

UDC: 664.858

## FUNCTIONAL AND TECHNOLOGICAL PROPERTIES OF THE FOOD ADDITIVE MAGNETOFOOD IN THE PRODUCTION OF MOULDED AGAR-BASED AND PECTIN-BASED MARMALADE JELLY SWEETS

DOI: <https://doi.org/10.15673/fst.v15i3.2119>

### Article history

Received 04.11.2020

Reviewed 18.01.2020

Revised 25.04.2021

Approved 31.08.2021

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### Cite as Vancouver style citation

Tsykhanovska I, Yevlash V, Trishch R, Lazarijeva T, Alexandrov A, Nikulina A. Functional and technological properties of the food additive *Magnetofood* in the production of moulded agar-based and pectin-based marmalade jelly sweets. Food science and technology. 2021;15(3):143-154. DOI: <https://doi.org/10.15673/fst.v15i3.2119>

### Цитування згідно ДСТУ 8302:2015

Functional and technological properties of the food additive *Magnetofood* in the production of moulded agar-based and pectin-based marmalade jelly sweets / Tsykhanovska I. et al // Food science and technology. 2021. Vol. 15, Issue 3. P. 143-154 DOI: <https://doi.org/10.15673/fst.v15i3.2119>

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**Abstract.** Marmalade jelly products are lyophilic colloidal dispersed (i. e. microheterogeneous polyphasic) systems based on high-molecular-weight compounds (gelatine, pectin, agar, etc.). That is why to expand and modernise the manufacture of these products, it is necessary to search for simpler technologies, both resource- and energy-saving, to increase the stability of a colloidal dispersed system, and to improve the quality of finished products. This paper suggests solving the problem of stabilising the polyphase structure of fruit jelly products by using the food nanoadditive *Magnetofood* (FeO-Fe<sub>2</sub>O<sub>3</sub>). *Magnetofood* is highly dispersed powder with the particle size 70 to 80 nm. It produces a compound effect, has a chemically active surface layer, is clusterophylic, and has complex-forming, structure-forming, thickening, stabilising, and thixotropic properties. This allows us to recommend *Magnetofood* as a polyfunctional food additive to improve the quality of fruit jelly products. The surface-active properties of *Magnetofood* nanoparticles have been determined. Such parameters as the ζ-potential value (34–44 mV) and amphiphilicity (Θ<90° both in polar and in non-polar media) provide polyphasic colloidal dispersed systems with features of stability, which increases, on average, by 55±5% in acidic environments and in solutions of polysaccharides and proteins. It has been found that *Magnetofood* added in the amount 0.10–0.20% of the mass of the structure-forming agent makes aqueous solutions of the gelling agents more viscous (by 1.22–1.27 times for agar and by 1.24–1.29 times for pectin) and increases the rate of structure formation in gel masses (by 1.73±0.01 times for agar and by 1.67±0.01 times for pectin) due to the structure-forming action of the additive. The gelling temperature rises by 5°C (for both agar and pectin), the capacity of a gel structure for thixotropy increases by 1.4–1.5 times and the mechanical strength of the gel by 1.32–1.80 times (for agar) and by 1.49–1.57 times (for pectin) due to the stabilising action of *Magnetofood*. This allows reducing the amount of the gelling agent (by 9.0–11.0% for agar and by 7.0–9.0% for pectin) and shortens the maturation time of a gel system (by 20 min for pectin and by 4 min for agar).

**Key words:** food additive *Magnetofood*, functional and technological properties, lyophilic colloidal dispersed systems, marmalade sweets.

### Introduction. Formulation of the problem

Marmalade jellies are “lyophilic colloids,” that is, they have the colloidal dispersed structure based on

high-molecular-weight compounds (gelatine, agar, pectin, etc.). This makes it difficult for a manufacturer to maintain the stability of technological processes, and

prevents a consumer from getting high quality products. That is why stabilising polyphasic microheterogeneous structures is a problem of current importance. In particular, the issues to be solved include improving their gelling, water-binding, and water-holding capacities and forming their stable supramolecular structures (monolayers, micelles, etc.) [1,2].

The above makes it necessary to study and develop new food-improving additives, in particular, nanoscale agents. Nanoadditives typically have stable physicochemical parameters and are polyfunctional. It should be noted that food-improving additives (especially those with nanosized particles) make it possible to process raw materials with different properties. This processing results in finished products that meet all the requirements for quality and storability [3-5].

#### Analysis of recent research and publications

Marmalade jelly manufacture is a branch of production most actively using food-improving additives, gelling agents, stabilisers, etc.

Recently, researchers have been paying much attention to finding and developing new gelatinising and stabilising components that have the required functional and technological properties and can modify the content of traditional gelling agents (agar, pectin, gelatine) [5,6]. These new components include, in particular, byproducts of the canning and sugar-beet processing industries, winemaking, cotton farming, melon cultivation, etc. [7]. Application of these ingredients improves the mechanostuctural characteristics of gels. Marmalade jelly products are enriched with raw materials obtained from fruit and vegetables: chitosan [8,9], tropical fruit [10], extracts from aromatic herbs, fruit, and berries [11]. This improves the moisture retention capacity and the rheological characteristics of gels and the nutritional value of the finished products. However, these components lack multifunctionality, which is a disadvantage.

For a better course of gelation, various hydrocolloids are used: sorbitol [12], carrageenan with its sodium, potassium, and ammonium salts, furcellaran, xanthan, tara, gums, etc. [13], combined hydrocolloid systems: gelatine with pectin and  $\kappa$ -carrageenan [14], pectin with  $\kappa$ -carrageenan [6,15], agar with the animal protein concentrate ScanPro [16]. One of their weak points is the absence of a compound effect. It is also worth noting that complex hydrocolloid compositions make gells stronger than simple hydrocolloidal gelling agents do. However, these compositions do not provide the required physicochemical parameters of marmalade jelly products.

There are a number of modifying food additives: sodium carboxymethyl cellulose (Na-CMC) and ferric sulphates (III), which increase the gelling power of

hydrocolloids [17], sodium lactate, sodium citrate, and calcium cations (increase the gelling power of polysaccharides and allow controlling their amount) [18], mannitol and sodium alginate (make jelly mass stronger and reduce the expenditure of the gelling agent) [19,20].

In recent years, technologists involved in fruit jelly production have been paying more attention to applications of nanoscale food-improving additives. The recipe components used to develop new-generation confectionery are protein additives combined with nanoadditives of plant origin (obtained from pumpkins, carrots, lemons, ginger) [21]. There are nanocomposites with a bacteriostatic effect:  $\text{Fe}_3\text{O}_4$ -MgO with nutmeg essential oil, and  $\gamma\text{-Fe}_2\text{O}_3$  with apple pectin [22]. Structure-forming ingredients with high functional and technological potential are developed based on modifications of metal nanoparticles and their oxides with high-molecular-weight compounds (polysaccharides, plant and animal proteins). Compounds used as polymer matrices include chitosan, gelatine, gliadin, elastin, zein, etc. [23, 24]. These nanoadditives can modify the functional and technological properties of gel systems and help in creating high-quality marmalade jellies, which opens the door to their wide application in industry.

The effectiveness of nanoadditives in innovatory jellies and marmalade sweets is due to their range of functional and technological features: their high dispersity, their structure, and physicochemical parameters. Achievements of modern experts in innovation marmalade jelly technologies and results obtained by them are helpful for further research and practical application of food nanoadditives (in particular, oxides of metals with stable physicochemical parameters), which can be used to modify the functional and technological characteristics of structure-forming agents and to improve the consumer properties of marmalade jellies [25,26].

*Magnetofood* is a food additive based on ferrous and ferric oxides:  $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ . It is highly dispersed powder coloured dark brown to black, tasteless and odourless. The size of its particles is  $\sim 75$  nm. Its structure is that of spinel: in the nodes of its lattice, there are cations  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  that have free 3d orbitals and are structure-forming. Its  $\zeta$ -potential is 33–44 mV, which facilitates formation of stable gel systems. *Magnetofood* has a compound effect: sorptive, water-binding, water-holding, structurising, stabilising, bacteriostatic, and antioxidative [26,27].

That is why it is so practical to use *Magnetofood* in the technologies of food with a gelatinous structure, including jellies and marmalade confectionery.

Therefore, studies of its effect on the quality parameters of marmalade jellies are of current importance.

**Purpose and objectives of the research.** The purpose of the paper is to study how the food additive

*Magnetofood* affects the quality of agar-based and pectin-based moulded marmalade sweets.

To achieve the purpose, the following objectives were set:

- to determine the surface-active properties of the food additive *Magnetofood* (FAM): contact angles of wetting, surface tension, elektrokinetic  $\zeta$ -potential);
- to study the effect of the FAM on the rheological properties (effective viscosity and thixotropic recovery) of colloid solutions of the two gelling agents – pectin and agar;
- to study the effect of the FAM on the mechanostructural characteristics of the samples of agar-based and pectin-based gel masses under study (mechanical strength, rate of structure formation).

### Research materials and methods

The food additive *Magnetofood*, or FAM (Technical Specifications of Ukraine 10.8-2023017824-001:2018. Food additive based on iron oxides *Magnetofood*), is high-dispersed brown or black powder. The size of its particles is 70–80 nm. The chemical composition of the FAM includes double iron oxide ( $\text{FeO}\cdot\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ ) obtained by chemical co-precipitation of salts of ferrous and ferric iron from aqueous solutions in an alkaline medium (Patent UA No. 126507.53. Method of producing the food additive *Magnetofood*); food grade agar (Gelagar CT 1.2 by the company B&V, Italy); apple pectin (DSTU 6088:2009); dried egg white (DSTU 8719:2017); chloride acid (DSTU 2904-94); sodium chloride (DSTU 3583:2015); rectified ethanol (DSTU 4221:2003); sodium dodecyl sulphate, or SDS (DSTU 2161:2010); distilled water (DSTU 7525:2014).

The following model systems were used: water+FAM, HCl+FAM, gelling agent (pectin or agar)+FAM, egg white + FAM, egg white + agar or high-ester pectin+FAM. They had the form of suspensions of *Magnetofood* nanoparticles (MNP) in a 5% (or 3%; 0.01%) aqueous solution of HCl, HE pectin, agar, or egg white. The suspension of the FAM in water was obtained by dispersing a weighed portion of the FAM in deaerated and demineralised drinking water at 18–20°C for (5–7)×60 s followed by resting for (10–12)×60 s [28]. The suspension of the FAM in an HCl solution was obtained by adding a calculated portion of the FAM to a 3% HCl solution at 30–40°C, stirring it continuously at  $n=2.0\text{--}2.2\text{ s}^{-1}$  for (40–50)×60 s, and then cooling the mixture down to 18–20°C and resting for (10–12)×60 s. The suspension of the FAM in 5% (or 3%; 0.01%) solutions of egg white was prepared by adding a calculated portion of the FAM to a 5% (or 3%; 0.01%) solution of egg white at 18–20°C, stirring it continuously at  $n=2.0\text{--}2.2\text{ s}^{-1}$  for (3–5)×60 s followed by resting for (5–7)×60 s [28]. The suspension of the FAM in 5% (or 3%; 0.01%) solutions of agar or HE pectin was obtained by adding a weighed portion of the FAM to a 5% (or 3%; 0.01%) polysaccharide solution at 55–60°C, stirring it

continuously at  $n=2.0\text{--}2.2\text{ s}^{-1}$  for (5–7)×60 s, and then cooling the mixture down to 18–20°C, stirring it continuously at  $n=2.0\text{--}2.2\text{ s}^{-1}$  [31]. The suspension of the composition “egg white + agar” or “HE pectin + FAM” was made by adding a calculated portion of the FAM to a 5% (or 0.01%) polysaccharide solution at 55–60°C, stirring it continuously at  $n=2.0\text{--}2.2\text{ s}^{-1}$  for (5–7)×60 s, and then cooling the mixture down to 18–20°C, stirring it continuously at  $n=2.0\text{--}2.2\text{ s}^{-1}$  and adding a weighed portion of egg white powder, while stirring the mixture continuously at  $n=2.0\text{--}2.2\text{ s}^{-1}$  for (3–5)×60 s, followed by resting for (5–7)×60 s [29].

The elektrokinetic  $\zeta$ -potential of the aqueous suspensions of the FAM was determined by microelectrophoresis (moving-boundary electrophoresis) in a glass three-column container with calibrated tubes [28]. The surface tension was measured by the du Noüy ring method using a Kruss tensiometer in model 0.01% solutions in polar and non-polar solvents [29]. The “instantaneous photography” method was used to determine the contact angles when wetting the FAM substrate with droplets of oil and water material. The instrument to measure the contact angle was a meter of the ACAM family (Russia). The shape of the droplets was determined when they were projected on a screen and photographed (5–10 units) [30].

The rheological and mechanostructural properties were studied by standard, conventional methods [31]. The effective viscosity and thixotropic properties were determined on a rotational viscosimeter Rheotest-2. The strength of the gel masses was studied by the critical shear stress using Kargin and Sogolova’s modified scales. The rate of structure formation in the gel masses was found by the formula (1):

$$V_{str} = \frac{\tau_{max} - \tau_0}{B_{str}} \quad (1)$$

where  $V_{str}$  is the rate of structure formation, kPa/s;

$\tau_{max}$  is the maximum strength value, kPa;

$\tau_0$  is the initial strength value, kPa;

$B_{str}$  is the rate of structure formation,  $\tau\cdot 60\text{ s}$ .

### Results of the research and their discussion

The stability of colloidal dispersed systems can be assessed by their elektrokinetic potential ( $\zeta$ -potential). Its value depends on the physicochemical characteristics of the dispersed phase and the dispersed medium. For FAM nanoparticles, high  $\zeta$ -potential (>30 mV) means that the colloidal dispersed system is resistant to aggregation and stable. Fig. 1 shows *Magnetofood* nanoparticle layers in a water medium.

The results of determining  $\zeta$ -potential in the studied samples of colloidal dispersed systems with the FAM added are presented in Table 1.

Table 1 makes it clear that in the samples under analysis (2–5), the elektrokinetic potential is quite high (41.6–44.2 mV) and increases by 1.2–1.3 times as

compared with Sample 1 (33.8 mV). This proves the stabilising capacity of *Magnetofood* nanoparticles, in particular, of colloidal dispersed systems – “lyophilic colloids” (microheterogeneous systems based on polysaccharides, proteins, etc.). The effectiveness of stabilising dispersed systems with FAM nanoparticles is due to the formation of an electrical double layer (EDL) on its surface (Fig. 2) [28].

In the colloidal dispersed system  $\text{FeO}[\text{Fe}_2\text{O}_3](\text{C}_{13}\text{H}_{14}\text{O}_{13})_n \text{H}_2\text{O}$  (Sample 4), a monolayer around *Magnetofood* nanoparticles is formed from anions of D-Galacturonic acid. Then,  $\text{H}_2\text{O}$  molecules help in the formation of a hydration shell, which reduces the surface tension on the phase interface and increases the aggregate stability of the colloidal dispersed system. Besides, the like charge of acyl anions contributes to the action of electrostatic repulsive force among them, promotes their disaggregation, increases the electrokinetic potential and the stability of a microheterogeneous dispersed system [28].

It should be noted that formation of gel-like colloidal dispersed food systems (jellies, marmalade sweets, etc.) is accompanied by the action of mechanisms responsible for arranging the solvent on the interface with another phase (in particular, a solid one). In this process, the surface activity of FAM nanoparticles is important.

Table 2 presents the results of studying the surface activity of the FAM in the colloidal solution samples under analysis.

The data in Table 2 show that the FAM is by 19–25% less surface-active than egg white is with its tendency for hydrogen, ionic, and hydrophobic interactions. The hydrophobic properties of the FAM are less pronounced than the hydrophilic ones.

In the lyophilic colloidal dispersed systems “polysaccharide + FAM” and “egg white + FAM,” both in the aqueous and in the saline solutions, the surface tension decreases (compared with the pure solvent) by 3.0–4.5%, whereas in the 70% ethanol solution, it is lower by 3.0–4.5%, and in the 1% SDS solution, by (2.9±1)%. This indicates interaction between FAM nanoparticles and polysaccharide or egg white due to noncovalent bonds. The hydrophobic interactions are less significant than the hydrophilic ones due to hydrogen and ionic bonds. In the colloidal dispersed systems “egg white + polysaccharide + FAM,” both in water and in the saline solutions, the surface tension is by (1.0±0.1)% higher than it is in the colloidal system “egg white + FAM.” In the 70% ethanol solution, it increases by 3–4%, and in the 1% SDS solution, by 4.7–8.2% [23,28].

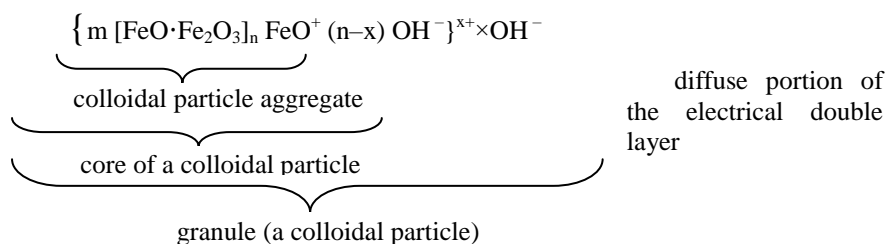


Fig. 1. *Magnetofood* nanoparticle layers in a water medium

Table 1 – Electrokinetic potentials of the analysed samples of colloidal dispersed systems containing FAM nanoparticles ( $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ) ( $n = 5$ ,  $p \leq 0.05$ )

Analysed samples of colloidal dispersed systems containing FAM nanoparticles	$\zeta$ -potential, mV
Aqueous suspension: $\text{FeO}[\text{Fe}_2\text{O}_3]\text{H}_2\text{O}$ – Sample 1	33.8±1.2
Suspension in a 3 % solution of HCl: $\text{FeO}[\text{Fe}_2\text{O}_3]\text{Cl} \text{H}_2\text{O}$ – Sample 2	41.6±1.8
Suspension in a 3% solution of agar: $\text{FeO}[\text{Fe}_2\text{O}_3](\text{C}_{12}\text{H}_{18}\text{O}_9)_n \text{H}_2\text{O}$ – Sample 3	42.7±1.8
Suspension in a 3% solution of pectin: $\text{FeO}[\text{Fe}_2\text{O}_3](\text{C}_{13}\text{H}_{14}\text{O}_{13})_n \text{H}_2\text{O}$ – Sample 4	43.2±1.9
Suspension in a 3% solution of egg white: $\text{FeO}[\text{Fe}_2\text{O}_3]$ egg white   $\text{H}_2\text{O}$ – Sample 5	44.2±1.9

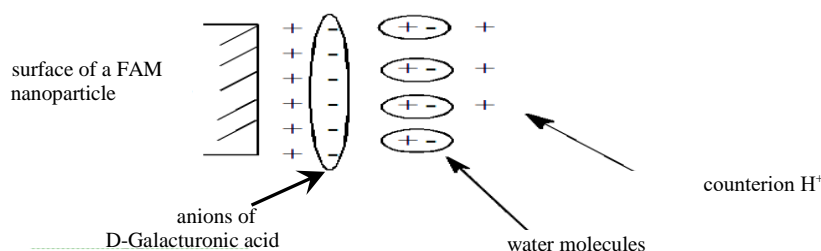


Fig. 2. Structure of the EDL on the surface of a pectin-containing FAM nanoparticle (3% solution)

Table 2 – Surface tension in the colloidal solutions of the tested samples of the surface-active substances (n=5, p≤0.05)

Surface-active substances	Surface tension, mN/m			
	Solvent			
	H <sub>2</sub> O	0.05 N NaCl	70% ethanol	1% SDS
Solvent	72.8±4.1	74.0 ±4.1	28.9 ±1.4	39.0 ±2.1
FAM	65.0 ±3.4	63.0 ±3.4	28.5 ±1.3	38.2 ±2.1
HE pectin	72.7 ±3.4	73.8 ±3.4	28.8 ±1.4	38.9 ±2.1
Agar	71.7 ±3.4	73.2 ±3.4	28.9 ±1.4	38.5 ±2.1
FAM + HE pectin	69.8±3.4	69.9 ±3.4	28.8 ±1.4	38.1 ±2.1
FAM + agar	67.5 ±3.4	67.8 ±3.4	28.7 ±1.3	38.0 ±2.1
Egg white (EW)	51.0 ±2.7	48.0 ±2.4	28.6 ±1.3	35.0 ±2.0
EW + FAM	53.0 ±3.1	50.5 ±3.1	28.5 ±1.3	34.0 ±2.0
EW + FAM + HE pectin	58.0 ±3.1	60.0 ±3.2	29.7 ±1.4	36.8 ±2.0
EW + FAM + agar	53.5 ±3.1	51.0 ±2.7	29.5 ±1.4	35.6 ±2.0

Thus, the FAM has chemical surface activity, which manifests itself in electrostatic and co-ordinate interactions with different substances (proteins, polysaccharides). That is why adding the FAM to polyphasic food systems slows down the breaking of electrostatic interactions, thus helping the formation of new bonds. This allows colloidal dispersed systems (gels, foams, etc.) to stabilise [23,29].

To check the hypothesis that the FAM has diphilic properties, we determined the contact angles ( $\Theta$ ) of wetting the surface of the compacted FAM with a droplet of water (Fig. 3a) and of sunflower oil (Fig. 3b), using the sessile drop technique (the “instantaneous photography” method) [30].

From Fig. 3, it can be seen that in the water-wetted FAM sample, the contact angle ( $\Theta$ ) is smaller by  $(15\pm 1)^\circ$ , i. e. the FAM manifests its affinity for water to a larger extent. In both cases, though,  $\Theta < 90^\circ$ , which proves that the FAM has an affinity both for water and for oil. This means that the FAM is an amphiphile, hence its ability to form various supramolecular structures: monolayers, micelles, liposomes. In other words, it is the ability to form lyophilic colloidal dispersed systems, i. e. the foaming and gelling (in particular, structure-forming) power [23,26].

Fig. 4 shows how the effective viscosity ( $\eta$ ) of the colloidal dispersed systems “gelling agent + FAM” depends on the mass fraction of the FAM.

Fig. 4 makes it clear that in all the samples tested, adding the FAM causes an increase in the viscosity throughout the whole range of shear stress:  $\dot{\gamma} = (1.5 - 40) \text{ s}^{-1}$ . For agar, it increases by 1.22–1.27 times, and for pectin, by 1.24–1.29 times (compared with the reference sample). The increase is due to the presence of structure-forming cations  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  on the surface of FAM nanoparticles and to electrostatic co-ordination of these particles with polysaccharide macromolecules. This results in the formation of a three-dimensional network made up by molecules of hydrocolloids structured by FAM nanoparticles [26]. The most practical proportion of the FAM is 0.15%: its further increase produces almost no changes in the viscosity of colloidal solutions of gelling agents.

For the tested samples of colloidal dispersed systems of gelling agents, the coefficient of thixotropic recovery of their primary structure has been found (Fig. 5). Analysis shows that the thixotropy coefficient  $K_{(\text{thix})}$  increases, on average, by 1.4–1.5 times when the FAM is added to a system (compared with the reference sample).

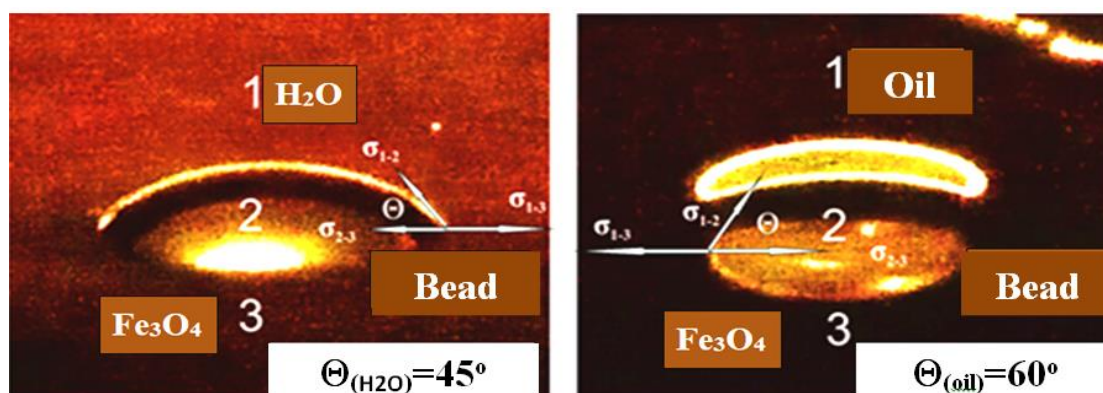


Fig. 3. Results of determining the contact angles ( $\Theta$ ) of wetting the FAM surface with a – a droplet of water; b – a droplet of sunflower oil

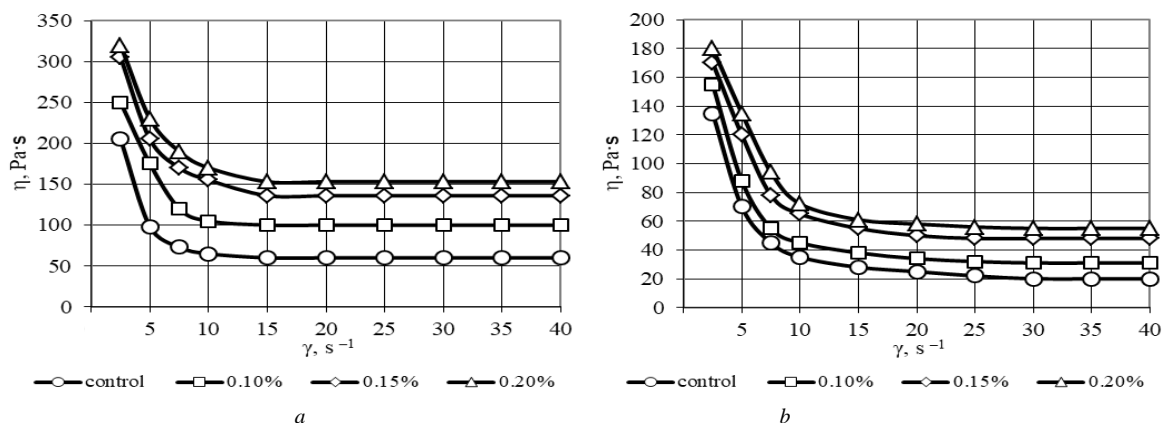


Fig. 4. Dependence of the effective viscosity of gel systems on the FAM concentration: a – agar-based samples; b – pectin-based samples

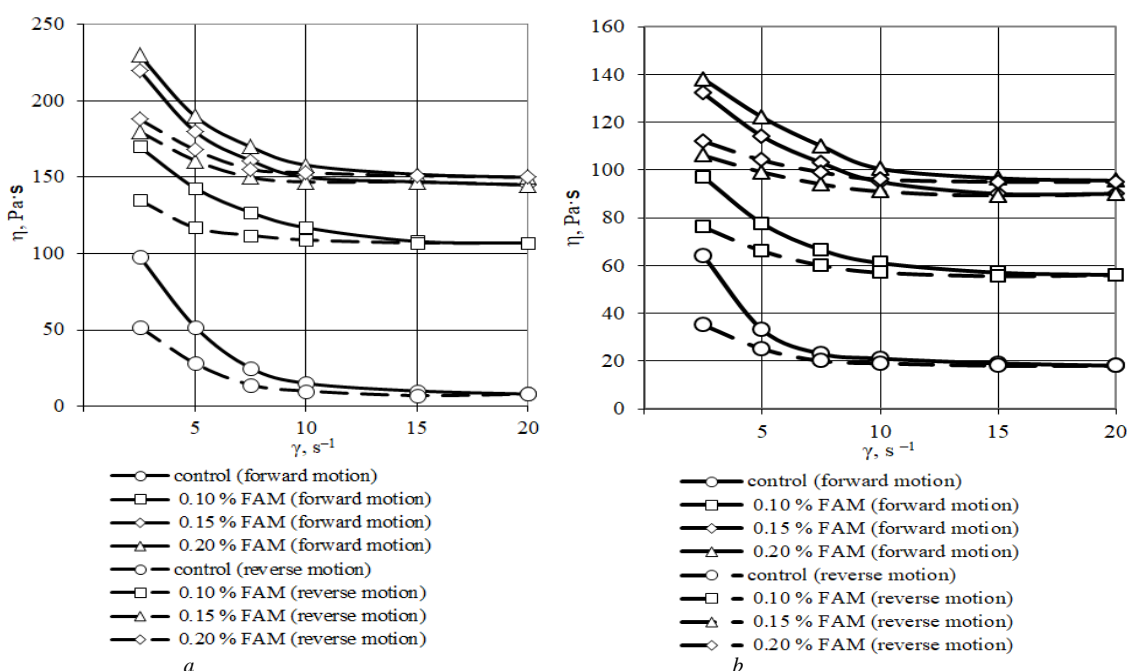


Fig. 5. Dependence of thixotropic recovery of gel systems on the FAM concentration: a – in the agar-based samples; b – in the pectin-based samples

Thus, “lyophilic colloids” (gelling agent + FAM) have thixotropic properties. In particular, adding the FAM to aqueous solutions of gelling agents (including agar and pectin) slows down the breaking processes by 1.15–1.22 times and by 8.8–9.2% accelerates the gel structure recovery after the mechanical action has stopped. Thus, the structure’s capacity for thixotropy increases by 1.4–1.5 times. This is due to the surface-active properties of the FAM and to its ability to form a dispersed system of a certain consistence and to stabilise it, thus preventing its breaking [23, 27]. So, the study of the rheological properties of lyophilic colloidal dispersed systems “gelling agent + FAM” with different agents used (in particular, agar and pectin) confirms the hypothesis that these properties of gel systems can be adjusted when influenced by *Magnetofood* nanoparticles.

Changes in the hydrocolloidal composition tell on the viscosity of gel systems, and this has an essential effect on

the quality parameters of marmalade jellies. In a hot gel system, gelling agent molecules form different structures due to Brownian motion. When the system is cooled down to the gelling temperature, hydrogen bonds appear among macromolecules of the gelling agent, and three-dimensional structures are formed. The further aggregation of these structures is accompanied by gel formation. In our case, the contribution to the gelling process is made by amphiphilic nanoparticles of *Magnetofood*, whose electrokinetic potential is quite high [28, 29]. The temperature the gelling process starts at after the system is cooled down depends on the gelling agent type and on the nanoeffects of *Magnetofood*. Fig. 6 illustrates how the temperature affects the viscosity of the test samples of the gel systems “gelling agent + FAM” with different gelling agents used.

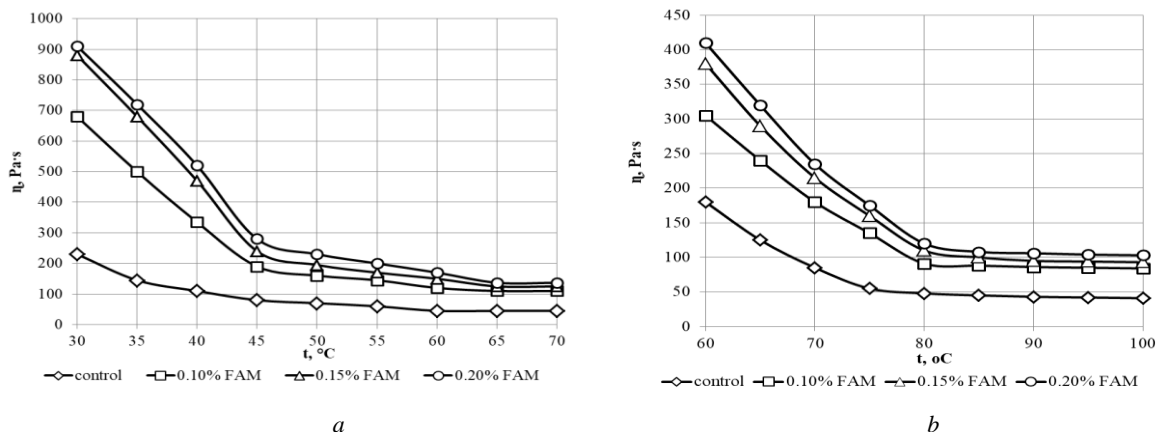


Fig. 6. Dependence of the viscosity of gelling systems “gelling agent + FAM” on the temperature: a – in the agar-based samples; b – in the pectin-based samples

As can be seen from Fig. 6, at high temperatures (65°C and higher for agar-based gel systems, and 85–100°C for pectin-based gel systems), the viscosity of gel systems depends on the type of a gelling agent but insignificantly. This can be explained by weakening of the intermolecular forces acting among the recipe components (which is caused by their more intense thermal vibrations). The value of the viscosity and the rate of its change with the decrease of the temperature depend on the composition of the dispersed medium. With the FAM added, the increase in the viscosity of a gel system as the temperature drops becomes more pronounced. Besides, the temperature has a bigger effect on the rheological properties of the samples of gel systems under study: the viscosity of the reference samples in the considered temperature range changes by 5.1 times in the samples with agar and by 4.4 times in the ones with pectin. In the test samples containing 0.1%, 0.15%, and 0.2% of the FAM, the viscosity changes, respectively, by 6.2, 7.0, and 6.6 times (for agar) and by 3.6, 4.1, and 4.0 times (for pectin). The smaller change in the viscosity of the pectin-based gel systems is due to the insufficient number of active areas on the surface of a pectin molecule. These areas are needed to form new intermolecular bonds responsible for higher viscosity of the system “pectin + FAM” when the temperature decreases. Adding the

FAM to the system slows down this process due to the formation of new supramolecular nanoassociates with pectin (or agar) macromolecules. Also, introduction of the FAM increases the gelling temperature: 45°C in the samples with agar (40°C in the reference) and 75°C in those with pectin (70°C in the reference). At these temperatures, an increase in the viscosity is observed, which means that the temperature is close to the value needed for structure formation [26].

The gelling process determines the structure and the mechanical strength of marmalade jellies and, consequently, the quality of the finished marmalade sweets. To assess the maturation time of the test samples of gel systems “gelling agent + FAM,” the critical shear stress ( $\tau$ , kPa) was determined in the course of maturation ( $\tau \cdot 60 \text{ s}^{-1}$ ) (Fig. 7). The maturation time was defined as the period in which gel with constant critical shear stress (constant resilience) is formed.

Fig. 7 makes it evident that the gelling time is different in gel systems made with the use of different gelling agents. For the systems “agar + FAM,” it is 60–80 min (60 min for the sample containing 0.15% of the FAM, 80 min for the reference sample), and for the systems “pectin + FAM,” it is 12–16 min (12 min for the sample containing 0.15% of the FAM, 16 min for the reference sample).

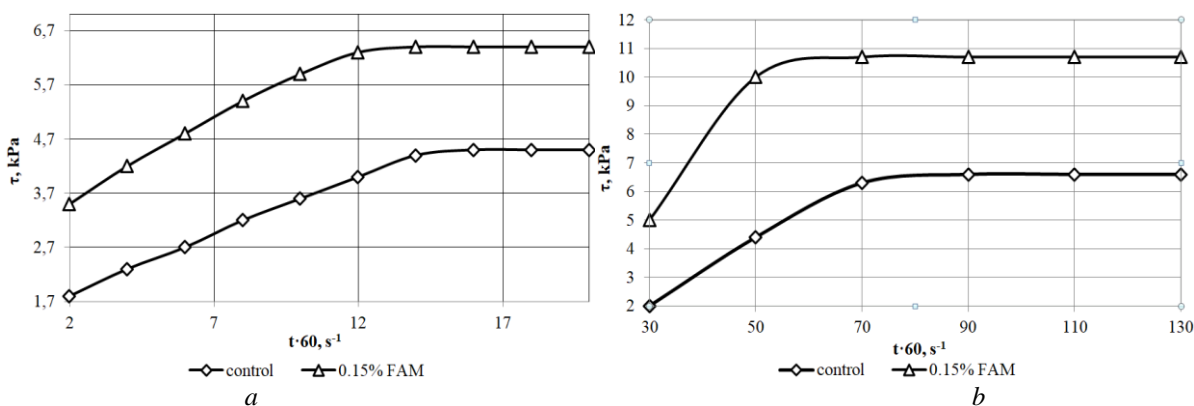


Fig. 7. Dependence of the critical shear stress of gel systems “gelling agent + FAM” on the duration of maturation: a – on agar; b – on pectin

Thus, the food additive *Magnetofood* reduces the maturation time of the systems “gelling agent + FAM”: by 20 min in the agar-based samples, and by 4 min in the pectin-based ones. This positive effect can be explained by the chemically active surface of *Magnetofood*, by its clusterophilic nature, and by the ability of FAM nanoparticles to form three-dimensional nanoassociates with hydrocolloids (agar,

pectin, etc). Besides, adding the FAM strengthens gel: by 1.32–1.80 times for the agar-based samples, and by 1.49–1.57 times for the pectin-based ones, as compared with the reference.

Table 3 shows the rate of structure formation in the test samples of gel masses. It was found by the formula (1).

**Table 3 – Rate of structure formation in the test samples of gel masses (n = 5, p ≤ 0.05)**

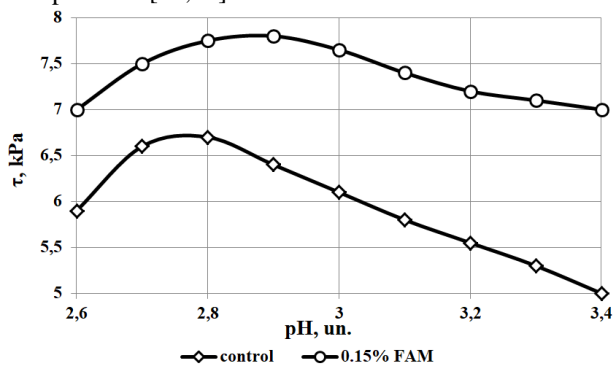
Samples analysed/Parameters	$\tau_0$ , kPa	$\tau_{max}$ , kPa	$T_{str}$ , $\tau \cdot 60$ s	$V_{str}$ , kPa/min
Agar-based samples of gel masses				
Sample 1 – reference	3.4±0.2	10.1±0.5	60.0±3	0.11±0.01
Sample 2 with 0.15% of FAM	4.4±0.2	11.9±0.6	60.0±3	0.19±0.01
Pectin-based samples of gel masses				
Sample 3 – reference	1.8±0.1	5.6±0.3	12.0±0.6	0.28±0.01
Sample 4 with 0.15% of FAM	2.8±0.1	7.2±0.4	12.0±0.6	0.47±0.02

From Table 3, one can see that adding the FAM increases the rate of structure formation of gel masses, as compared with the reference samples: by (1.73±0.01) times for agar, and by (1.67±0.01) times for pectin. This is due to the ability of FAM nanoparticles to interact with polysaccharide molecules. This interaction leads to formation of a regular three-dimensional framework that strengthens gel structures. This results in a good texture of jelly products, their high consumer qualities, and their longer freshness retention (in particular, they give out far less moisture when stored).

High-ester pectin is known to be characterised by so called sugar-acid gelation, for which, in the presence of a dehydrant (sucrose), the acid provides the required pH of the medium by inhibiting dissociation of carboxyl groups. This prevents the repulsion of pectin chains and allows molecules to come close together, which is followed by their further arrangement in a three-dimensional structure. The required amount of acid depends on its nature and on the recipe formulation of a gel system. Fig. 8 shows how the mechanical strength (i. e. the gelling power) of the pectin-based gel mass samples under study (the reference and the one with 0.15% of the FAM) depends on the concentration of hydrogen ions (pH of the medium).

It is clear from Fig. 8 that the gel strength is the greatest in a dispersed medium with the following active acidity: pH=2.7–2.8 (reference), pH=2.8–2.9 (jelly mass with 0.15% of the FAM). The lower pH in the FAM-containing jelly is due to the amphoteric action of cations  $Fe^{2+}$  and  $Fe^{3+}$  of the FAM. The three-dimensional framework of gel formed under these conditions is the strongest due to the appearance of hydrogen bonds. The FAM introduced into a gel system strengthens it by 1.13–1.4 times, compared with the reference. The reason for this is the formation of additional electrostatic interactions between pectin molecules and nanoparticles of *Magnetofood*. With an increase in acid to pH=2.6, the mechanostructural

properties of the gel system samples change for the worse. This can be explained by too early gelation of the system, which is accompanied by the irreversible destruction of gel that has been partly formed, and by a weak, inhomogeneous gelling process. At higher acidity values (pH=3.0–3.4), a gel system loses its strength and becomes “long,” “tractile” in its structure. Adding *Magnetofood* slows down these processes due to the stabilising and structuring action of its nanoparticles [23,26].



**Fig. 8. Dependence of the critical shear stress of pectin-based gel masses (reference and the sample with 0.15% of the FAM) on the concentration of hydrogen ions (pH of the medium)**

Thus, the research of the mechanostructural characteristics of lyophilic colloidal dispersed systems with different structure-forming agents (agar and pectin) confirms the hypothesis that FAM nanoparticles can stabilise the polyphasic structure of “lyophilic colloids.” The most practical proportion of the FAM is 0.15% of the weight of a structure-forming agent. Adding this dose of *Magnetofood* to colloidal dispersed systems allows reducing the amount of the structure-forming agent: that of agar by 9.0–11.0%, and that of pectin by 7.0–9.0%. Besides, this strengthens the gel: by 1.32–1.80 times for agar, and by 1.49–1.57 times for pectin, in comparison with the reference.



When the food additive *Magnetofood* based on double ferrous and ferric oxide is introduced into a colloidal dispersed system, it accelerates and reinforces structure-forming processes in “lyophilic colloids.” The experiments have confirmed the thickening, thixotropic, and stabilising properties of the additive and its structure-forming capacity. These properties are important for gel systems.

### Approbation of results

The findings of the research were the topics of laboratory classes for students of Speciality 181 “Food technologies,” the field of expertise “Technologies of foods of plant origin,” at the Educational and Research Institute of Food Technologies and Business (Kharkiv State University of Food Technology and Trade).

### Conclusion

The surface-active properties of *Magnetofood* nanoparticles have been determined. It has been proved that quite a significant  $\zeta$ -potential value (34–44 mV) and the wetting contact angle  $\Theta < 90^\circ$  in both polar and non-polar media (i. e. the amphiphilic properties of *Magnetofood*) provide polyphasic colloidal dispersed systems with features of stability, according to their kinetic properties and to the sedimentation ones as well. The stability of these systems increases, on average, by 55±5% in acidic environments and in solutions of polysaccharides and proteins. This is due to the interaction between *Magnetofood* nanoparticles with the above components (the hydrophobic interactions being less significant than the hydrophilic

ones) and due to their three-dimensional structure formation.

The findings on the effect of *Magnetofood* on gel formation (compared with the reference) have shown that, when introduced in the amount 0.10–0.20% of the mass of the gelling agent, this food additive:

- increases the viscosity of aqueous solutions of gelling agents throughout all the range of shear stress ( $\gamma = (1.5–40 \text{ s}^{-1})$ ) by 1.22–1.27 times for agar and by 1.24–1.29 times for pectin;

- slows down the destruction processes by 1.15–1.22 times, and accelerates (by 8.8–9.2%) the gel structure recovery after the mechanical action has stopped, thus increasing the structure’s capacity for thixotropy by 1.4–1.5 times;

- increases the rate of structuring of gel masses by 1.73±0.01 times for agar and by 1.67±0.01 times for pectin; raises the gelling temperature by 5°C (for both agar and pectin); increases the mechanical strength of the gelled mass by 1.32–1.80 times for agar and by 1.49–1.57 times for pectin, which allows reducing the amount of the gelling agent by 9.0–11.0% for agar and by 7.0–9.0% for pectin, and shortens the maturation time of the gel system by 20 min for pectin and by 4 min for agar;

- reduces the active acidity of pectin-based jelly mass by 0.1–0.2 pH units, and contributes to stabilising the mechanostructural properties of a gel system throughout all the range pH=2.6–3.4.

The results obtained allow recommending the food additive *Magnetofood* as a stabiliser, structure-former, and improver of polyphasic colloidal dispersed gel-structured food systems.

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## ФУНКЦІОНАЛЬНО-ТЕХНОЛОГІЧНІ ВЛАСТИВОСТІ ХАРЧОВОЇ ДОБАВКИ «МАГНЕТОФУД» У ВИРОБНИЦТВІ ФОРМОВОГО ЖЕЛЕЙНОГО МАРМЕЛАДУ НА АГАРІ Й ПЕКТИНІ

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**Анотація.** Желейно-мармеладні вироби є ліофільними колоїдно-дисперсними тобто мікрогетерогенними поліфазними системами на основі високомолекулярних сполук (желатину, пектину, агару тощо). Тому розширення й удосконалення виробництва желейно-мармеладної продукції вимагає пошуку спрощеної ресурсо- та енергозберігаючої технології, підвищення стабільності колоїдно-дисперсної системи та поліпшення якості готової продукції. Проблеми стабілізації поліфазної структури желейно-мармеладних виробів у роботі запропоновано вирішувати шляхом використання харчової нанодобавки *Магнетофуд* (FeO-Fe<sub>2</sub>O<sub>3</sub>). *Магнетофуд* – високодисперсний порошок з розміром частинок (70–80) нм та з комплексною дією має хімічно активний приповерхневий шар; кластерофільність; комплексоутворювальні, загущувальні, структуроутворювальні, стабілізувальні, тиксотропні властивості. Це дозволяє рекомендувати *Магнетофуд* як поліфункціональну харчову добавку для підвищення якості

желейно-мармеладних виробів. Визначено поверхнево-активні властивості наночастинок *Магнетофуд*: величина  $\zeta$ -потенціалу 34–44 мВ, амфільність ( $\theta < 90^\circ$  як в полярних, так і в неполярних середовищах) – чинять на поліфазні колоїдно-дисперсні системи ознаки стійкості та стабільності, які підвищується в кислих середовищах, у розчинах полісахаридів, білків в середньому на 55±5%. Встановлено, що додавання *Магнетофуд* у масовій частці 0,10–0,20% до маси структуроутворювача збільшує в'язкість водних розчинів гелеутворювачів в 1,22–1,27 рази для агару та в 1,24–1,29 разів для пектину та швидкість структурування гелевих мас в 1,73±0,01 рази для агару і в 1,67±0,01 рази для пектину за рахунок структуроутворювальної дії *Магнетофуд*. Підвищується температура гелеутворення на 5°C (для агару й пектину); здатність гелевої структури до тиксотропії в 1,4–1,5 рази та механічна міцність гелевого студню в 1,32–1,80 рази для агару і в 1,49–1,57 рази для пектину за рахунок стабілізуючої дії *Магнетофуд*, що дозволяє скоротити кількість гелеутворювача на 9,0–11,0% для агару і на 7,0–9,0% для пектину та час вистоювання гелевої системи на 20 хв для пектину й на 4 хв для агару.

**Ключові слова:** харчова добавка *Магнетофуд*, функціонально-технологічні властивості, ліофільні колоїдно-дисперсні системи, мармелад.

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