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Aqueous polyurethane–alginate compositions: Peculiarities of behavior and performance

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Abstract

A series of polyurethane–alginate (APU/AG) compositions with pH/temperature-responsive character and regulated viscosity were obtained by adding different quantities of sodium alginate into an aqueous polyurethane anionic dispersion. Rheological, thermoresponsive, mechanical properties and swelling behavior dependencies on composition have been determined. APU/AG compositions reached equilibrium swelling and deswelling states within about 60 min. They display non-Newtonian flow and posses thixotropic properties. The strength of the films increases after their treatment with $CaCl_2$ at the expense of cross-linking of alginate with divalent calcium ions and of forming an alginate network.

Keywords: Polyurethane; Alginate; Compositions; Temperature-responsive

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1. Introduction

One of the main directions of modern polymer technology, along with the synthesis of new compounds, is the search for rational ways of using traditional polymers by means of creating new compositions. Polymer blending constitutes a most useful method for the improvement or modification of the properties of polymeric materials. Polymer blends have been the subject of study for decades. However, much less attention has been paid to blends of aqueous dispersions with natural polymers, such as polysaccharides. Environmental and legislative pressure has driven industry to concentrate on waterborne polymer based mixtures. Interest to polymer water dispersions is increasing due to their pollution-free status, high performance properties, and ease of tailoring materials to specific end user requirements. The interest to polysaccharides is based on their availability and water-soluble character. Systems obtained by mixing of polysaccharides and synthetic polymers are of particular significance because they can be used as biomedical and biodegradable materials in various fields of industry. We choose alginate with carboxylic acid groups because it is widely implemented as a gel-forming agent in food, pharmaceutical, cosmetic industries and in biotechnology [1–4]. Gels are formed by adding multicharged non-organic cations (Ca^{2+}, Ba^{2+}, Al^{3+}, etc.) into an aqueous sodium alginate solution [5]. These cations serve as linkagents by interaction with carboxylic groups of polysaccharides. As a result, alginate gels are physically cross-linked systems. Besides, alginates posses unique functional properties, such as

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thickening and jellification. When added into an aqueous solution, they swell and thicken the solution, increasing its viscosity. Solution viscosity and gel strength depend on temperature, pH and presence of metal cations.

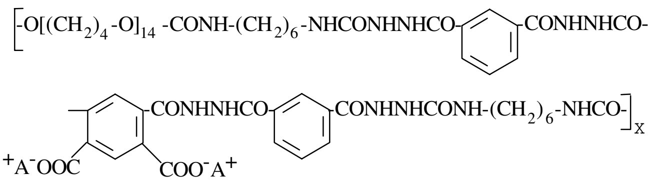
In this study, we prepared polyurethane/alginate gel compositions which were able to respond to both temperature, and pH variations, displayed high colloidal stability and mechanical properties and rapidly reached equilibrium swelling and deswelling states.

2. Experimental

2.1. Synthesis of anionic dispersion

Anionic water based polyurethane (APU) [6] was formed as a result of interaction of an isocyanate precursor on the basis of oligooxytetramethylene glycol (MM1000) and hexamethylenediizicyanate (1:2) with dianhydride of pyromellitic acid and dihydrazide of dicarbonic acid in acetone solution followed by carboxylic groups transfer to a salt form and consequtive dispersion in water.

Scheme of the elementary unit of APU:

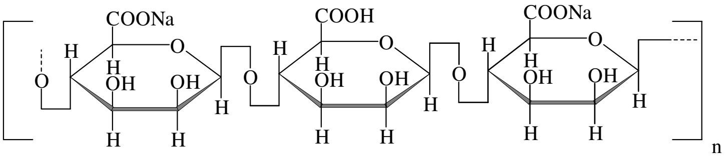


where A = K^+.

2.2. Alginate

Sodium alginate with mannuronate/guluronate residues ratio of 1; $M_w \sim 369{,}100$ g/mol was received from Aldrich Chem. Inc.

Schematic performance of AG unit



2.3. Preparation of APU/AG compositions

The APU (22.7 wt.%) and aqueous solution of alginate (sodium alginate solution with a concentration of 5 wt.% was prepared by stirring preliminary swollen sodium alginate in distilled water for 3 h) were mixed in various compositions (95/5, 90/10, 85/15, 80/20, 50/50 by weight). The sample films were cast by pouring the compositions on glass substrates, dried at room temperature for 72 h, and then dried at 60 °C to constant weight in a vacuum oven.

Gel compositions were prepared by cutting, dry films into squares with sides of $1.2 \times 1.2\ \mathrm{cm}^2$ and immersing them in 10 ml of $CaCl_2$ aqueous solution (0.5 wt.%). After shaking for 10 min at room temperature, gel compositions were washed in water and dried to constant weight at room temperature in a vacuum oven.

2.4. TGA measurements

Thermogravimetric analysis (TGA) was carried out using a Q-1000 derivatograph, (MOM, Budapest) under the following conditions: temperature range: 20–800 °C; average heating rate −10 °C/min; initial weight of samples: 100 mg; inert substance: Al_2O_3; medium: air (static), sample holder: a ceramic cone-like crucible.

2.5. Swelling properties

Swelling studies of APU/AG gel compositions were conducted as functions of time, temperature, and pH of swelling medium (water). The swelling ratio $[(W_s - W_d)/W_d]$ was defined as the weight of absorbed water per weight of dried gel composition, where W_s and W_d were the weight of the gel composition in the swelled and dry states, correspondingly. In order to determine the swelling ratio, pre-weighed dry samples were immersed in water. Then the excess water was removed with filter paper and the swelled samples were weighed. For swelling and deswelling kinetics studies, gel compositions swelled in water at 20 °C were weighed at fixed time intervals until the swelling ratio became constant.

2.6. Characterization

The mechanical properties were tested using a RM-30-1 test machine (a device constructed in Ivanovo Measure-works, Russia). The number of samples used in each mechanical measurement was three. Samples were prepared in a form of strips (width—4 mm, operating length—2 mm). Measurements were carried out in accordance with standard 14236–81; allowed error—3%. The viscosity was measured with a rotational Rheotest-2 viscometer, with a cylindrical measuring device, at room temperature. Particle sizes were determined from the turbidity spectrum using a FEK-56M Photoelectrocalorimeter, according to [7].

3. Results and discussion

3.1. Preparation of APU and APU/AG gel compositions

White opalescent dispersion of anionic polyurethane has been obtained by using APU synthesis. Particle size of APU is about 0.17 μm, the content of dry substance reaches 23%. APU possess a high stability, do not break down for years, and form a flexible transparent film with high mechanical characteristics.

During the preparation of gel compositions of APU and AG, each solution of AG and APU was mixed well. After film forming, the alginate was crosslinked with divalent calcium ions. Treatment of as-cast samples with $CaCl_2$ solution results in ionic cross-links between alginate and polyurethane chains, providing the formation of a three-dimensional network structure with linked molecules in the network units [8,9]. The strength of an alginate gel decreases with the reduction of the $CaCl_2$ concentration at time of gelation [10,11]. The highest gel strength was observed for equimolar concentration of Ca^{2+} [12]. Densely cross-linked hydrogels are formed when the guluronic sequence of the samples is rich and Na ions are fully converted to Ca ions. In our case we cannot estimate how much Ca^{2+} incorporates to the network, because we do not know the degree of conversion of COOH groups of alginate to COONA groups. Besides, before Ca^{2+} introduction there are ionic centers both in the polymer matrix, and the AG. After Ca^{2+} is added into the system, ionic type reactions of different nature and completeness occur. The complexes of α-L-guluronate with calcium served as network units, whereas the guluronate blocks in contrast to mannuronate displayed a high affinity to Ca^{2+}, which interacted with carboxylic groups of two neighboring chains. Due to folding conformation [13] of α-L-guluronate calcium cations were placed inside cavities. The structure formed by polysaccharide and cations is usually presented by the egg-cell model [14]. Molecules of APU are fixed between cross-linked alginate chains.

Table 1
Average particle size and pH value versus APU/AG compositions

Indexes	Sample, APU/AG (wt.%)						
	100/0	95/5	90/10	85/15	80/20	50/50	0/100
r, μm	0.17	0.18	0.17	0.18	0.18	0.17	–
pH	7.8	7.45	7.6	8.0	8.0	7.6	8.3

3.2. Colloid-chemical properties

Aqueous APU/AG compositions were characterized in terms of their pH value and particle size (Table 1).

The average particle size of compositions does not change much with composition variation, indicating an aggregative stability of the mixed systems. These systems are stable and do not separate into layers within six months. In case of anionic polyurethane dispersions, the stabilization arises solely from the ionized carboxylic groups; consequently, they are unstable at a low pH (i.e., below the pK_a of the stabilizing acid group). However, pH of APU/AG compositions does not significantly change with the increase of AG content.

3.3. Rheological properties

Most probably APU/AG systems (out of Ca^{2+}) present a mixtures of two polymers, in which a net of physical bonds occurred due to the adsorption of alginate molecules on the polyurethane globule surfaces. According to rheological data, aqueous 5% alginate solution displays the Newtonian flow; its viscosity insignificantly depends on shear stress.

The rheological behavior of compositions is typical for structural non-Newtonian liquids exhibiting thixotropic flow (Fig. 1).

The character of curves is not affected by the variation of AG content. The viscosity of APU/AG compositions depends on shear rate only at the initial stage, when γ is below 20 s^{-1}. Transition from Newtonian flow at low shear rates to unsteady flow occurs in the narrow area of stresses, so the range of γ, in which the viscosity anomaly is observed, is rather narrow. One of the reasons of viscosity anomaly of APU/AG compositions is thixotropy. A high viscosity at low shear rates manifests thixotropic flow. However, as the shear rates increase, the viscosity drops correspondingly until it reaches a low limiting value. When the shearing force is removed, the viscosity recovers, but not instantaneously. This phenomenon is conditioned by changes of the supramolecular structure

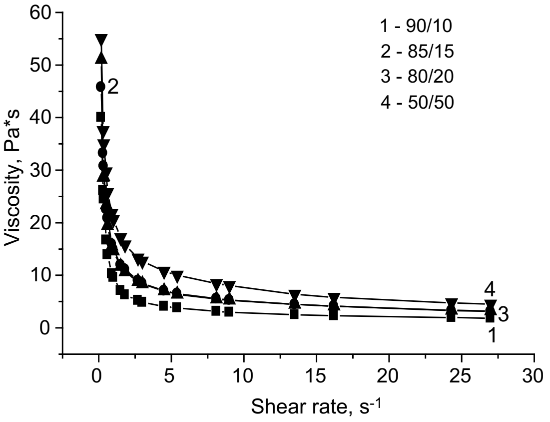


Fig. 1. Viscosity of APU/AG versus shear rate.

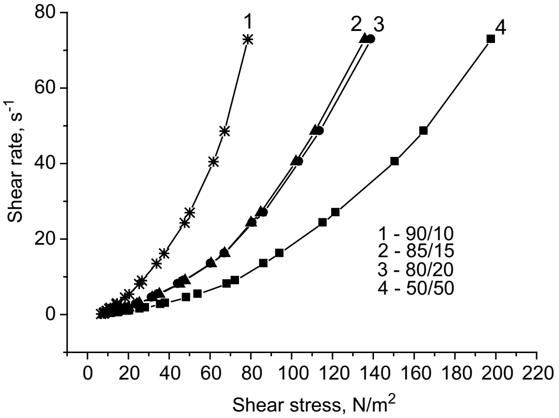


Fig. 2. Rheological curves of flow of APU/AG.

and macromolecule shape under stress and their recovery after the stress is eliminated. Viscosity values of APU/AG compositions are higher in comparison to that of initial components (Fig. 2). The higher the AG content the more viscous is the system. Alginate is widely used as a thickener for aqueous polymers and based systems. As has been shown previously, alginate acts as a thickener of anionic polyurethanes [15]. The thickening effect is connected with formation of colloid-structural hydrophilic covers that determine a viscous flow of thickened dispersion. During transition from structural-viscous to Newtonian flow (with the increase of shearing force), a desorption of thickener molecules from polyurethane globule surfaces is observed and aggregates are destroyed.

3.4. Thermal analysis

Thermal stabilities of APU, AG and APU/AG gel compositions were measured using TGA analysis. As shown in Fig. 3, thermal stability of gel compositions increases in comparison with alginate. This result may be due to the introduction of APU, which shows a higher initial thermal decomposition temperature of 173 °C, while AG displays decomposition at 60.5 °C, and also because of network formation after the films are treated with $CaCl_2$.

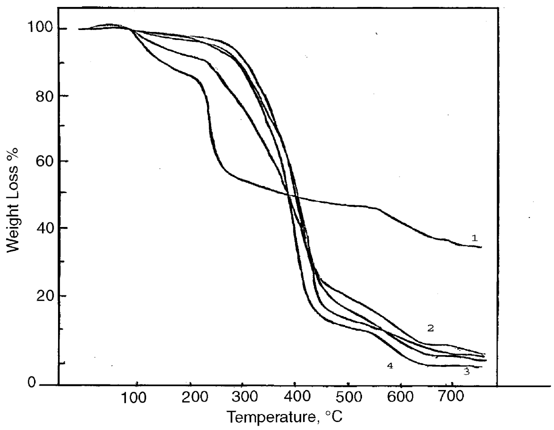


Fig. 3. Thermal gravimetric analysis of APU/AG gel compositions: 1—AG, 2—APU, 3—APU/AG 95/5, 4—APU/AG 85/15, 5—APU/AG 50/50.

The thermal decomposition process of all studied samples may be divided into three steps. The first one covers the temperature interval of about 52–268 °C and is characterized by a 5–10% samples weight loss. The process runs with the formation of decay products. The second stage of 238–460 °C is defined by a maximum decomposition rate between 318 and 341 °C with an exothermic peak in the temperature range of 250–300 °C. At this step the weight losses reach 70–80%. With temperatures above 250 °C, the evolving decay products fall to radicals that essentially increase the combustion rate. Besides heterolytic destruction, the process of deep homolytic decomposition of the main structure takes place at this step. The third stage after 420–460 °C is characterized by an intensive exothermic peak with a maximum in the region of 500–600 °C and by complete burning of carbonic residual [16].

3.5. Swelling–deswelling kinetics of gel compositions

Fig. 4 shows swelling kinetics of gel compositions and APU, treated with $CaCl_2$. Swelling ratio acquires an equilibrium swelling state within about 30 min. Rapid swelling kinetics of the samples is due to the fast and strong hydration of the alginate chain. The lower the alginate content in the system, the slower it reached equilibrium. Composition of APU/AG 50:50 acquires its equilibrium state in 15 min.

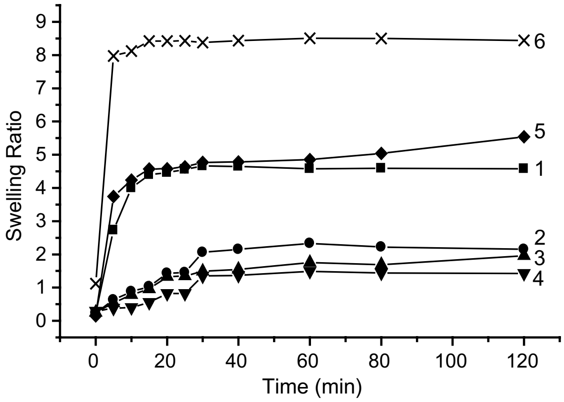


Fig. 4. Swelling kinetics of APU/AG gel compositions in water at 20 °C: 1—APU, 2—APU/AG 95/5, 3—APU/AG 90/10, 4—APU/AG 85/15, 5—APU/AG 80/20, 6—APU/AG 50/50.

The swelling ratio of gel compositions depends on the degree of cross-linking. The higher the ratio of alginate to APU, the higher the degree of cross-linking. As a result, APU/AG 50/50 has the highest swelling ratio, while samples APU/AG 95/5, 90/10, 85/15 exhibit lower swelling ratios depending on the amount of alginate for cross-linking. The swelling ratio of studied gels decreases with the increase of the AG content up to 15% and then it increases. The low values of swelling ratio of APU/AG 95/5, 90/10, 85/15 samples may be attributed to the compact complex structures due to the reaction of ionic exchange between carboxyl groups in alginate and salt groups in APU. If there is a small amount of AG component, the quantity of its carboxylic groups is comparable to the quantity of APU salt groups and the probability of compact complex formation is higher. It captures the hydrophilic groups and produces the tight and ionic bonded structures. Namely, the swelling ratio of APU/AG 95/5, 90/10, 85/15 series was influenced by the degree of complexation and physical cross-linking. It also should be pointed out, that in our case a lot of ion-exchange reactions with participation of COOH (AG), COO^-Na^+ (AG), COO^-K^+ (APU) and $CaCl_2$ are taking place. Besides, the ion–molecular interactions between carboxylate anions of AG and urethane groups of APU are very likely to be mostly realized at low AG concentrations. As a result the degree of physical cross-linking (due to ion–molecular interactions) increases up to some limit with AG introduction.

Fig. 5 shows the deswelling kinetics of gel compositions. The series exhibit a rapid deswelling and reach the equilibrium state within about 60 min. The sample of APU/AG 50/50 displays the drastic decrease of swelling ratio within 30 min, while samples with lower alginate content reach the equilibrium state faster.

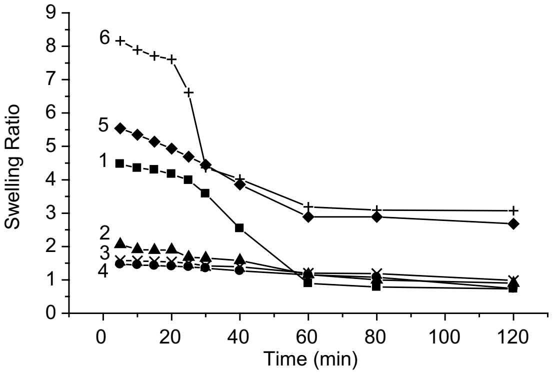


Fig. 5. Deswelling kinetics of APU/AG gel compositions in water at 20 °C: 1—APU, 2—APU/AG 95/5, 3—APU/AG 90/10, 4—APU/AG 85/15, 5—APU/AG 80/20, 6—APU/AG 50/50.

3.6. Responsive swelling behaviors

Temperature dependence of equilibrium swelling of APU/AG gel compositions is shown in Fig. 6. All the samples have significant changes in swelling ratio over the temperature range between 25 and 40 °C. APU/AG 50/50 displays the most drastic volume phase transition in comparison with APU/AG 20/20, and 95/5. This may be due to the temperature-responsive properties of crosslinked AG.

PH-sensitive characteristics of gel compositions were studied by swelling test with pH varying between 2 and 5. As shown in Fig. 7, the swelling ratio of APU/AG 50/50 continuously increased with the increase of pH values, because the carboxylic acid groups of AG and APU below pK_α values are in the COOH form. As pH of the solution increases, COOH becomes ionized (COO^-), and the resulting electrostatic repulsion causes the gel to swell.

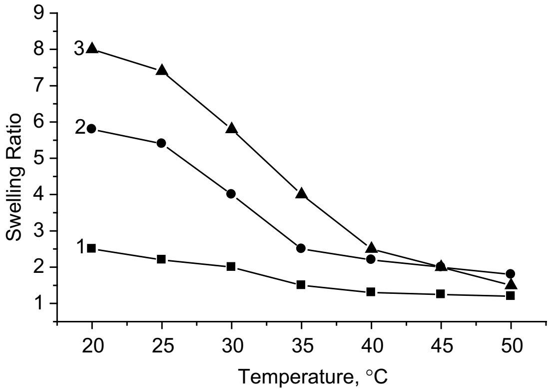


Fig. 6. Swelling ratio of: 1—APU/AG 95/5, 2—APU/AG 80/20, 3—APU/AG 50/50 gel compositions as a function of temperature in water.

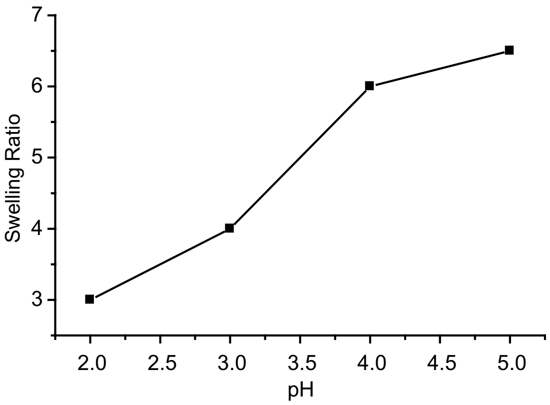


Fig. 7. pH-dependent swelling behavior of APU/AG 50/50 at 20 °C (0.01 N NaCl).

3.7. Mechanical properties of APU/AG gel compositions

The observed strength increase and elongation decrease of APU/AG films, treated with $CaCl_2$ (Fig. 8) is first of all connected with gel structure formation. The strength of gel films is determined by cross-linking agents (Ca^+) and by the AG content. Their increase promotes the increase of network density and assists in formation of a more rigid structure with high strength and, correspondingly, low elasticity indexes [9]. Besides, mechanical properties of gels depend on the proportion and length of the guluronate blocks in a given alginate chain [17]. The α (1–4) linkage of the guluronic acid residues introduces greater steric hindrance from the carboxyl groups and thus alginate chains with high mannuronic content are more flexible than guluronic. AG molecules at low $CaCl_2$ content turn out to be slightly cross-linked. The growth of the network density lowers the quantity of non-associated polysaccharide molecules and decreases the length of chain units between the cross-linked parts. It results in elimination of their mobility and transference in relation to each other, so the elasticity is lost. The tensile strength of the treated films is higher in comparison with untreated. The more AG in the system, the higher the film strength.

4. Conclusions

Polyurethane–alginate gel compositions with different component ratios based on an anionic polyurethane water dispersion and sodium alginate have been prepared by crosslinking with calcium ions. Obtained gels are physically cross-linked systems with mechanical properties dependent on the proportion and length of the alginate guluronate blocks and calcium ions quantity. Compositions reached the equilibrium swelling and deswelling states in a short time and displayed the fast response to temperature changes. The swelling ratio of gel compositions depends on the degree of crosslinking. The degree of gel compositions crosslinking increases with the ratio of alginate to APU. In the pH-sensitive swelling behavior, the swelling ratio of compositions increased continuously with the pH value. Thus, by adjusting the degree of crosslinking by varying the composition ratio and Ca^{2+} quantity, systems with controlled thermo- and pH-sensitivity, swelling ratio, and

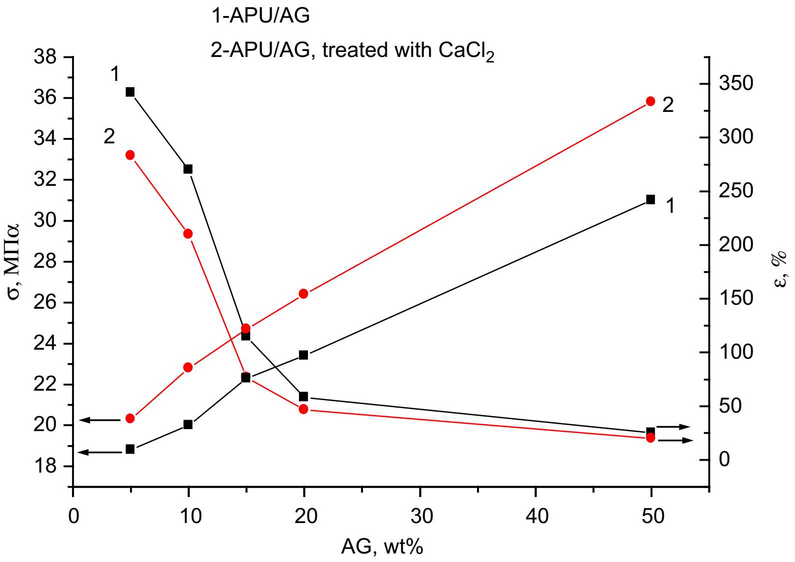


Fig. 8. Tensile strength and elongation at break point of APU/AG versus AG content.

strength indexes have been obtained. Mixtures of APU and AG in absence of divalent ions formed structural non-Newtonian stable systems with higher viscosity in comparison with initial components. APU/AG gel compositions could be promising materials for biomedical application and food industry.

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