

Pectin - a Functional Component of Diet

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Abstract: *A diet is an important factor in a healthy lifestyle of every man. An unreasonable diet can lead to many lifestyle diseases such as obesity, hypertension and cancer. Increasing consumer awareness regarding nutrition, makes that they reach for and search for the reduced-calorie products owing to their advantages. The reduction in sugar and fat, and introduction of food additives does not deteriorate the quality of such products, which are then perceived by consumers as even more attractive. Such additives include vegetable hydrocolloids. They are useful from the technological point of view because of their functional properties, particularly their high water binding capacity as well as their thickening and gelling capacities, but they are also valued for their health benefits. For instance, they play the role of dietary fiber and thus allow inducing the feeling of satiety. Hydrocolloids present in the reduced-calorie foods include pectins which are heteropolysaccharides. In food products, pectin preparations act as both substances with functions of thickeners, stabilizers, and gelling agents, and as bioactive ingredients in a soluble fraction of dietary fiber.*

Keywords: *pectin, dietetic food, aerated food, low-sugar jams, hydrocolloids*

1. INTRODUCTION

1.1. Dietetic Foods

Dietetic foods are foods for special purposes. In the EU including Poland they have a clear legal status [1]. According to the Act of 25 August 2006 on food safety and nutrition [2] "food for special nutritional purposes is the food that due to the special composition or method of preparation is clearly different from commonly consumed foods and according to the information posted on the packaging is marketed for the purpose of satisfying the specific nutritional needs of people whose digestion and metabolism are disturbed or individuals that due to the special physiological condition may particularly benefit from a controlled consumption of certain substances in foods and healthy infants and toddlers aged one to three years. "

Consumers are gaining increasing knowledge about proper nutrition, which is why manufacturers and researchers are looking at ways to preserve or even increase the nutritional and sensory values during processing. In order to achieve a satisfying and desirable effect, it is necessary to use a number of additives like, e.g. hydrocolloids including pectins [3, 4].

2. GENERAL CHARACTERISTICS OF PECTIN

Pectins (E440) are heteropolysaccharides, namely polysaccharides soluble in water. They are characterized by natural origin, as they occur in cell walls as well as in central plaques of the intercellular spaces of plants. Therein, they perform the function of the skin-forming material and control water management. The most popular on the market are pectins extracted from apple pomace and citrus peel [5]. Pectins are esters of methyl alcohol, and polygalacturonic acid. Galacturonic acid residues linked into long chains with $\alpha \rightarrow 1,4$ -glycoside bonds are the basic units of pectins [6]. Pectins are included among the hydrocolloids characterized by good gelling properties [7].

The gelling efficiency depends on the type of pectins (degree of esterification, the site of methyl ester groups in the molecule, concentration of biopolymers) and environmental conditions (concentration of divalent and monovalent ions, temperature, ionic strength of the solution, pH), while the gelling capability is affected by their molecular weight (pectins with molecular weights greater than 105 form gels, whereas these with low molecular weights are practically incapable of gelling) [8, 9]. During gelling, pectins form a three-dimensional network, owing to which the resultant gels are soft, concise and flexible [10].

The basic division of pectins comprises low-methoxyl pectins (LM) and high-methoxyl pectins (HM). This variety in pectin types depends on two main factors: the degree of chain polymerization and the degree of carboxyl groups of galacturonic acid esterification with methyl alcohol, wherein the degree of esterification could theoretically be in the range from 0 to 100% and the percentage of methoxyl groups in the range from 0 to 16% [11].

The low-methoxyl pectins (LMP) are compounds whose degree of esterification is below 50%, which means that less than 50% of carboxyl groups are esterified, and contain less than 7% of methyl groups and can therefore be used in products with low sugar content. These pectins form gels in the presence of divalent ions (e.g. calcium) in a wide pH range (2-6) and then sugar addition is not necessary [12], whereas a temperature decrease and an increase in the concentration of calcium ions (Ca^{2+}) increase the gel strength [13]. The sensitivity of this hydrocolloid to Ca^{2+} is reduced below pH 4.5 and becomes negligible below pH 2. Even in the absence of Ca^{2+} and pH above 3.5, low-methoxyl pectin aggregates to form weak gels. Increasing the addition of Ca^{2+} leads to the formation of gel which is becoming more varied, and the increase in the concentration of pectin above 3 g / l improves the flexibility, without changing the gelation temperature [13, 14].

Gelation takes place by the formation of contact zones between regions of pectin HG (Homogalacturonan) by the calcium bridges. At $\text{pH} > 3.5$, most of the carboxyl groups dissociate, which promotes the cross-linking of calcium. When calcium ion concentration is too high, the pectin may gel too early, and this leads to syneresis. The excess of metal ions causes precipitation of the pectin in the form of pellets [5]. Sugar is not required to form a gel with low-methoxyl pectin, but its addition (10-20%) reduces the syneresis and ensures the desired firmness of gel. The reduced amount of calcium is also required for gel formation. In contrast, high levels of sugar (60% or more) interfere the gelation process [15].

Low-methoxyl pectins are obtained by controlled deesterification of high-methoxylated pectin. This phenomenon takes place in an acidic or basic medium or under the influence of pectin esterases [16], but when deesterification is carried out in the presence of ammonia, the low-methoxyl pectins are obtained amidated (LMA) because they possess an introduced amide group ($-\text{CO}-\text{NH}_2$). Like LMP pectins, they form thermo-reversible gels, however, have lower requirements for calcium concentration in the medium. The good quality of gels formed by LMP and LMA pectins is ensured when these hydrocolloids possess chain fragments composed of 7-20 residues of galacturonic acid, which is free of methoxyl groups [17].

A few years ago, a new generation of pectins GENU® has appeared on the market, for which the CP Kelco company received a Gold Medal at the Food Ingredients fair in 2015 for the most innovative food additive. These pectins gelatinize with a very little extract and may be used in products having a low pH, thus retaining the fruity flavor. They may be the only texture-forming substance when the extract is even only 5%, and may provide a compact gel structure without the phenomenon of syneresis. It is also unnecessary to add calcium with fruit still being uniformly suspended in the gel. These pectins are used in the production of so-called healthy fruit desserts (jellies) and low-sugar jams [18].

High-methoxylated pectins (HMP) are compounds whose degree of esterification is above 50%, which means that more than 50% of carboxyl groups are esterified, and contain more than 7% of methyl groups. They form irreversible gels at $\text{pH} < 3.5$, in the presence of at least 55% of sugar [5]. These gels do not undergo syneresis, they are transparent and hard. The rate of HMP pectin gelation increases with decreasing pH and an increasing degree of esterification. High-esterified pectins can be divided into three groups: slowly gelling pectins (degree of esterification at 60-65%), pectins with a medium rate of gellation (degree of esterification at 65-75%), and fast gelling pectins (degree of esterification over 75%) [16, 19].

The HMP gelling ability is also affected by: the chain length (namely by particle size), and the type and the presence of metal ions and roughage [20, 21]. The necessity of adding large quantities of soluble sugars which are required for the HMP pectin limits their use as a gelling agent primarily in sweetened fruit products such as jams and marmalades [5].

2.1. The Use of Pectins in Food Technology

Pectins are widely used in the food industry as additional substances with properties of thickeners, gelling agents, stabilizers, and as carriers of other substances. They are applied on the surface of food products, and are used as bioactive components (the soluble fiber fraction) [22]. The selection of a suitable type of pectin depends on the extract of a finished product and on temperature of pouring of e.g. jams to jars. Products with a high extract of 55 - 60% like high-sugar jams may be manufactured with the addition of all types of amidated pectins, but the application of high temperature of pouring points to the use of pectins sensitive or medium sensitive to calcium, while at normal and low pouring temperatures it is recommended to use pectins with low calcium sensitivity. This type of pectins is also appropriate in the manufacture of products with a lower extract in the range from 45 to 55%, whereas in these with extracts below 45% and high pouring temperatures the best prove to be pectins sensitive or medium sensitive to calcium. Strong gels with the extract below 25% may also be formed using a calcium-sensitive pectin, but strong syneresis may occur in these gels when damaged [22].

High-methoxylated pectin preparations are commonly used in the processing of fruit to high-sugar jams with the extract at about 60-70%, at pH 3-3.3. The addition of pectin to such products depends on the type of fruit used, and the proportion of the native pectin. In the confectionery industry, high-methoxylated pectins are added to products with fruit filling, in which the fruit part (e.g. jam or marmalade) after baking remains inside the product. They can also be applied onto the surface of biscuits after baking as a jelly, which is then covered with other coating glaze. In the dairy industry, pectins are used as an ingredient in milk drinks and milk-fruit sour drinks, in which they act as stabilizers of consistency and prevent proteins coagulation, owing to the formation of soluble complexes with milk proteins. In fruit sorbets and Italian ice cream, pectin improves the consistency and smoothness by adjusting the amount of ice crystals formation. It also serves as a protective colloid, e.g. in the production of turbid beverages [23].

Preparations of low-methoxylated pectins are used in the processing of fruit to produce low-sugar jams in the amount of 0.7 to 1.2% of jam weight, confectionery fruit fillings, as well as fruit fillings of milk drinks. The dairy industry also exploits the properties of the low-methoxylated pectins. In the gelatin dessert products, pectins form a gel by combining with calcium ions present in milk. The addition of pectin in such products is at 0.6-0.9%. The consistency of such dessert depends on the amount of the additive as well as the type of pectin. Owing to the addition of pectins (stabilizing properties), fruit yogurts have enhanced fruity flavor compared to yogurts with added starch or other natural hydrocolloids. Low-methoxyl pectins are also used for the production of cream cheeses like "cottage" and melted cheese. The LMPs are also present in the composition of food concentrates and preparations of low-methoxylated amidated pectins are used for tarts baked with fruit topping, and confectionery products glazed by fruit jelly [22, 23, 24].

The pharmaceutical industry uses low-methoxy pectin as a drug carrier delivered to the gastrointestinal tract, for e.g. matrix tablets, gel beads, and membrane-coated dosage of drugs [25]. Pectin hydrogels are also utilized in the composition of tablets, as a binding agent and used in matrix tablet formulations of controlled-release drugs. By changing the degree of esterification of low-methoxylated pectin, Sriamornsak and Nunthanid [26] modified the form of drug release from gel beads of calcium pectinate. As pectins may react with calcium ions, calcium pectinate was examined as an insoluble hydrophilic coating applied to form a sustained release form in the process of interfacial complexation. The spherical granules which contain calcium acetate, were obtained by extrusion - spheronization followed by coating with the solution of pectin. Around the granules there are formed insoluble and uniform coatings of calcium pectinate gel [27].

The positive effect of applying pectin in food processing is the behavior of anthocyanin pigments. According to Le Bourvellec et al. [28] and Holzwarth et al. [29], pectins may form specific gel coatings that allow sealing the formed procyanidin complexes.

2.2. Health Benefits of Pectins

Pectins serve many functions in the human body, because their role is very important. They are considered some of the safest food additives for which no Acceptable Daily Intake (ADI) has been

stipulated. Pectins have also been included into a group of completely safe substances and are referred to as G.R.A.S. - Generally Regarded as Safe [23].

Pectins bind and remove excess fat supplied with food, thereby reducing the amount of cholesterol, reducing the incidence of atherosclerosis and preventing liver disorders. Indirectly, they also protect against heart attack [30]. By binding cholesterol and bile salts from food, apple pectins enforce the body to use fat tissue reserves in metabolic processes, thereby reducing the amount of total cholesterol that circulates in the blood and improving the ratio between concentrations of HDL and LDL cholesterol fractions [31].

Pectins reduce levels of phospholipids, triglycerides and free fatty acids in plasma and tissues to modify the distribution of lipoproteins, wherein their force is dependent on the degree of their methylation and amidation. The most positive effects have been ascribed to high-methoxylated pectins, including their contribution to weight loss, while low-methoxyl pectins have no such a clear effect on cholesterol and lipids metabolism. Thus, the high-methoxylated pectins are applied in the prevention and treatment of diseases (such as diabetes, obesity or hypercholesterolemia), whereas the low-methoxyl pectins may be used in diets to prevent these types of disorders [32].

Pectin preparations lower blood glucose and insulin levels after consumption foods with carbohydrates [23], by coating the mucosa they hinder the contact of glucose with the mucosa, they slow down the absorption of sugar, and then inhibit the process of stomach emptying and too big portions of sugar are not provided to the intestine. Due to the slower postprandial absorption of sugar, there is no large demand for insulin, which is important for patients with diabetes [31]. The presence of pectin in the diet increases the thickness of the surface layer of intestinal mucus and its viscosity. Kim [33] showed that the addition of pectin to a glucose solution increased its viscosity and reduced glucose absorption in the small intestine. Due to the formation of solutions with a significantly higher viscosity, a more significant effect on this phenomenon has been ascribed to the high-methoxylated pectins [32].

Pectins have also anticarcinogenic properties. Modified citrus pectins (MCP) have anti-metastatic effects [34]. These are derivatives of pectins treated with a base and then with an acid, which leads to their transformation into lower molecular weight unbranched, rich in galactose polysaccharides with improved absorption. Studies on the effect of the modified citrus pectin on the development of breast and prostate cancer have demonstrated that low concentrations of MCP 0.25-1.0 (mg/ml) did not inhibit the growth of cancer cells, however such an effect was confirmed after combining MCP with 2 newly tested phytochemicals responsible for the health of breast and prostate [35].

In clinical trials, the MCPs were investigated for their effect on the time of doubling the level of prostate-specific antigen (PSA) in men, in whom the PSA was still detectable in the blood and increased after local therapy for prostate cancer. The study did not allow to clarify the extent to which the therapeutic measures affected the suppression of metastasis, cancer cell growth or directly affected the cancer cells [34].

Due to their low digestibility, pectins are referred to as ballast ingredients of food products. Human digestive enzymes do not digest them, and the colonic microflora decomposes them into short chain fatty acids. When they are absorbed into the bloodstream, they are metabolized in the liver, which is why they are used in dietetic formulas. The ability to bind food components in the digestive tract by pectins results in a slower process of their digestion. Owing to the binding capacity of significant amounts of water and the ability to form coatings which cover food in the stomach, the contact with digestive enzymes is impaired and digestion is slowed down. The swelling of pectins in the digestive tract after ingestion increases the feeling of satiety, which is exploited in slimming diets used in the treatment of obesity and overweight [23].

Pectins are used in a therapeutic pectin diet for infants during diarrhea and constipation. In the case of diarrhea, the action of lactic fermentation bacteria is inhibited, they cannot grow and are removed with feces. During the treatment of diarrhea, pectins occurring in herbs (e.g. berberis fruit, leaves of wild strawberries or blackberries) protect gastrointestinal mucosa. In addition, pectins have a positive effect on peristalsis, thereby regulate constipation and help excreting undigested food residues [19].

2.3. Pectins in Dietetic Foods

Mainly low-methoxyl pectins are used in the dietetic foods. They absorb dietary components in the gastrointestinal tract and are applied as substances used to manufacture gluten-free baby formulas and foods for older children [10, 23].

Amidated pectins have an increasing share in the manufacture of food products with reduced sugar content, i.e. in products similar to those in which low-methoxyl pectin are being used [22]. According to the WHO, nutritionists and food technologists have focused their attention on the new evidence for the phenomenon of alarmingly increasing obesity worldwide [36]. A solution to this global problem may be aerated food.

Air bubbles are commonly found in foods, like e.g. beer or bread. Often consumers are not aware of their presence in the food they eat (ice cream contains up to 50% of air), and it turns out that a wide range of food products is aerated. Aerated foods are gaining increasing importance, therefore manufacturers are trying to use bubbles as food components, which is why aeration is one of the fastest developing unit operations in the food industry. Many food ingredients become functional thanks to the presence of air bubbles. The positive features of the aerated products include mainly their texture. Liquid food (whipped cream and mousses) gain smoothness, while solid products (cereals and snacks) become "light" and crispy. Aeration also increases the visual appeal of bread, bars, wine and beer, and may also be an indicator of their quality. The aerated structure helps in chewing and may enhance flavor. The aeration treatment changes also the rheological properties of foods, thereby enabling the originally liquid components to form more attractive shapes like meringue or chocolate [37].

One of the alternatives to develop products that provide satiety with low calorific value may be enclosing water and / or air in the gel matrix. The aerated products include e.g. aerated gels. The gels in food are a kind of delicate solids with a high content of the water phase, i.e. as much as 80%. Gel structures are present in most processed foods with a high moisture content, i.e. jelly, yogurt, meat products, and pectin is a very common ingredient of such products [38].

Aerated gels contain both the so-called "bubbles" and the entrapped water molecules, which is commonly used in food production. Scattered air (or other gases) are an additional phase within the gel, which makes that the structures formed in this way can play new functions and form an interesting texture. Many of the properties of the polymer forms of gels in food can be fortified by e.g. combining the materials and introducing a dispersed lipid phase (gels, emulsions). Investigated are both traditional methods and unconventional technologies (microfluidic systems, membrane systems) of "bubbles" formation in foods, including aerated gels. It is considered that the aerated gels may be used as carriers for flavors and nutrients to reduce the caloric value of food and to induce satiety and as innovative culinary products [36].

The introduction of the gas phase to the food matrix makes the product lighter, but at the same time changes its appearance, color and taste. Although the final texture of the aerated food can be either liquid, semisolid, or solid, the gas bubbles are always initially dispersed in the liquid. The aerated liquids are thermodynamically unstable, which necessitates the use of stabilizers such as proteins or emulsifiers. In turn, the "bubbles" suspended in the gel structure form a stable structure. One of the gel matrices used in the manufacture of aerated food is pectin matrix. Owing to the fact the aerated foods are manufactured with the aim to reduce the calorific value of food products and to make them "light", the preparations of low-methoxylated pectins fulfill their task as they form flexible gels or even sugar-free gels in the presence of Ca^{2+} . In addition, pectin which possesses a water binding capacity, by forming coatings helps to slow down digestion and to prolong the sensation of satiety [23, 39].

Due to the relatively low content of sugar, low-methoxyl pectin gels have many uses in dietetic and low-calorie foods, e.g. jams and jellies. The demand for jams and jellies with reduced or no sugar increases, partly due to the consciousness of consumers regarding calories, but also because of the demand for sugar-free products for diabetic patients. Low-methoxyl pectins that gelatinize in the absence of sucrose, but form gels with calcium are applied in such products. In products with a low sugar content, use is also made of hydrocolloids such as gums, carrageenans or agar. The advantage of using the low-methoxyl pectin instead of gums is their higher stability in the acidic medium, however a drawback may be difficulty in controlling the setting time of this type of gel [23, 40].

3. CONCLUSION AND SUMMARY

The awareness of consumers of food products is increasing. In care over their health, consumers are increasingly turning attention to what they buy and what they eat. More preferable are products with reduced fat, sugars, and calories, as well as the so-called "light" products. A fashion for healthy eating is observed as well. On the other hand, scientists, food technologists and manufacturers are facing a big challenge of satisfying the changing needs and demands of consumers. They are looking for new solutions, including additives that will improve products and make them healthier and more attractive, or explore the known substances, searching for their new properties and applications. One of these substances are the discussed pectins.

After analyzing the properties of pectins and their use in food technology, it may be concluded that they are highly suitable for the production of dietetic foods, mainly owing to the variety of their properties, including health-promoting ones. Pectins, in particular the high-methoxylated ones, added to foods bind and remove excess fat supplied with food, as well as reduce cholesterol level, which minimizes the risk of atherosclerosis incidence. Pectin preparations lower blood glucose levels and have anti-cancer properties. With the ability to bind food components in the digestive tract, in particular water, they are capable to swell and thus prolong the feeling of satiety. Low-methoxyl pectins are most often used in dietetic foods mainly due to the formation of gels without or with a small amount of sugar and the presence of ions, mainly calcium. A new trend in food technology is also the manufacture of aerated foods in which pectin can be successfully applied.

All these properties make that pectins are increasingly being used as additives to dietetic foods. They are considered one of the safest food additives, without specified ADI and included into the list of completely safe substances called G.R.A.S.

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