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Composite Films from Sodium Alginate and High Methoxyl Pectin - Physicochemical Properties and Biodegradation in Soil

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Abstract. The increased public attention on the waste pollution and the awareness of the hard environmental problems is the reason for the need of new materials which are susceptible to degradation in nature for a short period of time. The biopolymer films and coatings based on renewable natural sources are suitable for obtaining of biodegradable packaging. The newly developed composite films based on sodium alginate and apple high methoxyl pectin were studied for total soluble matter, swelling in water, water vapors transmission rate and biodegradation in soil. The analysis of their behavior in water medium showed a considerably higher rate and degree of dissolution of the pectin monocomponent film compared to the composite and alginate films. The composite alginate-pectin films showed lower water vapors transmission rate even under extreme conditions (38ºC, RH 90 %) compared to the monocomponent films. All investigated films degraded in soil up to 80 days. The good barrier properties to water vapors and the complete biodegradation in soil make the films based on sodium alginate and high methoxyl pectin potential ecological materials for packing and coating of foods and pharmaceutical products.

Key words: composite films, alginate, high methoxyl pectin, solubility, water vapors transmission rate, biodegradation.

Introduction

The rapid technological progress that has been seen during the last decades in its greatest part is owing to the plastics industry. The production and the use of plastic materials are increasing at extremely accelerated rates. For example, in 1950 the output of plastic was 1,5 million tons and in 2008 it reached up to 245 million tons (NOWAK *et al.*, 2011). Around 30% of the manufactured plastic in the world is used as packing. The dramatic increase of the production of synthetic plastics, however, increases their presence in nature after use because of their stability, resistance and the lack of biodegradation. This fact focuses public attention on their accumulation in environment and the merging of problems with pollution which may last for hundreds of years and which would have a disastrous effect on the ecosystem balance (ALBERTSSON *et al.*, 1987). The advanced ecological culture and the awareness of the hard environment problems is the reason for the need of new materials which are susceptible to chemical, biochemical and biological degradation processes as result of which their degradation in nature takes place in a short period of time.

A number of biopolymers have a potential to be used as a base for production of biodegradable materials for packaging and coatings with application in food industry and pharmacy. One of the main advantages of this type of materials is that they are obtained from renewable sources

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that are widely spread in nature and can be used in native or chemically modified form (SOLAK & DYANKOVA, 2011).

The development of biodegradable polymer coatings and films from natural and renewable sources diminishes the need of synthetic petroleum polymers, eliminates the negative effect on environment, gives a good possibility to meet the changing consumer requirements and market trends for healthy and safe foods, packed with natural materials, which do not pollute the environment (DYANKOVA *et al.,* 2013). In addition to their property to biodegrade they have a number of other advantages, namely – they are biocompatible and bioassimilable, edible, with aesthetic appearance and good barrier and mechanical properties. Besides that this type of materials allows the incorporation of biologically active substances (natural antibacterial and antioxidant components of plant and microbial origin, enzymes, probiotics or other functional ingredients), which gives a possibility for prolongation of the shelf life of the processed foods (KROCHTA *et al.,*1997; MARTÍN-BELLOSO *et al.,* 2009; QUEZADA-GALLO, *et al.,* 2009).

Very often the obtained biopolymer films and coatings are a monohydrocolloid layer of proteins or polysaccharides. In the last several years, however, the technological investigations have been directed towards the development of composite films combining the synergic effects of proteins, polysaccharides and/or lipid components. These materials show combines and/or completely new functional qualities (DA SILVA *et al.,* 2009).

The salts of the alginic acid and the pectin are an example of polysaccharides with good film forming properties, suitable for obtaining of biopolymer films and coatings. Alginates are hydrophilic polysaccharides extracted from various species of brown seaweed *(Phaeophyceae).* They are of interest because of their unique colloid properties and the capacity to form three dimensional networks in the presence of polyvalent cations (for example Ca^{2+}), when a gel or an insoluble polymer is obtained (DRAGET *et al.,* 2006; WILLIAMS, 2009). By chemical structure alginates are unbranched binary copolymers, built of β-D-manuronic acid and its isomer α-L-guluronic acid. There are three types structural elements in the alginate molecules - β (1–4)-D-mannuronate (M-block), α-(1-4)-L-guluronate (G-block), and the third structure contains both monomers in almost equal proportions (MG-block) (DRAGET *et al.,*2006; FANG 2008; WILLIAMS, 2009). From the alginic acid salts the sodium alginate is most often applied in practice.

Pectins are plant heteropolysaccharides whose main chain consists of acidic derivatives of the hexoses (D-galacturonic acid), and the side chains are built of pentoses (D-xylose and L - arabinose) and hexoses (D – glucose and D - galactose). In the main chain the units D-galacturonic acid are linked by α-(1-4) glycosidic bond i.e. it is polygalacturonic acid to which are attached the side chains by β-(1-6) glycosidic bonds. The carboxyl groups of the galacturonic acid are partially esterified with methanol and neutralized with metal or ammonia ions as different pectin substances are obtained – pectins, pectates, pectic acids (DUMITRIU , 2004; PHILIPS & WILLIAMS, 2000). The main characteristic with the greatest influence on the rheological and physicochemical properties of pectin is the degree of esterification (DE) by which is expressed the percentage of the esterified to the total number –COOH groups. Depending on the degree of esterification pectins are divided into two main categories: high methoxyl (HM) and low methoxyl (LM) pectins. The degree of esterification for HM pectins varies from 50 to 100%. LM pectins (DE under 50%) are usually obtained by demethoxylation of the extracted pectins by enzyme processes or by treating with acids or ammonia in alcoholic medium. HM and LM – pectins have a different mechanism of gel forming when dissolved in water (GIGLI *et al.,* 2009; THAKUR *et al.,*1997).

The wide use of alginates and pectins in food industry and medicine is dictated by the lack of toxicity and allergenicity and the unique colloid properties. Both biopolymers are capable to form gels in the presence of divalent cations (FANG *et al.*,2008; BRACCINI & PEREZ, 2001). The alginate and the pectin form synergic mixed gels which lead to structures completely different from those of the pure polymers. They are of particular interest in the creation of biodegradable films with new improved characteristics.

The mechanism of synergic interaction between pectin and alginate has not been fully clarified. The rheological behavior of the mixed solutions and hydrogels has been studied to a great extent (FANG *et al.*,2008; OAKENFULL *et al.*,1990; RAO & COOLEY, 1995), while the investigations in the field of the physicochemical properties of the resulting composite films and their biodegradation have been yet much more weakly examined.

The objective of the present investigation was to analyze newly developed composite biopolymer films based on sodium alginate and high methoxyl pectin in relation to the physicochemical and barrier properties and to determine the period of their biodegradation in soil.

Materials and Methods

Materials. Apple high methoxyl pectin (CpCelso), sodium alginate (Sigma Aldrich), glycerol pa (Merck), calcium chloride pa (Merck).

Obtaining of biopolymer films. The method for obtaining of the films is described in more details in one of our previous articles (DYANKOVA & SOLAK, 2014). Briefly: the film forming solutions (FS) were prepared by mixing of water solutions of sodium alginate (2,5%) and high methoxyl pectin (2,5%) in the following proportions: 100–0% (AG), 75–25% (C_1AG-P), 50–50% (C_2AG-P) and 25–75% (C_3AG-P). As *plasticizer* was used glycerol (0.6g/g polymer), and for the primary cross-linking to each composition was added 0.1 M $CaCl_2$ (1ml/100ml FS). The prepared hydrogel was treated under vacuum for removing of the air bubbles. After that the film forming solutions were poured into petri dishes (0,325 g FS/cm^2) and dried under vacuum (20 kPa, SPT-200 Vacuum Drier) at 35°C. The dry samples were put in 0.3 M solution of $CaCl_2$ for realization of main cross-linking and were washed with distilled water for removing of the excess Ca^{2+}. The films were dried at 25° C and preserved at 50 ± 1% relative humidity before testing.

Analysis of the source pectin - The content of the methoxy-groups, galacturonic acid and the degree of esterification was determined by method described in USP 23 (1995).

Moisture content - by express weight method with infrared dryer (Sartorius Thermo Control YTC 01 L).

Film thickness - The thickness of the film was determined with a digital micrometer with accuracy up to 0.01mm ±5% in five randomly taken sectors of the film.

Water vapors transmission rate (WVTR) determination. The test was carried out according to ISO 2528: (E) **(**1995) under two specific conditions: temperature 38°C and relative humidity (RH) - 90%; 2) temperature 25° C and RH -75%. Aluminum containers (with dimensions: height, h= 8cm; outer diameter, d= 5.5 cm, inner diameter, d= 5cm) filled with desiccant (anhydrous $CaCl_2$), were covered with samples of the films (diameter 5,5cm), which were attached by a thin layer paraffin wax and on the top was put a plastic ring. The containers were put in a chamber: 1) at 38±1,0°C, RH 90± 2,0% and 2) at 25±1,0°C, RH 75± 2%. The increase in weight was measured at identical time intervals. After the water transfer equilibrated (difference in weight between two consequent measurements was <5%), the water vapor transmission rate (WVTR) was calculated by the formula:

$$WVTR= W/(tA), \quad (1)$$

where W is the increase in weight (mg), t is the duration of the experiment (days) and A is the permeation area (23,75 cm^2). The results are presented as average values of three parallel experiments for a period of 10 days.

Total soluble matter(TSM). TSM was determined according to a method described by RHIM *et al.* (1998). Preliminary weighted samples of the films with equal size (d=2 cm) were put in flasks containing 100 ml distilled water (with sodium azide for inhibition of microbial growth). The flasks were put in a shaking system ("Inkubations-Schüttelschrank BS-4 B.Braun", 100 rpm) at temperature 25°C for 24 hours. The not dissolved particles were separated and dried at temperature 105°C for 24 hours after which they were weighted.

TSM was determined by the formula:

$$TSM=[(Wi-Wf)/Wi]x100, \quad (2)$$

where Wi is the initial weight and Wf is the weight after separation and drying.

Swelling ratio (S) Samples of the films were weighted (Wd) and put in 30 ml distilled water at room temperature for a specific time after which they were taken out, wipe with filter paper and weighted again (Ws). The swelling ratio of the samples was determined by the formula:

$$S= [(Ws -Wd)/ Wd] x100. \quad (3)$$

Biodegradation in soil. The biodegradability of the films was analyzed using a method previously described in the literature (MARTUCCI *et al.,* 2009). Biopolymer films with dimensions 2 x 3 cm were dried under vacuum (20 kPa, SPT-200 Vacuum Drier) at 65°C for 6 hours and weighted (W_0) with accuracy up to 0.0001 g. For better manipulation the samples were placed in aluminum nets and were put at a depth of 6 cm (aerobic degrading) in soil with given specifications: pH 7,1; NH_4^+ - 6,7 mg/kg; NO_3^- 5,4 mg/kg; K_2O - 21,5 mg/100g ; P_2O_5 - 4,1mg/100g; porosity 78%; total number of microorganisms - $2,1.10^8$ CFU/g. The experiment was carried out for a period of 80 days at temperature 18±5°C and soil moisture 48±4 % RH. At a given interval the samples were taken out of the soil, washed with distilled water, dried at 65° C for 6 hours and were weighted again (Wt), in order to calculate the average weight loss by the formula:

$$WL\%=[(W_0-Wt)/W_0]x100. \quad (4)$$

The results are presented as average values of three consequent experiments. Samples of polyethylene films (PE) were used for comparison.

Statistical analysis. Results were analysed by *statistical program Minitab 15.* One-Way ANOVA and Tukey Test were used to determine statistically significant differences ($p<0.05$).

Results and Discussion

Analysis of the source pectin

The quantitative analyses of the samples of the commercial apple pectin showed content of pure pectin - 71,50%. The content of galacturonic acid is 753,0 ± 14,76 mg/g, and of methoxy-groups - 68,50 ± 2,36 mg/g. From the obtained results was calculated the degree of esterification (DE) which is 56,90%. By this index the used pectin is determined as high methoxyl but also with present of a certain percentage free carboxyl groups.

pH of the film forming solutions varies from 2,88 for the pectin to 6,16 for the sodium alginate (AG). The different variants film forming mixtures show pH values in the acidic range: C_1AG-P - 4,25; C_2AG-P - 3,78 and C_3AG-P - 3,54.

Characteristics of the obtained films

The film variants are obtained with different proportions between the two polysaccharides (sodium alginate and pectin) - 1:0, 1:3, 1:1, 3:1, 0:1, glycerol as plasticizer and $CaCl_2$ as a cross-linking agent at two step cross-linking procedure. Visually the resulting films are homogeneous, uninterrupted, without brittle sectors and without presence of air bubbles (Table 1). They are manageable and flexible. The color of the alginate films varies from transparent to slightly opaque. The films with high pectin content are with slight yellowish nuance.

The thickness of the obtained materials depends on the composition, the used technology and on the drying conditions. When pouring of a constant quantity film forming mixture for a given area (0,325 g FS/cm^2), films with thickness from 0,043 to 0,062 mm were obtained (Table 1).

Table 1. Characteristics of the films.

Composition	Appearance	Thickness (mm)	Moisture (%)	WVTR (g x m^{-2}x day^{-1}) T 38°, RH 90%	WVTR (g x m^{-2}x day^{-1}) T 25°C, RH 75%
AG	transparent, flexible	0,054±0,003	11,52±0,30	1080,99±20,56	290,59± 8,90
P	lightly yellowish, flexible	0,062±0,005	14,80±0,20	995,63±15,52	283,87± 10,20
C_1AG-P	lightly opaque, flexible	0,050±0,004	12,82±0,35	337,23±10,80	150,41± 8,60
C_2AG-P	lightly yellowish, flexible	0,048±0,003	14,10±0,40	363,07±11,50	133,24 ± 5,70
C_3AG-P	lightly yellowish, flexible	0.043±0,035	14,20±0,29	460,11±9,08	160,73± 6,20

In this investigation the calcium chloride was used as a gel forming and cross-linking agent. The polyvalent cations like Ca^{2+}, play the role of bridges between the polymer chains of the alginate and build junction zone which form the hydrogel network. For the pectins with DE around 50% (the pectin used by us is with DE 56,90%), the gel forming force depends on a number of factors – pectin concentrations, dissolved sugars and polyols, pH-value of the solution and quantity of the present calcium cation. The degree of cross-linking and the synergy between the two biopolymers have a direct effect on the physicochemical characteristics of the resulting films and particularly on their barrier properties and behavior in water medium. The values of moisture content for the different compositions are relatively close except for the alginate and the pectin films for which a statistically reliable difference is observed ($p<0.05$). When the films are placed in water medium a comparatively fast swelling is observed yet in the first 10 minutes. On Fig. 1 are presented the data for the different film variants for swelling in water as a function of time.

According to the results the monocomponent pectin films are with the highest water absorption capacity – maximum value at the 20th minute after which they decompose. SRIAMORNSAK & KENNEDY (2008) have also observed a higher degree of swelling for the pectin films compared to the alginate. For the alginate and composite films the cross-linking with calcium chloride allows the building of a multitude of binding zones and forming of a polymer network which is more stable. Less water molecules are able to penetrate the sample, and hence the swelling is reduced. This tendency is confirmed by the test for determining of *total soluble matter (TSM)*. The applied test is a way to characterize the solubility of the film matrix in water medium. When the samples are in contact with the solvent, water is absorbed which causes breakage of the polymer-polymer bonds, forming of new bonds between the water and the polymer materials, dividing of the polymer, swelling and dissolving at the end. On Fig. 2 are presented the summarized test results. The composite films show a considerably lower solubility compared to the monocomponent pectin film for which the total quantity soluble matter is around 99,13%. Their results are similar to the values obtained for the alginate film. The applied two steps cross-linking with calcium chloride strongly diminishes the solubility in water of the resulting films. The combination of the film forming materials and their synergy, the temperature and the relative humidity of the environment influence the permeability of the resulting films. The tests for water va-

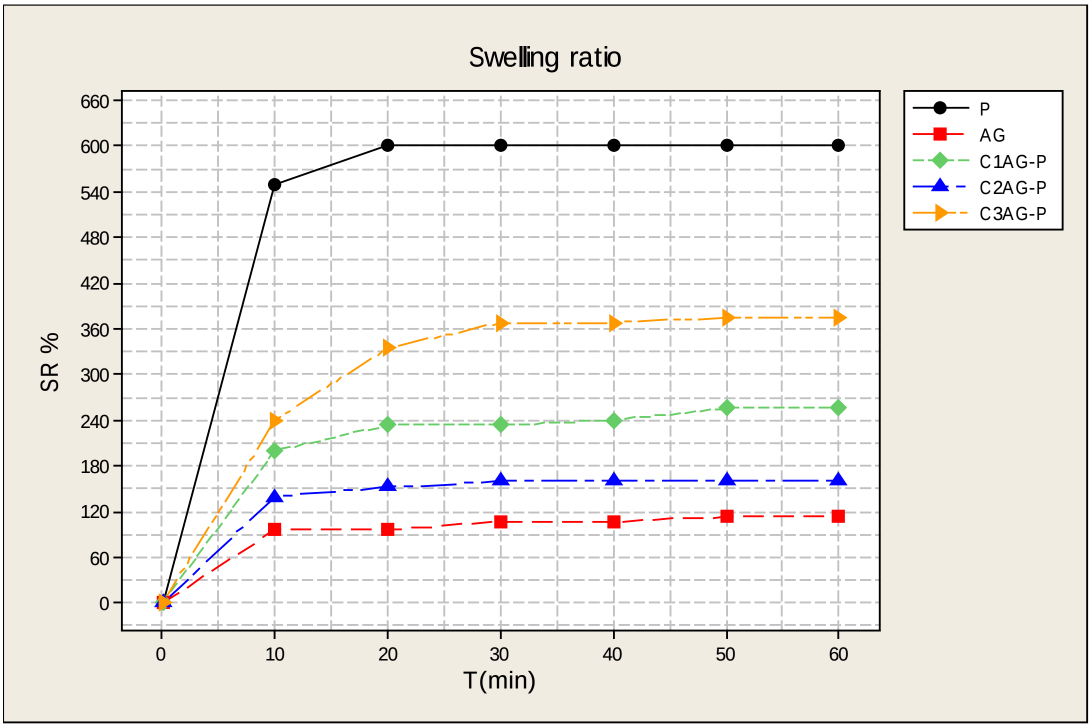


Fig.1. Swelling ratio of films in water

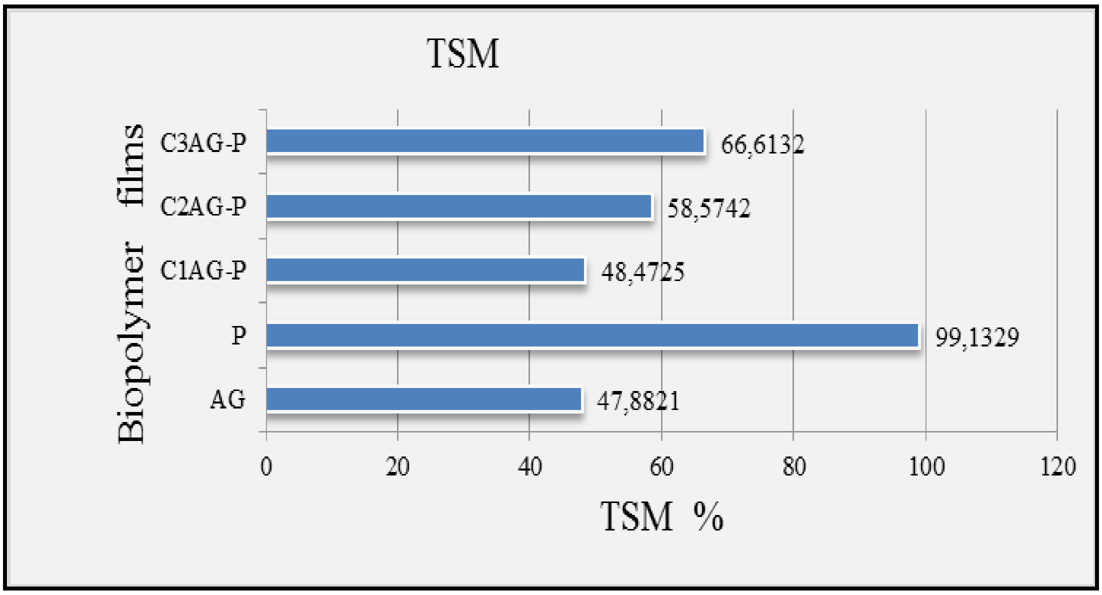


Fig. 2. Total soluble matter (TSM) for the different film variants.

pors permeability (WVP) give an idea of the barrier capacity to water vapors of the biopolymer films. This capacity is an important factor when they are used as packing. All films treated under regime 1 have from 2 to 3,5 times higher permeability to water vapors ($p<0.05$) compared to regime 2 (Table 1), due to the fact that the barrier properties to water vapors diminish with the increasing of the temperature during the WVP measurements (RHIM *et al.*, 2003). The temperature regimes applied during the measurement are above the admissible ranges for preservation of packed foods. These temperature values were selected because one of the objectives was to follow up the behavior of the film under more extreme conditions. The WVTR values for pectin films we obtained are slightly higher than those observed by

LINSHU LIU *et al.* (2007). This is probably due to the difference in the technology of obtaining producing the film and the lower temperature regime in the course of the test. For both regimes (1-38±1˚C, RH 90±2% and 2-25±1˚C, RH 75±2%) the monocomponent polysaccharide films show a higher WVTR than the composite films. This fact can be explained with the generation of continuous physical co-gels when mixing the synergic solutions of the two polysaccharides where the pectin component is dispersed in the gaps of the main alginate gel network. From these mixtures in the process of drying is obtained a more compact and stronger structure which is less permeable to water vapors. The increases in weight as a function of time for both measuring regimes are presented on Fig. 3 and Fig. 4.

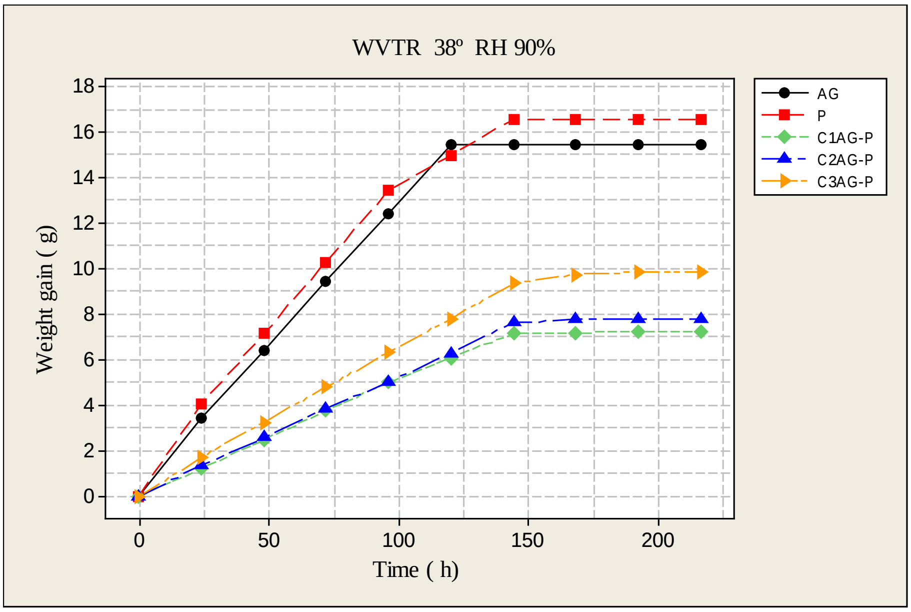


Fig. 3. Increases in weight as a function of time (regime 1).

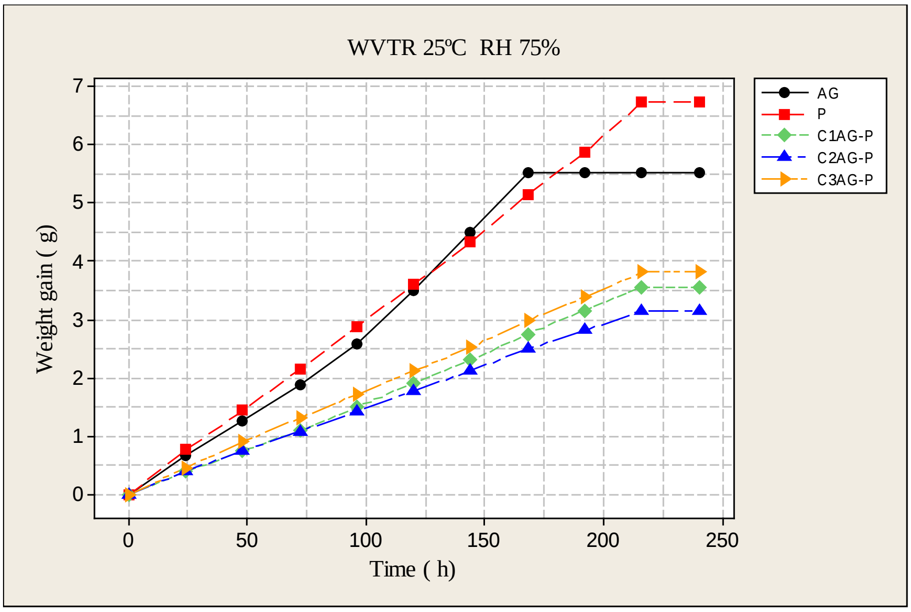
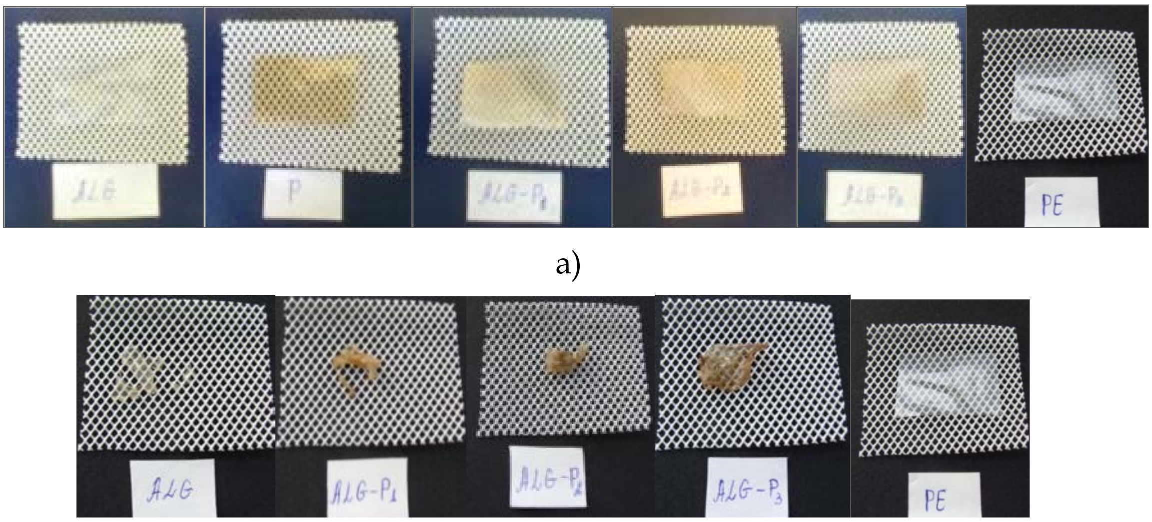


Fig. 4. Increases in weight as a function of time (regime 2).

Biodegradation in soil

The test for biodegradation was carried out by burying of the films in soil in laboratory conditions for 80 days at temperature 18±5°C. The moisture of the soil was kept around 48±4 %, for preventing the dissolving of the matrix. On Fig. 5 are presented photos of the studied samples before and during the test. The process of degradation begins yet on the second day after burying the films in the soil (Fig 5).

Till the seventh day the loss in weight of the samples is from 30% to 75% with visible changes in the form compared to the initial state (Fig.6). The fastest degradation is observed for the pectin films – on the 9th day the loss in weight is 100%. The alginate films at the end of the period- 80th day, are with 92,13% loss in weight. The composite film C_3AG-P (loss in weight up to 90,09%) degrades faster than the composite films C_1AG-P and C_2AG-P (respectively 76,13 and 77,17%). It has been established that after putting in the soil all films absorb water (to a lower or higher degree) and lose their initial form and structural integrity. After the 30th day a specific smell of decay is observed.



a)

b)

Fig 5. Macroscopic aspect of the films before (a) and after 14 days (b) of burying in soil.

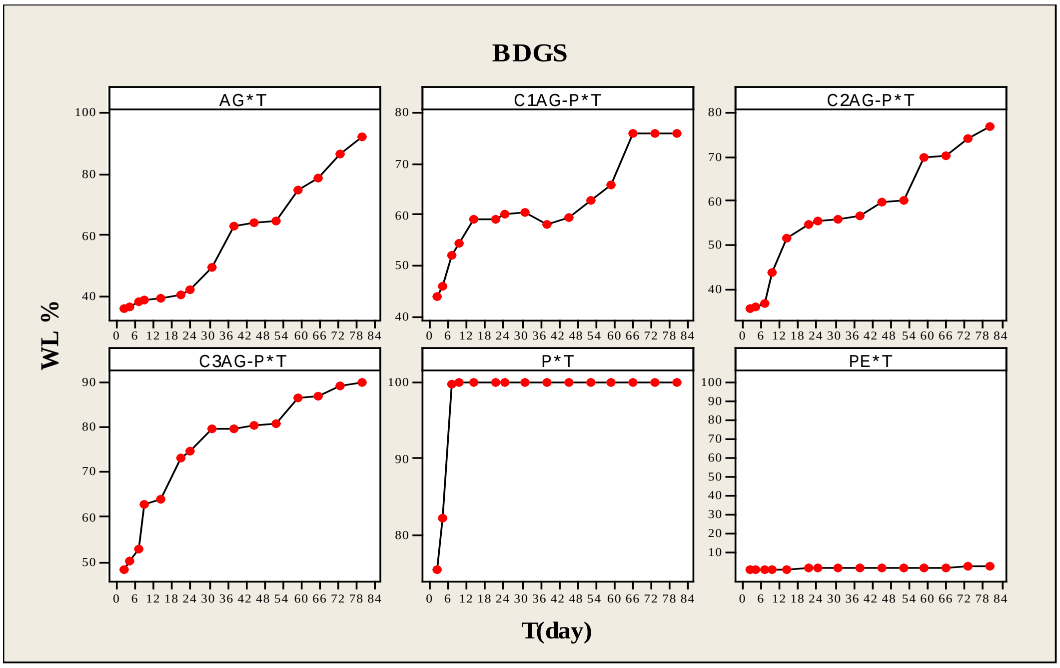


Fig. 6 Biodegradation in soil - weight loss (%) of the films as a function of time

The faster degradation of the pectin films is due to the more weakly cross-linked structure. Besides that the water absorption for the pectin films is 2 to 3 times higher than the other samples (test for swelling rate, Fig. 1). This effect is the cause for the greater susceptibility to microbial attack of the pectin films while the stronger structures of the alginate films make them hardly susceptible to the activity of the microbial hydrolytic enzymes. The situation is similar for the composite films where the degradation rate under the effect of the soil microorganisms is comparable to the alginate ones. The used as a comparison sample polyethylene (PE) remained unchanged.

Conclusion

The use of natural biopolymers with film forming properties gives a good potential to develop new possibilities for utilization of the agricultural raw materials. Alginates and pectins are very suitable plant biopolymers for obtaining of biodegradable (and in particular edible) films and coatings with various applications. The combining of sodium alginate and high methoxyl pectin allows the obtaining well shaped, homogeneous and semi-transparent films. The analysis of their behavior in water medium has shown considerably great differences in the rate and degree of dissolving of the pectin monocomponent film compared to the composite and the alginate films. The composite alginate-pectin films have better barrier properties to water vapors compared to the monocomponent. The test for biodegradation has shown that up to 80 days all studied films degrade in soil in contrast to the samples of synthetic folio which remain unchanged. The films based on sodium alginate and pectin are biodegradable and show low water vapors transmission rate even under extreme conditions which makes them potential materials for packing and coating of foods and pharmaceutical products. Their complete degradation in soil and the fact that they are obtained from renewable sources makes them ecology friendly products whose production turn out to be an investment for environment protection for the future generations.

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