Ecological packaging materials for bakery and confectionery products based on a new pectin modification

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Abstract

Introduction. Pectin is advisable to be used for biodegradable film production. There are a lot of types of modified pectin, but its modification potential has not yet been exhausted.

Materials and methods. Pectin, polyvinyl alcohol (PVA, E 1203), glycerol (E 422), oleic acid were used in this study. The vapor permeability of the film was determined according to BS EN 12086:1997. The physical and mechanical properties (strength and elongation) of the films were determined on the TIRAtest-2151 universal testing machine. Infrared (IR) spectroscopy was performed on a Nexus-475 Nicolet device.

Results and discussion. The effectiveness of the pectin modification was confirmed by IR spectroscopy and elemental analysis. Efficiency was confirmed by the modification of pectin, namely, the change in molecular weight and by the appearance of new bonds and/or functional groups. The formation of pectin amide can be judged by the ν(C-N) band at 1333 cm^{-1}. Unlike the reaction with ammonia product, the formation of salt groups with urea was not clearly visible. The disappearance of the NH_2-group deformation scissor oscillation band at 1592 cm^{-1}, as well as the shift of the C=O and C-N valence urea vibration bands may indicate the covalent bond formation between urea and pectin. The elemental analysis data indicate that the pectin esterification with ammonia, as well as with urea, took place. The film strength increased from 20.0 to 32.4 MPa and the vapor permeability decreased from 6.1 mg/(m·h·kPa) to 4.3 mg/(m·h·kPa) when content of pectin modified with ammonia in the film increased from 0.5 to 4.5%. The film elongation increased with an increase of the modified pectin content in the film. Pectin modified with urea showed a similar effect on the film properties as pectin modified with ammonia. However, the film containing pectin modified with urea was stronger, which could be explained by the formation of hydrogen bonds between the free urea amino group and OH groups in the polygalactouronic acid. The developed program based on Microsoft Office Access allows determining the biodegradable material composition based on the vapor permeability.

Conclusions. Fourier-transform infrared spectroscopy (FTIR) and elemental analysis confirmed modification of pectin with ammonia or urea. The resulting material could be used to obtain eco-friendly packaging material having better physico-mechanical and barrier properties than original one.

Introduction

The world community is currently determined to reduce the use of the polymer packaging materials. As alternative to conventional synthetic packaging new eco-friendly edible films and coatings that are materials used to wrap or coat food products to extend their shelf life and can be eaten together with the product should be proposed. These new packing materials are biodegradable and are decomposed in natural conditions to CO_2, H_2O and humus, so they do not require a separate collection or certain disposal conditions. Such natural substances as whey proteins, casein, wheat gluten, gelatin, polysaccharides such as starch, pectin, carrageen, alginate, gill, gum, chitosan, cellulose and its derivatives, fatty compounds, such as plant fats, animal fats, and waxes are used for the development of edible films and coatings (Caner, 2005; Díaz-Montes et al., 2021; Hammam, 2019).

It was shown that bread individual packaging and the extra plastic bags, which are used as an additional bread wrapping, leads to accumulation of a significant amount of used packaging materials (Svanes et al., 2018). Meanwhile, pectin, one of the natural polymers, can find an application in the production of biodegradable films for different food including bread (Espitia et al., 2014; Lazaridou and Biliaderis, 2020). Confectionery also usually has individual polymer packaging. Besides, confectionery products have an unbalanced composition with a predominant content of carbohydrates and a minimal content of biologically valuable substances. The adding functional components to the edible coating composition could increase the nutritional value of the products.

For effective use of biodegradable materials as a packaging they must have certain physico-mechanical and barrier properties. Based on our research, native and amidated pectins have insufficient physico-mechanical and barrier properties. The ecological packaging material for sandwiches has been patented in order to extend their shelf life (Patent 5543164 UA, Water-insoluble protein-based edible barrier coatings and films), and the edible material for the products of restaurant establishments against drying, moistening and microbiological spoilage was proposed (Patent 27608 UA, Food sprayed film-forming coating). The authors (Patent 3152 UA, Composition of edible film coating; Patent 45172 UA, Food sprayed film-forming coating) offer various coating composition based on different types of starch and its modification to protect bakery from drying. Biscuits (Panchev et al., 2005) and fondant candies (Patent 70679 A UA, Method for production of fondant candies) can also be protected from drying out with an edible coating. Appling of a film from whey proteins plasticized with sucrose in a 1:1 ratio on the surface of chocolate ensured its stable gloss for a long time (Lee et al., 2002). Cheese-based oriental sweets are better stored in an edible film coating based on kappa-carrageenan, chitosan, zein and whey protein concentrate (Guldas et al., 2010). So, currently, edible films and coatings are used for a limited number of products. It is advisable to expand of the packed products range in such materials and the materials range.

In order to further improve of the biodegradable materials properties, it is advisable to change of the raw materials properties for their production due to its modification. Currently, a number of the main raw materials modifications (natural polymers) are already known, in particular, the proposed enzymatic modification of pectin with pectinmethylesterase obtained from orange juice of the *Valencia* variety (Wicker et al., 2003). Cationic derivatives of pectin were obtained due to the interaction of pectin with 3-chloro-2-hydroxypropyltrimethylammonium chloride in the presence of sodium hydroxide (Fan et al., 2012). The chemical modification of amaranth pectin was investigated (Kostin et al., 2013). Salts of pectin with sodium hydroxide, ammonium and some amines were obtained. Modified products are homogeneous powders, with the exception of diethanolamine. It was established

that the introduction of additional groups into the molecule does not disturb the 4C conformation of the pectin pyranose rings and the α-conformation of glycosidic bonds. This article (Chen, Jun, et al., 2015) attempts to review the information about various methods used for pectin modification, including substitution (alkylation, amidation, quaternization, thiolation, sulfation, oxidation, etc.), chain elongation (cross-linking and grafting) and depolymerization (chemical, physical, and enzymatic degradation). Characteristics and applications of some pectin derivatives are also presented. In addition, the safety and regulatory status of pectin and its derivatives were reviewed.

The authors of the present article proposed a generalized classification for the modification of natural polymers based on the literary sources analysis, which is presented in Table 1.

Table 1

Classification of way modification of natural polymers

Classification sign	Example
Polymer type	a carbohydrate, a protein
Type of modifier	a crosslinker of polymer chains; a carrier of hydrophilic groups; a carrier of hydrophobic groups
Type of modification	mechanical (heating under excess pressure (extrusion), heating without excess pressure; biochemical (enzymatic, microbiological); chemical
Conditions	a catalyst (available, not available); a solvent (without solvent, water, organic solvent); environment (acidic, neutral, alkaline, in the air atmosphere, O_2, N_2, He); pressure (excess, atmospheric, vacuum)

According to the analysis of scientific literature, the most of proposed polysaccharide modification schemes are multistage, complex, require expensive and toxic reagents, which is unacceptable for the food industry. Consequently, the synthetic potential of pectin is far from exhausted.

The aim of the present research was to modify pectin to obtain material for bakery and confectionery eco-friendly packaging materials and study the properties of the resulting product.

Materials and methods

Materials

Pectin (esterification degrees 31.0%, 67.5%), polyvinyl alcohol (PVA, E 1203), glycerol (E 422), oleic acid were used in the present study.

Research methods

Films and coatings based on natural polymers were produced under the same conditions: polyvinyl alcohol (PVA) and the obtained modified pectin were mixed in dry

form, the calculated amount of solvent was added and heated until their complete dissolution and/or swelling. Next, a plasticizer (glycerol) was added and stirred until dissolved. The hydrophobic component (oleic acid) was emulsified after its addition in order to obtain a homogeneous mass of the forming solution of the biodegradable coating and/or film. The films were obtained by casting the film-forming solution (91 cm^3) onto a Teflon surface (293 cm^2). Complete drying of the film took place in 10-12 hours at room temperature. The coating was obtained by applying of a molding solution on the surface of the confectionery or bakery products.

Modification of pectin

By ammonia. 1.94 g of pectin and 40 cm^3 of water were added to a three-necked reactor with a Liebig refrigerator, a 100 °C thermometer, and a dividing funnel. The mixture was stirred at a temperature of 50 °C and 0.72 g of ammonia was added dropwise from a separator funnel. The stirring was continued for 15 hours. After mixing, the resulting solution was evaporated in a porcelain cup. The obtained product in the form of a film was crushed and washed with ethyl alcohol. The product was dried at a temperature of 50 ± 2 °C.

By urea. 1.94 g of pectin and 40 cm^3 of water were added to a three-necked reactor with a Liebig refrigerator, a 100 °C thermometer, and a dividing funnel. The mixture was stirred at a temperature of 50 °C and a solution of 3.0 g of urea in 15 cm^3 of water was added dropwise. The stirring was continued for 26 hours. After mixing and cooling, the product was filtered and dried at room temperature.

Physical and mechanical properties (strength, MPa; elongation, %) of the films were determined on the TIRAtest-2151 universal testing machine

The vapor permeability of the film was determined according to BS EN 12086:1997. The vapor permeability is a value that is numerically equal to the amount of water vapor in milligrams that passes in 1 hour through a layer of material with an area of 1 m^2 and a thickness of 1 m, provided that the air temperature on the opposite sides is the same, and the difference in partial pressures of water vapor is equal to 1 Pa according to ASTM E96/E96M–16.

FT-IR. Infrared studies conducted on the device Nexus – 475 firm Nicolet, KBr tablet (Chung et al., 2004). Automated composition calculation of biodegradable material using Microsoft Office Access software was developed.

Results and discussion

Pectin with different esterification degrees

Previous modeling studies have shown that films based only on pectin have insufficient properties as a packaging material, which coincides with the data of other researchers in this field (Mangiacapra et al., 2006). That is why a number of researchers suggest supplementing pectin films with other film formers (Alve et al., 2011; Jo et al., 2005) or clay, $CaCl_2$ (Kang et al., 2005; Silva et al., 2009).

We proposed to strengthen the properties of the pectin film by introducing an additional film former, namely PVA, since this polymer forms quite strong and transparent films. In

addition, it is known that the combination of pectin and PVA is expedient from the point of view of increasing the biodegradability of PVA (Patent 5646206 USA). The use of PVA increases the viscosity of the film-forming solution, which facilitates its application to the surface of products and allows reducing the consumption of pectin as a more expensive raw material. The given investigated quantitative content of pectin (Table 2) is due to previous model experiments, which showed that with a lower pectin content, the film either does not form or is extremely weak. In addition, if such a molding solution is applied to the surface of the products, the molding solution spreads without forming a coating layer. Under the condition of higher concentrations than given in Table 2, the formed film is difficult to chew because it has a rough structure, which can be explained by the insufficient amount of solvent to form a full-fledged film matrix.

In the composition of the film, we use a plasticizer – glycerol, taking into account the property of pectin to form jelly in the presence of a dehydrating agent, which is glycerol. Glycerol, like sucrose, is necessary for the formation of pectin jelly. In our case, glycerol is preferred to avoid the sweet taste of an edible biodegradable film or coating. Since sucrose will be added in quantities lower than the concentrations at which it exerts a preservative effect, such concentrations will have the opposite effect is a favorable environment for the development of microflora. Oleic acid was used as a hydrophobic component instead of linseed oil for economic reasons. The quantitative content of oleic acid was found by the active experiment method. The experimental results of the physico-mechanical and barrier properties of the pectin-based film are shown in Table 2.

Table 2

Changes in the properties of films depending on the type and quantity of pectin (n=5, p≤0.05)

Pectin content with different esterification degrees,%		Strength, MPa	Elongation,%	Vapor permeability, mg/(m·h·kPa)
31.0	67.5			
0.5	-	24.3±2	62±1	7.0±0.2
1.0	-	29.4±4	67±3	6.8±0.1
1.5	-	33.4±3	71±4	6.4±0.4
2.0	-	39.3±4	79±4	6.0±0.2
2.5	-	40.8±4	84±5	5.3±0.1
3.0	-	42.7±2	90±4	5.1±0.2
3.5	-	44.9±4	94±3	5.1±0.2
4.0	-	46.1±1	101±1	5.2±0.3
4.5	-	48.4±1	113±1	5.0±0.2
-	0.5	14.4±1	42±2	8.1±0.1
-	1.0	18.2±2	56±2	7.7±0.2
-	1.5	21.6±5	70±3	7.4±0.2
-	2.0	27.8±3	83±4	6.9±0.3
-	2.5	34.7±3	79±2	6.8±0.4
-	3.0	36.8±1	72±4	6.0±0.1
-	3.5	38.1±4	66±3	5.6±0.2
-	4.0	40.2±2	61±5	5.6±0.2
-	4.5	41.7±4	70±3	5.9±0.4

Note: the content of other components in the composition of the film: PVA, 1.5%, glycerol, 2%, oleic acid, 2%, water, the rest.

The obtained data (see Table 2) show that increasing the pectin content, depending on the esterification degree, affects the properties of the films in different ways. It is known that the conditions for the formation of jelly for pectin with different degrees of esterification are different. The advantage of low-esterified pectin is its ability to change to a jelly-like state without a dehydrating agent (sucrose). That is why the strength of films made of low-esterified pectin, under the condition of its minimum content, is greater compared to high-esterified pectin under the same conditions, since only in the presence of 0.5% pectin, a network is already formed, which is the film matrix. The change in the elongation index for films from highly esterified pectin occurs randomly, which is probably due to unfavorable conditions (sucrose absence in the amount of 65%, acid with the required dissociation level, and a sufficient amount of water) for the pectin gel-like state formation under the conditions of film production. The lowest values of vapor permeability are characteristic of films made of low-esterified pectin, since, as already mentioned, the conditions for its transition to a jelly-like state are more favorable, as a result of which a well-developed pectin network is formed, which ensures the necessary level of barrier properties. In addition, free carboxyl groups form hydrogen bonds, which also provide the necessary density of the film matrix to reduce vapor permeability, which is characteristic of low-esterified pectin. It is worth noting that a pectin concentration of more than 2.5% does not cause a significant decrease in vapor permeability, therefore, in order to reduce the use of raw materials, it is advisable to dose 2.5% of low-esterified pectin.

The ability of low-esterified pectin to form hydrogen bonds is confirmed by IR spectra (Figure 1).

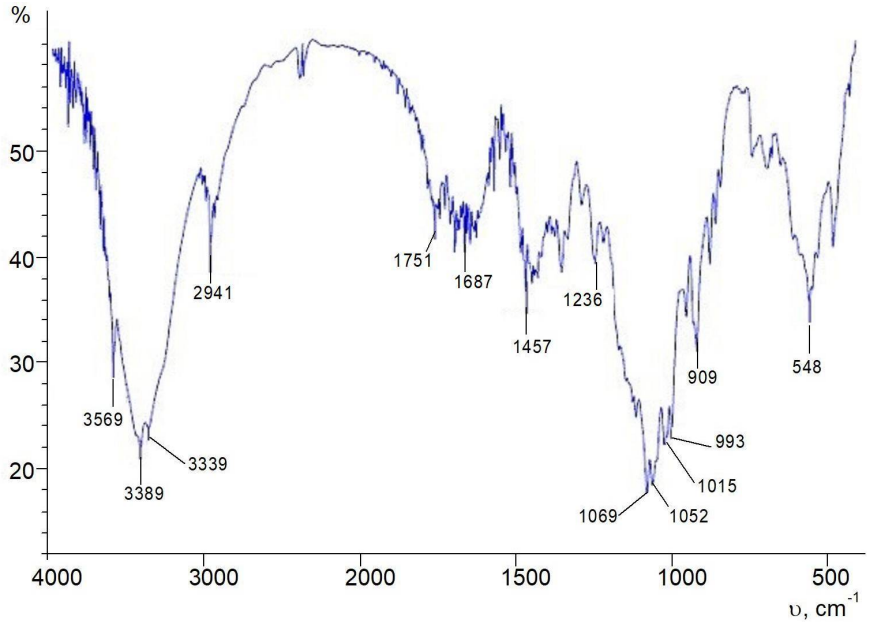
The analysis of the spectra showed (see Figure 1) that the spectrum of highly- esterified pectin has an intense band with three maxima at 3400.56 cm^{-1}, 3316.52 and 3271.70 cm^{-1}, which correspond to the valence νOH vibrations of the pectin glucourone rings. In the IR spectrum of low-esterified pectin (see Figure 1a), there is also an intense band with three maxima at 3568.62 cm^{-1}, 3389.35 and 3338.93 cm^{-1}, but the maximum is located in a more intense oscillations region at 3568.62 cm^{-1} and separated from the other two (3389.35 cm^{-1} and 3338.33 cm^{-1}), corresponds to the OH group valence vibrations of the free pectin carboxyl group, which takes an active part in the formation of hydrogen bonds, which indicates a greater number of hydrogen bonds, and, as a result, a lower esterification degree. Therefore, it is most appropriate to use low-esterified pectin for the production of biodegradable edible films and coatings.

In order to control the pectin esterification degree, especially in industrial conditions, the authors developed an express method, which was used to determine the degree of pectin modification (Shulga et al., 2020).

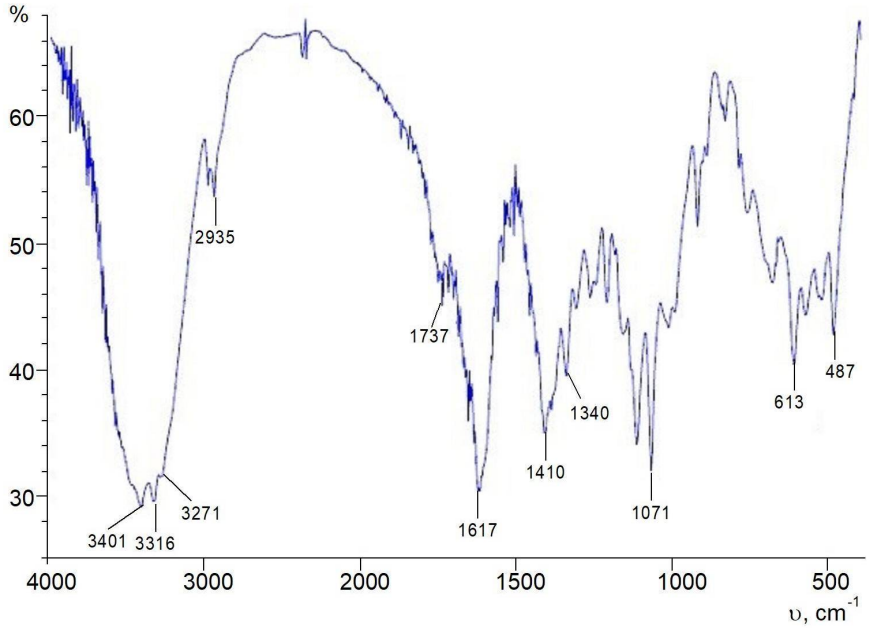
The existing types of pectin do not meet all the requirements as a film former, in particular, pectin films have insufficient barrier properties, so it is advisable to modify the film former (pectin). The following substances were chosen as pectin modifiers: ammonia and urea.

The given substances were chosen for the following reasons: ammonia is a modifier that already allows obtaining amidated low-esterified pectin, but its properties as a modifier have not yet been fully used; urea is an approved food additive E 927b, which is currently not used as a modifier for pectin. In addition, these modifiers are economically available.

The reactions of pectin with ammonia, urea were carried out in an aqueous environment, which is more acceptable than in methyl alcohol (Skoblya et al., 2004; Synytsya et al., 2003) from their use in the food industry (Mishra et al., 2009). In addition, on the basis of previous studies (Kobilins'kij et al., 2008; 2010) it was found that the interaction of pectin with polyethyleneimine in water led to the formation of amide groups due to the saponification of ester groups.



a



b

Figure 1. IR-spectrums of pectin: a, highly-esterified pectin; b, low-esterified pectin (n=3, p≤0.05)

One of the main requirements for the obtained products is the production of film packaging materials from them, which in terms of barrier properties were not inferior to materials based on synthetic polymers. In addition, natural polymers, depending on the thickness of the film, tend to form relatively strong materials.

Pectin modification with ammonia

The qualitative change of pectin can be confirmed by IR spectroscopy. The IR spectra of original pectin and modified pectin (pectinamide) are presented in Figure 2.

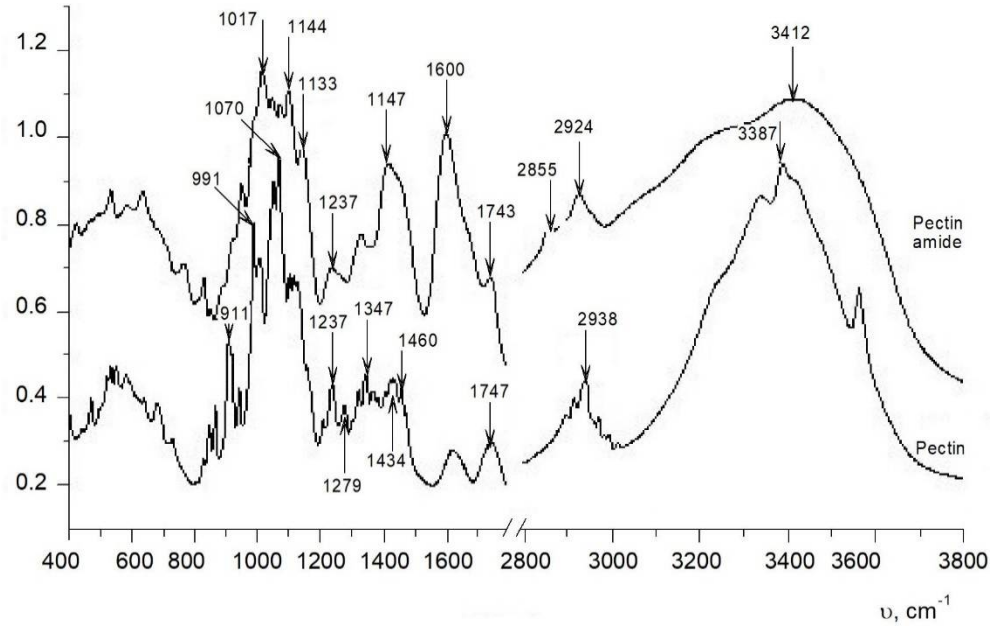


Figure 2. IR spectra of pectin and the product of its interaction with ammonia
(n=3, p≤0.05)

The bands of the original pectin (Mishra et al., 2009) can be interpreted as follows: 3387 cm^{-1} ν(OH), 2938 cm^{-1} ν(C-H), 1747 cm^{-1} ν(C=O), 1434 cm^{-1} δ(CH_3), bands in the range of 1000-1200 cm^{-1} refer to valence vibrations ν(C-C) and ν(C-O) of the pyranose ring, glycosidic bond and alcohol groups. In particular, the band at 1070 cm^{-1} refers to ν(C_3-OH primary), 1052 cm^{-1} to C-O-C of the pyranose ring, the band at 1130 cm^{-1} to ν(C-O-C) of the glycosidic bond, bands at 1237, 1279 cm^{-1} – ν_{ac} (C-O) of carboxyl and ester groups, respectively. In the reaction product of the pectin with ammonia, intense bands of 1600 cm^{-1} and 1417 cm^{-1} appear, which relate to asymmetric and symmetric valence vibrations of the ionized carboxyl group COO- and overlap the C=O and NH bands of the amide group.

The formation of pectin amide can be judged by the ν(C-N) band at 1333 cm^{-1}. The saponification reaction of the pectin ester groups are indicated by the disappearance of bands at 1279 cm^{-1} and 911 cm^{-1}, which refers to the pendulum oscillations of the ρ(CH_3) $COOCH_3$ group.

The elemental analysis data show the pectin esterification with ammonia took place on the basis of a fragment consisting of four galactourone rings containing amide, ammonium, methoxylated and free carboxyl groups. The amount of carbon was found to be 40.175%, calculated to be 40.595%; hydrogen was found to be 4.762%, calculated to be 5.142%; nitrogen was found to be 3.369%, calculated to be 3.789%.

Currently, low-esterified amidated pectin with the help of ammonia is presented on the Ukrainian market, which has a number of advantages compared to high-esterified and low-esterified pectin: gels are thermoreversible, at temperatures below gel formation they retain fluidity during mixing, and are tolerant to a larger range of calcium salt content. In the work, modification with ammonia is proposed, since studies of the modified product have shown that in the presence of an ammonia excess, salt ammonium groups (-$COONH_4$) are formed, which increase the pectin solubility. If there is a water limited amount in the formulation solution, the increase in solubility will contribute to a more complete formation of the film/coating matrix, which will positively affect their properties. The properties of the film obtained using ammonia-modified pectin are shown in Table 3.

Table 3

Properties of a film with pectin modified with ammonia (n=5, p≤0.05)

Content of modified pectin,%	Strength, MPa	Elongation,%	Vapor permeability, mg/(m·h·kPa)
0.5	20.0±2	84±2	6.1±0.3
1.5	23.8±2	98±2	5.6±0.3
2.5	28.3±2	114±3	5.1±0.2
3.5	31.2±3	128±3	4.5±0.2
4.5	33.4±3	147±5	4.3±0.2

Note: the content of other components in the composition of the film: PVA, 1.5%, glycerol, 2%, oleic acid, 2%, water, the rest.

The results show that the strength of the film increases from 20.0 to 32.4 MPa with increasing the content of ammonia-modified pectin in the film composition from 0.5 to 4.5%. The film elongation index increases with an increase in modified pectin in the film composition: it was 147% for sample with a modified pectin content of 4.5%, against 84% with a modified pectin content of 0.5%.

The film vapor permeability decreases with an increase in the content of modified pectin in the composition of the film from 6.1 mg/(m·h·kPa) (pectin content of 0.5%) to 4.3 mg/(m·h·kPa) (pectin content of 4.5%) (Table 3).

The obtained results are explained by the change of free pectin carboxyl groups to amide and salt groups, which increases solubility and allows the formation of a more developed pectin network. Free carboxyl groups that remained after the modification contribute to the formation of hydrogen bonds. The modifications carried out make pectin thermoreversible, which is important in working with it and will reduce the production waste amount.

Pectin modification with urea

The formation salt groups with urea is not clearly visible unlike the reaction with ammonia. The bands at 1453, 1627, 1664 cm^{-1} can be attributed to ν(C-N), ν(C=O), δ (NH),

δ (NH_2) of the urea fragment (Figure 3). The disappearance of the NH_2 group deformational scissor vibrations band at 1592 cm^{-1}, as well as the shift of the C=O and C-N valence urea vibrations band may indicate the formation of a covalent bond between urea and pectin. Similarly to the previous product IR spectrum, the band at 913 and 1279 cm^{-1} disappears, which is due to the saponification of ester groups. The band at 1747 cm^{-1} indicates that not all carboxyl groups are involved in the salt bonds formation.

The elemental analysis results indicate the pectin esterification with urea took place on the fragment consisting basis of four galacturonic rings containing imidoamide, methoxy and two free carboxyl groups. Carbon was found to be 40.693%, calculated to be 41.053%; Hydrogen was found to be 4.074%, calculated to be 4.737%; Nitrogen was found to be 3.404%, calculated to be 3.684%.

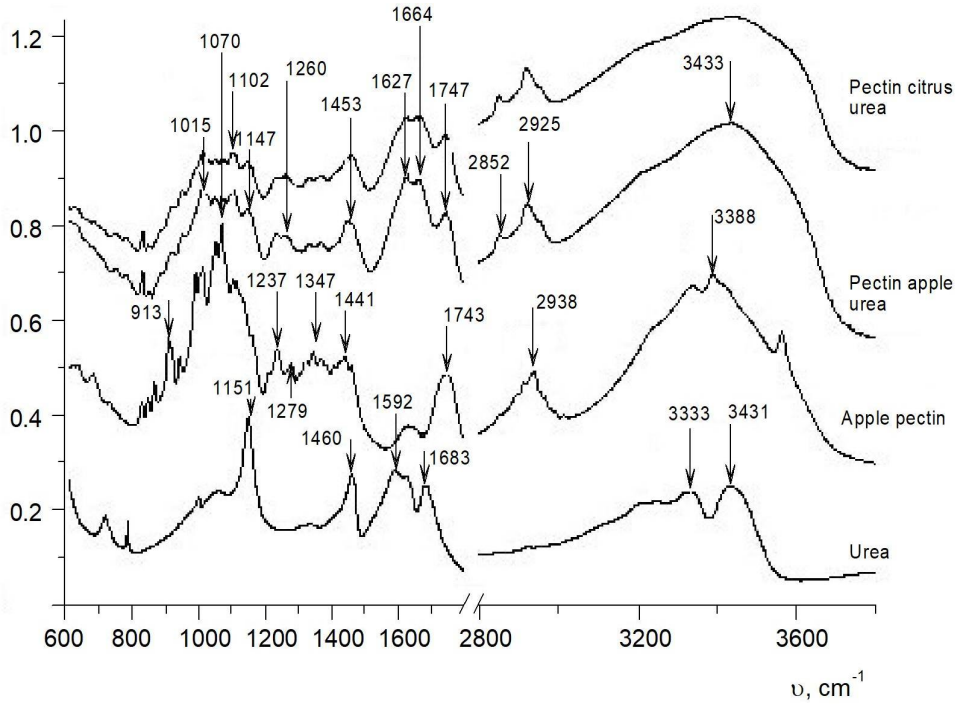


Figure 3. IR spectra of apple pectin, urea and two different pectins with urea products (n=3, p≤0.05*)*

Urea is used in the films production as a plasticizer that is why the modification of pectin with urea is of particular interest. Therefore, the film former modification with urea will avoid the technological stage is adding a plasticizer.

The pectin modification effect on the properties of biodegradable edible film is shown in Table 4.

Table 4

Properties of a film with pectin modified with urea
(n=5, p≤0.05)

Content of modified pectin,%	Strength, MPa	Elongation, %	Vapor permeability, mg/(m·h·kPa)
0.5	21.8±2	81±3	6.5±0.3
1.5	26.7±2	87±3	6.0±0.3
2.5	29.0±2	115±5	5.7±0.3
3.5	33.4±3	129±5	5.2±0.2
4.5	35.9±3	139±5	5.0±0.2

Note: the content of other components in the composition of the film: PVA, 1.5%, glycerol, 2%, oleic acid, 2%, water, the rest.

According to the experimental data (Table 4), pectin modified with urea exerts a similar effect as pectin modified with ammonia on the film properties. However, the formed film is stronger, 21.8 MPa (for pectin content of 0.5) (Table 4), against 20.0 MPa with the same pectin content (Table 3), which is explained by the formation of hydrogen bonds between the free urea amino group and OH groups of polygalactouronic acid. This property also leads to a decrease in elongation compared to a film containing pectin modified with ammonia. The vapor permeability value is at the same level as for a film with pectin-amide. The modification also makes pectin thermoreversible.

Conclusions

The obtained products novelty was confirmed by IR spectroscopy and elemental analysis. The elementary link of the pectin modification with urea consists of four galacturonic rings, which contain imidoamide, methoxy and two free carboxyl groups. The elementary link of the pectin modification with ammonia consists of four galactourone rings, which contain amide, ammonium, methoxylated and free carboxyl groups. Urea modification gives pectin thermal reversibility, the resulting modification products meet the level of food safety. The obtained new modifications of pectin will make possible to produce ecological packing materials with improved physico-mechanical and barrier properties.

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