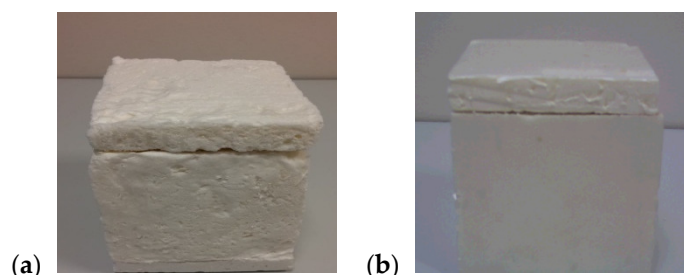


Figure 2. View of lyophilized protein structure of the sample B3 (a) and foamed polystyrene (b) packagings.

2.6. Thermovision Analysis of Lyophilized Protein Structures

For comparative assessment of the samples, the temperature fields recorded on their surface during thawing of the deep-frozen product (carrot with green peas) placed inside the packaging were tested. Thawing was carried out at an ambient temperature of 25°C until the thawed product inside

the packaging reached 23 °C. The temperature analyzer LB-515P cooperating with mini temperature and humidity data logger (type 23) was used to measure and record temperature. The mini data logger recorded temperature in a frozen product inside the packaging. The data obtained were used to compare thawing kinetics. For analysis of changes occurring during thawing of products on the surface of packaging walls, a Testo 882 thermal imaging camera (detector resolution 320 × 240 pixels, measuring accuracy ±2 °C, thermal sensitivity < 50 mK), cooperating with the Testo IRSoft program Version 3.4., was used. Thermovision analysis of lyophilized structures was based on the detection of thermal bridges, i.e., points on the surface of the packaging wall with the highest temperature and histograms of temperature distribution along the line passing through the point with the lowest temperature (CS).

2.7. Statistical Analysis of Results

The results were evaluated with statistical analysis methods (determination of mean values, standard deviation) using the *Statistica* 13.1 program and analysis of variance (ANOVA) at a at the 95% confidence level. To verify the significance of differences between the average values, the Student's *t*-test was used, where the distribution of variables, followed a normal distribution.

3. Results and Discussion

3.1. Physical Properties of Obtained Lyophilized Protein Structures

Materials used for food packaging should have appropriate density. This parameter is closely related to the thermal conductivity coefficient. This relationship determines the decrease in the thermal conductivity coefficient as the material density increases. Material density is also important when mechanical properties are formed [28]. Table 1 shows the density and hardness of lyophilized protein structures modified by the addition of carboxymethylcellulose and xanthan gum in varying percentages. It was found that the density of lyophilized protein structures defined as the ratio of mass to volume increases with the increase of xanthan gum share in the samples B2, B3 and B4. The highest density (28.22 kg·m⁻³), was noted for the sample B1 containing 10.0% albumin and 2.0% carboxymethyl cellulose, while the sample B2, which contained 10.0% albumin and 2.0% xanthan gum, had the lowest density (20.41 kg·m⁻³). The percentage and type of modification used had a statistically significant impact on the density of lyophilized protein structures. The values of density of the obtained materials were significantly lower compared to foamed polystyrene which served as the reference sample. The density of the material is determined by the volume and dimensions of air bubbles which in turn depend on the viscosity of the environment and the conditions for the formation and dispersion of the gaseous phase [29].

Table 1. Density and bending force of lyophilized samples and foamed polystyrene.

Properties	B1	B2	B3	B4	XPS
Density (kg·m ⁻³)	28.22 ± 0.28 ^b	20.41 ± 0.07 ^c	25.01 ± 0.11 ^d	24.51 ± 0.66 ^d	36.51 ± 1.17 ^a
<i>p</i> -value	0.01	0.001	0.003	0.002	
Bedning force (N)	0.68 ± 0.20 ^b	1.00 ± 0.21 ^b	4.49 ± 0.53 ^c	1.55 ± 0.11 ^d	20.84 ± 0.52 ^a
<i>p</i> -value	0.0001	0.0004	0.001	0.0004	

^{a,b,c,d} Means in the same line indicated by different letters were significantly different (*p* value < 0.05). The results are expressed as mean ± SD (*n* = 3).

The conducted fracture test showed a much greater hardness of lyophilized protein structures with xanthan gum than those with carboxymethyl cellulose. The sample B3 containing 6.0% albumin and 6.0% xanthan gum had the highest hardness (4.49 N), whereas the lowest hardness (0.68 N) was noted for the sample B1, which contained 10.0% albumin and 2.0% carboxymethyl cellulose. The obtained lyophilized protein structures had a statistically significantly lower hardness compared to the reference material, which was foamed polystyrene (20.84 N). Hazirah et al. [30] showed that physical and

mechanical properties of gelatin-carboxymethylcellulose films were best improved with 5% xanthan gum added. The use of xanthan gum a non-gelling nature, as an alternative crosslinking agent in gelatin/carboxymethylcellulose film blend have formed a blend of composite film and improved several physical and mechanical properties of gelatin/carboxymethylcellulose film blend alone. Results Lima et al. [31] demonstrated that films containing higher content of xanthan gum show the highest tensile strength and the lowest elongation. Xanthan gum addition did not affect the water vapor permeability, solubility, and moisture of films.

3.2. Characteristics of Thermophysical Properties of Obtained Protein Structures

Table 2 presents thermophysical properties (coefficient of thermal conductivity— λ , heat capacity— C , thermal diffusivity— a) of lyophilized protein structures modified with a different percentage of carboxymethyl cellulose and xanthan gum. The coefficient of thermal conductivity (λ) characterises the material's ability to conduct heat. It is defined as the heat flux per unit area of the material with a temperature gradient of $1 \text{ K}\cdot\text{m}^{-1}$ [28]. The study demonstrated that modification of material composition affected statistically significantly ($p < 0.05$) the value of thermal conductivity coefficient. The lowest value of this parameter ($0.06 \text{ W}\cdot(\text{mK})^{-1}$) was noted for protein structures obtained from 8.0% albumin and 4.0% xanthan gum (B4) and it was comparable to foamed polystyrene ($0.04 \text{ W}\cdot(\text{mK})^{-1}$), which is widely used as a material with insulating properties. Similar values of thermal conductivity were reported by Kozłowicz et al. [25]. The thermal conductivity of lyophilized gelatin structures ranged from 0.045 to $0.063 \text{ W}\cdot(\text{mK})^{-1}$. The values of thermal conductivity determined for lyophilized gelatin structures modified with hydrated paper pulp, ground extruded starch and hydrogel balls were in the range of 0.047 – $0.081 \text{ W}\cdot(\text{mK})^{-1}$ [32].

Table 2. Thermal properties of lyophilized samples and foamed polystyrene.

Properties	B1	B2	B3	B4	XPS
Thermal conductivity λ ($\text{W}\cdot(\text{mK})^{-1}$)	0.12 ± 0.01^b	0.13 ± 0.01^b	0.12 ± 0.01^b	0.06 ± 0.00^c	0.04 ± 0.00^a
<i>p</i> -value	0.000	0.000	0.000	0.000	
Heat capacity C ($\text{MJ}\cdot(\text{m}^3\text{K})^{-1}$)	0.40 ± 0.02^b	0.41 ± 0.03^b	0.41 ± 0.02^b	0.29 ± 0.02^c	0.26 ± 0.02^a
<i>p</i> -value	0.000	0.000	0.000	0.02	
Thermal diffusivity a ($\text{mm}^2\cdot\text{s}^{-1}$)	0.30 ± 0.01^b	0.30 ± 0.01^b	0.28 ± 0.01^b	0.21 ± 0.01^c	0.18 ± 0.01^a
<i>p</i> -value	0.000	0.000	0.000	0.000	

^{a,b,c} Means in the same line indicated by different letters were significantly different (p value < 0.05). The results are expressed as mean \pm SD ($n = 3$).

Lyophilized protein structures modified with carboxymethylcellulose 2% (B1) and xanthan gum 2% (B2) and 6% (B3) had a significantly higher heat capacity C ($0.40 \text{ MJ}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$ and $0.41 \text{ MJ}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$) than lyophilized protein structures with addition of 4% xanthan gum (B4) ($0.29 \text{ MJ}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$) and foamed polystyrene ($0.26 \text{ MJ}\cdot\text{m}^{-3}\cdot\text{K}^{-1}$). Heat capacity is defined as the ratio of the amount of heat absorbed by the material to the resulting increase in temperature. Materials with high heat capacity require more heat than those with low heat capacity to achieve the same effect of a temperature rise. In packaging, it is preferable to use materials with high heat capacity. Packagings made of such materials will maintain a constant temperature of the product inside.

Another value characterizing a material in terms of its thermal properties is thermal diffusivity a , which determines the ability of a given material to transfer heat within it and reduce temperature gradients. Thermal diffusivity in lyophilized protein structures, modified with carboxymethylcellulose and xanthan gum, ranged from 0.21 – $0.30 \text{ mm}^2\cdot\text{s}^{-1}$. The obtained thermal diffusivity values were significantly higher ($p < 0.05$) than those noted for foamed polystyrene ($0.18 \text{ mm}^2\cdot\text{s}^{-1}$). This value is determined by the structure, chemical composition and temperature describing the speed of heat conduction in the material [28].

3.3. Analysis of Thawing Kinetics

The thawing curve is a widely used data source for determining changes of the frozen product's temperature during thawing (Figure 3).

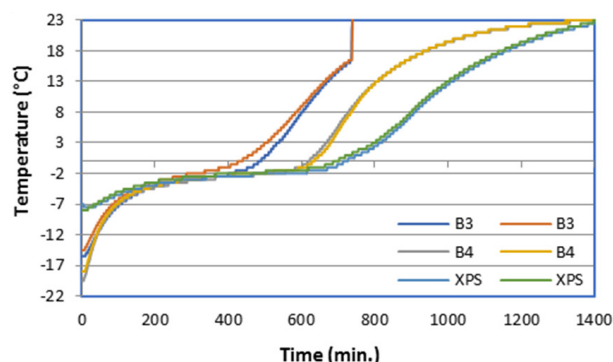


Figure 3. Thawing curves for carrots with green peas in packaging (B3—6.0% albumin, 6.0% xanthan gum, B4—8.0% albumin, 4.0% xanthan gum, XPS—foamed polystyrene).

Considering the temperature changes over time in the form of thawing curves summarized in diagrams (Figure 3), it was found that in a packaging made of lyophilized protein structures B3, the thawed product kept the temperature below 0 °C for the shortest time (temperature measured after 7.5 h). The temperature of 0 °C was reached by the thawed product in a packaging made of lyophilized protein structures B4 after 10 h. It was the time of thawing compared to that recorded for the product placed in the packaging made of foamed polystyrene (11.7 h).

3.4. Thermovision Analysis of Designed Packaging

The operation of the thermal imaging camera is based on the phenomenon of infrared radiation. The temperature distribution on the surface of the tested packaging is presented in the form of colored isotherms, where the individual color corresponds to points having the same temperature [33].

The packagings were subjected to thermovision analysis when testing changes in temperature during defrosting of the product. Figure 4 presents a thermovision image of packaging made of lyophilized protein structures of the B3 sample with characteristic parameters. The point CS1 specifying the lowest temperature occurring on the packaging wall (20.1 °C) and temperature profiles on the straight lines P1 and P2 are presented. A histogram was prepared for the thermovision image shown in Figure 5. The histogram is used to present the empirical distribution of features, so it is possible to use it to present the results obtained for certain quantitative variables. It was found that temperatures in the range of 21.4–22.5 °C had the largest share of the entire area, constituting about 65%. Analysis of the temperature distribution profile on the line P1 shows a minimum temperature of 20.1 °C (uneven material structure, uneven aeration) and a maximum temperature of 22.5 °C. The temperature distribution on the line P2 shows the minimum value of 21.8 °C and the maximum value of 24.6 °C (Figure 6).

Figure 7 presents a thermovision image of a packaging made of lyophilized protein structures (8.0% albumin, 4.0% xanthan gum) of the sample B4. At CS1, the lowest packaging surface temperature was 19.9 °C. The largest share in the whole area, constituting 82.0% of the total individual temperatures, was recorded for the range of temperature 23.3–25.0 °C (Figure 8). Analysis of the temperature distribution profile on the line P2 shows the temperature with minimum of 20.8 °C and maximum of 25.2 °C, while the temperature distribution on the line P3 shows the minimum value of 20.0 °C and the maximum value of 24.8 °C (Figure 9).

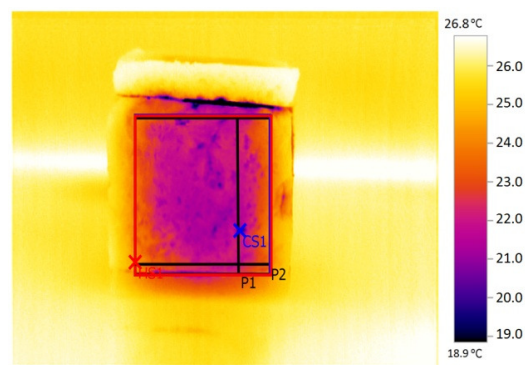


Figure 4. Infrared image of packaging surface with analysis of temperature profile and its extreme values (B3).

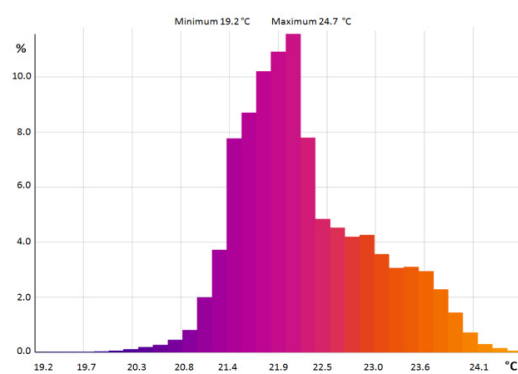


Figure 5. The histogram of temperature distribution on packaging surface (B3).

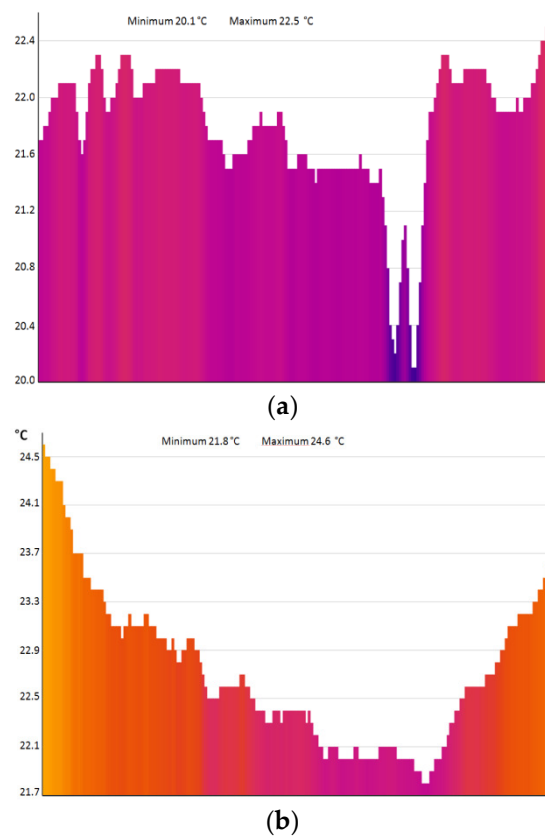


Figure 6. The temperature distribution profile of pack surface samples B3 in line (a) P1, (b) P2.

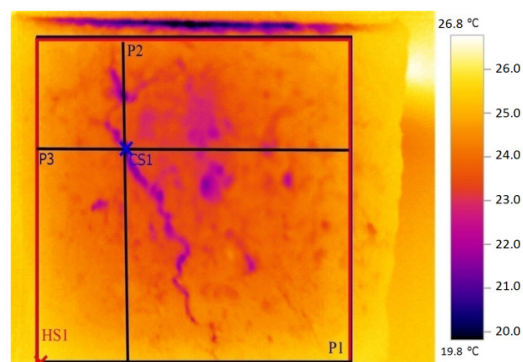


Figure 7. Infrared image of packaging surface with analysis of temperature profile and its extreme values (B4).

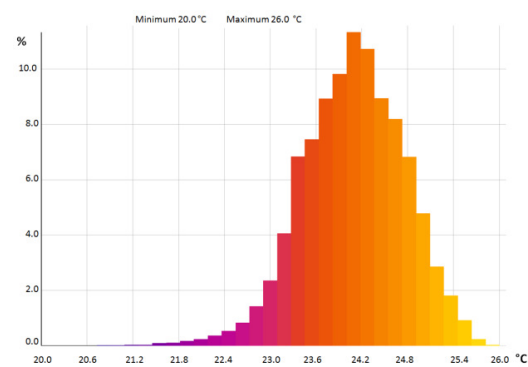


Figure 8. The histogram of temperature distribution on packaging surface (B4).

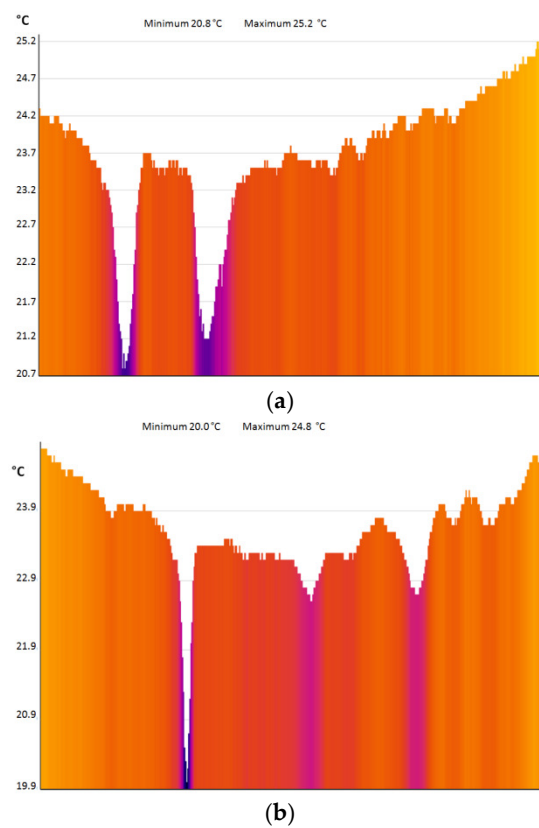


Figure 9. The temperature distribution profile of packaging surface samples B4 in line (a) P2, (b) P3.

For comparison purposes, packagings made of foamed polystyrene (XPS) were also subjected to the thermovision analysis. The image of the surface of packaging wall is shown in Figure 10 together with the profile analysis and indication of extreme values. The histogram of the temperature distribution for the entire surface area of the packaging (Figure 11) shows that about 40% of the total temperature is in the range 23.5–24.0 °C. Analysis of the temperature distribution profile on the line P1 shows the minimum temperature of 23.3 °C and maximum temperature of 24.8 °C. Whereas these values on the line P2 are, respectively, 24.7 °C and 25.7 °C (Figure 12).

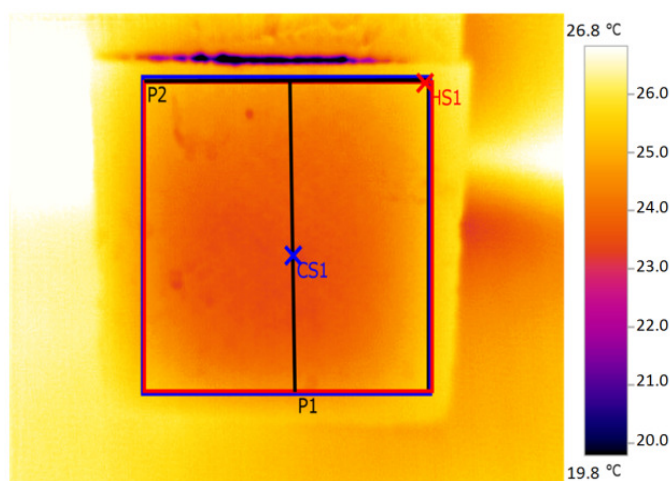


Figure 10. Infrared image of packaging surface with analysis of temperature profile and its extreme values (XPS).

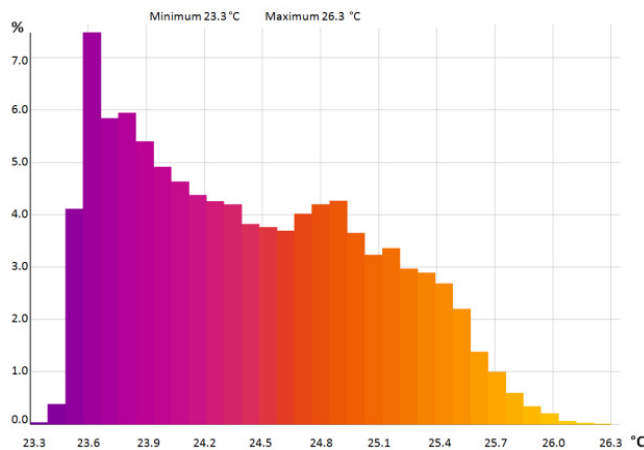


Figure 11. The histogram of temperature distribution on packaging surface (XPS).

The obtained results are consistent with the results of studies conducted previously by other authors who used lyophilized gelatin structures and lyophilized protein structures modified with agar and gelatin as packaging with good thermal insulation properties for frozen food [25,26]. The possible biodegradability of such material means that it can be a suitable replacement for foamed polystyrene used in the production of packaging.

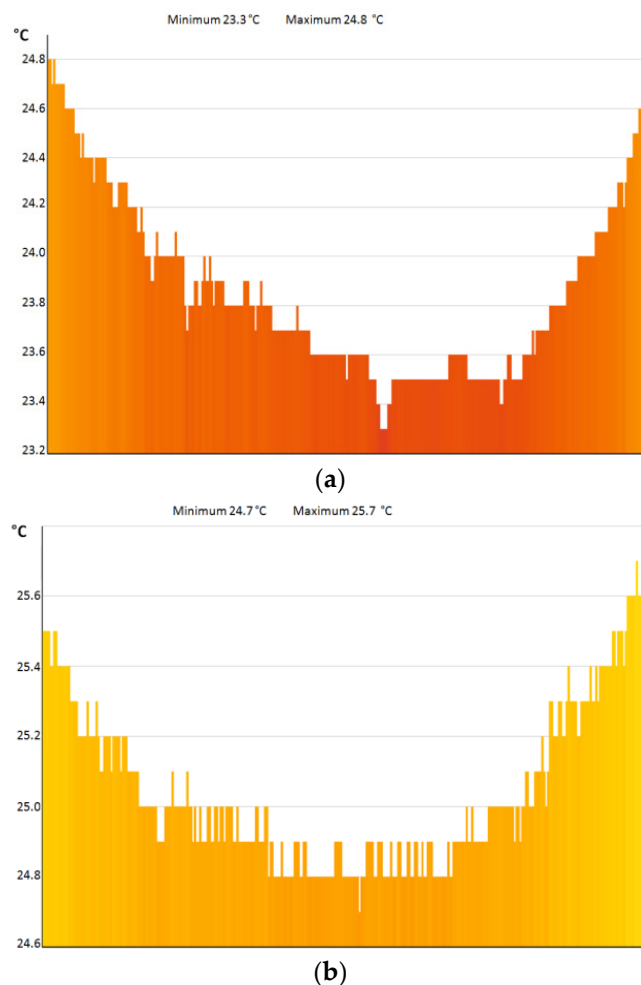


Figure 12. The temperature distribution profile of the foamed polystyrene packaging in line (a) P1, (b) P2.

The trend of using natural resources to produce packaging materials is now very common. Such materials include polysaccharides (corn and potato starch, cellulose, gums), animal proteins (casein, collagen, gelatin), vegetable (soy, gluten) and lipids (oils from fats) [34,35]. The use of proteins of animal and vegetable origin has proved to be promising in obtaining films and mixtures development of biodegradable packaging. The proteins hake films were more resistant and soluble in water, while gluten films showed greater elongation on cracking [36]. Microbial biopolymers such as gellan, bacterial cellulose, xanthan, pullulan, and curdlan are non-toxic, biocompatible, and biodegradable. They are used in the food industry as material for coating and packing purposes. The packagings prepared from these polymers are transparent and have good mechanical, moisture, and oxygen barrier properties, but weak water barrier properties. The blending of microbial gums with lipids, hydrocolloids or reinforcement agents improves the functional properties of materials [37]. However, it should continue to look for strategies that promote the improvement of the mechanical and barrier properties of these materials. Only in this way will it be possible to replace, partly or completely synthetic polymers with biodegradable polymers. These materials allow to maintain an appropriate quality of packaged raw materials. In addition, packaging made of natural materials does not require biodegradability testing.

4. Conclusions

The conducted research confirmed the possibility of using albumin foams in the form of lyophilized structures as an alternative material for frozen food packaging. In terms of thermal insulation, the proposed structures are also well suited to packaging material for frozen products as foamed

polystyrene The best thermophysical properties were obtained for the sample B4 with thermal conductivity of $\lambda = 0.06 \text{ W} \cdot (\text{mK})^{-1}$, thermal capacity $C = 0.29 \text{ (MJ} \cdot (\text{m}^3\text{K})^{-1})$ and thermal diffusivity $a = 0.21 \text{ (mm}^2 \cdot \text{s}^{-1})$. The density of the obtained lyophilized protein structures was significantly lower compared to the reference material (foamed polystyrene). The obtained materials had statistically significantly lower hardness than foamed polystyrene. The analysis of thawing curves of frozen carrots with green peas showed that the product placed in a packaging made of foam polystyrene reached temperature 0°C after the longest time (11.7 h). A slightly lower defrosting time was recorded in the product kept in packaging from material B4 (10 h). Thermovision analysis of the tested packagings showed the occurrence of local freezing. Lyophilized protein structures obtained from natural ingredients can be classified as materials made in accordance with the principles of sustainable development that meet the needs of consumers and which are environmentally friendly. These are completely biodegradable materials, suitable for composting and made from natural resources. In addition to biodegradability, lyophilized protein structures are distinguished by high insulation and low density, which provide adequate protection for stored frozen food. In addition, all the ingredients in the obtained lyophilized structures are 100% approved for contact with food, hence they can be a substitute for foamed polystyrene in the production of packaging.

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