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MODIFICATION OF FOOD POLYSACCHARIDE GUM ARABIC WITH POLYBASIC CARBOXYLIC ACIDS

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This work investigates the chemical modification of food-grade gum arabic (GA) using various polycarboxylic acids (citric, adipic, succinic, and oxalic) to enhance its functional properties for advanced applications. The esterification reaction was confirmed through a combination of elemental analysis and FTIR spectroscopy, which indicated the successful incorporation of carboxyl and ester groups into the polysaccharide structure. X-ray diffraction analysis revealed a further amorphization of the modified samples, confirming structural changes. Gel permeation chromatography showed a significant increase in the average molecular weight (M_w) and polydispersity of the derivatives, indicating both cross-linking and chain extension reactions. Atomic force microscopy demonstrated the formation of homogeneous, defect-free films consisting of spherical particles agglomerated into a continuous matrix. Thermal analysis (TGA/DSC) revealed modified thermal degradation patterns and showed that the oxalate derivative (GA-OxA) exhibited the highest thermal stability with a residual mass of 80.73% at 500 °C and the maximum activation energy for decomposition (295 kJ/mol). The results demonstrate the successful synthesis of tailored gum arabic derivatives with improved thermal properties and altered solubility, making them promising materials for applications in food packaging, edible coatings, and as carriers for controlled delivery systems.

Keywords: gum arabic, chemical modification, polycarboxylic acids, esterification, cross-linking, thermal properties, film formation.

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Introduction

Gum arabic is a natural polysaccharide isolated as an exudate mainly from trees of the genus Acacia senegal and Acacia seyal, and is one of the most widely used food hydrocolloids [1]. Due to its unique structure, which includes a complex branched polysaccharide framework with residues of arabinose, galactose, rhamnose and glucuronic acid, as well as protein components, gum arabic exhibits high emulsifying, stabilizing, film-forming and adsorption properties [2]. These characteristics determine its use in the food industry as an emulsion stabilizer, flavor carrier, tablet coating, as well as in pharmaceuticals and cosmetics [3]. Despite its widespread use, the functional capabilities of gum arabic are limited by a number of factors: its sensitivity to changes in pH, ionic strength, temperature, as well as its tendency to microbial degradation and insufficient adhesion to hydrophobic surfaces [4]. In addition, when stored under conditions of high humidity and temperature, the emulsifying activity may decrease due to partial hydrolysis of glycosidic bonds [5]. In order to expand the range of application and improve the performance properties of natural polysaccharides, their chemical modification is increasingly used. One of the promising areas of polysaccharide modification is the introduction of new functional groups through esterification, acylation or cross-linking reactions. In this context, polybasic carboxylic acids are of particular interest – such as citric,

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tartaric, maleic, succinic and fumaric acids. These compounds contain several carboxyl groups that can react with the hydroxyl groups of polysaccharides in the presence of catalysts (e.g. acids or enzymes), forming ester bonds [6]. Modification of polysaccharides with acids allows not only to increase the content of free carboxyl groups, improving its ionic and surface activity, but also to potentially increase thermal stability, water solubility and the ability to form gels or films [7].

Research in the field of modification of polysaccharides with citric acid has already shown its effectiveness in improving the functional properties of starch, cellulose and pectin [8, 9]. For example, esterification with citric acid leads to an increase in viscosity, improved thermal stability and an increase in the adsorption capacity of modified polysaccharides [10, 11]. However, data on the use of polybasic acids for the modification of gum arabic remain limited, especially in the context of food applications, where safety, biocompatibility and preservation of the natural origin of the product are important. In addition, modification of gum arabic can facilitate the creation of new functional ingredients with improved rheological properties, the ability to control the release of active substances or increased resistance to degradation in the gastrointestinal tract, which opens up prospects for use in drug delivery systems or prebiotic supplements [12].

This paper examines the possibility of chemical modification of food gum arabic using various polybasic carboxylic acids and the study of the obtained products using physicochemical methods.

Materials and Methods

Gum arabic was modified with carboxylic acids: citric, adipic, succinic, oxalic.

The synthesis was carried out according to the method [13]: Five grams of acid were dissolved in 50 ml of distilled water with stirring. After the acid was completely dissolved, a 1 N NaOH solution was added until the reaction mixture reached a pH of 3.5, followed by the addition of 5 g of polysaccharide. The resulting solutions were stirred for 24 hours.

The sample was placed in an oven and dried at 50 °C for 24 hours, after which the temperature in the oven was increased to 80 °C and maintained at this level for 3 hours.

The synthesized derivatives were ground in a porcelain mortar, placed in a funnel and washed with ethyl alcohol to remove unreacted carboxylic acids until the washing water acquired a neutral pH value.

Elemental analysis was performed on a Thermo Quest Flash EA-1112 elemental analyzer (Italy).

IR spectra of the samples were recorded on a Tensor-27 FTIR spectrometer (Bruker, Germany). Potassium bromide powder was used as a binder for the preparation of tablets. For this purpose, it was pre-ground in a porcelain mortar, dried in a drying cabinet at 170 °C and stored in a desiccator over a P_2O_5 desiccant. 1000 mg of KBr and 1–5 mg of the test substance were weighed on an analytical balance and placed in a DDR-GM 9458 vibration mill. The matrix was mixed with the substance for 2–5 minutes. From the mill, the sample was quantitatively transferred to a tablet press mold. The press mold was connected to a vacuum pump, and the press mold was evacuated throughout the pressing period. The press pressure was 400 kg/cm^2, the pressing time was 20–60 sec. Then the tablet with the test substance was placed in the cuvette compartment of the device and the IR spectrum was recorded in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}, the number of scans was 32. The result of the analysis is the IR absorption spectrum. Similar manipulations were carried out with a tablet of pure potassium bromide. The potassium bromide spectrum was subtracted from the IR spectrum of the sample. The spectrum was processed using the OPUS version of the software package.

X-ray phase analysis was performed on a DRON-3 X-ray diffractometer (monochromatic radiation CuKα (λ = 0.154 nm), voltage 30 kV, current 25 mA). The scanning step was 0.02 degrees, intervals were 1 s per data point. Measurements were performed in the range of Bragg angles 2Θ from 5.00 to 70.00 degrees. To obtain data on the average molecular weight (Mn), average molecular weight (Mw) and polydispersity of the original and modified polymers, an Agilent 1260 Infinity II Multi-Detector GPC/SEC System chromatograph (with two detections: refractometer (RI) and viscometer (VS) was used. Three PL aquagel-OH columns were used for separation. A 0.1 M $LiNO_3$ solution in deionized water was used as a mobile phase. Calibration was performed using polyethylene glycol standards (Agilent, USA). The eluent flow rate was 1 ml/min, the volume of the sample used was 100 µl. Before analysis, the samples were dissolved in the mobile phase (1–5 mg/ml) and filtered through a 0.22 µm PES membrane filter (Agilent). Agilent GPC/SEC MDS software was used for data analysis. The films were prepared as follows: modified polysaccharide (1 g) was dissolved in distilled water (30 ml) at room temperature. The resulting solution of the modified polysaccharide was poured into a Petri dish and dried in a drying oven at a temperature of 45 °C to

constant weight. The resulting films of the modified polysaccharide were separated from the Petri dish with tweezers, after which they were analyzed by atomic force microscopy.

The films were studied by AFM in the semi-contact mode using a Solver P47 multimode scanning probe microscope (NT-MDT, Moscow). Scanning was performed at least in 3–4 points in several places. The scanning speed was 1.5–2.0 Hz, the resolution of the resulting image was 256 × 256 pixels.

A synchronous thermal analyzer (STA-449 F1 Jupiter (NETZSCH, Germany) was used for DSC and TGA. Thermal analysis was carried out in a nitrogen atmosphere at a flow rate of 50 ml/min. Heating was carried out to 500 °C at a rate of 10 °C/min.

The solubility of modified gum arabic samples in water was determined gravimetrically at 25 °C. 100 ml of distilled water were placed in 150 ml conical flasks, and an excess amount of the test sample (~10 g) was added. The flasks were thermostatted with constant stirring for 24 hours. After 24 hours, the samples were allowed to settle for 1 hour to precipitate the undissolved fraction. An aliquot (25 ml) of the upper solution layer was then removed and centrifuged at 8000 rpm for 15 minutes. An aliquot of the filtrate (20 ml) was quantitatively transferred into pre-weighed weighing bottles (W_1) and dried in an oven at 105 °C to constant weight. After cooling in a desiccator over silica gel, the weighing bottles were weighed (W_2).

Solubility (S, g/100 mL) was calculated using the formula:

$$S = ((W_2 - W_1) \times V_{total}) / (V_{aliquot} \times 100) \quad (1)$$

where W_1 and W_2 are the weights of the weighing bottle before and after drying, g; V_{total} is the total volume of the solution, mL (100 mL); $V_{aliquot}$ is the volume of the aliquot, mL (20 mL).

Each measurement was performed in triplicate. Results are presented as the arithmetic mean ± standard deviation.

Results and Disscussions

The results of the elemental analysis (Table 1) show the successful introduction of polybasic carboxylic acids into the structure of the polysaccharide, as indicated by the change in the content of carbon, hydrogen and oxygen.

The data in Table 1 demonstrate a clear trend in the change in the elemental composition after the modification reaction. Compared to the original polymer, all modified samples show a decrease in the mass fraction of carbon and a significant increase in the mass fraction of oxygen. This is direct evidence of the successful esterification reaction, as a result of which additional carboxyl (-COOH) and ester (-COOR) groups enriched with oxygen were introduced into the polysaccharide structure.

The most indicative changes are observed for the sample modified with oxalic acid (GA-OA). Its composition differs sharply from the others: the mass fraction of carbon is minimal (21.90%), and oxygen is maximal (76.73%). This is explained by the peculiarity of oxalic acid: it is the shortest and most reactive dibasic acid in this series. The high density of carboxyl groups per unit molecular weight of the acid leads to the maximum degree of substitution of the hydroxyl groups of the polysaccharide, which is reflected in such a significant change in the elemental composition. The changes in the samples modified with other acids (citric, adipic, succinic) are less pronounced, but statistically significant. The carbon content in them decreased, and the oxygen content increased compared to the original gum arabic, which confirms the fact of chemical modification. Small differences between these samples (GA-CA, GA-AA, GA-SA) can be due to different molecular weights, reactivity and steric accessibility of carboxylic acids, which affects the efficiency of their binding to the polymer chain. Thus, the elemental analysis data clearly confirm the successful covalent attachment of all the studied polybasic acids to the gum arabic structure, which is a fundamental condition for the subsequent change in its physicochemical and functional properties.

Table 1. Results of elemental analysis of the samples

Code	Org. acid	Content of C, wt. %	Content of H, wt. %	Content of O, wt. %
Initial GA	–	44.23	5.74	47.72
GA-CA	Citric	34.33	4.66	61.01
GA-AA	Adipic	40.71	6.25	53.04
GA-SA	Succinic	40.85	6.12	53.03
GA-OA	Oxalic	21.90	1.37	76.73

Interpretation of IR spectra of gum arabic derivatives. IR spectroscopy showed that in all samples, interaction between gum arabic and carboxylic acids occurs to varying degrees. The IR spectra of the original gum arabic and gum arabic modified with citric acid (GA-CA) are shown in Figure 1.

The absorption peak in the region of the wave 3444 cm^{-1} corresponds to the vibrations of the -OH group of gum arabic. However, the upper part of the -OH group of gum arabic and gum arabic citrate looks different: in the original gum arabic the -OH group is slightly wider, whereas for gum arabic citrate the -OH group is slightly narrowed due to the fact that part of the -OH group of gum arabic is replaced by citric acid [14]. The absorption peak in the region of the wave 2932 cm^{-1} corresponds to the stretching of the OH and C-H bonds, are characteristic of the inter- and intramolecular binding of alcohol with gum arabic fragments [15], and is characteristic of the CH_2 group of gum arabic [16]. The absorption peak in the 1727 cm^{-1} region is characteristic of vibrations of the ester group, which also indicates the ongoing interaction, as evidenced by the presence of carbonyl groups (C=O) obtained from citric acid [13].

The absorption peak in the 1404 cm^{-1} region corresponds to the bending of OH-H due to the presence of alcohol groups. The absorption peak in the 1230 cm^{-1} region shows the formation of an ester bond, as well as the presence of C-O, C-C bonds [17]. The absorption peak in the 1075 cm^{-1} region corresponds to the stretching of the C-O bond of the C-O-C group in the anhydrous gum arabic ring [16].

The IR spectra of the original gum arabic and gum arabic modified with adipic acid (GA-AA) are shown in Figure 2.

The absorption peak in the region of 3440 cm^{-1} is characteristic of the absorption bands of the stretching vibrations of OH groups [17]. The absorption peak in the region of 2930 cm^{-1} corresponds to the asymmetric vibrations of -CH_2 groups and is characteristic of the inter- and intramolecular binding of alcohol with gum arabic fragments [15]. The absorption peak in the region of 1712 cm^{-1} corresponds to the appearance of absorption bands of carboxylic acid esters [13], also indicates a characteristic peak of gum arabic esters, this range is associated with the stretching vibrations of the C=O bond of the ester group. The absorption peak in the region of 1428 cm^{-1} indicates the presence of both carboxylic acids and aldehydes [16]. The absorption peak in the region of 1064 cm^{-1} is attributed to the stretching of the C-O bond of the C-O-C group in the anhydrous gum arabic ring. The IR spectra of the original gum arabic and gum arabic modified with succinic acid (GA-SA) are shown in Figure 3.

The absorption peak in the region of 3439 cm^{-1} wave corresponds to the stretching vibrations of -OH groups. The absorption peak in the region of 2931 cm^{-1} wave is a characteristic of inter- and intramolecular binding of alcohol with gum arabic fragments and is typical of the CH_2 group of gum arabic. The absorption peak in the region of 1729 cm^{-1} wave is associated with stretching vibrations of the C=O bond of the ester group [13], is typical of stretching vibrations of CO – groups in esters, which confirms the formation of gum arabic succinate, also, this range corresponds to the absorption of carboxylic acid esters [17]. The absorption peak in the region of 1423 cm^{-1} wave corresponds to the bending of OH-H due to the presence of alcohol groups [15]. The absorption peak in the region of 1248 cm^{-1} wave shows the deformation vibration of CH_3 symmetry and the stretching vibration of C-O, respectively. The absorption peak in the region of 1064 cm^{-1} is attributed to the stretching of the C-O bond of the C-O-C group [16].

The IR spectra of the original gum arabic and gum arabic modified with oxalic acid (GA-OA) are shown in Figure 4.

The absorption peak in the 3442 cm^{-1} region is characteristic of the absorption bands of the OH-group stretching vibrations [18]. The absorption peak in the 2934 cm^{-1} region is characteristic of the inter- and intramolecular binding of alcohol with gum arabic fragments and is characteristic of the CH_2 group of gum arabic. The absorption peak in the 1740 cm^{-1} region indicates the presence of carboxylic acid esters [13] and the C=O ester group [15]. The absorption peak in the 1638 cm^{-1} region indicates the content of the carbonyl group [13] and is attributed to the tightly bound water present in gum arabic. The absorption peak in the 1032 cm^{-1} region is attributed to the stretching of the C-O bond of the C-O-C group.

X-ray phase analysis. The X-ray diffraction pattern of the original gum arabic and its derivatives is shown in Figure 5.

According to the XRD data, the original gum arabic is an X-ray amorphous substance, which is manifested in the diffraction pattern by a low-intensity halo in the region of 15–30 (angles 2ɵ). In the process of modifying these polysaccharides with di- and tribasic carboxylic acids, the halo is significantly reduced, which indicates further amorphization of the materials. The lowest intensity is observed in samples obtained using citric acid. The absence

of sharp peaks of high intensity indicates the absence of residues of the used carboxylic acids (and therefore the purity of the products), which are crystalline substances. Similar patterns were observed during the esterification of polysaccharides [19] – due to the disordering of the structure when introducing additional functional groups.

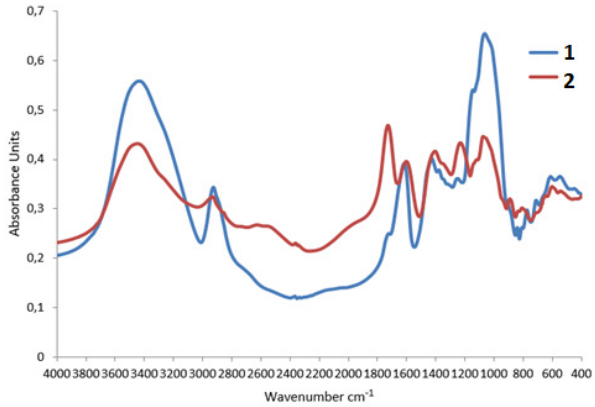


Fig. 1. IR spectra of the original gum arabic (1) and gum arabic modified with citric acid (2)

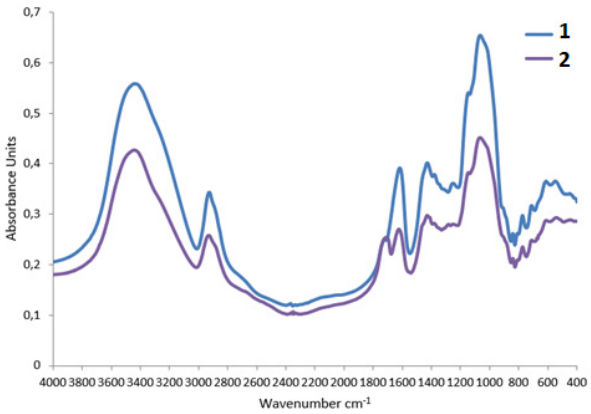


Fig. 2. IR spectra of the original gum arabic (1) and gum arabic modified with adipic acid (2)

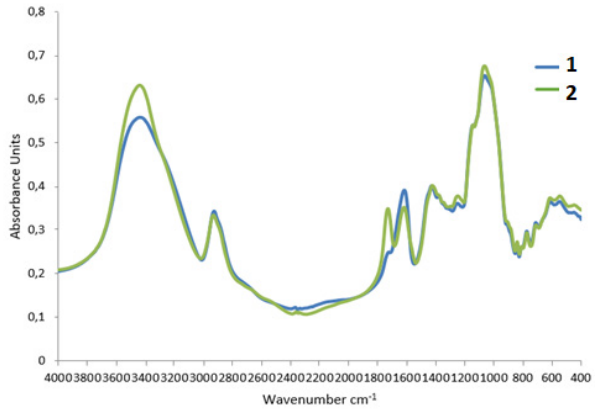


Fig. 3. IR spectra of the original gum arabic (1) and gum arabic modified with succinic acid (2)

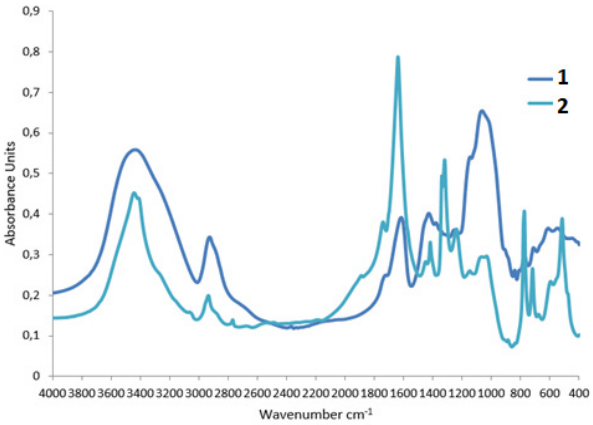


Fig. 4. IR spectra of the original gum arabic (1) and gum arabic modified with oxalic acid (2)

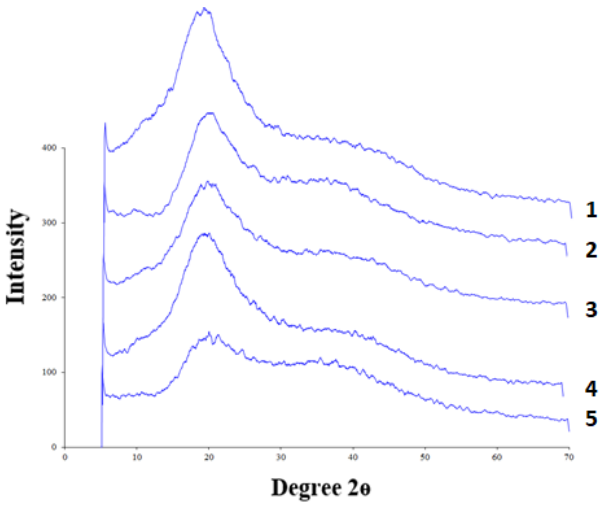


Fig. 5. X-ray diffraction pattern of gum arabic and its derivatives: 1 – initial GA, 2 – GA-OA, 3 – GA-AA, 4 – GA-SA, 5 – GA-CA

Gel permeation chromatography. The use of certain crosslinking agents is important in binding, stabilizing and suspending natural gums during film formation, which subsequently determines the scope of application of the obtained materials from emulsifiers and thickeners to food and pharmaceutical products. Gum arabic is one of the most common gums that have the potential of film-forming substances. A comparative study of crosslinked films based on acacia gum and polybasic carboxylic acids was carried out using the gel permeation chromatography method. Based on the obtained data presented in Table 2, a general trend of increasing average molecular weights (Mw) can be observed regardless of the crosslinking agent used. However, the solubility of the obtained samples varies significantly. Citrate and oxalate of gum arabic have limited solubility in an aqueous medium, which may indicate inter- and intramolecular interactions between the polysaccharide and carboxylic acid. Despite the fact that gum arabic succinate and adipate are characterized by the greatest increase in molecular weight, reaching a maximum of 296916 and 306116 g/mol, respectively, the solubility of these samples is much faster. Apparently, in the presence of succinic and adipic acid, esterification reactions occur to a greater extent without cross-linking.

The profiles of the molecular weight distribution curves of the gum film samples are identical to each other (Fig. 6). During modification, two additional shoulders become pronounced in the high-molecular region (~20×10^5 and 10^6 g/mol). In addition, a significant broadening of the main gum peak and an increase in the polydispersity index values from 1.97 to 5.11 indicate the inclusion of additional fragments in the polysaccharide structure, which together allows us to judge the successful modification of the original structure.

Atomic force microscopy. The surface morphology and microrelief of the obtained films based on modified gum arabic were characterized by atomic force microscopy (AFM) in two modes: relief recording and phase contrast (Table 3). Topography analysis showed that the surface of all the studied samples (GA-CA, GA-SA, GA-AA, GA-OA) is not monolithic, but is formed from individual spherical and near-spherical particles combined into agglomerates. Such a structure is typical for polysaccharide films obtained by drying aqueous solutions and reflects the process of self-assembly of macromolecules during solvent removal. The size and shape of the agglomerates turned out to be relatively uniform for all modified samples, indicating the absence of a fundamental effect of the type of polybasic acid used on the mechanism of formation of the supramolecular structure of the film. The absence of large defects, such as cracks or delamination, indicates good film-forming ability of the obtained derivatives. Critical data were obtained from phase contrast analysis, which is sensitive to local variations in mechanical properties such as elasticity and adhesion. The images did not reveal any distinct phase boundaries or foreign inclusions on the film surface. A uniform phase pattern over the entire scan area indicates the absence of significant amounts of unreacted carboxylic acid or other impurities. This result confirms the effectiveness of the sample washing procedure with ethyl alcohol and is consistent with the XRD data, which did not show the presence of crystalline impurities. The obtained AFM data allow us to conclude that deep modification was successful, as a result of which covalently bound carboxylic acids were uniformly distributed throughout the polymer matrix, rather than simply adsorbed on its surface. The formation of a homogeneous nanoscale structure of films consisting of spherical agglomerated particles explains the good structural and mechanical properties of the materials and predetermines their potential efficiency for use as functional coatings or delivery systems. Thus, the results of AFM analysis confirm the production of pure and homogeneous gum arabic derivatives modified with polybasic carboxylic acids.

Thermal analysis. The thermal transitions occurring during heating in an inert atmosphere were analyzed using differential scanning calorimetry (DSC).

Table 2. Molecular weight characteristics of the initial gum arabic and products of modification with carboxylic acids

code	M_n, g/mol	M_w, g/mol	PD
Initial GA	65880	129939	1.97
GA-CA	68403	271456	3.97
GA-SA	92142	296916	3.22
GA-AA	92033	306116	3.32
GA-OA	55331	282494	5.11

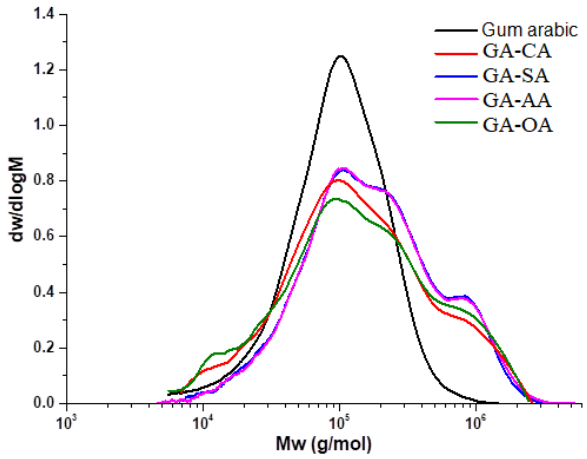
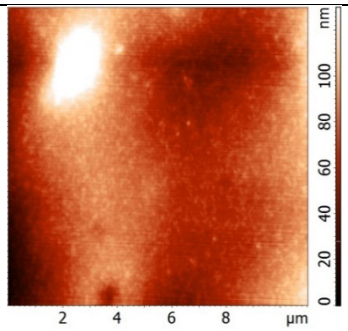
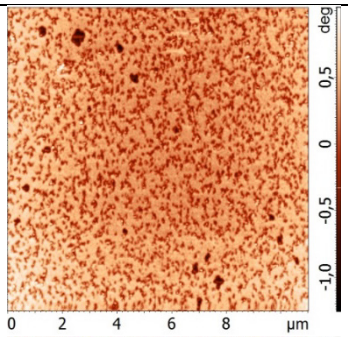
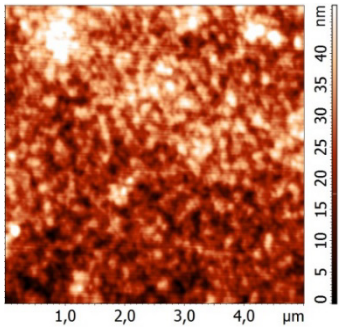
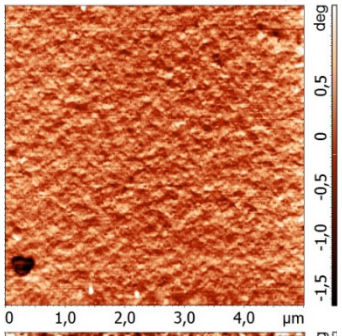
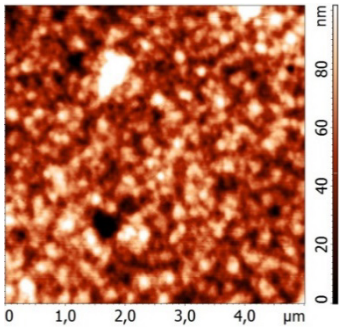
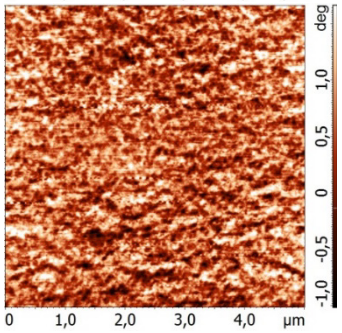
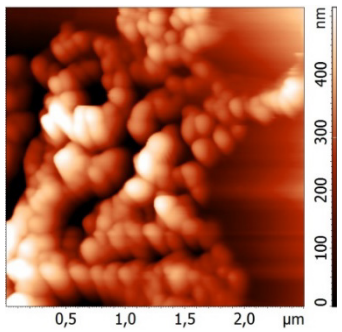
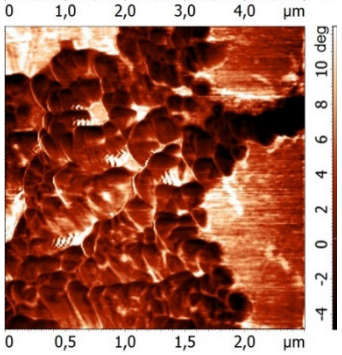


Fig. 6. Molecular weight distribution curves of the initial gum arabic and the products of its modification with carboxylic acids

Table 3. AFM images of products of gum arabic modification with carboxylic acids

№	Relief	Phase contrast
GA-CA		
GA-SA		
GA-AA		
GA-OA		

Typical DSC thermograms of GA-CA, GA-SA, GA-AA, and GA-OA samples are shown in Figure 7. The peak temperatures of the various thermal effects, as well as the corresponding enthalpy changes for all the studied polysaccharides, are given in Table 4.

Most of the DSC curves show early endotherms with maxima in the temperature range of 72–94 °C. The transitions associated with water loss (0.6–8 wt.%) correspond to the hydrophilic nature of the functional groups of the corresponding polymer. Probably, GA-CA and GA-OA samples have a smaller number of hydrophilic OH groups, which is the main reason for the low moisture content.

The glass transition temperature (Tg) was not recorded. The reason may be due to the interference of the Tg transition with the endothermic peak of humidity. Glass transition temperatures can also be located at temperatures below the initial temperature of the DSC analysis.

The main intense peak recorded in the DSC thermograms is an exothermic transition (at about 300 °C), followed by weaker exotherms. Except for the GA-OA sample, which showed two endothermic transitions with peaks at 225 and 360 °C (Fig. 7). Generally, dehydration, depolymerization and pyrolytic decomposition are involved in these high temperature steps leading to the formation of H_2O, CO, CH_2. The studied polysaccharide samples consist of carboxylate or carboxyl functional groups. Therefore, thermal cleavage of carboxylate groups and release of CO_2 from the corresponding carbohydrate backbone can be a probable mechanism of thermal transitions. The exact definition of thermal transitions is a matter of debate. At the same time, due to the differences in structures and functional groups, the thermal degradation pathways or the fragments formed will be different. Thermogravimetric analysis is a simple and accurate method for studying the degradation behavior and thermal stability of polymers. Figures 8 and 9 show the result of TG and DTG analysis. Table 2 shows the detailed data on the thermal behavior from the results of the integral (TG) and differential (DTG) mass loss curve of the sample.

The minor weight loss in the samples at the initial stage is explained by the desorption of moisture in the form of hydrogen bonding of water with the saccharide structure. The GA-SA and GA-AA samples lose the most moisture, 8 and 7%, respectively. During further heating, these samples decomposed in one stage.

The main decomposition of the GA-SA and GA-AA polysaccharides occurs in the temperature range of 188–378 °C and 187–340 °C, respectively. During this period, the samples lose about 70% of their initial mass (Table 4).

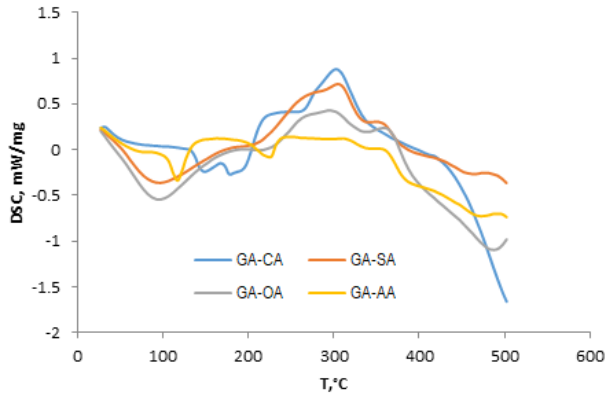


Fig. 7. DSC curves of samples GA-CA, GA-SA, GA-AA и GA-OA

Table 4. Results of TG/DTG analysis of gum arabic samples with carboxylic acids

Sample	Temperature range, °C	Maximum on the DTG curve, °C	Weight loss, %	Activation energy, kJ/mol	Remainder at 500 °C, %
GA-CA	30–131	–	0.55	–	32.43
	131–246	198	30.24	93	
	246–349	304	24.34	129	
	400–460	432	6.40	–	
GA-SA	30–188	91	7.99	–	34.60
	188–378	306	49.47	84	
GA-AA	30–167	92	7.05	–	29.18
	187–340	296	48.77	123	
GA-OA	30–95	–	0.11	–	80.73
	98–132	114	1.85	164	
	193–237	223	4.86	240	
	285–334	307	5.07	295	

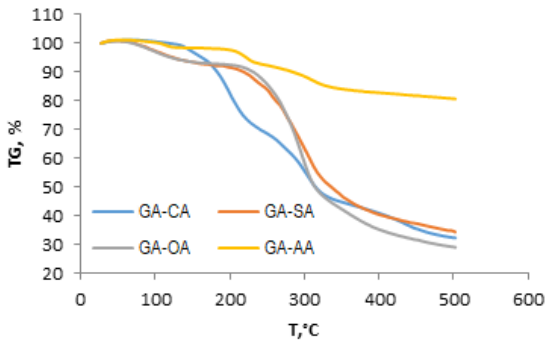


Fig. 8. Results of TG analysis

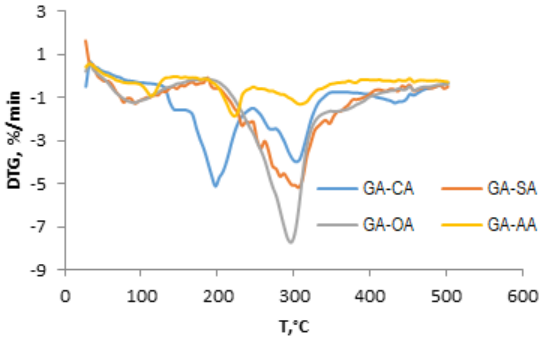


Fig. 9. Results of DTG analysis

The GA-CA sample begins to decompose at a temperature of (130 °C). During thermolysis, three peaks of different intensity (198, 304 and 432 °C) were noted on the DTG curve. The residue at the end of pyrolysis was 32%.

A completely different picture is demonstrated by the thermolysis of the GA-OA sample. Despite the lowest temperature of the onset of decomposition (98 °C), during the three-stage decomposition, the sample loses only about 20% of its initial weight, which may indicate high thermal stability.

The acceleration of thermal degradation can be quantitatively assessed by determining the apparent activation energy (E_a) for different stages of material degradation. The activation energies of different polymers were calculated using the Broido integral method [20]. The Broido equation has the form:

$$\ln\ln\left(\frac{1}{y}\right) = -\left(\frac{E_a}{R}\right)\cdot\frac{1}{T} + const \qquad (2)$$

where y is determined by the relation

$$y = \frac{(W_t - W_\infty)}{(W_0 - W_\infty)}.$$

W_t denotes the weight of the sample at any given time, and W_0 and W_∞ denote its initial and final weights, respectively. T is the absolute temperature recorded on the thermogram. The activation energy for each main stage of decomposition was estimated from the slope of lnln(1/y) versus 1/T, and the results are presented in Table 1. Based on the Ea values, the activation energy of thermal decomposition of the substances under study is:

GA-OA > GA-CA > GA-AA > GA-SA

Based on the Ea values, the highest activation energy for thermal degradation of the studied polysaccharides is shown by the GA-OA sample with a value of 295 kJ/mol, followed by the GA-CA sample and the GA-AA sample with values of 129 and 123 kJ/mol, respectively. The lowest activation energy is shown by the GA-SA sample. Thus, the modified polysaccharides exhibit different thermal behavior due to differences in structural and functional groups. For example, GA-OA exhibits the slowest degradation (high Ea value) with the formation of a large carbon residue at 500 °C (81%). In contrast, GA-SA and GA-AA show the lowest activation energy and similar thermal behavior.

The solubility of gum arabic derivatives with carboxyl acids is presented in the table 5.

The obtained data (Table 5) demonstrate a clear dependence of GA solubility on the nature of the modifying acid used. Modification with aliphatic dicarboxylic acids-succinic (GA-SA) and adipic (GA-AA)-did not result in significant changes in solubility compared to the original sample.

Table 5. Solubility of gum arabic samples in water at 25 °C

Sample	Modifying acid	Average solubility, g/100 ml
Initial GA	–	45.0±1.5*
GA-SA	Succinic	42.0±2.5
GA-AA	Adipic	40.5±2.0
GA-CA	Citric	15.5±1.5
GA-OA	Oxalic	8.5±1.0

In contrast, treatment of GA with citric and oxalic acids caused a significant decrease in solubility. The solubility of the GA-CA and GA-OA samples decreased to 15.5±1.5 and 8.5±1.0 g/100 ml, corresponding to a decrease of ~66% and ~81%, respectively. This significant effect is likely due to the ability of citric and oxalic acids to act as effective cross-linking agents due to their high functionality and acid strength, resulting in the formation of a dense polymer network with limited hydration and dissolution capacity. The observed trend indicates the potential of using oxalic and citric acids as modifiers to specifically reduce the solubility of GA, which can be used, for example, to create prolonged-release systems.

Conclusions

A series of modified gum arabic derivatives was successfully synthesized via esterification with polycarboxylic acids (citric, adipic, succinic, and oxalic). The effectiveness of the modification was unequivocally confirmed by elemental analysis, which showed a decrease in carbon content and an increase in oxygen content, and by FTIR spectroscopy, which revealed the appearance of characteristic absorption bands of ester bonds (C=O stretch at ~1720–1740 cm^{-1}).

X-ray phase analysis indicated that the chemical modification led to a further amorphization of the naturally amorphous gum arabic structure, with the most significant decrease in halo intensity observed for the citrate derivative. The absence of sharp crystalline peaks confirmed the purity of the products and the absence of unreacted acid crystals.

Gel permeation chromatography revealed a substantial increase in the weight-average molecular weight (M_w) and polydispersity index (PDI) of all modified samples compared to native gum arabic. The most significant increase in M_w was observed for the adipate (306.116 g/mol) and succinate (296.916 g/mol) derivatives, indicating effective polymer chain extension. The high PDI value (5.11) for the oxalate derivative suggests a predominance of cross-linking reactions.

Atomic force microscopy studies showed that the modified polymers form homogeneous, continuous films composed of agglomerated spherical particles. Phase contrast images revealed no foreign inclusions or phase separation, confirming the homogeneity of the products and the effectiveness of the washing procedure.

Thermal analysis demonstrated that modification significantly alters the thermal behavior of gum arabic. The oxalate derivative (GA-OA) exhibited exceptional thermal stability, with a residual mass of 80.73% at 500 °C and the highest activation energy for decomposition (295 kJ/mol), indicating its potential for high-temperature applications. The degradation mechanism and number of degradation stages varied depending on the acid used.

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Conflict of Interest
The authors of this work declare that they have no conflicts of interest.

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