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Research on innovation of smart packaging by biomaterials with antiseptic properties

Steluta V. Radu[1], Stefan -Lucian Toma[2]

[1]University of Life Science "Ion Ionescu de la Brad" Iasy, Faculty of Agriculture, Food Technologies Departament, No.3, Aleea Sadoveanu street, Iasi, Romania
[2]University "Gheorghe Asachi" Iasi, Romania

Abstract

Applied research aimed at innovating smart packaging made of biodegradable materials. The experimental aimed to identify the type of biomaterial and the proportion needed to develop a material with improved physical and mechanical characteristics, as well as to establish the biopolymers that will be used to obtain the new single-use smart biofilms. After the research activity, an edible material for single-use packaging was obtained: its testing and characterization, benefits in use, applicability were performed. Creating smart biofilms with various additives, phytoncide extracts - in order to present alternatives to the materials for packaging dehydrated and candied food, existing today in the trade with foods. Also, a series of substances with antiseptic properties were extracted from plants containing phytoncides and biomaterials were impregnated to improve their antiseptic characteristics. The final results also aimed at establishing the products that can be packed in newly developed materials, with the possibility of obtaining and immediate application in the specialized industry.

Keywords: biofilms, hydrocolloids, phytoncides

1. Introduction

By origin, all polymers are divided into synthetic and natural. Natural polymers come form the basis of all animal and plant organisms. These include polysaccharides (cellulose, starch), proteins, nucleic acids, natural rubber and other substances. Although modified natural polymers find industrial applications, most plastics are synthetic. Plastics are classified according to various criteria: chemical composition, hardness. The main criterion that explains the nature of the polymer heating of plastic. On this basis, all plastics are divided into three main groups: thermoplastics, thromdes, elastomers. Belonging to a particular group is determined by the shape, size and location of macromolecules, along with their chemical composition. Thermoplastics are plastics that melt when heated and return to their original state when cooled. These are composed of linear or slightly branched molecular chains. At low temperatures, the molecules are tightly bound together and difficult to move. Under these conditions, the plastic is hard and brittle. If it heat the plastic even more, the intermolecular bonds become even weaker and the molecules begin to slide against each other - the material passes into an elastic, viscous flow state. As the temperature drops and cools, the whole process goes in reverse order [26]. Bioplastics are materials produced from renewable sources biomass sources, such as vegetable fats and oils, corn starch, vegetable waste, recycled, etc. Bioplastic can be made from by-products and used plastics (ie plastic bottles and other containers) by using microorganisms. Bioplastics are usually derived from sugar derivatives, including starch, cellulose and lactic acid. A dedicated bio-based pathway allows the production of products that cannot be obtained by traditional chemical reactions and can create products that have unique and superior properties. In 2014, bioplastics accounted for approximately 0.2% of the global polymer market (300 million tonnes) [20]. Starch is the most widely used bioplastic, accounting for about 50% of the bioplastics market [10]. The simple bioplastic starch film can be made by gelatinizing and pouring the solution [11]. Pure starch is able to absorb moisture. Plasticizers such as glycerol, glycol and sorbitol, can be added so that the starch can be processed thermoplastic [12].

Corresponding authors: E-mail: stelaradu@yahoo.com

The characteristics of 'thermoplastic starch' can be adapted to specific needs by adjusting the quantities of these additives. Conventional polymer processing techniques can be used to process starch into bioplastics, such as extrusion, injection moulding, compression, and solution casting [12]. The properties of starch bioplastic are largely influenced by the amylose / amylopectin ratio. Starch with a high amylose content may have better mechanical properties [13]. However, amylose-rich starch has lower processability due to its higher gelatinization temperature [14] and higher viscosity on melting or solubilization [15]. Starch bioplastics are often mixed with biodegradable polyesters to produce mixtures of starch / polylactic acid, [16] starch/polycaprolactone [17] or starch/Eco-flex [18] (polybutylene-adipate-co-terephthalate [26]). These mixtures are used for industrial applications and are also compostable. Other manufacturers have developed other starch/ polyolefin blends that are not biodegradable but have a lower carbon footprint than petroleum-based plastics used for the same applications [20]. Due to the origin of the raw material, starch is cheap, abundant and renewable [21]. Starch plastics are complex mixtures of starch with biodegradable or compostable plastics, such as polylactic acid, adipate polybutylene terephthalate, polybutylene succinate, polycaprolactone, and polyhydroxy alkanoates. These complex mixtures improve water resistance as well as mechanical and processing properties [21]. Starch films (mainly used for packaging) are mainly made of starch mixed with thermoplastic polyesters to form biodegradable and compostable products. These films are especially seen in the packaging of consumer goods in magazine packaging and bubble wrap. In food packaging, these films are seen as bakery or fruit and vegetable packages. Composting bags with these films are used in the selective collection of organic waste [21]. Moreover, a new starch-based film was developed by scientists from the Agricultural Research Service and can even be used as paper. Starch nanocomposites have been extensively studied with improved mechanical properties, thermal stability, moisture resistance, and gas barrier properties [22]. *Environmental impact*. Materials such as starch, cellulose, wood, sugar and biomass are used as substitutes for fossil fuel resources to produce bioplastics; this makes the production of bioplastics a more sustainable activity compared to conventional plastic production.

The environmental impact of bioplastics is often debated, as there are many different values for "green" (eg.water or energy use, deforestation, biodegradation, etc.). Therefore, the bioplastic impact on the environment is classified into the use of non-renewable energy, climate change, eutrophication and acidification. Firms around the world could increase the environmental sustainability of their products by using bioplastic. Biomass production during industrial agricultural practices causes filtration of nitrates and phosphate in water bodies; this causes eutrophication, the process by which a body of water gains an excessive richness of nutrients. Eutrophication is a threat to water resources around the world, as it causes harmful algae blooms that create dead zones of oxygen, killing aquatic animals. The large increase in eutrophication and acidification caused by bioplastics is caused by the use of chemical fertilizers in the cultivation of renewable raw materials to produce bioplastics. Bioplastics also cause carbon dioxide emissions. Other minor environmental impacts include high water consumption for biomass cultivation, soil erosion, soil carbon loss and biodiversity loss and are mainly the result of land use associated with bioplastics. Land use for bioplastics leads to carbon loss and increases carbon costs, while diverting land from its existing uses. Some bioplastics are made from the edible parts of crops [21]. This makes bioplastics compete with food production, as crops that produce bioplastics can also be used to feed people. These bioplastics are called "first generation bioplastics". Second-generation raw material bioplastics use non-food crops (cellulosic raw material) or waste from first-generation raw material (eg residual vegetable oil). The third generation of raw material bioplastics uses algae as raw material [20].

2. Materials and Method

The experiment was aimed to obtain intelligent biofilms with additives or antiseptic extracts, which by drying can be sufficiently resistant and elastic to form a package. The ecological tendencies of reusing some materials and the need to replace plastics or cardboard determine new techniques for obtaining packaging in the food industry. Without the physical and mechanical properties, the biomaterials from which food packaging is built today must also have antiseptic properties.

In this sense, plant extracts, containing phytoncides, were used to prevent the penetration of microorganisms inside the packaging, so that the biological risk of microorganisms entering is eliminated. The way of obtaining the biofilms that were tested for the evaluation of the physical and mechanical properties was materialized by: determining the breaking strength and elasticity. The DUH 211S hardness micro instrument (Shimadzu) and the Mark 10 ESM 301 micro instrument for measuring texture, equipped with fixing systems for films and thin foils, according to STAS ASTM D 882 [17] were used for this purpose. In addition to the tests related to the determination of the resistance, there are also the tests related to the determination of the solubility of the films. The moisture content of packaged products - instant coffee, nesscafe, powdered milk, dehydrated vegetables and fruits - in the biomaterials under test was determined using the reference method STAS 90-88 [18]. Solubility was determined according to the method described by [4]. The swelling index, the moisture content of the material, the water activity index (aw), which provide information on the stability of the products, were also evaluated, using the AquaLab equipment, a test performed at the temperature of 20°C. So that, the microorganisms which grow in the food can be influenced by reducing the water content (dehydration) or binding it to the food. Microorganisms cease their activity at values of water activity index lower than 0.7. Throughout, water has often been removed or added to change the value of the water activity (aw) index in order to preserve the food quality [1]. The application of the Peleg model was investigated to estimate the water uptake by seven biomaterials during soaking between temperatures (T) of 20°C and 100°C. The Pelek model can predict the kinetics of softening biomaterials to equilibrium, using short-term data under given conditions. Its specific shape for infinite time can be used to estimate the equilibrium moisture content (Me). The samples did not show any significant difference ($P < 0.05$) in the Peleg velocity constant (k1) and the Peleg capacity constant (k2); and between groups at all temperatures except k1 [6]. This method provides accurate information about the moisture content and water absorption at different times, which characterizes both the hydrophobic properties of the biofilms and the interaction between biomaterials and water; parameters of practical significance for the interpretation of hydration kinetics [2].To observe the microstructure and roughness of the films, the Optika scanning microscope (X40) was used, accompanied by the OptiKa Microscopes Digital D3 video camera software. optical properties, the colour was tested using the CR-400 Konika Minolta colorimeter and the Ocean-Optics HR 4000 spectrophotometer, and the reading was made at a wavelength of 660 nm. The outer appearance of the membranes was also monitored - the adhesion to the silicone substrate used for drying, the fineness, the presence of pores and cracks that can be seen with the naked eye, the regularity of the edges and the uniformity of the films, the taste and smell. The characterization of the texture profile was performed with the help of the Perten TVT 6700 measuring instrument of texture and the related software, TexCalc 5. The obtained membranes were also characterized from a microbiological characteristics, an aspect related to the antiseptic properties of biofilms. For this purpose, both the films obtained and the ingredients used were tested to determine the incidence of *Coliform bacteria*, *Enterobacteria*, *Staphylococcus Aureus*, *Escherichia Coli*, but also yeasts and moulds. Culture media Standard I nutrient agar 107880500 for bacteria, Roth Yeast Extract, nongranulated 2904.2, VRB Fluor cult Agar were used for the determinations of moulds.

3. Results and Discussion

In order to test, agar films-films 1, agar-starch films-films 2, sodium agar-alginate-films 3, agar-starch-alginate-films 4, plasticizer films-films 5 were obtained, and agar films and plasticizer-films 6, (according to the method described by Rhim, J.W., (2015) [5], the optimal amount of plasticizer used, being a maximum of 30% of the total ingredients used. This composition determines the obtaining of a thin, fine, uniform film, without pores or cracks (fig.1).

The films with an agar-plasticizer composition are very good for packaging powdery products, which require solubilization before consumption. The solubility was improved by the addition of lipids or other hydrocolloids to the composition. Thus, all the obtained films showed low adhesion to the drying surface, were easily removed from the silicone support, were flexible and did not break, allowed bending and had a pleasant, uniform appearance; they had no taste or smell. The colour varied according to the ingredients used, so that the samples with high agar content in the composition

had a higher intensity of yellow colour. The use of the Peleg model to evaluate solubility was performed for temperatures of 20°C, 30°C, 40°C, 50°C and 60°C, respectively. The optimum solubility temperatures were between 20°C and 40°C, at values higher than 50°C-60°C, the samples were completely solubilized, re-quantification was impossible. The values of the constant k1 decreased, with the increase of the temperature (table1), finding experimentally, that with the increase of the temperature, the water transfer intensifies. (fig.1)

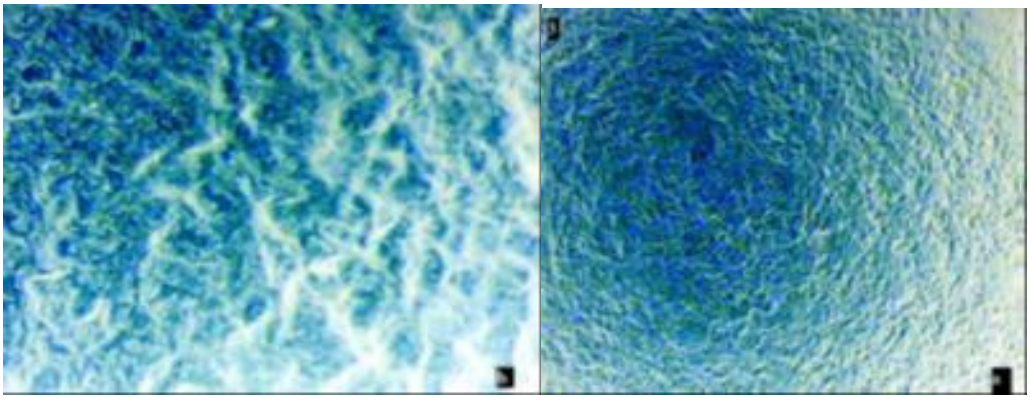

Figure 1. Microstructure of the film obtained from 70% agar and 30% plasticizer wet version, b- dry version)

Table 1. Values of the constant k2 as a function of temperature variation

Samples	K2 min.%⁻¹ at 20°C	R²	K2 min. %⁻¹ at 30°C	R²	K2 min. %⁻¹ at 40°C	R²
S1	78.4	0.997	77.89	0.998	77.27	0.998
S2	80.00	0.999	80.95	0.999	81.38	1.000
S3	80.68	0.999	80.41	0.999	82.98	1.000
S4	Completely solubilized					
S5	89.74	0.999	89.51	0.999	89.36	1.000
S6	87.44	0.999	87.38	0.999	87.12	0.999
S7	88.65	0.999	88.98	0.999	89.72	0.999

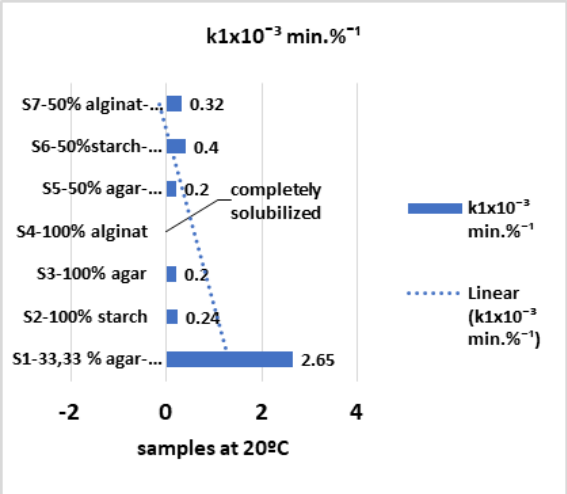

Figura 2. Dinamics of constant K1 function by temperature 20ºC

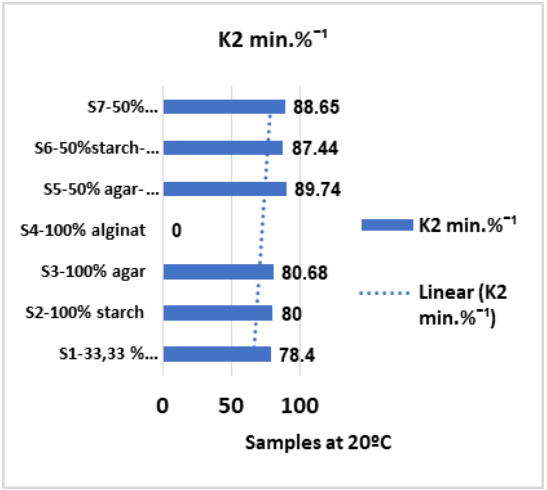

Figure 3. Dinamics of constant K2 by temperature 20ºC

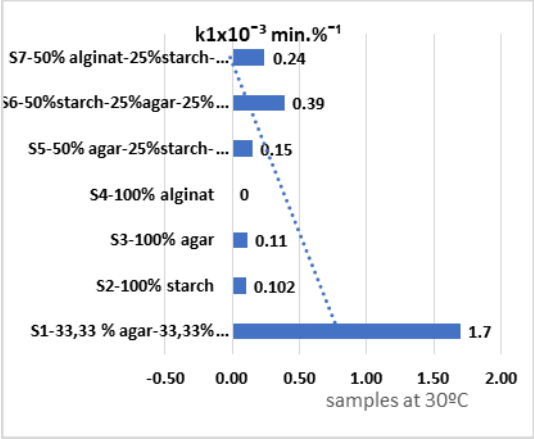

Figure 4. Dinamics of constant K1 function by temperature 30ºC

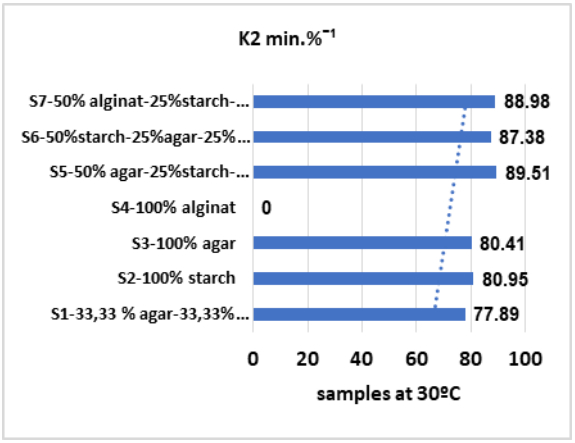

Figure 5. Dinamics of constant K2 by temperature 30ºC

S1-sample with equal content of sodium agar-starch-alginate -33.33%, S2-sample with high starch content (100%) without agar, S3-sample with high agar content (100%) without alginate, S4-sample with high alginate content (100%) without agar, S5-sample with high agar content (50%), equal to starch (25%) and alginate (25%), S6-sample with high starch content (50%), equal to agar (25%) and alginate (25%, S7- sample with high alginate content (50%), equal to starch (25%) and agar (25%). of sodium agar-starch-alginate for powdered foods, has a combination of hydrocolloids and 30% glycerol as a plasticizer, so it was made in seven types of films with different content, varying the amount of biopolymers and glycerol. distillate remained constant at 150 ml. The discrepancy for k1 was attributed to the characteristic water permeabilities of biomaterials. Peleg k1 decreased from 2.65 × 10−3 to % -1 for S1- the sample with equal content of sodium agar-starch-alginate, to 1.3% for the increase in temperature from 20°C to 40°C and at 0.2-0.4 × 10−3 at % -1 for samples S2, S3, S5, S6, S7 at 0.17-0.37 × 10−3 at% -1 with increasing temperature from 20 to 40°C. (fig.2,4,6). Peleg k2 for samples ranged from 77.27 to 89.72% -1 with increasing temperature from 20 to 40°C. The recording of R^2 values above 0.99 (Table 1) indicates the possibility of using this model to show the kinetics of water absorption in the case of material biofilms, in the temperature range 20-40°C (fig.3,5,7).

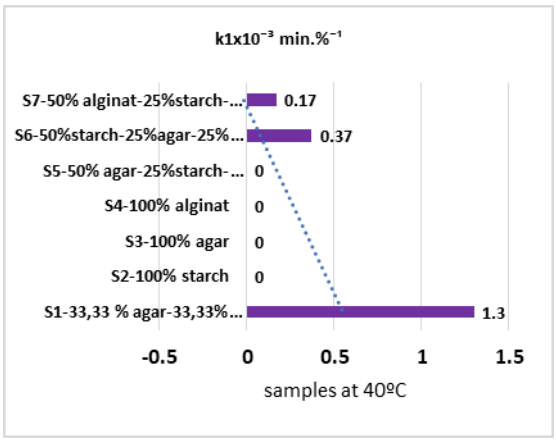

Figure 6. Dinamics of constant K1 function by temperature 40ºC

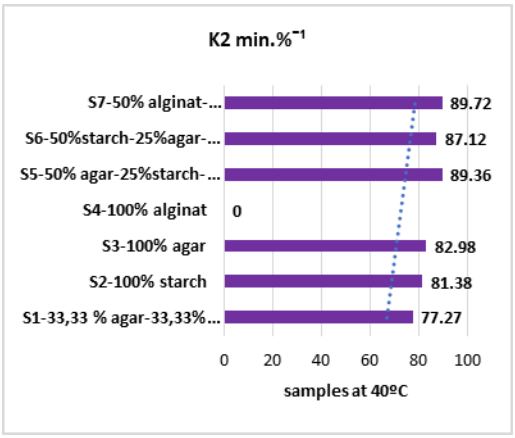

Figure 7. Dinamics of constant K2 function by temperature 40ºC

Experimental research has aimed to develop an edible material based on biopolymers with the addition of inulin which has a low energy effect and a beneficial effect on lipid metabolism, facilitating the absorption of calcium and magnesium ions, iron [3]. All the films were easily removed from the silicone support, they were flexible, with a pleasant, homogeneous appearance. The colour varied depending on the ingredients used: the samples with a high agar content in the composition were yellow, those with a higher starch content were yellowish-

white, and those with only starch were white. The safety of use and consumption of this material was also demonstrated by microbiological tests performed during the test period (from 0 → 10 weeks), when no microorganisms were identified on the surface of the films or on the raw material used to obtain them. The samples were tested to determine the total number of germs, Staphylococcus Aureus, Escherichia Coli, coliform bacteria, but also yeasts or moulds. The low values of water activity (0.32-0.39), constant over time, as can be seen from the determinations made, contribute to preventing the development of microorganisms.In the case of the 7 biofilms, they were impregnated with plant extracts with phytoncidal effects for the evaluation of the antifungal and fungicidal potential in vivo, under controlled conditions.

The effect of phytotoxic oil extracts, plant extracts and citrus peels and by-products on the germination of plant matrices was established.

The seven biofilms whose water activity aw was from 0.32 to 0.39, the most playful values showed no signs of microbial development regardless of the concentration of extract used. The phytoncide extracts used were 5%, 10%, 15%, 20% for any type of extract obtained from Inula Orientallis Aloe Vera, buds from Abies Alba. In the case of these plants, the liqueur was extracted or an alcoholic extract was obtained which was used in concentrations of 5%, 10%, 15%, 20%. Within 6 days to 10 weeks, the presence of microorganisms was tested with sanitary tests to identify them.

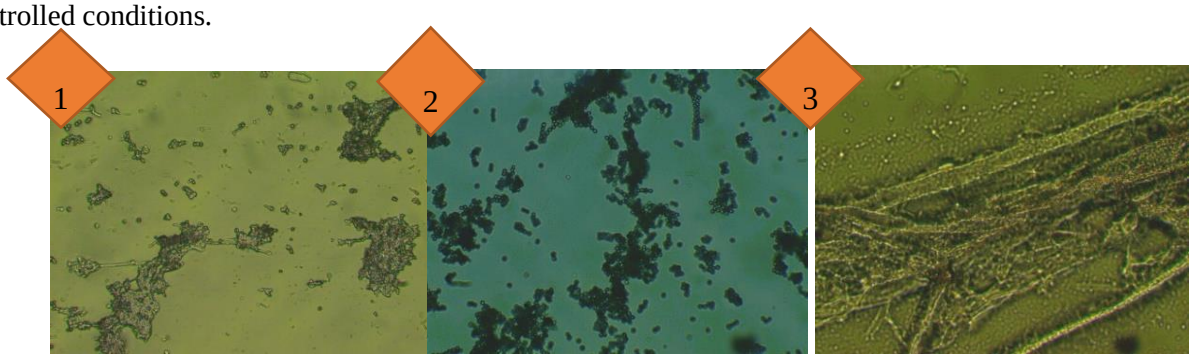

Figure 8.1. *Penicillium digitatum* (blue mold) on biofilms impregnated with 5% Inula Orientallis Aloe Vera extract towards the end of the 10th week (image1), and in the 11th week (images 2, 3)

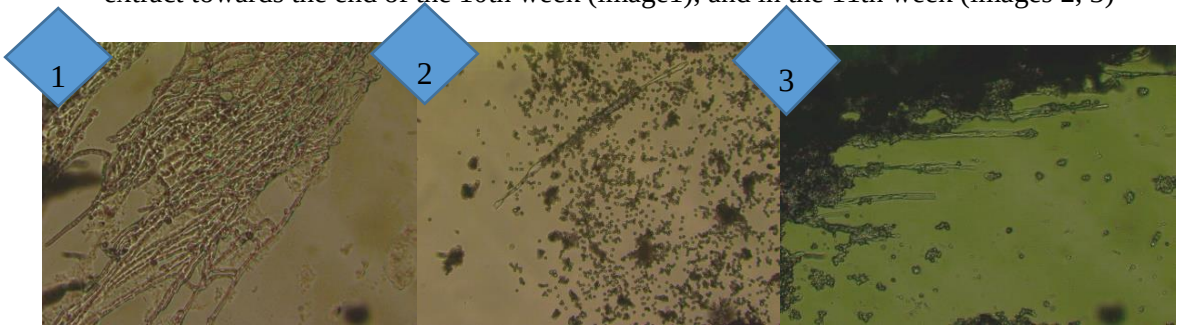

Figure 8.2. *Rhizopus Nigricans* (black mold) on biofilms impregnated with 5% Abiens Alba extract towards the end of the 10th week (image 1) and in the 11th week (images 2,3)

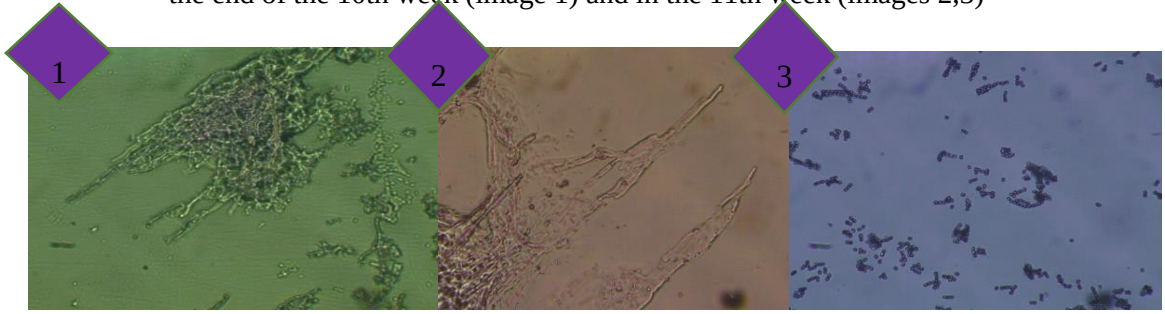

Figure 8.3. *Aspergillus Oryzae* (white mold) appears in the 10th week at 20% extract. (images 1,2,3)

4. Conclusion

1. The experimental research aimed to develop an intelligent, biodegradable packaging, obtained from biopolymers and various additives. In addition to the optimal amount of plasticizer, a number of plant materials were incorporated into the matrix – starch, agar, alginate - known for their hydrocolloidal properties, which determined superior characteristics of the packaging material. Various types of films have been made, which can successfully replace conventional, synthetic packaging.

2. The biofilms obtained were tested using a polysaccharide biomaterial for packaging powdery products with very low humidity and a very high degree of dispersion of instant-cappuccino, instant coffee, powdered milk or concentrated cubes of dehydrated vegetables, which requires solubilization before consumption.

3. All the materials obtained were rapidly solubilized in water at a temperature above 80°C and about 1 minute after immersion in water at the temperature of 20-23°C.

4. The effects of phytoncides proved to be exceptional, when no significant change in the microscopic field was recorded, for 10 weeks, ie 49 days. In weeks 8-9 *Enterobacter* and *Coliform bacteria* were below the allowable limits. No mold was reported. In the 10 week and after that 11 week was reported the presence of mold *Penicillium digitatum, Rhizopus Nigricans, Aspergillus Oryzae.*

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human or animal subjects (if exist) respect the specific regulation and standards.

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