

Aqueous Polyurethane Dispersions - Sodium Alginate Based Blends and Hydrogels

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Abstract: The film forming binary polyurethane-alginate blends and based hydrogels, containing different alginate content, were prepared by blending of anionic polyurethane dispersions (APD) and aqueous sodium alginate (SA) solution. Binary blends of APD and SA were cast in film form from mixed aqueous polymer solutions by solvent evaporation. Post-treatment of as-cast films with CaCl_2 led to the hydrogels formation. The thermal stability, thermal transition, water-swelling, mechanical properties and gas permeance for O_2 and CO_2 of two kinds of films were examined according to alginate content. Irrespective of composition, blend samples gave a single glass transition temperature (T_g), indicating the formation of thermodynamically miscible phase. The shift of T_g in hydrogels to the higher temperatures indicated the possible simultaneous occurrence of a chelate complexation of SA with Ca^{+2} cations, cross-links between polyurethane chains, having carboxylate anions, with Ca^{2+} cations, and interactions between SA and anionic polyurethane, resulting in the formation of a semi-interpenetrating network structure. The relationships between the films structure, their physicochemical properties and alginate content have been discussed.

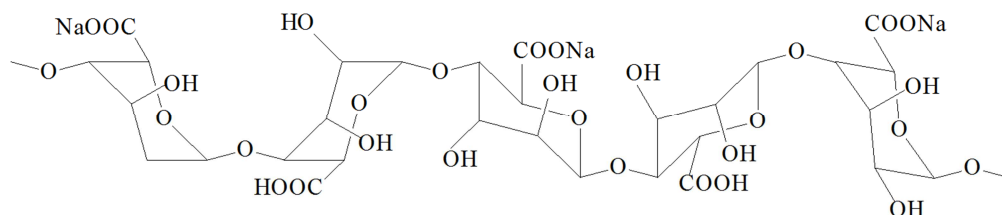
Keywords: Sodium Alginate, Polyurethane Ionomer, Hydrogels, Blended Films

1. Introduction

The growing urgency to develop novel renewable resources based products and innovative technologies that can reduce the dependence on fossil fuels and environmental pollution has turned considerable attention of scientists to green chemistry [1]. Biobased products provide the basis for sustainable and green materials able to compete with materials based on synthetic polymer. Alginate is known as easily available natural polymer with good biodegradability (naturally degraded by *Pseudomonas alginolyticus*) and low cost [2, 3]. It has been used in dietology, medicine, food packaging, pharmaceutical industry, biomedicine, etc. [4]. It can be combined with different synthetic polymers in order to exploit new polymer materials with required properties. Among widely used synthetic polymers polyurethanes occupy a special place due to their valuable properties and biocompatibility. The development of ecologically-friendly waterborne polyurethane formulations has been increased primarily due to the control of volatile organic compound

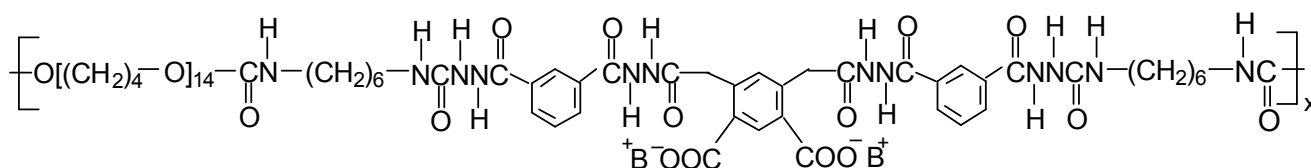
emission to atmosphere as well as to the superior properties presented by these resins in comparison to similar ones obtained in organic medium. Waterborne polyurethanes as nontoxic and nonflammable materials have been abundantly used as an environmental coatings, adhesives, etc. [5]; they are endowed not only with excellent mechanical properties, but also have a hydrolytic character, which makes them easy to degrade [6] and, therefore friendly to the environment. The presence of hydrophilic groups provides the miscibility between waterborne polyurethane and natural polysaccharides, including alginate. Therefore, it is possible to obtain polyurethane – alginate transient networks – polymer hydrogels in which the physical cross-links can be broken and recovered. Furthermore, polyurethane blends with natural polysaccharides are shown to be easily degraded by microorganisms [7, 8]. The results of alginate use for creation of pH/temperature-responsive polyurethane-alginate compositions with regulated viscosity [9] as well as for thickening of water based polyurethane [10] indicated the increase of mechanical strength, thermostability, and viscosity of thickened polymers in comparison with initial

polymer. The potentiality to use such polymers as binding, saturating and covering materials has been shown. This suggests that polymer blending is an important and simple method for modification or improvement of properties of both natural and synthetic polymers. It makes a chance to replace the endangered oil resources on available renewable raw materials and impart the polymer with new properties, namely, biodegradability. In this work we obtained the polyurethane - alginate blends and based hydrogels with adjustable properties and studied their structure-properties relationships depending on alginate content.



2.2. Preparation of Anionic Polyurethane Dispersion

Anionic water based polyurethane ionomer (PUI) was synthesized by a two-stage prepolymer method. On the first stage a prepolymer with terminal NCO groups was obtained using oligooxytetramethylene glycol (MM 1000) and hexamethyldiisocyanate taken in a molar ratio of 1:1.9. On



where $B=K^+$

2.3. Preparation of Polyurethane-Alginate Blends and Hydrogels

Polyurethane alginate blends (PUI/SA) were prepared by gentle mixing at room temperature of the polyurethane dispersion and the alginate solution in varying ratios. The resulting viscous solutions showed neither visible separation into layers nor any precipitation on standing. The relative composition of two polymers in the mixed solutions ranged from 95/5 – 50/50 in PUI/SA weight percent ratio. An appropriate amount of each blended solution was poured into a glass substrate and cast in the film form by solvent evaporation at room temperature for 72 h, and then dried at 60°C to constant weight in a vacuum oven. Intermolecular cross-links were introduced into the films by subjecting them to a post-treatment with calcium chloride: dried PUI/SA films were immersed into 0.5 wt% $CaCl_2$ aqueous solution. After shaking for 10 min at room temperature, formed hydrogels were washed in water to allow excess calcium to leach out and dried once again at 50°C to constant weight in a vacuo.

2.4. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements

2. Materials and Methods

2.1. Preparation of Alginate Solution

Sodium alginate (SA) solution was prepared at concentration of 4 wt% by dissolving powdered freeze-dried alginate, (Aldrich, weight average 380,000; fraction of G residues, 0.68) in deionised water vortex created by a magnetic stirrer for 60 min. Alginate solution was then stored at 4°C overnight before use to ensure the solution was homogeneous and free of bubbles.

the second stage, stoichiometric amount of isophthalic acid dihydrazide and pyromellitic acid dianhydride in a molar ratio of 0.35:0.70 was added to the reaction mass and this mixture was stirred for 2 hours at 60°C with subsequent transmission of carboxylic acid groups into a salt form and dispersing in water.

were performed on ca. 10 mg samples with a Model MDSC 2920 of TA Instruments, equipped with a DSC cooling can. The samples placed in aluminum pans with lids were first cooled to -150°C by means of liquid nitrogen and then heated at a rate of 5°C/min up to 200°C. All the measurements were performed under a nitrogen atmosphere.

2.5. Thermogravimetric Analysis

Thermogravimetric analysis (TG) 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.

2.6. Mechanical Properties

The mechanical properties of dried hydrogels were tested using the tensile machine FU-1000 (VEBMWK "FritzHeckert", Germany). The number of samples used in each mechanical measurement was 3. Samples were prepared in a form of strips (width – 4mm, operating length – 2 cm). Measurements were carried out in accordance with standard 14236-81 "Polymer films. Tensile strength test method"; allowed error – 3%.

2.7. Water Content

The water content (W_{H_2O} , wt%) in the gels was defined as the weight of absorbed water per weight of dried gels, $W_{H_2O} = [(W_w - W_d)/W_d] \times 100$, where W_w and W_d were the weight of the films in the wet and dry states, correspondingly. In order to determine the water content, pre-weighed dry samples were immersed in water. Then the excess water was removed with filter paper and the swelled samples were weighed.

2.8. Gas Permeance

Gas permeance was determined using gas analyser UL-B2P at 23°C, standards ASTM D1434, GB 1038, pressure 0.5 MPa

3. Results and Discussion

3.1. Thermogravimetric Analysis

The results of TG studies (Table 1) show, that thermal stability of treated with $CaCl_2$ PUI/SA films is higher as compared with initial films. As SA content increases the thermal stability of blended samples falls, while hydrogels exhibit higher thermal stability in the initial stage of decomposition. Thus, weight losses of sample PUI/SA (95/5) amount 5% and 10% at 235 and 291°C, correspondingly, while a hydrogels of the same composition loss 5% and 10% at 253 and 303°C, respectively.

Table 1. Thermogravimetric data of PUI/SA blends and hydrogels.

Mass loss temperature, °C												
The component ratio of PUI/SA, % in blended films and hydrogels(*)												
Mass loss, %	0/100	100/0	95/5	95/5*	90/10	90/10*	85/15	85/15*	80/20	80/20*	50/50	50/50*
5	84	240	235	253	223	235	222	235	220	242	135	147
10	120	320	291	303	278	287	269	289	250	263	220	229
50	260	400	403	410	400	407	397	408	400	407	405	410

Shift to the higher temperatures is a consequence of physical bonds network occurred in PUI/SA hydrogels: SA forms the network by means of Ca^{2+} bridges, while PUI forms a network of ion, intra- and intermolecular hydrogen bonds, including COOH groups of SA. Above 340°C the difference in the decomposition temperatures of the treated and untreated samples becomes smaller as a result of degradation of urethane groups generally forming the network of intra- and intermolecular bonds [11, 12].

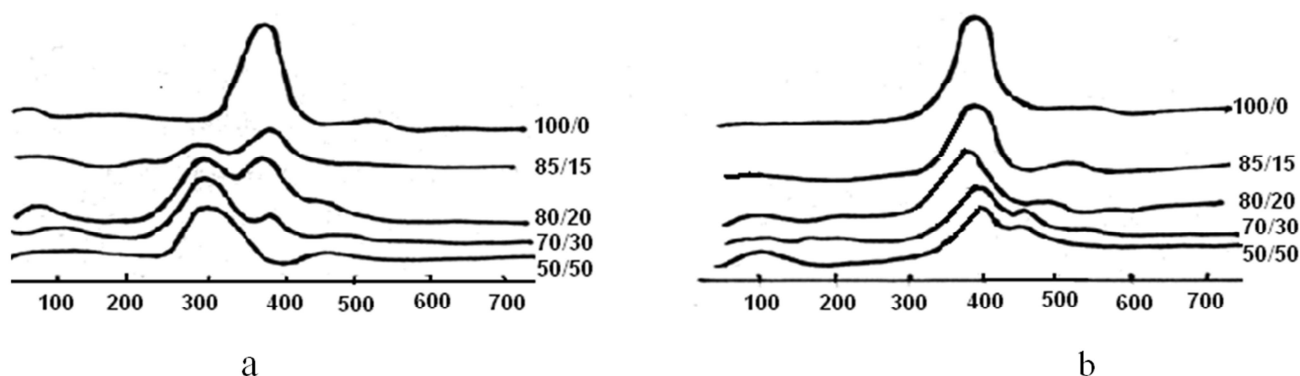


Figure 1. DTG curves of blended films (a) and hydrogels (b).

Regardless of the SA content there are two clear peaks observed in differential thermogravimetric (DTG) curves of blended films (Figure 1, a), whereas hydrogels (Figure 1, b) exhibit one large DTG peak indicating a unified mechanism of decomposition assuming the strong interaction between the two components of hydrogel.

3.2. DSC Results

DSC measurements were used to characterize PUI, SA and PUI/SA compositions, both untreated and treated with $CaCl_2$. Results are presented in Table 2, while Figure 2 illustrates heating scans of samples of the latter case. All samples containing PUI exhibit a clear baseline gap, absent on the SA scan and reflecting the glass transition in a temperature range

of -83°C - -71°C , which is characteristic of polyurethane component [13]. An endothermic effect in temperature interval of 75° - 150°C (with the peak of about 120°C) corresponds to the ability of hydrogels to hold a structured water [14]. This peak is most clearly expressed in alginate due to its hydrophilic character (Figure 2, curve 5). The increase of alginate content does not affect significantly the T_g of the blended films (Table 2), however, an additional treatment of as-cast samples with $CaCl_2$ increases their T_g . Lowering of the intensity of the α -transition at T_g , probably is the direct result of PUI content decrease in the composition. However, it should be noted that at SA content in the compositions more than 15 wt%, the effect of $CaCl_2$ becomes more evident and appears in intensive decrease of the α -transition value as the result of tightening of general structure

of composition. T_g of cross-linked samples is shifting systematically to higher temperatures with the increase of SA content (Figure 2). The endothermic peak of cross-linked samples is increased and shifted systematically to lower

temperatures with the increase of SA content (Figure 2). These changes in thermal transition behavior are probably owing to specific cross-linking reactions of the polymer components caused by films' post-treatment.

Table 2. DSC results: glass transition temperature and specific heat discontinuity.

Sample, PUI/SA (wt.%)		100/0	95/5	90/10	85/15	80/20	50/50	0/100
T_g (°C)	Blended films	-77.6	-77.9	-77.6	-77.5	-77.4	-77.8	-
	Hydrogels	-76.2	-75.7	-75.3	-75.0	-74.5	-73.0	-
ΔC_p (J/g°C)	Blended films	0.41	0.40	0.38	0.39	0.38	0.27	-
	Hydrogels	0.40	0.38	0.36	0.34	0.30	0.21	-

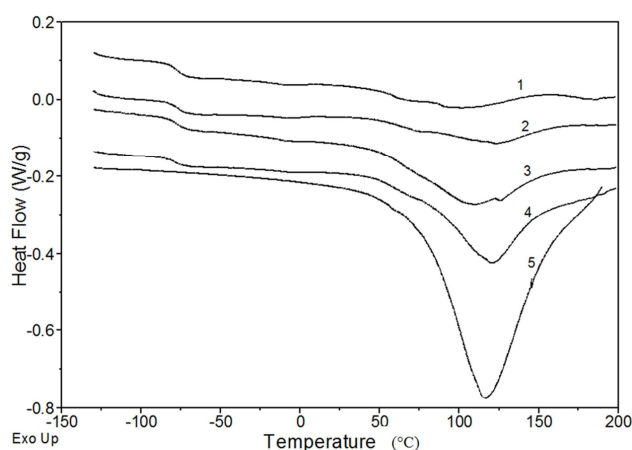


Figure 2. DSC scans of PUI/SA hydrogels: 1 – PUI, 2 – PUI/SA 90/10, 3 – PUI/SA 80/20, 4 – PUI/SA 50/50, 5 – SA. (All data are plotted on the same relative scale but the curves are shifted vertically for clarity).

Treatment PUI/SA samples with CaCl_2 provides the occurrence of three simultaneous cross-linking reactions. Alginate is known to be readily cross-linked in the presence of divalent metallic ions by chelate complexation between carboxylate anions and the metal cations [15]. In one's turn, PUI under the influence of CaCl_2 can form a network through complex formation, reactions of electrostatic interaction of ionic centers, as well as by internal and external hydrogen bonds between the functional groups of the PUI and SA.

It should be noted the only single, composition dependent T_g for all binary samples (Table 2, Figure 2), indicating the compatibility of the components and the formation of mixed amorphous microphase in which an interpenetration of the

components has been observed [16]. The specific heat discontinuity decreases in hydrogels with the increase of SA content as a result of immobilization of oligoether microphase fraction because of intermolecular interactions of PUI and SA. The results have shown that the increase of alginate component and, consequently, degree of cross-linking produces an increase in the glass transition temperature and a more homogeneous morphology.

3.3. Mechanical Properties

Tensile strength and breaking elongation dependencies on the SA content are shown in Table 3. The tensile strength of the films increases with the increase of SA content for both blended films and hydrogels. The maximum value of tensile strength (36.5 MPa for hydrogel) is observed at 50% of SA content. The increase of SA and Ca^{2+} cations content leads to a higher cross-linking degree and to the more rough structure. The growth of network density reduces the quantity of free polysaccharide molecules and lowers the chain units' length between the linkages. It results in elimination of their mobility in relation to each other, and consequently in the decrease of breaking elongation. Thus, the higher the SA content in the films, the lower the breaking elongation. Though the gel is formed by rather steady cross-linkages of polysaccharide molecules with calcium cations, their quantity is essentially less in comparison with the number of physical bonds. Therefore the structure of PUI/SA hydrogels should be related to weakly cross-linked ones with low network density.

Table 3. Dependence of tensile strength (σ) and elongation at break point (ϵ) of blended (bl) PUI/SA and hydrogels (hg) on SA content.

SA, wt. %	5		10		15		20		50	
	bl	hg	bl	hg	bl	hg	bl	hg	bl	hg
σ , MPa	15.8	20.5	17.6	23.8	18.0	27.6	20.0	29.0	24.3	36.5
ϵ , %	350	280	275	201	150	75	100	50	75	25

3.4. Effect of Alginate Content on Water Uptake

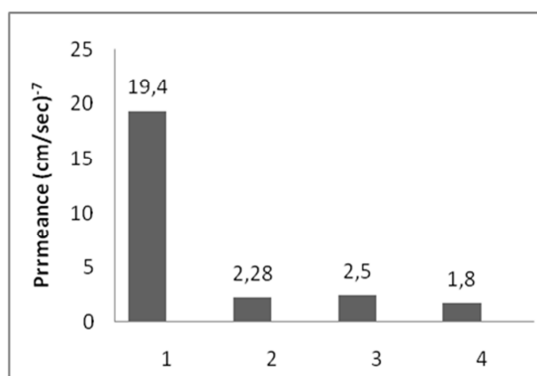
The effect of SA content on the absorbed water for PUI/SA hydrogels is shown in Figure 3. With the increase of SA content, the degree of water uptake of the cross-linked films

increases. During the crosslinking of SA with calcium chloride, SA formed a network through Ca^{2+} bridges, PUI penetrates into the SA - Ca^{2+} network and forms a structure of semi-IPN. The higher the alginate content in the system, the more Ca^{2+} it includes [17]. The increase of charged

groups' content results in growth of network density. The most essential growth of water uptake was observed at small SA content. The high ability of weakly cross-linked gels to swell is firstly connected with the existence of effective repulsion between charged gel units. Most often it is caused by the strutting off osmotic pressure of mobile counter-ions, enclosed in gel. That is why the main effect is observed at a small alginate and, consequently, charged units content (up to 15%), when the contribution of Coulomb repulsion between the likely charged units is absent due to a large distance between them.

3.5. Gas Permeance

With the addition of SA both samples (blended and hydrogels) presented significant reduction of permeances for gases O_2 and CO_2 (Figure 4 a,b). In comparison with the commercial polylactide (PLA) known as biodegradable, biocompatible aliphatic polyester of natural origin widely used for biodegradable packaging, personal hygiene



products, surgical sutures, implants, both blended samples and hydrogels exhibit comparable permeance (the same order of size) and this perhaps means that materials with possible commercial potential have been developed.

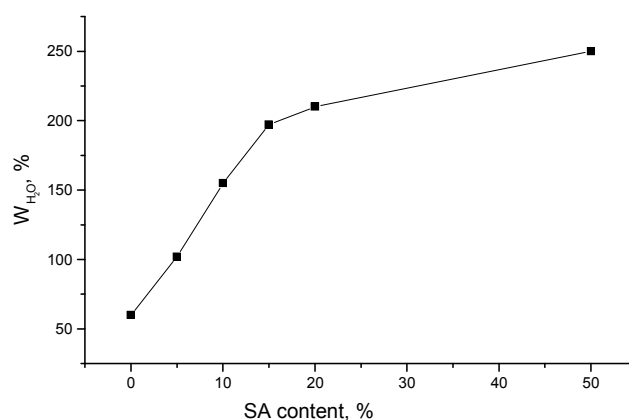


Figure 3. Effect of sodium alginate content on the water uptake of the PUI/SA gels.

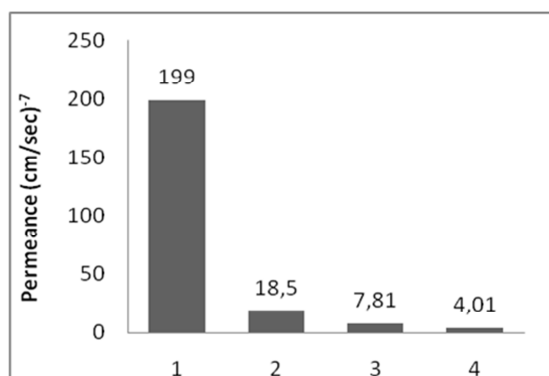


Figure 4. Permeance of O_2 (a) and CO_2 (b) of the PUI (1), PUI/SA 50/50 blend (2), PUI/SA 50/50hydrogel (3) in comparison with the PLA (4).

Such reduction of the permeance is the result of cross-linking phenomena of calcium ions between the polymeric and polysaccharide chains. This cross-linking was evident and it appears that, contrary to the results for the O_2 gas, where the treatment with $CaCl_2$ has no noticeable effects, the permeance for CO_2 was significantly decreased due to calcium cross-linking. This indicates that the average length of the gas molecules' leap or jump decreased significantly and this resulted in a corresponding reduction of permeance. The cross-linking phenomenon assists the packing of the macromolecular chains, while at the same time the plasticization caused by CO_2 through its interaction with the macromolecules (dissolution - diffusion) has been observed. In any case however, for the studied samples the permeance was significantly higher for the CO_2 as compared to the O_2 . This comes as a direct indication of the explicit alleviation of the CO_2 plasticization effect by means of the samples' treatment with the $CaCl_2$ solution.

4. Conclusions

Binary blended films composed of carbohydrate sodium

alginate and anionic polyurethane were prepared from mixed aqueous polymer solutions by solvent evaporation. By post-treatment of as-cast samples with calcium chloride, presumably, three kinds of polymer networks were introduced into the blended films: one is based on cross-linking between alginate chains and Ca^{2+} ions, while the second on the cross-linking of polyurethane chains having carboxylate anions with Ca^{2+} ions and the third one – due interactions between sodium alginate and anionic polyurethane. On the basis of the observations of a single, weakly composition-dependent T_g and its shift to the higher temperatures in cross-linked samples with increasing of alginate content, it is reasonable to conclude that the polyurethane and alginate form a thermodynamically miscible phase in their blends, without giving rise to a definite phase-separation. The physical properties of gels can be modulated over a broad range by altering the alginate content and calcium concentration. Mechanical properties and thermal stability of the blend films were improved by cross-linking. The swelling degree of the cross-linked films increased with the increase of sodium alginate content, suggesting that the cross-linked films have potential

application for water storage materials with good thermal and mechanical properties. Both blended samples and hydrogels exhibit comparable with commercial PLA permeance (the same order of size) for O₂ and CO₂ that provide them with possible potential as films for packages.

References

- [1] Anastas P., & Warner J. (1998). *Green Chemistry: Theory and Practice*. London: Oxford University Press;144 p.
- [2] Comaposada, J., Gou, P., Marcos,B., & Arnau, J. (2015). Physical properties of sodium alginate solutions and edible wet calcium alginate coatings. *LWT - Food Science and Technology*, 64, Issue 1, 212-219.
- [3] Wallen, L. L., Stodola, F. H., & Jacson, R. W. (1959). Type reactions in fermentation chemistry. ARS-71-13. *Agricultural Research Service*. US Department of Agriculture. May.
- [4] Sellimi, S., Younes, I., Ayed H. B., Maalej, H., Montero, V., Rinaudo, M., Dahia, M., Mechichi, T., Hajji, M., & Nasri M. (2015). Structural, physicochemical and antioxidant properties of sodium alginate isolated from a Tunisian brown seaweed. *International Journal of Biological Macromolecules*, 72, 1358-1367.
- [5] Xing Zhou, Yan Li, Changqing Fang, Shujuan Li, Youliang Cheng, Wanqing Lei, & Xiangjie Meng (2015). Recent Advances in Synthesis of Waterborne Polyurethane and Their Application in Water-based Ink. *Journal of Materials Science & Technology*, 31, 7, 708-722.
- [6] Gary T. Howard. (2002) Biodegradation of polyurethane. *International Biodeterioration & Biodegradation*, 49, 4, 245-252.
- [7] Khalid, M. Zia, F. Zia, M. Zuber, S., Rehman, & Mirza N. Ahmad. (2015). Alginate based polyurethanes: A review of recent advances and perspective. *International Journal of Biological Macromolecules*, 79, 377-387.
- [8] Travinskaya, T., Savelyev, Yu., & Mishchuk E. (2014). Waterborne polyurethane based starch containing materials: Preparation, properties and study of degradability. *Polymer Degradation and Stability Journ.* 101, 102-108.
- [9] Travinskaya, T. V., Savelyev Yu. V. (2006). Aqueous polyurethane-alginate compositions: Peculiarities of behaviour and performance. *European Polymer Journal*, 42, 388-394.
- [10] Sukhorukova, S., Travinskaya, T., & Chumak L. (1988). Influence of waterborne polymers on rheological properties of anion-active polyurethane latexes. *Plasticheskie massy*, 10, 23-24, (in Russian).
- [11] Herrera, M., Matuschek, G., & Kettrup A. (2002). Thermal decomposition of thermoplastic polyurethane elastomers (TPU) based on MDI. *Polym.Degr.Stab.* 78, 2, 323-331.
- [12] Lattimer R. P., & Williams R. C (2002). Low-temperature pyrolysis products from a polyether-based urethane. *J.Analyt.Appl.Pyrol.* 63, 1, 85-104.
- [13] Petrovic, Z. S., Javni I., & Divjakovic, V. (1998). Structure and physical properties of segmented polyurethane elastomers containing chemical crosslinks in the hard segment, *Journal of polymer science, Part B, Polymer. Physics*, 36, 221-235.
- [14] Xiao, C. B., Gao, S. J., & Zhang, L. N. (2000). Blend films from konjac glucomannan and sodium alginate solutions and their preservative effect. *J.Appl.Pol.Sci.*, 77, 3, 617-626.
- [15] Schipunov Yu. A., Koneva E. L., & Postnova I. V. (2002). Homogeneous alginate gels: phase behavior and rheological properties. *Vysokomoleculiarnye soedinenia A*, 44, 7, 1201-1211 (in Russian).
- [16] Demi, H., Barikani, M., & Barmar M. (2013). Compatible compositions based on aqueous polyurethane dispersions and sodium alginate. *Carbohydrate Polymers*, 92, 1, 490-496.
- [17] Wang, J., Ying, X., Li X., & Zhang, W. (2014). Preparation, characterization and swelling behaviors of polyurethane-grafted calcium alginate hydrogels. *Materials Letters*, 126, 263-266.