

Розроблено та досліджено новий склад екологічно безпечного казеїнового клею на водній основі з підвищеною адгезією до субстрату (скло, поліетилентерефталат та ін.) і водостійкість. Клей легко змивається при етикетуванні продукції, яка фасується до тари багаторазового використання, але при цьому має високу адгезію до різних поверхонь. Визначено оптимальний склад розробленої клейової композиції за допомогою досліджених властивостей. Вивчено вплив кількості модифікуючої добавки на динамічну в'язкість на різних швидкостях деформації, липкість клейової композиції, показник водневих іонів (рН).

Досліджено технологічні властивості клейової композиції: в'язкість – 170 Па·с; рН – 7,21; масова частка сухого залишку – 38,2 %; липкість – 58,17 ум. од.; робоча температура – +20...+25 °С.

Підібрано оптимальні технологічні параметри для використання клею: оптимальна в'язкість від 120 Па·с до 170 Па·с, температура 25 °С і 35 °С відповідно. Адгезійна міцність паперової етикетки до скла – 4 бали, до поліетилентерефталату – 3 бали. Експлуатаційні властивості оцінювали по стійкості клейової композиції до зміни температури і умов навколишнього середовища, вологи і механічного впливу.

Сформовано вимоги до клею, які необхідно враховувати при його експлуатації: а – стійкість до конденсованої води, а саме: 5–15 °С; б – стійкість до крижаної води при температурі 3–5 °С; видалення етикетки в миючій машині при температурі 70–80 °С з додаванням NaOH або поверхнево-активних речовин.

Проведено дослідження клейової композиції методом SAB Miller для оцінки якості при проведенні тесту на стійкість до крижаної води. Для оцінки якості наклейки етикетки був використаний метод з застосуванням копійовального паперу. Сформовано вимоги до клею, які повинні враховуватися при його експлуатації (стійкість до конденсованої і крижаної води і видалення етикетки в миючій машині при температурі 70–80 °С з додаванням NaOH або поверхнево-активних речовин)

Ключові слова: клейова композиція, казеїн, модифікуюча добавка, липкість, адгезійна міцність, водостійкість, технологічні властивості, експлуатаційні властивості, етикетування, тара

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DEVELOPMENT AND RESEARCH OF A LABEL CASEINE ADHESIVE FOR PACKAGING THE INDUSTRIAL AND HOUSEHOLD PRODUCTS

A. Cherkashina

PhD, Associate Professor*

E-mail: annikcherkashina@gmail.com

A. Rassokha

PhD, Professor*

E-mail: rassan2000@ukr.net

I. Ryshchenko

Doctor of Technical Sciences, Professor

Department of General

and Inorganic Chemistry**

E-mail: ryshchenko@kpi.kharkov.ua

O. Komarova*

E-mail: olyakomarova2407@gmail.com

*Department of Plastics and

Biologically Active Polymers Technology**

**National Technical University

«Kharkiv Polytechnic Institute»

Kyrpychova str., 2, Kharkiv, Ukraine, 61002

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1. Introduction

Natural adhesives are renewable and environmentally friendly. The advantage of casein adhesives is eco-friendliness (manufacturability, the absence of harmful chemicals and odor). The use of water-based adhesives solves the issues related to resource and energy conservation [1, 5], as well as the protection of the environment [2–5], as the renewable energy sources are used and the environment is not polluted: the atmosphere, hydrosphere, and lithosphere. Resolving these issues focuses on the creation of new composite materials from renewable raw materials and the use of modern methods to control their technological and adhesive properties.

In the process of gluing, casein adhesives may lose the capability to dissolve or soften when heated, so their use when sticking labels leads to difficulties in washing them

away from industrial and household containers if it is necessary to reuse them. In addition, the application of casein adhesives requires special conditions for their transportation and storage.

The need for easily washed adhesives arises when labeling products packaged in reusable containers, primarily, glass containers. Such adhesives are subject to the most stringent requirements – high stickiness, adhesion, and water resistance; at the same time, they should be capable of keeping a label on the glass container, including under conditions of high humidity. The label should be compatible with the capability of glue to ensure a light separation from the container when laundering it with harmless liquids, most often aqueous soda solutions or surface-active substances. Therefore, it is a relevant task to develop a glue adhesive composition with high stickiness for sticking labels at high-speed machines.

2. Literature review and problem statement

The production of packaging products in various industries is associated with the use of such materials as paper, cardboard, microcorrugated board, polymeric films, glass, fabrics, foil, etc. Label adhesives are used to label glass containers and polyethylene terephthalate (PET) packaging. The following types of polymeric adhesives for packaging are used for these materials:

- a) silicate;
- b) pulp, rosin, rubber;
- c) gluten (starch, dextrin) [6], protein (casein, bone, albumin), etc. [7, 8];
- d) polyvinyl acetate, acrylic [9], copolymer;
- e) melt adhesives [10];
- f) insoluble single-component and multi-component adhesives.

There are adhesives based on liquid reactive oligomers [11] for labeling technical products made from metals, plastics, and glass.

A promising direction of modern polymer science is to study the structure and stability of the casein microparticles [12, 13], to create and study the nanocomplexes of the casein protein, the solubility of the casein protein and the whey protein [14, 15].

Water-resistant adhesives are used to glue various whey protein-based materials, modified by oligomers (isocyanate, phenol-formaldehyde oligomer) [16, 17] and a polymer (polyvinylpyrrolidone) [18].

One of the reasons why natural polymers are replaced by synthetic polymers is their cost. However, the concepts of natural and environmentally friendly adhesives are attracting increasing public attention.

The environmentally friendly water glues have been developed with whey protein and the addition of polyvinyl alcohol (PVA), modified with isocyanate and containing the nanoparticles of CaCO_3 calcium carbonate as a dispersed filler [19]. Other whey protein-based adhesives are modified by phenol formaldehyde oligomer (PFO). The glue adhesive composition possesses a dry shift strength of 1.98 MPa, a wet shift strength of 1.73 MPa. These indicators are higher than those required for a regular application under the JIS K6806-2003 standard. The release of formaldehyde from the adhesive is 0.067 mg/dm^3 , which is much lower than the required value in accordance with the standard JIS A5908 [20]. Such adhesives have high adhesive strength and durability but do not belong to an environmentally friendly group of adhesives.

Until now, the promising adhesive, mainly in water-based labeling glues, has been casein – a complex protein with the gross formula $\text{C}_{81}\text{H}_{125}\text{N}_{22}\text{O}_{39}\text{P}$ [1, 3, 4], given its functional unique features of the structure of the macromolecule protein and the supramolecular structure of the polymer in general. On an industrial scale, a modified glue adhesive composition is used [21], containing a mixture of casein solution with active additives with a mass concentration of 28–31.4 % and an alkaline solution of oxidized starch with a mass concentration of 23–24.8 %. The glue adhesive composition possesses the increased frost resistance and withstands at least four cycles of freezing and thawing, but not sufficient adhesive strength.

In recent years, attempts have been made to reduce the content of casein in the formulations of adhesives by modifying with functional additives as there is an increase in the price of the raw material, casein. On the other hand, the glues for labeling at high-speed machines are subject to special

requirements: high initial grasp not only to dry containers but also cold and wet containers. It is obvious that the glue adhesive compositions based only on casein or starch cannot be used to meet these requirements. Dextrin adhesives are also excluded due to the relatively low water resistance and insufficient adhesion to the substrates.

Therefore, new natural and synthetic modifying substances are being developed, compatible with casein adhesives. The ester of hydroxypropyl oxidized starch, the ester of phthalic acid and hydroabietyl alcohol, methyl, di- or tri-ethylene glycolic ester of rosin, have been proposed as the modifying substances. For the labeling of containers, it is proposed to introduce PVC and other components to the environmentally friendly casein glue [22]. The introduction of PVC to the glue adhesive composition increased its water resistance and acid resistance.

Recently, there has been a need to develop glue adhesive compositions that would possess the technological and operational advantages over the casein adhesives currently used in the industry. Owing to the development of modern technologies, the chemical composition, structure, and functionality of milk proteins are carefully studied. This new knowledge is useful in developing more effective and safe adhesives. The use of milk protein in the formulations of environmentally friendly adhesives is discussed [23]. To quickly cure the adhesives, the casein protein molecules need crosslinking. Protein crosslinking is achieved by the physical (irradiation, thermal treatment), enzymatic, or chemical (adding a crosslinking agent) methods.

It is obvious that the requirements for casein glues (adhesives) to maintain stability in storage, to have the original stickiness of 5–45 s with when sticking complex labels with a density of $70\text{--}80 \text{ g/m}^2$ to the glass are stricter. At the same time, a casein glue should demonstrate high adhesive characteristics after sticking a label to both glass and plastic containers and should not be washed off in industrial washing machines when working with various return containers (glass, PET, etc.).

Casein adhesives contain casein as a binder derived from skimmed milk when it is treated with rennet enzyme or from mineral acids (usually, sulfur H_2SO_4 or hydrochloric HCL). To increase the viability of an adhesive, the alkaline agents (in the form of hydroxides or sodium salts) are introduced into its formulation, and, to increase the water-resistance of an adhesive, casein is pre-modified with heavy oxides or hydroxides of heavy (alkaline earth metals), typically calcium hydroxide $\text{Ca}(\text{OH})_2$.

Paper [24] studied the effect of salt concentration, the pH and temperature, on the structure of the casein micelles and showed that the elevated temperatures do not affect the structure of the micelles. At the protein polymer preparation stage, the focus was on how to improve the strength of the protein network. Mixing protein polymers with chemical crosslinking agents is one of the most common methods of curing protein adhesives.

The nano micelles from casein and keratin were studied in [25]. The results demonstrate that the complex nano micelles, obtained at neutral pH, in the mass ratio of casein to keratin 4:1, take the shape of a sphere, the diameter of which is about 40–70 nm. Casein was dispersed in water by magnetic mixing at $50 \text{ }^\circ\text{C}$. A casein solution was prepared and brought to pH 7.0 with the help of a NaOH solution and an HCl solution. Complex nano micelles in solution have excellent stability during dilution and storage; they are relatively

hydrophilic and have a good potential for industrial use as a base for adhesives.

Paper [26] reported the developed casein glue for sticking labels, in the form of an aqueous solution. The glue was obtained from sodium caseinate with the addition of starch, carbamide, zinc oxide, sodium tetraborate, and fluoride. The authors solved the issues related to regulating the glue viscosity, limiting the storage temperature and working temperature; the glue, however, possesses insufficient adhesive strength, it should be stored at a temperature of at least 15 °C, used at 27 °C of the environment.

A technique has been proposed to prepare a labeling adhesive based on casein, cornstarch, and urea, as well as additives including a crosslinking agent, a thinner, a viscosity regulator, and an antifoam agent. All components are placed in the reactor where the heating, mixing, and gelatinization occur, then the pH value is brought to 6.5–7.5, the temperature is lowered to 40 °C, then the glue viscosity is brought to the desired value with the help of a viscosity regulator. The advantage of the obtained glue adhesive composition is the stability of viscosity in storage [27].

Work [28] proposes a water-resistant nanomodified environmentally friendly binder (an adhesive) on a water base, which, in addition to casein, includes the soy protein. Zinc nano oxide and zirconia nano oxide are introduced into the binder as a nano modifying filler. The advantage of the glue is only high water resistance.

A glue for pulp was suggested, which includes soy protein and lignin. Lignin reacts with the active groups on the protein molecules and forms a crosslinking and interpenetrating mesh that increases the water resistance and thermostability of the adhesive [29].

Different techniques for obtaining dry powdered modified casein adhesives [30] were proposed as well [31]. Casein glue is obtained by purifying the sodium caseinate in the alkaline solution and drying it by spraying. Next, the caseinate is mixed and ground with different components. The resulting dispersed system (in the form of powder) is subjected to antioxidant treatment. Dry casein adhesives require hot water with temperatures ranging from 80 to 85 °C and a long swell process, from 20 to 24 hours.

Paper [32] proposes a water-resistant fast-capture glue based on casein, containing carbamide, starch, and a zinc oxide-based crosslinking agent as the functional modifiers. A significant advantage of the adhesive is its high thermostability and resistance to enzymatic, acidic, and alkaline hydrolysis; the glue, however, has insufficient adhesion to the polymeric substrates.

Study [33] describes a glue adhesive composition containing, as a modification additive, glycerin ester of tall oil rosin, as a plasticizer – orthophthalic acid diethyl ester, as a surface-active substance – the ALM-10 syntanol, and an additional hydrophilic agent. The adhesive composition differs in that the composition includes not the original casein but the product of its processing, which makes the adhesive composition more expensive.

A study on the development of an adhesive, which contains zinc stearate and oxidized potato or cornstarch as a viscosity modifier was reported in [34]. However, the adhesive possesses low stability and low gluing efficiency under complex adhesive compounds.

It should be noted that the industry still uses, to stick labels on various surfaces, a water adhesive containing (% by weight) casein – 100; trisodium phosphate – 12.5; sodium hy-

droxide – 4; soda ash – 16; ammonia – 3.7; water – 1,000 [35]. The glue adhesive composition demonstrates low vitality, adhesion, and a lack of stable viscosity.

Our analysis of literary sources [22, 23, 25, 26, 28–31, 33–35] suggests that, for the packaging industry, it is a promising direction to develop, create, and study a set of properties of the functionally modified environmentally friendly adhesive compositions based on animal proteins. The technological methods of obtaining glue adhesive compositions and their practical application are relatively simple. The casein adhesives used in the industry dry up quickly, produce a thin and even layer and possess good adhesion to the glass and polymeric surfaces. However, they do not meet the appropriate requirements when used in the high-speed processes of labeling the surface of household and industrial containers. Some adhesives do not demonstrate stable viscosity in their dissolution and storage, sufficient adhesion to different types of substrates. Therefore, they do not fully meet the requirements for the quality of the adhesive and technological aspects at the stage of the formation of an adhesive composition and in the process of labeling the surface of the container. The glue should possess high adhesive characteristics after sticking the label to both glass and plastic containers, increased moisture resistance; at the same time, it must be easily and quickly washed off in washing machines when working with return containers.

3. The aim and objectives of the study

The aim of this work is to study and develop a new composition of an adhesive with improved technological and operational properties based on the animal protein – casein, with a functionally modifying additive. This would make it possible to obtain a label casein glue for packaging industrial and household products with the increased stickiness and adhesive strength to the glass and polymeric containers at high-speed labeling machines.

To achieve the set aim, the following tasks have been solved:

- to study the parameters of the technological process of obtaining glue adhesive compositions with a functional modifier;

- to investigate the technological, adhesive, and operational properties of glue adhesive compositions in order to select the optimal composition of the adhesive based on casein and functional modifying additives; to investigate the properties of the optimally-composed adhesive, and to determine the technological parameters for the adhesive and the requirements that must be taken into consideration when applying it to the packaging and during operation.

4. Research methods and materials

The subjects of this study were:

- technical casein, which is a loose powder measuring 0.25 to 0.50 mm from light yellow to yellow with the following elementary composition (% by weight): carbon, 53.1; hydrogen, 7.1; oxygen, 22.8; nitrogen, 15.4; sulfur, 0.8; phosphorus, 0.8. All casein fractions are phosphoproteins; the presence of polar functional groups (amino, carboxyl, hydroxyl, and other groups), present both on the surface and inside the micelles of technical casein, contributes to significant water-binding (3.7 g per 1 g protein). Casein contains in its

composition (% by weight): protein, 84; moisture, 12; fat, 2.3. Casein is a complex protein formed from its predecessor, caseinogen when curdling milk;

– the surface-active substance OP-10 (auxiliary material OP-10), which is a liquid product of the treatment of the mixture of mono- and dialkyl phenols with ethylene oxide;

– the glycerin ester of gum rosin – a complex ester of triatomic alcohol, transparent, vitreous mass, the color of the solution of the ester on the iodometric scale is no more than 60, the acid number is no more than 11 mg KOH/g;

– potato starch – a pure white powder, particles with a diameter of 0.5–1.0 mm have a characteristic oval shape;

– dextrin – a white, fawn, yellow powder, particles with a diameter of 0.5–1.0 mm;

– carbamide (urate, coal acid diamide) – the colorless, white crystals, soluble in polar solvents (water, 104.7 g at 20 °C; ethanol; liquid ammonia);

– butyl alcohol (chemically pure – c. p.);

– ethyl alcohol (c. p.);

– dibutyl ester of orthophosphoric acid;

– zinc oxide (c. p.);

– zinc stearate (c. p.);

– sodium tetraborate.

This study used the standard, industry-common testing methods, described below.

The study determined: the thickness of an adhesive layer (ASTM D3652 method), the mass share of dry residue (GOST 18992-80), the hydrogen ions index (pH) (GOST 14231-88), the dynamic viscosity η of the adhesive at the viscosimeter Reotest (GOST 25276). The device makes it possible to measure the deformation rate from 0.56 to 4,860 s⁻¹, the shear stress τ – from 40 to 2.2·10⁵ Pa. The magnitude of the measured dynamic viscosity η ranges between 8 and 40·10⁷ MPa·S. The viscosity measurement limits: 10⁻² to 10⁴ Pa·s; the shear rate (deformations): from 0.1667 to 1.458·10³ s⁻¹; the shear stress, from 12 to 3·10³ Pa; temperatures, 30 to 150 °C, the adhesion capacity (detachment) and the separation of glue from a substrate, at an angle of 90°, (ASTM 3330), the adhesion by lattice incisions (DSTU ISO 2409:2015), the stickiness, a «loop method», (ASTM D6195 (A)), the resistance of glue to water condensate (the method of exhibiting samples in the atmosphere of saturated water vapor, DIN 50017, at 40 °C), the resistance of glue to ice water (a SAB Miller method) [36].

The adhesive capacity of glue adhesive compositions was evaluated by determining the strength of adhesion contact for the detachment of the adhesive composition from the substrate (glass, polyethylene terephthalate – PET) at an angle of 90°.

In addition, we estimated the adhesion of the glue adhesive composition by the method of lattice incisions in accordance with Table 1.




The operational parameters of the examined glue adhesive systems under real and critical operating conditions were studied taking into consideration the widely used and rated parameters: the resistance to condensed and icy water.

The test was conducted in the laboratory at a temperature of 25 °C and relative humidity of 50 %.

Wet bottles were cooled to a temperature of 4 to 5 °C. The tests lasted for 6.5 hours under constant conditions. The result was estimated by the condition of the label and the turbidity of the water released under the label. In the end, the test results were compared to the documented values for the practical conditions of the trial.

Table 1

Assessment of adhesion by a lattice incision method

Point	Description of the surface of the coating after making incisions in the form of a lattice	The physical appearance of a coating
1	The edges of the incisions are completely smooth, there are no signs of exfoliation within each square of the lattice	
2	A slight exfoliation of the coating in the form of small scales at the intersection of the lattice lines. The disruption is observed over no more than 5 % of the surface of the lattice	
3	Partial or complete exfoliation of the coating along the lattice incision lines or at their intersections. The disruption is observed over at least 5 % but no more than 35 % of the lattice surface	
4	Full exfoliation of the coating, or partial, exceeding 35 % of the lattice surface	

Wet bottles were cooled to a temperature of 4 to 5 °C. The tests lasted for 6.5 hours under constant conditions. The result was estimated by the condition of the label and the turbidity of the water released under the label. In the end, the test results were compared to the documented values for the practical conditions of the trial.

The resistance to cold water by the developed glue adhesive composition can be determined by different methods. Table 2 gives different methods for assessing the resistance of glue to ice water.

Table 2

Comparison of different methods for testing the resistance of glue to cold water

Indicator	Test method			
	Inbev	Heineken	SAB Miller	VLB Berlin
Drying duration	24 h, 21 °C; 24 h, 40 °C; 7 days, 23 °C	7 days, 21 °C	24 h, 21 °C	24 h, 21 °C
Water temperature	5±1 °C	5±1 °C	4±2 °C	5±2 °C
Mechanical load	Rotating five times at 180° every 3 hours	Removal after 24 hours	Rotating five times at 180° every 3 hours	Rotating in equal periods
Estimate	1. Label position. 2. Part of the open area, %	Label position	Label displacement	Label position

A comparative analysis of the methods for testing glued parts for cold-water resistance (extreme conditions) revealed the high efficiency, reproducibility, and accuracy of the SAB Miller research method. According to it, the bottles were placed in water for 24 hours at a temperature of 4 to 2 °C. Every 3 hours, the bottles were rotated at 180°. Next, the bottles were taken out of the water and manually checked if the label had shifted or not. The label remained on the bottle after being in the water for 12 hours and at the constant rotation of the bottle at 180°; thus, the adhesive composition successfully passed the test.

In assessing the quality of the developed adhesive compound based on the functionally modified systems, a rather simple but extremely effective method of assessing the quality of the adhesion was used when labeling containers using copy paper. The correct placement in the labeling process affects the consumption of glue and the physical appearance of the packaging. The labels or corresponding samples of paper were glued on the backside and applied to a glass plate. Next, two sheets of wet filter paper were placed on the examined samples, which were covered with another glass plate. All this was left for 2 hours in a drying chamber at a temperature of 70 °C.

When selecting the objects and research methods for this study, important factors are the requirements for the glue being developed, which must be taken into consideration when using it:

- a) the resistance to condensed water at 5–15 °C because such water under actual operation conditions covers a bottle with a thin layer;
- b) the glue resistance to ice water at 3–5 °C;
- c) the removal of a label in a washing machine at 70–80 °C with the addition of NaOH (to create a high pH value) or the surface-active substances.

Experimental data were statistically treated by the STATISTICA software.

The number of parallel experiments in property studies was 10 per experimental point.

The experimental samples were the paper strips of 150 to 300 mm, 0.18–0.20 mm thick, the density of the label paper, 70–80 g/m².

The glue curing time ranged from 10 to 20 minutes at 50±5 °C.

5. Experimental results of the study

5.1. Exploring the parameters of the technological process of obtaining glue adhesive compositions with a functional modifier

When preparing the adhesive composition, a calculated amount of demineralized water at a temperature of 18–23 °C is loaded into a laboratory reactor with a heated jacket with a constantly working stirrer using a metering device (batcher) and casein powder is added (in portions). After the initial stage of stirring and wetting (up to 3 minutes), the mixer is turned off, the mass is left for 10–15 minutes at rest to saturate casein particles with water and to partially dissolve it. Next, with a constantly working mixer, other components of the adhesive composition are portioned in accordance with the formulation. Then the adhesive composition is mixed for 4 hours at a stirrer speed of 50–70 rpm until a homogeneous, uniform adhesive solution is obtained, gradually bringing the temperature in the reactor to 75 °C, then the mixer is stopped, the contents in the reactor are cooled to room temperature.

During the experiment, two formulations of glue were brewed, which were taken as the base for preparing adhesive compositions with different contents of a modifying ingredient, the glycerin ester of gum rosin (GER) in the amount of 1–5 % by weight.

The preparation of an adhesive (formulation No. 1) was carried out in the following sequence: we poured water to a laboratory reactor with a capacity of 0.5 dm³ in an amount of 60 % by weight at a temperature of 20–25 °C together with a surfactant of the brand OP-10, 0.2 % by weight, and zinc stearate, 0.2 % by weight. This mixture was aged for

10–15 minutes. After the mixture was aged at a temperature of 25 °C, we added to it the modified starch (dextrin), 4.5 % by weight, at constant stirring. After aging the mixture for 15–20 minutes at 20–25 °C, casein in the amount of 20 % by weight was added to it; it aged another 30–40 minutes at 25–30 °C. Then we added the dibutyl ester of orthophosphoric acid, 1.5 % by weight, it aged for 5 minutes, next we added carbamide (urea), 20 % by weight, it aged for 15 minutes at the same temperature (25–30 °C). Then we added sodium tetraborate, 4.0 % by weight, and the mixture was heated to 80 °C, aged for 10–15 minutes at constant stirring; the mixture was then cooled to 40 °C. The finished glue was divided into 3 portions, to each of which we added the functionally modifying additive GER in the following ratios: 1, 2, 5 % by weight, at constant stirring and aging for 20 minutes.

The preparation of an adhesive (formulation No. 2) was carried out as follows: we poured to a laboratory reactor with a capacity of 0.5 dm³ water in the amount of 60 % by weight at a temperature of 20–25 °C together with a surfactant of the brand OP-10, 0.1 % by weight, and zinc oxide, 1 % by weight. The mixture was aged for 10–15 minutes. After aging the mixture at a temperature of 25 °C, we added to the mixture carbamide (urea), 10 % by weight, butyl alcohol, 0.5 % by weight, and ethyl alcohol, 2.0 % by weight, potato starch, 5.5 % by weight, at constant stirring. After aging the mixture for 20–30 minutes at a temperature of 20–25 °C, we added casein in the amount of 30 % by weight to it and aged for another 30–40 minutes at the same temperature. Next, we added sodium tetraborate, 4 % by weight, and the temperature of the mixture was raised to 80 °C, it was aged for 10–15 minutes at constant stirring, after which the mixture was cooled to 40 °C. The finished glue was divided into 3 portions, to each of which we added the modifying additive GER in the following ratios 1; 2; 5 % by weight, at constant stirring, and aging for 20 minutes.

5.2. Studying the set of technological, adhesive, and operational properties of adhesive compositions with a functional modifier in order to choose the optimal formulation

We have studied the dynamic viscosity (at different deformation rates), hydrogen ions (pH) indicators, after introducing to adhesive compositions 1 and 2 the developed formulations, defined at the stage of preliminary, «starting» studies, with different contents of the functionally modifying additive GER.

The values of the dynamic viscosity and hydrogen ions indicators are given in Table 3.

Table 3

Values of the dynamic viscosity and the adhesive ions' hydrogen indicators based on casein dependent on the concentration of the functional modifier GER (formulation No. 1)

GER concentration, % by weight	Hydrogen ion indicator pH	Dynamic viscosity, Pa·s (rate 2)	Dynamic viscosity, Pa·s (rate 5)
0	7.45	112	88.7
1	7.21	168	130.6
3	7.16	182	134.3
5	7.12	168	134.3

Table 3 shows that when the content of the functionally modifying ingredient GER in the casein adhesive composition increases, the hydrogen ion indicator is reduced while the dynamic viscosity changes non-monotonously (a ma-

ximum of the parameter over this range of modifier concentrations is achieved at 3 % by weight), which indicates a significant influence of the modifying additive GER on the technological characteristics of the developed glue adhesive composition. Fig. 2 shows the chart of the dynamic viscosity dependence on the concentration of GER.

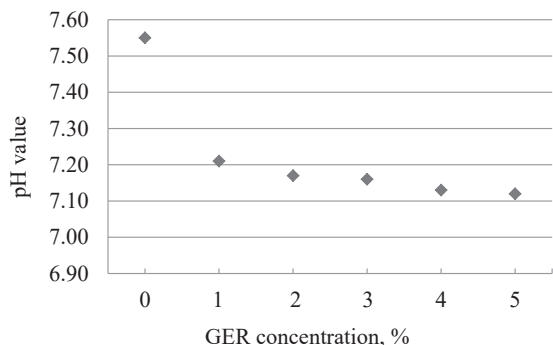


Fig. 1. Dependence of pH index on the concentration of the GER modifier in a casein glue adhesive composition (formulation No. 1)

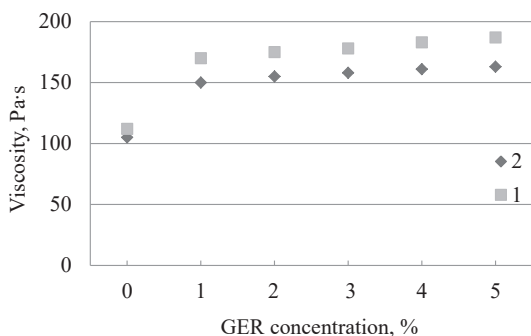


Fig. 2. Dependence of dynamic viscosity on the concentration of the GER modifier in a casein glue adhesive composition (formulation No. 2): 1 – viscosity measured at rate 2; 2 – viscosity measured at rate 5 (different deformation rates at the rotational viscosimeter «Reotest»)

The results of studying the dynamic viscosity (at different deformation rates) and the indicators of hydrogen ions (pH) after introducing to the adhesive casein composition 2 the formulation of the modifying additive GER in the range of the examined concentrations are given in Table 4.

Table 4

Values of the dynamic viscosity and the indicators of hydrogen ions for the casein adhesive ions dependent on the concentration of the functional modifier GER (formulation No. 2)

GER concentration, % by weight	Hydrogen ion indicator pH	Dynamic viscosity, Pa.s (rate 2)	Dynamic viscosity, Pa.s (rate 5)
0	7.44	280	223.2
1	7.43	410.6	316.2
3	7.36	476.0	372.0
5	7.26	578.7	427.8

The effect of the modification additive GER in a given adhesive composition was expressed in the reduction of the hy-

drogen ion indicator and the increase in the dynamic viscosity with an increase in the concentration of the ingredient GER. The charts of experimental dependences of the hydrogen ion indicator and dynamic viscosity on temperature are shown in Fig. 3 and Fig. 4. The study results have shown that the dynamic viscosity of a given adhesive composition has high values and cannot be considered as a glue adhesive composition for labeling the household and industrial containers under standard production conditions at high-speed industrial plants.

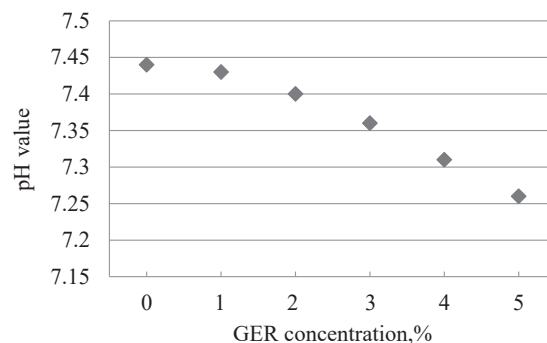


Fig. 3. Dependence of pH indicator on the concentration of the GER modifier in a casein glue adhesive composition (formulation No. 2)

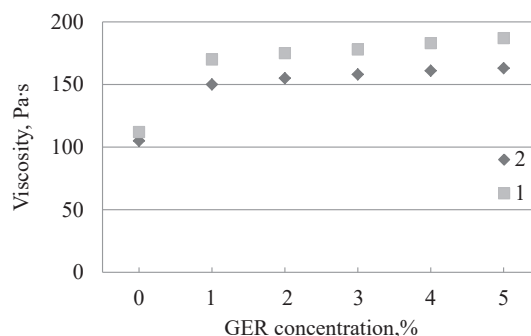


Fig. 4. Dependence of dynamic viscosity on the concentration of the GER modifier in a casein glue adhesive composition (formulation No. 2): 1 – viscosity measured at rate 2; 2 – viscosity measured at rate 5 (see explanation to Fig. 2)

We studied the technological properties of casein adhesive compositions with the functional modifying additive GER. The study results are given in Table 5. Based on the data from Table 5, it is clear that in terms of dynamic viscosity, pH level, and operating conditions requirements, it is advisable for further research aimed at practical application to use the casein adhesive composition containing the functional modifying GER additive in the amount of 1 % by weight.

The adhesive properties of a glue (stickiness and adhesive strength) are the main technological and operational characteristic of a glue adhesive composition when labeling the household and industrial containers, as well as during operation over the «life cycle» of a system (adhesive – substrate).

The capacity to form an adhesion when in contact with the hard surface of the casein adhesive composition is an important indicator, so we studied the stickiness of an adhesive composition.

The stickiness was tested at different concentrations of the functional modifier GER and the time of contact between an adhesive layer and the substrate of the device.

Table 5
The technological properties of the casein adhesive compositions with different concentrations of the functional GER modifier

Parameter	Indicator		
	GER modifier concentration, %		
	1	3	5
Dynamic viscosity at 20 °C, Pa·s	170	180	189
The optimal pH level of an adhesive composition	7.21	7.15	7.10
Mass share of dry residue in the adhesive composition, % by weight	38.2	36.9	37.0
The optimal working temperature for labeling a container, °C	+20...+25	+20...+25	+20...+25

The values of stickiness at different concentrations of the GER modifier in an adhesive composition are given in Table 6.

Table 6
Values of stickiness at different concentrations of the GER modifier in a casein adhesive composition

GER concentration, % by weight	Stickiness (a. u.) over the time of contact, s		
	10	15	20
0	32.5	36.7	40.5
1	47.82	58.17	58.58
3	44.14	54.17	57.59
5	50.20	54.80	55.38

The stickiness values, given in Table 6, showed that the best indicators of stickiness were demonstrated by the adhesive composition with the content of the GER modifier of 1 % by weight. The stickiness values for a given casein adhesive composition are much higher than those of other adhesive compositions at different times of contact in the formation of the system «label – adhesive – container surface». The glue adhesive composition possesses high primary stickiness: 47.82–58.58 a. u. during the contact time between surfaces (10–20 s), which contributes to the rapid sticking of a label to the surface of the household and industrial containers.

The results of the experimental tests of adhesive strength by the examined systems are given in Table 7.

Table 7
Adhesive strength for detachment for a casein adhesive composition at different concentrations of the GER modifier

Substrate surface	Adhesive strength for detachment (MPa)		
	The concentration of the GER modifier in an adhesive, % by weight		
	1	3	5
glass	5.8	5.5	5.0
polyethylene terephthalate	5.4	5.3	4.9

Table 7 shows that the casein composition with the content of the modifying additive GER in the amount of 1 % by weight demonstrates the higher adhesive strength: it is 5.8 MPa and 5.4 MPa, respectively, to glass and polyethylene terephthalate.

The experimental data on the strength of the formed adhesion contact of the examined adhesive systems based on the functionally modified casein adhesive by the standard method of lattice incisions are given in Table 8.

Table 8
The adhesive strength of a casein adhesive composition with different content of the functional modifier GER

Substrate	Adhesive strength (points) of adhesive composition at a concentration of the GER modifier, % by weight		
	1	3	5
glass	1	2	3
polyethylene terephthalate	2	3	4

Our study of the adhesive strength of an adhesive composition showed that the adhesion to glass and plastic (polyethylene terephthalate) is much higher for adhesive compositions with the content of the GER modifier in the amount of 1 % by weight, namely: the adhesion to glass – 1 point, to polyethylene terephthalate – 2 points.

Based on the experimental research and an analysis of the technological and adhesive properties of adhesive compositions, we have determined the formulation of a casein glue adhesive composition based on formulation 1 with a functional modifier (a concentration of 1 % by weight) for applying it in the labeling of household and industrial containers at high-speed production plants.

Based on our set of studies and for practical reasons, the casein adhesive composition based on formulation 1 with the content of a functional modifier in the amount of 1 % by weight was used for further study.

At the next stage, we investigated the chosen adhesive composition of the optimal formulation. We studied a change in the dynamic viscosity dependent on a temperature change over the technologically sound range. Fig. 5 shows a chart of changes in the dynamic viscosity of the casein adhesive composition with the content of the modifying additive GER in the amount of 1 % by weight at different temperature values.

The chart of changes in the dynamic viscosity of the adhesive composition with the content of the modifying additive GER in the amount of 1 % by weight (shear-deformation rate 2) is shown in Fig. 6.

The result of our study is the defined optimal technological parameters for the use of casein glue for labeling the surface of household and industrial containers: optimal dynamic viscosity, within 130–150 Pa·s at a temperature of 25–35 °C.

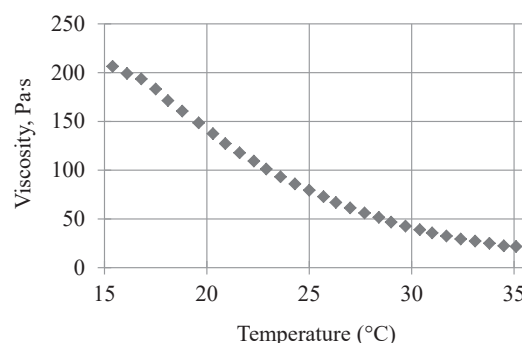


Fig. 5. Dependence of the glue dynamic viscosity on temperature

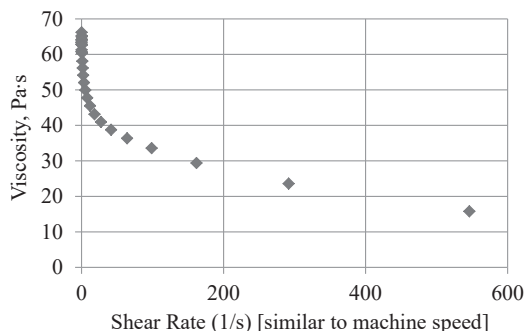


Fig. 6. Dependence of the dynamic viscosity of a casein glue adhesive composition on the shear rate (deformation)

Fig. 7 shows the comparative experimental charts of the dependence of dynamic viscosity on temperature for the starting composition without the functional modifying additive GER (starting: basic glue adhesive composition) and for the developed adhesive formulation with the content of the modifying additive GER in the amount of 1 % by weight.

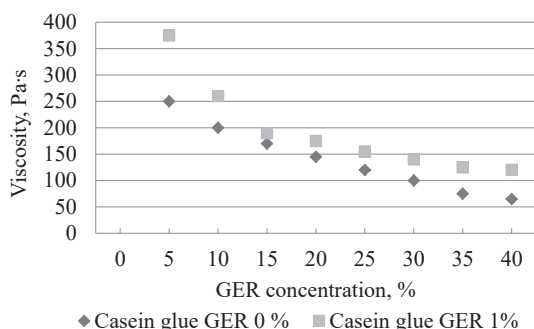


Fig. 7. Optimal conditions for using the developed casein glue adhesive composition

The maximum stickiness value of the developed adhesive composition is 58.17 a. u. in contact with a hard surface for 15 s, the adhesion for detachment to glass – 5.8 MPa, PET – 5.4 MPa.

The amount of adhesion strength is significantly influenced by factors due to the chemical nature of label glue, the quality of preparation of the surface of the substrate for gluing, the technological conditions of labeling, the conditions of transportation of a product with the label, storage and consumption of household and industrial goods with the label applied to it.

The surface of the substrate was cleaned from dust, fats, residues of chemicals used in the packaging. This allows the formation of a strong adhesive compound based on a functionally modified casein adhesive. The adhesive joint obtained after curing involving a casein adhesive, following the application of labels for preparing the surface of the substrate for bonding, required in the framework of this technological process, would have sufficient adhesive strength. That would allow the use of a glue adhesive composition based on the functionally modified materials for labeling at high-speed industrial machines.

Before applying the functionally modified casein adhesive, the surface of containers was prepared in accordance with the recommendations currently in place at the industrial enterprises of this production profile: the glass and polyethylene terephthalate surfaces were treated with ethanol.

The practical testing of this development was carried out by applying casein glue on the container at the labeling machine at an enterprise of AB InBev. The rated requirements for glue consumption at this equipment are 8–15 g/m², at an adhesive layer thickness of 0.1 mm to 0.2 mm. The layer thickness can be obtained with high reproducibility in the range of 0.1–0.15 mm.

As part of this study, at the stage of experimental and industrial testing, we studied the effect of the dependence of the consumption of the optimal formulation of the developed casein adhesive on the thickness of the adhesive layer. Experimental data are given in Table 9.

Table 9

Consumption of casein glue (a concentration of GER in the amount of 1 % by weight) depending on the thickness of the adhesive layer

Experiment	The thickness of the adhesive layer, mm	Consumption of adhesive, g/m ²
1	0.1	10.00
2	0.12	13.80
3	0.15	30.48

Table 9 shows that when the distance between a glue knife and the adhesive shaft changes from 0.1 mm to 0.12 mm, the glue consumption increases by about 40 %.

To select the optimal technological parameters for rational use, under industrial conditions, of the developed adhesive based on the functionally modified casein, we performed a representative assessment of the adhesive consumption at actual industrial high-speed equipment. The area S (m²) of samples to be glued was calculated. The glue consumption (g/m²) was determined from the following formula: $Pp = N \times a \times B / 100$, where: a is the thickness of a single-layer coating, μm . The standards of adhesive consumption were determined from the following formula: $N = (L_i - L_0) / S$, where L_0 is the mass of a sample, g; L_i is the mass of a sample with an adhesive composition, g. The results of calculating the consumption of the functionally modified casein glue of optimal formulation with the content of the modifier GER in the amount of 1 % by weight at different temperatures of forming the adhesive system are given in Table 10.

Table 10

Consumption of the optimal casein glue adhesive composition with the content of the GER modifier in the amount of 1 % by weight at different temperatures (thickness of the glue layer of 0.1 mm)

Experiment	Temperature, °C	Glue consumption, g/m ²
1	25	14.00
2	27	9.52
3	29	10.48
4	31	10.00
5	33	9.75
6	35	9.61

During the «life cycle», glass containers of household and industrial purposes can be exposed to the outside influence: being in the premises with finished products during storage, in retail, during transportation, in a refrigerator, or during washing. The same exposure applies to the label glued to it,

which positions the brand, and informs the consumer about the formulation of the drink's components. A label is subject to various effects, such as changes in the temperature and environmental conditions, humidity, and mechanical impact. Therefore, the casein adhesive should not only glue a label but should be characterized by a wide range of technological and operational properties. A label should not be separated from a bottle under the influence of condensation but should be easily washed off in a washing machine.

Therefore, at the next stage of our study, following the development of a casein adhesive material and choosing the optimal functional modifying formulation, it was appropriate to investigate the operational properties of the developed material under conditions as close to the actual (sometimes critical) operating conditions as possible. We examined the parameters of the operating properties of casein glue, which are «sensitive» to a given type of products: the resistance to condensed and icy water. Resistance to condensed water means that the glue, still moist under a label, should demonstrate good resistance to diluting by the flowing condensed water (assuming that the glue and condensed water at this point have the temperature of the product, which is inside the container, namely 5–15 °C because water covers the container with a thin layer). To be resistant to ice water, casein glue, on the other hand, must dry for many days before succumbing to water at 3–5 °C. The removal of a label in the washing machine typically takes place at a temperature of 70–80 °C with the addition of caustic soda NaOH (a high pH value) or special brands of the surface-active substances.

The low temperature at bottling, as well as the high humidity at the bottling and storage premises, lead to significant condensation of moisture on the surface. As a result, labels can be jarred, shifted, and in some cases, when washing out a casein adhesive, to lose its functional purpose («fall off» containers, bottles).

The developed casein glue adhesive composition with the content of the functional modifier GER in the amount of 1 % by weight within the framework of this study has successfully passed complex laboratory tests. At a total number of parallel experiments of 1,125 (the number of glass bottles with labels glued by the casein adhesive of optimal formulation and the rational thickness of the adhesive compound), the comprehensive operational tests were passed by 1,118 samples (bottles). Thus, the percentage of defects in the test was 0.62 %.

The adhesive is designed for use in product labeling, both to dry containers at 70 °C and to wet containers at 4 °C.

The quality of the adhesive compound depends to a large extent on the nature and properties of the connected surfaces, as well as on the properties of a glue (adhesive).

Along with the type of glue, the properties of the label material exert a significant effect on the resistance to cold water, as they can change not only because of the «dissolution» of the adhesive layer but also due to the loss of glue adhesiveness to paper. The less adhesion in a dry state, for example, as a result of the slight roughness of the paper surface, the faster the sticking in the wet state decreases.

Important is not only the temperature of the water but the movement of a bottle in it along a certain trajectory. The test results will be very different depending on how the bottle is positioned for control, or how it is subjected to increased mechanical loads by repeatedly rotating in the water. Some methods also manually test the strength of label fixing at the surface of the bottle.

As a result of our tests, the developed functionally modified casein glue adhesive composition has successfully passed these tests by having demonstrated the high efficiency of the developed adhesive.

6. Discussion of results of studying the properties of the developed adhesive composition

To create a new formulation of the casein-based adhesive, we investigated the dependence of dynamic viscosity and hydrogen ion indicator (pH) that affect the structure and stability of casein particles on the amount of the functional modifier introduced into the adhesive formulation (Table 3) and at different shear rates (Fig. 2). At pH=8, the structural changes in casein particles take several hours, and a few seconds at pH=14. Casein particles consist of blocks, which under a microscope are detected in the form of a microstructure with a characteristic size of several μm . The blocks are stretched in the first phase of the swell process. This leads to the assumption that at base pH values, the microstructure swells in the first stage, and then in the second stage, the swollen microparticle disintegrates due to the weakening of stabilizing contacts between the blocks [13]. A casein protein solution is only stable in a certain pH region. When approaching the isoelectric point, the casein solution becomes less and less stable, which is expressed in its deposition. Therefore, it is necessary that the pH of a glue formulation based on casein should be in the range of 7.12–7.28.

Introducing the functional modifier GER to the formulation of an adhesive composition reduces pH, compared to the adhesive composition without GER content, that is, the functional modifier helps reduce pH and stabilize the structure of casein; the dynamic viscosity varies from 130 to 180 Pa·s (Table 3). The created adhesive, based on a glue adhesive composition with formulation 2, the pH values are 7.26–7.44, the dynamic viscosity is in the range of 220–580 Pa·s (Table 4). The viscosity takes high values obviously because in the glue adhesive composition with formulation 2 the content of the regulator of viscosity (urea) is twice as much.

It should be noted that the technological properties are influenced by the concentration of the introduced functional modifier and the formulation of adhesive compositions created using different formulations (Table 5).

It was noted earlier that some adhesive compositions had insufficient adhesion [33–35]. It is obvious that in order to obtain strong adhesive strength and rapid graspability, the casein protein molecules may need crosslinking [23]. The crosslinking of proteins in a casein glue adhesive composition was achieved by a physical method (thermal treatment at a temperature of 50 ± 5 °C for 10 minutes). To assess the adhesive properties of the adhesive compositions, the stickiness and adhesive strength for detachment were determined. To increase the adhesiveness of GER, we implied the dispersing of a functional modifier in the presence of a plasticizer (dibutyl ester of orthophosphoric acid). With little contact time with a hard surface (15 s), the adhesive composition with a GER content in the amount of 1 % demonstrated the higher stickiness values (58.17 a. u.) (Table 6) compared to other compositions. With greater contact with the surface (20 s), the stickiness by compositions with a GER content of 3 % and 5 % is higher. The data given in Table 7 demonstrate that the casein composition with the content of the modifying additive GER in the amount of 1 % by weight showed higher

adhesive strength than that of other compositions, and is 5.8 MPa and 5.4 MPa, respectively, to glass and polyethylene terephthalate. The high values of adhesion strength are confirmed for the adhesive with the content of the modifying additive GER in the amount of 1 %, tested by the method of «lattice incisions».

The result of our experimental research and analysis of the formulations and properties of the resulting glue adhesive compositions is the established optimal formulation of the adhesive, including (% by weight): casein, 20.5–22.5; glycerin ester of gum rosin, 1.0; OP-10, 0.1–0.3; zinc stearate, 0.1–0.2; dibutyl ester of orthophthalic acid, 1.5–2.6; dextrin, 3.5–4.5; sodium tetraborate, 3.0–3.5; water, 50.5–60.7).

A comprehensive study of the technological, adhesive, and operational properties of the casein adhesive composition of optimal formulation has been carried out. Based on these studies, conducted in the laboratory, and tested under industrial conditions, the optimal technological parameters for the use of a modified casein adhesive at high-speed equipment for labeling household and industrial containers have been adjusted.

The advantages of this study, compared to those known in this subject area [32, 33], are the high stickiness over a narrow temperature interval, which is an important indicator for the use of the adhesive at high-speed equipment. However, the goal set in the development of a modified casein composition is achieved in a limited range of viscosity and temperature.

It has been established that it is recommended, for the use of casein glue, to observe the following conditions of operation: dynamic viscosity, 150–170 Pa·s; temperature interval, 25–35 °C.

It is shown that the adhesive is intended for use in the labeling of products, both dry containers at 70 °C and wet containers at 4 °C.

It should be noted that the results of our study are of practical value as we developed an adhesive by adjusting the formulation to standard industrial equipment and production conditions.

It is advisable in the future to develop adhesive compositions based on casein with high durability at storing for use in the printing industry.

7. Conclusions

1. The technologically justified parameters for the process of obtaining casein adhesive compositions containing a functional modifier have been experimentally defined; their technological and adhesive properties have been studied.

2. Based on the examined complex of technological and adhesive properties, the optimal composition of the functionally modified casein adhesive for effective use at high-speed technological equipment has been determined. The technological, adhesive, and operational characteristics of the developed casein glue adhesive composition have been investigated: stickiness, 47.82–58.17 a. u., in contact with the substrate for 10–15 s; the strength of adhesive contact when the label is detached from the substrate: to glass – 5.62–5.85 MPa, polyethylene terephthalate – 5.28–5.40 MPa; the resistance of the glue system to moisture exposure under different operating conditions.

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