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Effect of rheological properties of composition based on modified starch on film formation

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This study investigated the use of carboxymethylated corn starch with sodium alginate for films preparation. The rheological properties as well as water absorption and mechanical properties of aqueous solutions and films of corn starch, carboxymethylated starch, sodium alginate and mixtures of starch and sodium alginate were studied. It was found that application of modified starch allows obtaining of water resistant films characterized by better physical-mechanical properties comparatively to the corn starch based films. It was found that mechanical strength of the formed films is due to the fact that alginate and carboxymethylated corn starch are hydrocolloids with an unbranched structure. This composition is characterized by stronger structure gels and higher viscosity of the solutions.

1. Introduction

Recently, in the field of medicinal preparations, obtaining of additional therapeutic properties by introducing other polymeric material in dressing systems became very popular [1, 2].

The ideal polymer coating for wounds and burns should be characterized by the following properties: protective (prevents the penetration of infection from the outside, prevents from external mechanical injury), absorptive and healing (coatings should block the development of infection in the wound, have anesthetic and hemostatic effects, and stimulate healing of wounds).

Classic polymers that are widely used in medicine as the main component of dressing agents are cellulose and other derivatives of polysaccharides. At the same time, the greatest interest are protective coatings based on natural hydrocolloids (agar-agar, pectin, carrageenan, starch, cellulose and alginates) [3].

Currently, among the new wound bandages, composite materials predominate and are used in the form of gels, films and applied by the method of "printing" on the textile basis of plaster [4].

Polymers that have antimicrobial properties represent a valuable alternative to conventional antibiotics and is currently gaining interest in coatings, personal care, active food packaging, and biomedical applications. Typical antimicrobial agents used with polymers are organic or inorganic acids, metals, alcohols, ammonium compounds or amines. However, due to the low molecular weight of these antimicrobial agents, their retention capacity has been reported to be poor causing them to leach out when applied directly to a substrate or polymer system, thereby inhibiting their antimicrobial performance. The interest in starch as an antimicrobial agent carrier is accrued from its film-forming properties, and high molecular weight.

Native starch is hydrophilic in nature, insoluble in water at room temperature. Furthermore, it cannot be melt-processed as it degrades under relatively low temperature and lacks mechanical integrity. These shortcomings have limited its use for polymer applications requiring mechanical strength and thermal stability, especially in the plastic industry where starch should be melt processed in most cases. Also, the poor solubility of starch in cold water limits its potential applications.

Thus, starch modification is desirable not only to mitigate these challenges but also to bring about other functional properties. Some of the properties that can be achieved via starch modification include thermal stability, hydrophobicity, amphiphilicity, paste clarity, mechanical strength, freeze-thaw stability and others [5-10]. Several starch modification processes are reported in literature including, physical processes [11, 12], chemical modifications [13–16], and enzymatic approaches [17–19] or their combinations.

This work aimed to study the possibility of using polysaccharides to develop a film having healing properties by casting the mixture of biopolymers: sodium alginate and carboxymethylated corn starch.

2. Materials and methods

2.1. Materials

All materials were supplied at Sigma Aldrich as following grades: Corn starch (CAS 9005-25-8), sodium alginate (CAS 9005-38-3), chloroacetic acid (CAS 79-11-8), acetic acid (CAS 64-19-7), sodium hydroxide (CAS 1310-73-2), and glycerol (CAS 56-81-5).

2.2. Preparation of carboxymethylated (modified) starch (Na-CS)

Composition recipe, %
Corn starch 13.7
Water ………………….. 76.6
Chloroacetic acid 3.1
Sodium hydroxide ……….6.6

Corn starch had been dissolved in deionized water to a milk-like state, afterwards, pre-dissolved in water chloroacetic acid was added. After stirring, sodium hydroxide was added as 40 % solution. Synthesis was carried out at 50-60 °C for 30 minutes. After cooling down to 20 °C, the viscous solution was neutralized by 30 % acetic acid to pH 8.

2.3. Film formation

Films were produced by casting method of the colloidal solution. The resulting mixture has the appearance of a viscous solution, which was applied onto the glass plate. Then the samples were further dried at 40-50 ºC, after, were thermostabilized at 90-110 °C.

2.4. Rheological properties

The rheological properties of the samples were performed on the rheometer "Brookfield" DV-III (USA) using a thermoplatform block with a temperature range of 23-25 ^{o}C.

2.5. Water absorption

For the study of water absorption samples 10×10 mm having 1 mm thickness we prepared, they were weighed to an accuracy of 0.0001 g. Measurements were made after a certain period of time (10, 20, 30, 40 minutes). Water absorption of the sample, X (%), was calculated by the formula:

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$$X = (m - m_o) / m_o \cdot 100\% \qquad (1)$$

where: m - mass of the sample at a certain time of stay in water, g;
m_o - mass of the dry specimen, g.

2.6. Mechanical properties

Tensile strength and elongation at break were determined by the ASTM D882-18, Standard Test Method for Tensile Properties of Thin Plastic Sheeting [20] at a humidity of 45%, 65%, 80%.

3. Results and discussion

In this work, the effect of the addition of starch and modified starch on the viscosity of sodium alginate was studied, the influence on the mechanical properties of films at 45%, 65%, and 80% humidity was determined and the water absorption of films based on the composition of biopolymers was determined. Concentrations were adjusted as well as ratios for sodium alginate and modified starch in compositions (table 1). The glycerin as plasticizer was used in order to improve the mechanical properties (elasticity) of the films.

Typically, for preparing of the compositions, 10-15 % aqueous solutions of polysaccharides are used. Studies of the low concentration solutions (3-7 %) are required for better understanding of the mechanism of changing of the starch viscosity by different shear stresses. Significance of the flow index of the two-component system (starch-sodium alginate, modified starch-sodium alginate) are within the range of 0.303-0.445 by the Ostwald-de-Waele equation.

Table 1. Composition of films based on starch and Na-CS with sodium alginate, %*

Sodium alginate	Corn starch	Na-CS
7.5	2.5	–
7.5	–	2.5
5.0	5.0	–
5.0	–	5.0
2.5	7.5	–
2.5	–	7.5
10	–	–
–	10	–
–	–	10

*Note: Deionized water, % - 88; Glycerol, % - 2.

The rheological properties of the material were determined by parameters of temperature, pressure, stress or shear rate using a rheometer. The obtained results (fig 1.) are used to assess the storage stability of the substance, melting temperature, solidification temperature, shear stability, molecular weight, quality of production, chemical, mechanical and thermal processing of this material.

It was found that the composition based on the studied polysaccharide refers to structured systems with anomalously viscous properties, i.e. when increasing shear stress, the effective viscosity decreases: the viscosity of such composition in the coordinates $\eta = f(\gamma)$ obeys a power law and is described by the Ostwald-de-Waele equation. The values of the flow index of the two-component compositions are in the range of 0.29-0.45 and have a complex of properties predicting the possibility of their effective use for the production of films by casting.

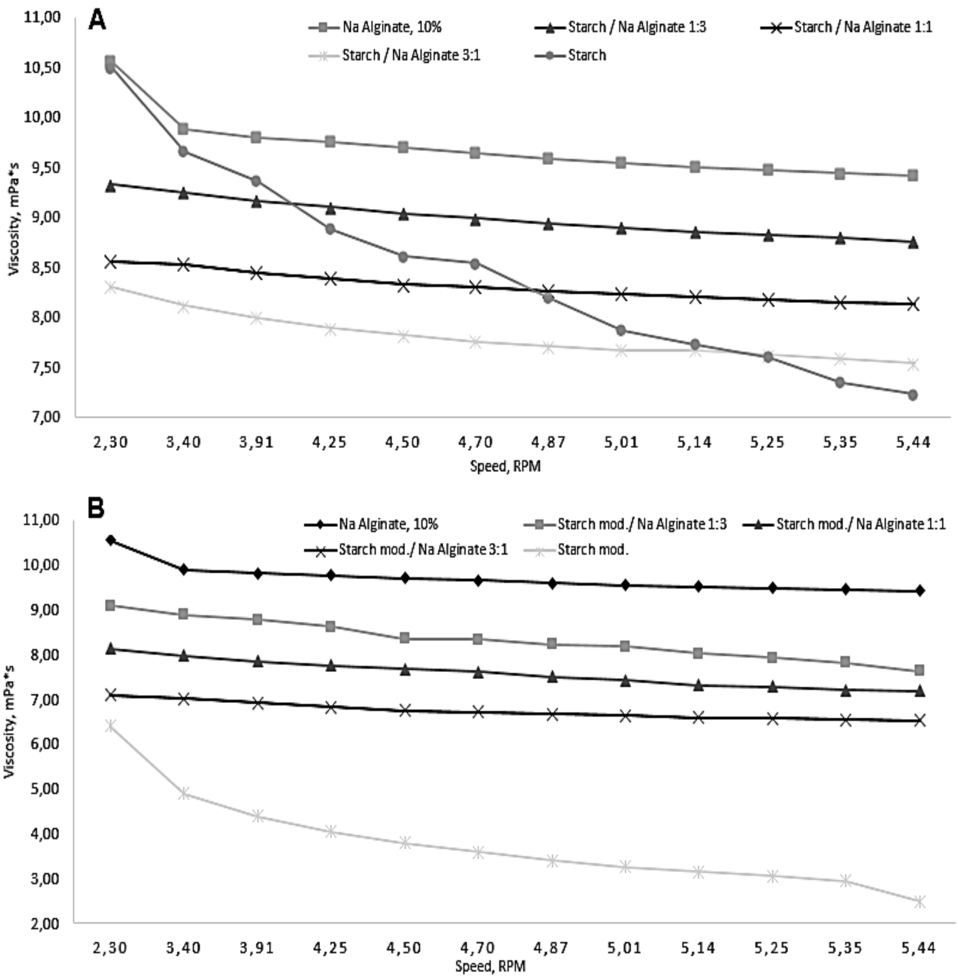

Fig.1 Dependence of changes of the viscosity of aqueous solutions on the content of starch (A) or Na-CM (B) in composition with sodium alginate.

It has been found that films containing carboxymethylated corn starch and sodium alginate show higher mechanical characteristics (fig.2) at 65% humidity, for the sample Starch mod./Sodium Alginate-1:1 stress ups to 2.0 N/mm^2, but it is less elastic. If the main indicator for the film is elasticity, then films based on starch are better than modified starch. However, films containing 3 vol. mass of carboxymethylated corn starch has an average strength of 2.1 N/mm^2 and elasticity up to 45%, which is the precursion case for the following studies determining water absorption of films and stability to their dissolution.

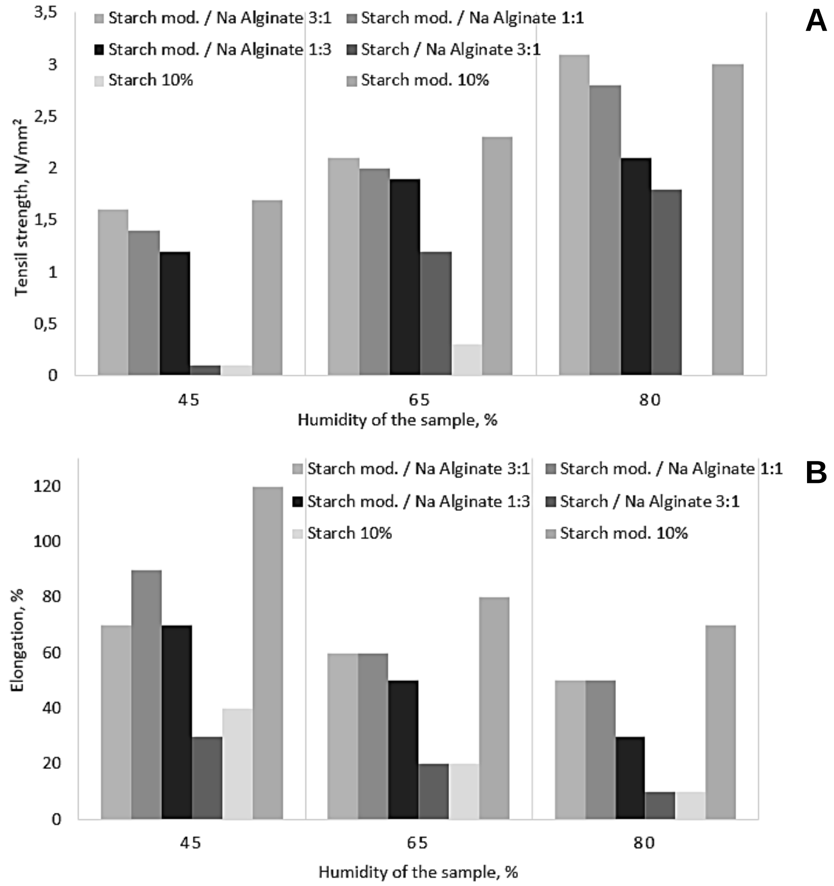

Fig. 2 Physical and mechanical properties (A – tensile strength; B – elongation) of films depending on humidity

The mechanical strength of the formed films is due the fact that alginate and carboxymethylated corn starch are hydrocolloids with an unbranched structure. This composition is characterized by stronger structure gels and higher viscosity of the solutions. The partial association of alginate and modified starch molecules results the homogeneity of the structure. Association of molecules and colloidal particles occurs due to the electrostatic interaction of charged groups, groups with high electron density, by the formation of so-called "chemical bridges" between the molecules and, also, due to the mechanical involvement of molecules. The addition of glycerol had led to an increase of the elasticity of the film but, at the same time, there was some increase of strength.

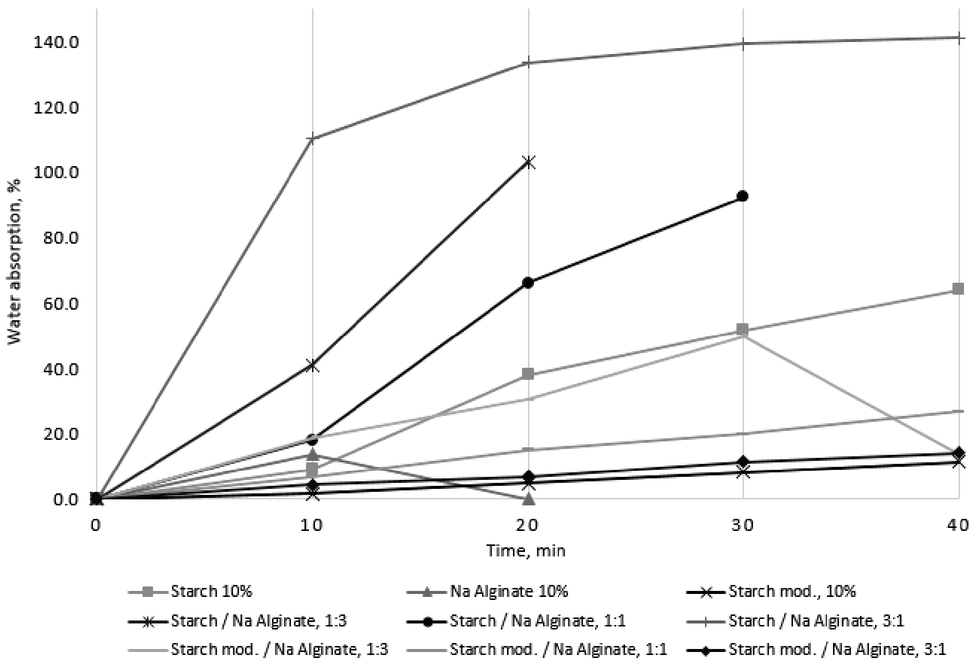

Fig.3 Dependence of water absorption of samples on the content of starch in the films

The films (fig.3) based on the pure sodium alginate and with ratio Starch mod./Sodium Alginate-1:3 are not water resistant and dissolve in 15 minutes. Films based on pure corn starch show greater water absorption, but also are not resistant to water solubility, films based on carboxymethylated corn starch show uniform swelling in water, indicating their resistance to water. Since carboxymethylated corn starch films has shown greater resistance to water solubility, this allows to develop the possibility of obtaining compositions with adjustable properties, namely prolonged water solubility.

4. Conclusions

Films based on a mixture of sodium alginate, modified starch and glycerine have the best physical and mechanical properties comparing with the starch based films. Rheological studies have shown that the values of the flow index of the two-component compositions are in the range of 0.29-0.45, and the compositions have a complex of properties predicting the possibility of their effective use for the production of films by casting method.

The addition of modified starch led to an increase of water absorption resistance of films based on sodium alginate up to 20-50% and prolonged their dissolving in time. The tensile strength of the films varies from 1.3 to 3.1 N/mm^2 and elongation varies from 30 to 130%. Thus, the use of sodium alginate in a mixture with carboxymethylated starch and glycerol has sufficient real prospects for further studies of the films and improvement of the films properties.

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