CHAPTER 13

Innovative potential of sea buckthorn pectin in providing textural properties to food and pharmaceutical products

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Abstract

The innovative potential of sea buckthorn pectin in food structure formation has been demonstrated, attributed to its unique functional properties. This study presents the results of theoretical and experimental investigations into the characteristics of pectin extracted from the peel of Hippophae rhamnoides (cv. "Leikora") grown in the right-bank region of Kherson, Ukraine.

In food and pharmaceutical processing technologies, there is a growing need for viscous solutions with adjustable rheological properties, which depend on equipment specifications and the desired characteristics of the final product. To assess possible structural transitions, the influence of sea buckthorn pectin concentration on the activation parameters of viscous flow – namely, activation enthalpy and activation entropy – was examined.

The studied sea buckthorn pectin exhibited a notably low "critical" concentration, indicating a high thickening capacity. Within the studied concentration range, the activation enthalpy and entropy changed in parallel. As the polysaccharide concentration increased, both activation parameters initially increased and subsequently declined, while viscosity increased throughout the entire concentration interval. At sub-critical pectin concentrations, the effective shear viscosity was primarily governed by the activation enthalpy. In contrast, above the critical concentration, viscosity was mainly determined by the entropic component.

It was shown that aqueous solutions of sea buckthorn pectin can be effectively used as model fluids for simulating the complex rheological behavior of materials employed in various technological processes. The rheological properties of food

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systems incorporating sea buckthorn pectin were also investigated, and deformation parameters of experimental model formulations of combined meat-vegetable-pectin pastes were determined.

In samples containing sea buckthorn pectin, a decrease in total, plastic, and elastic deformation was observed. The results of rheological and physico-mechanical tests demonstrated that the incorporation of sea buckthorn pectin into the formulation significantly influenced the structural integrity of the composite mixtures. Experimental data confirmed that sea buckthorn pectin improved the stability and homogeneity of highly concentrated meat-plant systems, facilitating the formation of a cohesive and stable food matrix.

The influence of sea buckthorn pectin on the techno-functional properties of food and pharmaceutical systems holds promising potential for further research, especially in light of its innovative applications.

Keywords

Sea buckthorn pectin, innovation potential, rheological properties, activation enthalpy and entropy, mechanical stability, deformation parameters, food and pharmaceutical systems.

13.1 Introduction

Sea buckthorn pectin is typically classified as a low-methoxyl pectin, consisting of a mixture of linear and branched polymers of α-*D*-galacturonan and other polysaccharides. Its innovative potential for food structure formation is considerable due to its unique functional properties. Pectins, owing to their ability to modify solution behavior through thickening, emulsification, stabilization, encapsulation, flocculation, swelling, and gelation, are used across a wide range of industrial sectors, including food, chemical, pharmaceutical, cosmetic, textile, paint, ceramic, petroleum, ecological technologies, and medicine.

The core aspects of the innovative potential of sea buckthorn pectin include its thickening, gelling, and emulsifying capabilities; its use as a functional food ingredient; valorization of processing by-products; and expansion of product ranges. In the context of rising demand for natural and "clean-label" food ingredients, pectin extracted from sea buckthorn offers an appealing alternative to synthetic thickeners and stabilizers. It can be obtained from pomace and other sea buckthorn processing waste, contributing to sustainable raw material utilization and waste reduction. Moreover, it presents economic opportunities at the regional level by fostering local agriculture and food industry development.

The distinctive properties of sea buckthorn pectin open new possibilities for designing products with novel textures and enhanced functional attributes. Its application enables manufacturers to meet growing consumer demand for healthy, natural, and innovative food products. However, certain challenges must be considered. The properties of pectin vary significantly depending on the sea buckthorn variety, maturity stage, cultivation conditions, and extraction methods. This may lead to variability in the quality and functional performance of the final pectin, including its thickening capacity. The molecular weight and degree of branching of pectin molecules also influence their rheological behavior, such as viscosity and gel-forming ability. These parameters may differ depending on the raw material source and extraction process, complicating standardization of pectin properties.

Compared to traditional pectin sources, research into the functional properties and applications of sea buckthorn pectin remains limited, potentially hindering the development of optimal formulations and processing techniques. Currently, quality and functionality standards for sea buckthorn pectin are less clearly defined than for commercially available pectins, which may limit its industrial scalability.

Nonetheless, ongoing research into extraction, characterization, and application of sea buckthorn pectin remains active. Due to its functional relevance, the investigation of the rheological properties of sea buckthorn pectin is particularly timely. Rheological properties – such as viscosity, elasticity, flow, and gelation capacity – are crucial for understanding how sea buckthorn pectin behaves in various food matrices. Such data enable the definition of quality benchmarks for its use as an ingredient, ensuring production process stability and predictability of end-product characteristics.

Understanding rheological behavior supports the optimization of mixing, heating, cooling, and other technological operations involving pectin, thus enhancing production efficiency and product quality. In certain food applications or drug delivery systems, the rheological properties of pectin may impact the release rate of active compounds, making this an important area for development of controlled-release products. Furthermore, these studies contribute to a deeper understanding of pectin's molecular structure, gelation mechanisms, and molecular-level interactions with other components. Comparing the rheological characteristics of sea buckthorn pectin to pectins from other sources broadens scientific knowledge and informs its potential applications. Ultimately, such research is essential for optimizing the use of sea buckthorn pectin in food and pharmaceutical industries, expanding its applications, and developing higher-quality, health-promoting products.

Although pectin is generally a valuable polysaccharide in the food and pharmaceutical industries, research on sea buckthorn pectin is limited and its applicability

is not well characterized. Gaps exist in the understanding of the specific properties of pectin extracted from sea buckthorn peel. The potential of sea buckthorn pectin, although recognized for providing textural properties, requires deeper investigation of sea buckthorn peel pectin to optimize its use in various products. There are a number of unresolved issues regarding its application for shaping the texture of food products that require further research. Sea buckthorn pectin from different geographical regions or different varieties may have different chemical and physicochemical properties, so it is necessary to study in more depth how the structural features of sea buckthorn pectin, which grows in the south of Ukraine, affect its ability to form viscous systems, to obtain a thermodynamic understanding of the structural aspects of the processes occurring in solutions of this polysaccharide, to identify the features of its functional behavior in food and pharmaceutical matrices. Solving these issues will allow for more effective use of sea buckthorn pectin as a valuable, natural and functional ingredient for innovative food products and pharmaceuticals, which, in turn, will contribute to expanding the range of functional products and efficient use of resources.

Therefore, the research topic "Innovative potential of sea buckthorn pectin in providing textural properties to food and pharmaceutical products" is both timely and relevant.

The primary aim of this study is to provide scientific evidence and practical data that substantiate and expand the application potential of sea buckthorn pectin as a valuable, innovative, and functional ingredient. Specifically, the objective is to reveal the potential of sea buckthorn-derived pectin in enhancing the textural properties of food and pharmaceutical products.

The scientific novelty of the study "Innovative potential of sea buckthorn pectin in providing textural properties to food and pharmaceutical products" lies in its focus on an underexplored but promising source of pectin – sea buckthorn. The novelty is not limited to the identification of pectin within sea buckthorn, but extends to a detailed analysis of its textural properties. Analysis of the textural properties of sea buckthorn pectin opens up opportunities for innovative and effective use of this natural polymer in the food and pharmaceutical industries.

13.2 Justification of using sea buckthorn pectin feasibility as regulators of food and cosmeceutical products consistency

Pectin can be extracted from agricultural biomass and fruit and vegetable processing waste using various methods. Naturally, pectin exhibits physicochemical

properties suitable for applications in both food and pharmaceutical industries. Pectin is a complex polysaccharide found in plant cell walls and consists of galacturonic acid residues. Pectin can be extracted from agricultural biomass, fruit and vegetable processing waste by several methods. Naturally, pectin has characteristics that are considered for application in the food industry. These characteristics include gelling, thickening, emulsifying, food encapsulation, and food coating. Reference [1] provides a comprehensive review of the structure of pectin, various extraction methods, and its applications in the food industry. However, pectin obtained through conventional extraction may exhibit certain limitations that restrict its broader utilization. To address these challenges, the review also discusses several modification techniques aimed at enhancing the functional properties of natural pectin. As a natural biomolecule, pectin acts as a biological modifier and is widely utilized in biochemistry, nutrition, and medicine. Due to its safety, biological activity, and biodegradability, pectin has attracted significant scientific interest. Studies have shown that plant-derived pectin possesses antioxidant [2], antitumor [3], and prebiotic [4] properties. Its unique emulsifying and gelling properties also make it a valuable functional food additive [5].

In [6], pectins from citrus peels of common varieties from different growing regions in China were characterized, and their comparison was carried out in terms of basic structure, composition (Fourier transform IR spectra, molecular weight distribution, monosaccharide composition), and functional properties (thermal stability and rheological properties). The relationship between chemical structure and antioxidant activities *in vitro* of these CPPs were also investigated comprehensively. Among the 10 kinds of citrus peel pectins, Shatangju (CPP-6) and Xuecheng (CPP-7) own superior antioxidant biological activity and Dahongpao (CPP-3) and Buzhihuo (CPP-9) had excellent functional properties (thermal stability and viscosity). According to the correlation analysis, molecular weight, galacturonic acid content and degree of methyl-esterification were beneficial to increase the thermal stability and viscosity of citrus peel pectins, while the rhamnose content, rhamnogalacturonan I region and lower molecular weight can improve citrus peel pectins antioxidant activity. Findings suggest that CPP-6 and CPP-7 may be useful as a potential natural antioxidant in pharmaceutical and cosmetic industries. Meanwhile, CPP-3 has great application potential in high temperature food and CPP-9 can be used as a thickener or stabilizer in the food industry [6].

Recently, extracting pectin from plant by-products has gained traction due to its low toxicity and inherent bioactivity. Sea buckthorn peel, a by-product of processing, contains a notable amount of pectin. Pectin is a non-toxic, natural, and multifunctional heteropolysaccharide, and one of the primary components of plant

cell walls, comprising 0.5 to 4.0% of the total fresh weight of plant materials [7]. Chemically, pectin is composed mainly of D-galacturonic acid residues, along with L-rhamnose (Rha), D-galactose (Gal), L-arabinose (Ara), and up to 13 other monosaccharides [8].

Determining the structure of pectin is complex, as its composition is influenced by plant origin, extraction conditions, growing location, and environmental factors [9]. Additionally, pectin undergoes modifications during plant maturation, processing, isolation, and storage [10]. Its biological activity is dictated by the composition of constituent sugars and substituent groups, and their interactions can enhance pectin's functional properties [11].

The chemical composition and molecular architecture of pectin vary significantly depending on the plant tissue type and extraction method [12]. Present consensus defines pectin as a heterogeneous polysaccharide with four main structural domains: homogalacturonan (HG), xylogalacturonan (XGA), rhamnogalacturonan I (RG-I), and rhamnogalacturonan II (RG-II) [13]. Although their relative proportions differ, HG and RG-I are the predominant components. RG-I consists of a repeating disaccharide backbone of rhamnose and galacturonic acid, decorated with linear or branched arabinan and/or galactan side chains. RG-II features a conserved structure composed of a short HG segment substituted with complex side chains made up of thirteen different monosaccharides and over twenty glycosidic linkages [14].

Pectin molecules are structurally organized into alternating regions: smooth, unbranched HG domains and branched, flexible RG-I-rich "hairy" regions. The hairy regions display greater compositional and structural diversity than the smooth ones, containing a wide array of monosaccharides [15].

In one study, high-methoxyl sea buckthorn pectin (SBHMP) was extracted from sea buckthorn peel with a yield of 8%. The SBHMP had a degree of esterification of 57.75% and contained 65.35% uronic acids. Structural and morphological analyses using HPLC, FTIR, and SEM revealed that SBHMP had a sheet-like, layered morphology and was mainly composed of galacturonic acid, arabinose, galactose, rhamnose, and mannose, indicating predominance of HG and RG-I domains [16].

In recent years, increasing attention has been devoted to the rheological properties of food colloids due to their strong correlation with functional performance. Compared to other colloidal systems, pectin solutions exhibit Newtonian-like flow at low concentrations and pseudoplastic (shear-thinning) behavior at higher concentrations [17]. Pectin viscosity is not only determined by its structure but also by concentration, pH, and ionic strength [18]. Pectin obtained via ultrasound-assisted extraction under optimized conditions exhibited clear non-Newtonian shear-thinning behavior at concentrations between 1.5% and 3.0% [19].

Sea buckthorn peel is a by-product of sea buckthorn processing, rich in various bioactive compounds. In [20], sea buckthorn high methoxyl pectin (SBHMP) was extracted, yielding 8% of light-colored product. SBHMP was classified as high methoxyl pectin, with a degree of esterification of 57.75% and a uronic acid content of 65.35%. The structural and morphological characteristics of SBHMP were analyzed using high-performance liquid chromatography (HPLC), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The results indicated that SBHMP exhibited a sheet-like, layered, and stacked morphology. It was mainly composed of galacturonic acid, arabinose, galactose, rhamnose, and mannose, suggesting that the extracted polysaccharides were primarily of the homogalacturonan (HG) and rhamnogalacturonan-I (RG-I) types.

In addition, SBHMP demonstrated significant gelling, thickening, and emulsifying properties. The results showed that SBHMP could form jelly-like gels under acidic and high-sucrose conditions, exhibiting shear-thinning behavior and increasing apparent viscosity with higher concentrations of both pectin and sucrose. Furthermore, SBHMP was capable of forming oil-in-water emulsions at pectin concentrations ranging from 1.0% to 3.0%. At concentrations of 2.0% and 3.0%, the emulsions remained stable over a storage period of 7 days. The findings of this study highlight the potential of SBHMP as a food-grade thickener and emulsifier, supporting the value-added utilization of sea buckthorn processing by-products [20].

In recent years, studies have shown that extracts from sea buckthorn berries, leaves, and seeds possess a wide range of biological activities [21, 22]. With the advancement of the sea buckthorn industry, substantial amounts of pomace, peel, seed meal, and other by-products have been generated. However, these materials have not been fully utilized, resulting in considerable resource wastage.

Currently, the extraction of pectin from plant-based by-products has attracted considerable attention due to its low toxicity and beneficial biological activity. Previous research indicates that fruit and vegetable peels contain significant amounts of pectin, with notable variability in composition and functional characteristics depending on the plant source. However, studies focused specifically on sea buckthorn pectin remain limited, and its functional application properties are not yet well defined.

Moreover, the composition of bioactive compounds in sea buckthorn is known to vary depending on growing conditions. Notably, sea buckthorn cultivated in plateau regions tends to exhibit higher concentrations and enhanced functionality of bioactive components compared to those grown in plains [23]. Therefore, exploring the potential of plateau-grown sea buckthorn peel as a pectin source, and characterizing its functional properties, holds significant promise for the development of innovative food and nutraceutical products.

13.3 Research materials and methods

An alternative source was used to obtain pectin, namely sea buckthorn peel [24]. This by-product of sea buckthorn fruit processing contains a significant amount of biologically active compounds. To date, research on pectin derived from sea buckthorn remains limited, and its application characteristics are not yet well defined. Furthermore, the composition and function of bioactive components in sea buckthorn vary depending on the habitat, influencing both their concentration and biological activity.

The aim of this study was to extract pectin from sea buckthorn peel. The test samples included cultivated *Hippophae rhamnoides* of the "Leikora" variety and wild-growing sea buckthorn. Both samples were collected from the right bank of the Kherson region (Ukraine).

According to a previously described method [25, 26], the sea buckthorn peel was mixed with distilled water at a raw material-to-liquid ratio of 1:10 (w/v), with the addition of 0.5% citric acid, 0.5% sodium ascorbate, and 0.2% ethylenediaminetetraacetic acid (EDTA). The pH of the mixture was adjusted to 2.0 using 1 M HCl, followed by incubation at 80°C for 1 hour.

After incubation, the mixture was centrifuged at 6500 rpm for 15 minutes. The resulting supernatant was concentrated using rotary evaporation, and 0.0004% sodium metabisulfite was added for mild decolorization. The solution was then mixed with 1.5 volumes of ethanol and allowed to stand for 4 hours. Pectic polysaccharide was recovered by dialysis and lyophilization.

The optimal extraction conditions were: temperature of 70 ± 2°C, pH 2.5–3.0, and extraction time of 10–12 hours. Acidification was performed with sulfuric acid. The extraction process was accompanied by filtration.

To obtain low-methoxyl (LM) pectin, de-esterification was carried out in ethanol with the addition of either an acid or a base.

Pectin was precipitated from the filtrate/ethanol mixture (up to 96 vol. %) at a ratio of 70:30. The precipitate was separated by filtration, again using a canvas filter.

Drying. Pectin obtained from the filtrate was placed in plastic trays and dried in a drying oven at a constant temperature of 60°C for 48 hours to remove excess moisture.

After drying, the product was stored in an airtight container until further use. The final powder moisture content should not exceed 5% by weight.

The appearance of the obtained pectin is shown in **Fig. 13.1**.

The obtained extract contained a mixture of pectic substances with varying molecular weights and degrees of esterification.

The following ingredients were used in the study:

– chicken meat (DSTU 3143:2013 "Poultry meat. General technical specifications", with Amendment No. 1);

– beans (DSTU 8672:2016 "Edible beans. Technical specifications", effective from 01.10.2017);

– drinking water (DSTU 7525:2014 "Drinking water. Requirements and methods of quality control", effective from 01.02.2015).

Measurements of rheological parameters of pectin solutions and a model mixture of canned poultry with pectin were performed using a Brookfield Model DV-III rheometer (Brookfield, Great Britain) (**Fig. 13.2**).

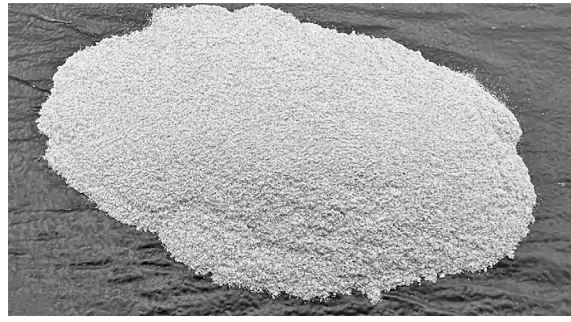

Fig. 13.1 Pectin obtained in the laboratory from sea buckthorn peel

Fig. 13.2 Brookfield Model DV-III rheometer

A sample of the tested solution weighing about 0.5 g was placed in the rheometer bowl under the spindle. Rheological parameters were measured when the spindle rotated at different shear rates, from low to high and back. During the studies, the solution samples were thermostated with an accuracy of ± 0.1°C using a Brookfield TC-350 thermostat (Brookfield, Great Britain) equipped with a flow cell (thermostat fluid – purified water). The results were used to construct rheograms showing the dependence of shear stress (τr) and dynamic viscosity (η) on the velocity gradient (Dr) in the range from 0 to 500 1/s.

The steady-state flow behavior of the prepared pectin solutions was measured at shear rates ranging from 0 to 500 s^{-1}. The effect of temperature on the flow behavior of pectin substances solutions at 0.5–2.5% (w/v) concentrations and pH 2.0–6.0 (prepared at a concentration of 1.0% (w/v)) was determined by measuring with a gradual temperature increase in the temperature range from 10 to 60°C at a heating rate of 10°C/min and an angular velocity of 0.1 rad/s.

The flow characteristics were determined using the Ostwald-de Waele rheological model, which describes plastic behavior or thickening under shear and is calculated by formula (13.1)

$$\tau = K \cdot \gamma^{n}, \tag{13.1}$$

where τ – shear stress (Pa); K – consistency index (Pa·s); γ – shear rate (s^{-1}); n – flow behavior index (dimensionless). In the investigated shear rate range, the viscosity of solutions was determined by formula (13.2)

$$\eta = \frac{P}{\gamma} = K\gamma^{n-1}. \tag{13.2}$$

The consistency index is relevant for the consistency of a liquid: if $n = 1$, the liquid is Newtonian, and the parameter K has the value of the Newtonian viscosity η. The flow behavior index is a deviation from Newtonian behavior. If $n < 1$, the viscosity decreases with increasing shear rate, which is characteristic of non-Newtonian plastic liquids [27–29] The mechanical stability (MS) of the samples was calculated as the ratio of the strength limit of the structure before fracture (τ_1) to the strength limit after fracture (τ_2) according to the formula (13.3)

$$MS = \tau_1 / \tau_2, \tag{13.3}$$

where τ_1 – the strength limit of the structure before failure; τ_2 – the strength limit of the structure after failure.

The value of the *MS* characterizes the degree of destruction of the structure of the samples in the process of irreversible deformation [30, 31].

To calculate the deformation characteristics, used the fundamental equation for elastic materials is Hooke's Law, which states

$$\sigma = E \cdot \varepsilon, \tag{13.4}$$

where σ – the stress; E – the modulus of elasticity; ε – the strain. For materials with elastoplastic behavior, more complex models such as the Prandtl-Reuss equations are used to describe stress-strain relationships during plastic deformation.

The Prandtl-Reuss equations consider both elastic and plastic strains

$$d\varepsilon = d\varepsilon_e + d\varepsilon_p, \tag{13.5}$$

where $d\varepsilon_e$ – the elastic component; $d\varepsilon_p$ – the plastic component of the strain [32].

All rheological behavior measurements were performed in triplicate and the values are presented as mean ± standard deviation ($n = 3$). The viscosity of the solutions was analyzed and statistically compared using the *t*-test.

13.4 Research results and discussion

13.4.1 Study of rheological properties of sea buckthorn pectin

In the practice of food and pharmaceutical technologies, there is a need to use viscous solutions with different viscosity values, which are determined by the characteristics of the equipment and the properties of the finished product. A necessary condition for creating an optimal recipe for a product with the required viscosity is the availability of data on the nature of the dependence of the system viscosity on the thickening agent concentration. There are several approaches to the graphical interpretation of the polymer solutions viscosity concentration dependence. The relationship between the solutions viscosity of almost any polysaccharide and its concentration is exponential. Representation of such a dependence in the "viscosity–concentration" coordinates clearly displays a sharp increase in viscosity with an increase in the concentration of the polysaccharide, but makes it difficult to assess some features of their rheological behavior. It was proposed to construct the concentration dependences of the viscosity of polymer solutions using the "viscosity-concentration" coordinates, which allows presenting these dependences

in linear form over a wide range of concentrations [33]. At the same time, in the area of moderately and highly concentrated solutions of polysaccharides, the use of semi-logarithmic coordinates seems to be the most preferable. The resulting simplification of the obtained dependencies does not prevent an objective assessment of the thickening capacity of various polysaccharides.

Fig. 13.3 shows the dependence of the viscosity of a sea buckthorn pectin solution on concentration at 25°C and a shear rate gradient of 500 s^{-1}.

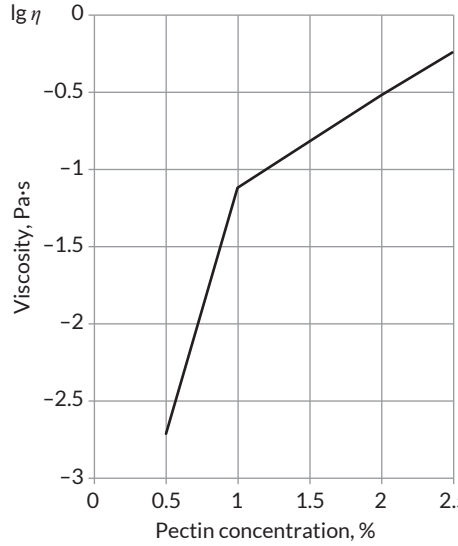

Fig. 13.3 Dependence of solution viscosity on the concentration of sea buckthorn pectin

The concentration dependence of viscosity in semi-logarithmic coordinates is expressed by two intersecting straight lines. The presence of an inflection point corresponds to a certain "critical" concentration. The presence of an inflection point on the viscosity concentration dependence is evidence that two straight-line sections of the dependence correspond to two different mechanisms of viscous flow.

To assess possible structural changes, the effect of the concentration of sea buckthorn pectin on the activation parameters of viscous flow of solutions was studied, since such indicators as heat and entropy of activation of viscous flow are very sensitive to the strength of the structure and its orderliness [34].

It is proposed to calculate the activation parameters based on the Frenkel-Eyring equation [35], which describes the temperature dependence of the viscosity

of a liquid from the standpoint of the theory of absolute reaction rates. However, during relatively large changes in temperature, the viscosity of the liquid begins to differ more and more from the values calculated by the Frenkel-Eyring formula. The real physical reason why the viscosity begins to differ from the values calculated by the Frenkel-Eyring formula during large temperature changes is that the temperature dependence of the activation free energy of viscous flow is not only in the form Gibbs energy of activation, but it can also be in a very complicated way due to the dependence of ΔH and ΔS on temperature: $\Delta G(T) = \Delta H(T) - T\Delta S(T)$.

If the structural temperature of the liquid has increased due to the influence of any substance, then when cooling that liquid, the temperature at which the viscosity is infinitely large will arrive sooner, that is, the liquid will be structured more quickly. From this point of view, it can be said that the increase in the structural temperature of the liquid due to the effect of any dissolved substance and other physical parameters means its structuring compared to the pure liquid as a result of this effect. Likewise, it can be said that the decrease in structure temperature is equivalent to the collapse of the structure of the liquid. Let's note that liquids with a structural temperature equal to zero, that is, the temperature dependence of viscosity can be expressed quite well by the Frenkel-Eyring formula, are called free liquids, and vice versa, liquids with a certain internal structure, that is, a non-zero structural temperature, are called non-free liquids [36].

In this work, the activation parameters were calculated using the following equation (13.6)

$$\Delta H - T\Delta S = 4 + 2.303RT\lg\eta. \quad (13.6)$$

The dependence of the heat and entropy of viscous flow activation of sea buckthorn pectin solutions on concentration at a shear rate of 500 s^{-1} and a temperature of 25°C is shown in **Fig. 13.4**.

The concentration dependence of the activation parameters has an extreme character. Both the heat and the entropy of the activation of the viscous flow reach their maximum in the region of the critical concentration of the solution, that is, at the same point where the viscosity change curve undergoes a break. With an increase in the concentration of sea buckthorn pectin in the interval up to the critical concentration, there is an increase in the number of macromolecules involved in the process of viscous flow, which is accompanied by an increase in the entropy of the system from 12.13 to 26.48 kJ/mol. As a result of the increase in the total number of macromolecules of the polysaccharide, the number of links between individual segments of macromolecules increases. This process is accompanied by an increase

in the number of elementary flow acts and intermolecular bonds, which are redistributed under the action of shear stress. This is evidenced by the increase in the heat of activation of the viscous flow.

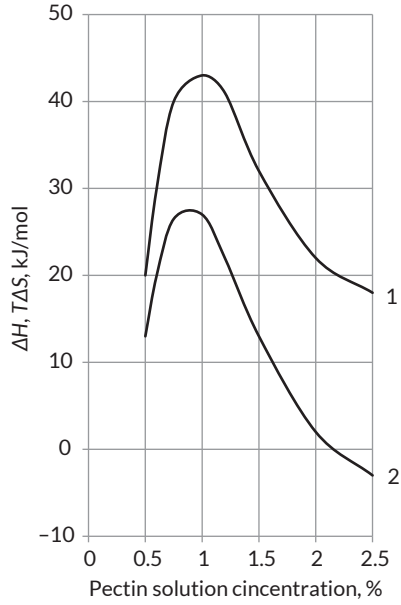

Fig. 13.4 Dependence of the activation parameters of the viscous flow of solutions on the concentration of sea buckthorn pectin:
1 – heat of activation (ΔH); 2 – entropy of activation ($T\Delta S$)

When the sea buckthorn pectin concentration is equal to the "critical" one, the total number of macromolecules becomes sufficient for the formation of a continuous three-dimensional mesh, and an ordered structure appears in the viscous solution. A further increase in the concentration of polysaccharide comes down to the involvement of new macromolecules in the resulting structure. The increase in the order of the system with an increase in the concentration of sea buckthorn pectin in the interval above the critical concentration is characterized by a significant decrease in the entropy of the activation of the viscous flow.

Taking into account the results of studies of polysaccharides, it can be assumed that when the structured system of pectins is sheared, the process of viscous flow is no longer due to the jumping of segments and individual macromolecules, but mainly

by the movement of larger supramolecular formations – aggregates and "domains". It is natural that the number of such kinetic units as aggregates or "domains" is significantly less than the total number of macromolecules, therefore, as the degree of aggregation increases, the number of contacts between kinetic units should decrease. In addition, the energy of interaction between individual aggregates is not so great, compared to the interaction of macromolecules within supramolecular structures. This is reflected in a decrease in the heat of activation of the viscous flow.

In the investigated concentration range of sea buckthorn pectin, the heat of activation and entropy change smoothly. As the polysaccharide concentration increases, the heat and entropy of activation first increase and then decrease, while the viscosity increases throughout the interval. It follows that at a concentration of sea buckthorn pectin less than the critical one, the effective shear viscosity depends mainly on the value of the heat of activation, while at a concentration greater than the critical one, the viscosity is determined mainly by the contribution of the entropy component.

Compared to the majority of industrial types of pectins that are currently used in the food and pharmaceutical industry, sea buckthorn pectin, which was studied, is characterized by a minimal value of the 'critical' concentration, which indicates its high thickening ability.

13.4.2 Research on the rheological properties of food systems containing sea buckthorn pectin

The study of rheological properties of food systems is a place for controlling the parameters of technological processes during the formation of optimal properties of the final product.

The tasks that study the influence of the components of the food system (in our case, new types of meat-vegetable canned food) on its rheological parameters are extremely important.

The inclusion of various components in the minced meat composition can cancel the quality indicators, in particular the structural and mechanical properties.

The object of the next study in this work was minced meat and vegetables with the addition of sea buckthorn pectin. The main components of the mass are water/food system (90/10).

Chicken fillet was ground in a meat grinder to a particle size of 1–2 mm. Bean flour and pectin were added to the minced chicken according to the recipes given in **Table 13.1**.

Table 13.1 Recipe for combined meat and vegetable minced meat

Component	Amount of component, g/100 g of raw material			
	F1	F2	F3	F4
Chicken trimmings	100	90	99	89
Bean flour	–	10	–	10
Sea buckthorn pectin	–	–	1	1

The components were thoroughly mixed, the minced meat samples were packed in polyethylene bags and stored at 4°C until testing.

The rheological parameters of the minced meat and vegetables were studied at 20°C.

In the food industry, the study of the dynamics of the ultimate shear stress is important for determining the consistency of products during storage or technological processing. Therefore, the dynamics of the ultimate shear stress of combined minced meat and vegetables with sea buckthorn pectin were studied depending on the shear rate.

The results of the studies are shown in **Fig. 13.5**.

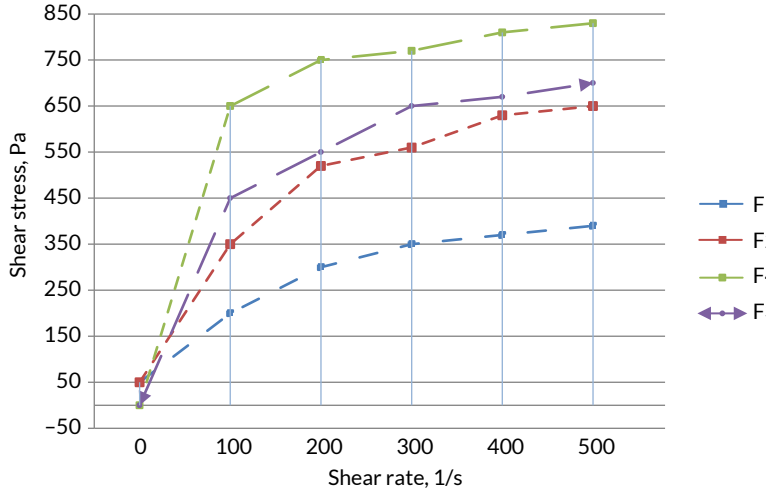

Fig. 13.5 Dynamics of ultimate shear stress of samples of combined meat and vegetable minced meat depending on the shear rate: F1 – chicken trimming; F2 – chicken trimming + bean flour; F3 – chicken trimming + sea buckthorn pectin; F4 – chicken trimming + bean flour + sea buckthorn pectin

In viscoelastic materials, the ultimate shear stress can depend on the rate of application of the load. With rapid loading, the material can behave as an elastic body with a higher ultimate stress, and with slow loading, as a viscous fluid with a lower ultimate stress. Changes in temperature can affect the strength of the material and its shear resistance. Typically, the ultimate shear stress decreases with increasing temperature. A material that has already undergone plastic deformation may have a different ultimate shear stress compared to an undeformed material. This phenomenon is called hardening. Chemical composition and microstructure are important factors. The presence of impurities, lattice defects, grain size, and other microstructural features can significantly affect the shear resistance of a material. Pressure, humidity, and other environmental factors can also affect the ultimate shear stress.

Analysis of the obtained rheograms (graphs of rheological parameters) allows to assess the mechanical stability of the paste and predict its behavior during production, storage and consumption. The mechanical stability of the paste means its ability to maintain a uniform consistency and physical structure for a certain time and under the influence of various mechanical factors. A mechanically stable paste should be uniform, plastic, spread well and not lose its properties under the influence of external factors. The work determined how the addition of sea buckthorn pectin affects the mechanical stability of experimental samples of the model base of the paste. For model samples F1 – chicken trimming; F2 – chicken trimming + bean flour; F3 – chicken trimming + sea buckthorn pectin; F4 – chicken trimming + bean flour + sea buckthorn pectin, the following results were obtained: for sample F1 – *MS* value = 1.22; for F2 – *MS* value = 1.29; for F3 – *MS* value = 1.12; for F4 – *MS* value = 1.14. A *MS* value greater than 1 indicates that the structure of the pate after destruction becomes weaker than it was before destruction. The higher the *MS* value, the greater the loss of structural strength after its disruption. For samples containing sea buckthorn pectin, a relatively small decrease in strength was found (*MS* ≈ 1.12–1.14). The *MS* value = 1.29 (sample containing chicken trimmings and bean flour) indicates a more significant loss of structural strength after destruction. Sample F2 lost approximately 30% of its initial strength, which may cause brittleness or a lower ability to restore its structure after damage. According to the results of the study, it can be concluded that the addition of sea buckthorn pectin leads to the fact that the product structure becomes less prone to significant loss of strength after mechanical impact, which leads to its destruction, i.e. such an additive improves the stability of the structure.

The dynamics of the ultimate shear stress shows how the value of the shear stress at which plastic deformation or fracture of the material begins varies depending on various factors.

In the context of food systems, the values of total, plastic and elastic strains reflect the response of a food product to an applied force or stress. Total deformation of a food system is the total change in the shape or volume of the product under the action of an external force. It includes both reversible (elastic) and irreversible (plastic) components. Total deformation is the total result of all changes that occur in the structure of the product under load. Plastic deformation of a food system is the irreversible part of the total deformation. This means that after the load is removed, the food product does not return to its original shape, but retains residual deformation. The magnitude of plastic deformation indicates the degree of irreversible changes in the structure of the product. For example, when spreading butter or pate on bread, the butter or pate undergoes plastic deformation, retaining its new shape after the force is removed.

Elastic deformation of a food system means that when an external force or stress is applied to a food product, it temporarily changes its shape or volume, but after the force is removed, it completely returns to its original state.

In the process of elastic deformation, changes occur in the interatomic or intermolecular distances in the structure of the food product. These changes are reversible, and when the load is removed, the molecules return to their original positions, restoring the original shape of the product.

The key characteristics of elastic deformation of food systems are: reversibility, temporality and dependence on the applied force. The first shows how after the load is removed the product completely restores its original shape and dimensions. Temporality shows that the deformation exists only as long as the external force acts. The dependence on the applied force characterizes the magnitude of the elastic deformation in relation to the applied force (within the limits of the elasticity of the material), which is described by Hooke's law (for solids) or similar dependencies for liquids and gels.

Elastic deformation can be clearly seen when analyzing various food systems, for example, during compression of sponge bread: when lightly compressed, the bread deforms slightly, but after the pressure is removed it returns to its original shape. An example such as the elasticity of jelly shows that slight oscillations or pressing on the jelly causes it to deform, but it quickly returns to its original shape. The elasticity of some fruits is also a visual demonstration of food systems, in which gently pressing a ripe but resilient peach can cause a small deformation that disappears when the pressure is removed. Elastic deformation is also characteristic of the change in volume of a liquid under pressure, since to some extent liquids can also undergo a small elastic deformation (change in volume) under pressure that disappears when it is removed.

Understanding elastic deformation is important for characterizing the textural properties of foods, their behavior during processing and storage, and for developing products with desirable sensory qualities. For example, elasticity is an important attribute for foods such as bread, paste, jellies, and some confectionery.

Understanding the relationship between elastic and plastic deformation is important for evaluating the texture, consistency, and behavior of foods during their production, storage, and consumption.

Products with high plastic deformation may be soft and easily deformable (e.g., paste).

The study of these deformations helps technologists develop products with desired properties and control their quality at different stages of production.

Fig. 13.6 shows the deformation parameters of experimental samples of the model base of combined meat-vegetable-pectin minced meat determined in the work.

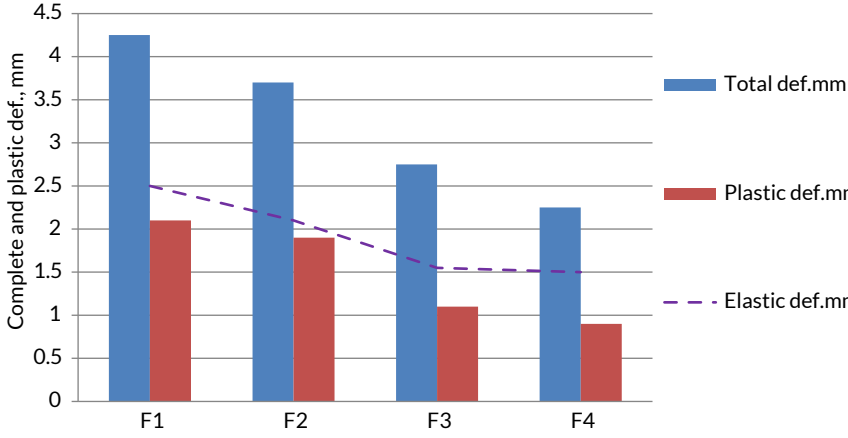

Fig. 13.6 Deformation parameters of experimental model samples of combined meat-vegetable-pectin minced meat: F1 – chicken trimming; F2 – chicken trimming + bean flour; F3 – chicken trimming + sea buckthorn pectin; F4 – chicken trimming + bean flour + sea buckthorn pectin

The highest values of total, plastic and elastic deformations were found in samples with the lowest shear stress – F1 and F2 (**Fig. 13.6**).

Small total, plastic and elastic deformations were found in samples F3 and F4, which contain sea buckthorn pectin. Small deformation of the pâté means that under the influence of external force (for example, when spreading, cutting or squeezing) it slightly changes its shape and at the same time retains its integrity, without

spreading or collapsing. After removing the external influence, the pâté can partially or completely return to its original shape.

In contrast, large total deformation may indicate too soft or liquid consistency, possible delamination.

From the point of view of the quality and properties of the pâté, small total deformation is a sign of high-quality pâté with a dense, but at the same time delicate structure.

Thus, the addition of sea buckthorn pectin led to a decrease in the total deformation of the model sample, which is a positive characteristic for the pate and indicates its high-quality consistency and stable structure.

13.4.3 Rheological study of composite pharmaceutical formulations based on sea buckthorn pectin

In the pharmaceutical sector, pectins represent a beneficial application for the creation of hydrogels. Hydrogel films have significant potential in pharmacy, as they provide a long-term and controlled release of drugs. This allows to reduce the frequency of drug administration, increase the effectiveness of therapy and reduce side effects. In addition to pharmaceutical applications, hydrogels are actively used in regenerative medicine to stimulate tissue regeneration. Thus, polymer hydrogels are a promising material for innovative technologies in biomedicine, in particular in drug delivery systems. Their unique properties provide a wide range of opportunities for the development of effective and safe therapy methods.

The physicochemical properties of hydrogels, in particular the degree of swelling, permeability and mechanical strength, determine their functionality. Pectins demonstrate high stability and can be modified by adding other polymers to achieve the desired characteristics. Polymer hydrogels based on pectin are three-dimensional polymer networks capable of absorbing and retaining a significant amount of water. One of the key characteristics of hydrogels is their ability to swell in an aqueous environment without losing structural integrity. This is achieved by chemical or physical crosslinking of polymer chains. The type of crosslinking determines the mechanical properties, stability and suitability of the hydrogel for a particular application. Despite the attractive properties of pectins, due to their hydrophilic nature and low water resistance, their use in sustained-release dosage forms is limited. One approach to further improve the characteristics of biopolymer films, in particular those based on pectin, is to combine them with other polymer matrices. Pectins can be modified by adding other polymers to achieve the desired characteristics. For a hydrogel with sea buckthorn pectin, it is most appropriate to use sodium alginate if one is aiming for

a completely natural, biodegradable hydrogel with good encapsulation capabilities and easy gelation (with the help of calcium). Sodium alginate is an ideal choice for food, pharmaceutical and biomedical applications where softness and compatibility with biological systems are important. Therefore, this study investigated the possibility of modifying sea buckthorn pectin by adding sodium alginate.

The study of the rheological properties of hydrogels is extremely important for many reasons, as they determine how the material will behave under the action of various forces and loads, as well as how it will interact with the environment and biological systems. These properties directly affect the production process, functionality and application of hydrogels.

Rheological studies of polymer compositions were carried out at different concentrations of pectin in the studied compositions. Based on the obtained results, flow curves were constructed (**Fig. 13.7**) illustrating the viscosity of sea buckthorn pectin-based solutions as a function of shear rate.

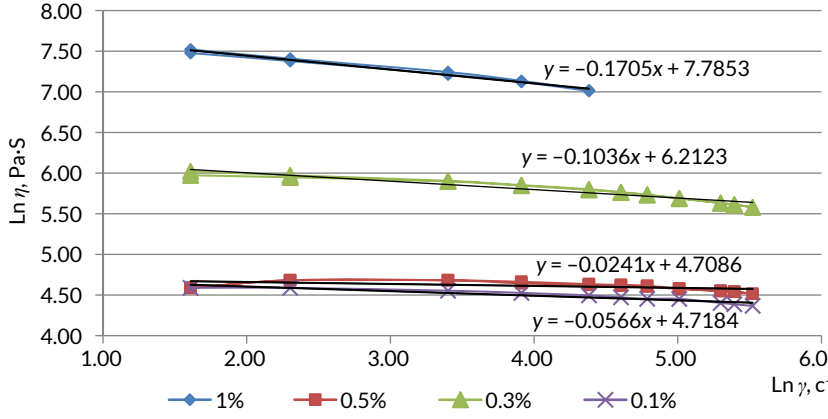

Fig. 13.7 Viscosity dependence of sea buckthorn pectin-based compositions on shear rate gradient

For all the curves presented, a decrease in viscosity (Ln η) is observed with increasing shear rate (Ln γ). This indicates pseudoplastic behavior (or shear thinning). This is a very common behavior for polymer solutions and hydrogels, which is explained by the orientation and deformation of polymer chains under shear loads, which reduces their resistance to flow. All slopes of the regression lines (the coefficient at x in the equation $y = mx + b$) are negative, which confirms the decreasing dependence of viscosity on shear rate. All points for each sample are approximated

by straight lines, which indicates that the dependence of Ln η on Ln γ is linear. This is typical for flow models, such as the Ostwald-de Waele power law, which in logarithmic coordinates has the form

$$\text{Ln}\,\eta = (n - 1)\,\text{Ln}\,\gamma + \text{Ln}\,K,$$

where n – the flow behavior index; K – the consistency coefficient.

For example, for the upper curve ($y = -0.1705x + 7.7853$), let's obtain: $n - 1 = -0.1705 \Rightarrow n = 1 - 0.1705 = 0.8295$, indicating pseudoplastic behavior ($n < 1$), and $\text{Ln}\,K = 7.7853 \Rightarrow K = e^{7.7853} \approx 2404.9$.

The difference in slopes and initial viscosity values between the curves indicates that the concentration significantly affects the rheological properties of the hydrogels, with the sample with a pectin content of 1.0% being the most viscous and the most pronounced pseudoplastic. It is known that classical pseudoplastics, unlike Bingham plastics, do not have a yield point. This means that they begin to flow even under very low shear stresses, albeit with very high viscosity. The graph does not show an initial viscosity "shelf", which may indicate the absence of a yield point. The high initial viscosity at rest provides shape stability (e.g. for encapsulation). At the same time, the shear thinning ability makes the material easily pumpable, extruded or injected under pressure. This is very important for applications such as injectable hydrogels for drug delivery. After the shear stress is removed (e.g. after extrusion from a nozzle), the viscosity of the material increases rapidly, allowing it to hold its shape and preventing it from flowing. The pseudoplastic behavior provides a pleasant tactile sensation when applied (easy spreading) and the stability of the product in the package.

So, in this case, the composition of sea buckthorn pectin polymers (concentration 1%) and sodium alginate is a material that is very well structured at rest, but easily deforms and flows under mechanical stress, after which it can restore its original structure, which makes it very valuable for many practical applications.

13.5 Conclusion

This work shows that sea buckthorn pectin is a promising ingredient with a wide range of applications in the food and pharmaceutical industries. Its unique structural-forming and functional properties open up new opportunities for creating innovative products with improved quality characteristics and benefits for consumers.

The dependence of the solution viscosity on the concentration of sea buckthorn pectin has been established and it has been proven that the studied pectin from sea buckthorn peel is characterized by a minimum value of the "critical" concentration – 1%, which indicates its high thickening ability.

The heat and entropy of activation of the viscous flow of a sea buckthorn pectin solution have been determined in order to obtain a thermodynamic idea of the structural aspects of the processes occurring in solutions of this polysaccharide. In the studied range of sea buckthorn pectin concentrations, the heat of activation and entropy change symbiotically.

A correlation between the formation of the structure and the rheological properties of pectin solutions has been revealed. The results of rheological and physicomechanical studies showed that sea buckthorn pectin added to the raw materials significantly affects the structure of combined minced meats – chicken trimming + bean flour + sea buckthorn pectin. It was found that both total deformation and its components – plastic and elastic – decreased upon addition of sea buckthorn pectin to the food system (from 4.15 mm to 2.25 mm). The experimental data obtained indicate that the addition of sea buckthorn pectin improved the stability and deformation parameters of experimental model samples of combined minced meats, which contributes to the formation of a stable combined food system with a strong structure.

The rheological analysis of pharmaceutical composite formulations based on sea buckthorn pectin modified with sodium alginate demonstrated that the 1.0% pectin sample behaved as a classical viscous pseudoplastic fluid, which is highly relevant for various applied uses.

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