Structure and Physical–Mechanical Properties of Interpolymeric Complexes Based on Sodium Carboxymethylcellulose

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ABSTRACT: The structure and physical–mechanical properties of films of interpolymeric complexes (IPCs) based on sodium carboxymethylcellulose (Na-CMC) with urea–formaldehyde oligomers (UFOs) of different structure are studied in this article. It is shown that films of IPC have higher rate of deformative–strength properties and elasticity, minimal rate of solutions' viscosity with equimolar proportion of components of Na-CMC and UFO. The excess of Na-CMC or UFO causes the decrease of strength and elasticity which in turn is connected with decreasing of intermolecular links frequency. The decreasing of IPC elasticity with excess of Na-CMC or UFO is connected with creation of heterogenic structures, which can be seen in electronic microscope images. As a result, there were obtained films of IPC with various concentrations of triazinon cycle, which have a globular structure with different values of diameters (from 200 to 500 é), mechanical strength (80–140 MPa), modulus of elasticity (from 3×10^3 to 3.8×10^3 MPa), and the viscosity of solutions with a value in the range from 0.16 to 0.20 Pa s. Changing the structure of the interacting components gives the possibility to control substantially structure and properties of IPC based on Na-CMC and UFO. Regulation of physical–mechanical properties of the IPC films provides numerous opportunities for their applications as soil conditioners in agriculture and as a base for semisolid medicinal forms in pharmacy. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1749–1757, 2011

Key words: interpolymer complexes; structure; physical–mechanical properties; sodium carboxymethylcellulose; urea–formaldehyde oligomers

INTRODUCTION

Interpolymer complexes (IPCs) are promising products in the pharmaceutics[1–6] and are increasingly used as thickeners and stabilizers of suspensions', prolongator of drugs, film-forming capsules and tablets, and as a basis for ointments and other forms of soft drugs, since they exhibit several unique and most valuable properties.[6]

IPC is a product of interaction of chemically complementary macromolecules—polyanions and polycations or donors and acceptors of protons. In contrast to conventional chemical reactions between low molecular weight substances, the interaction between macromolecules is cooperative in nature. The emergence of communication links between complementary strands, the strength of which coincides with the strength of the relevant links between small molecules, greatly facilitates the subsequent formation of interpolymeric contacts. It provides an exceptionally high stability of IPC, even under the condition that the free energy of formation of a unified communications is not so big.[6]

IPC is divided into two groups—the stoichiometric IPCs (SIPCs) in which chemically complementary units are included in the equimolar (1 : 1) ratio of the components [Scheme 1(a)] and nonstoichiometric IPCs (NIPCs) containing an excess of one component [Scheme 1(b)].[1,7–12] In the structure of IPC, it is possible to identify uniformly related sites created with each other (section A), the defective areas that are not related to each other (section B), and excess IPC (section C).

It is interesting to note that the particles of IPC have colloidal properties, the analog of protein structures, the most typical of which are the charge, hydrogel structure controlled by the permeability of water and the solution comprising the components of body fluids.[12] The consequence is an unusually good IPC biocompatibility and hemocompatibility.

These features of the structure and properties of IPC offer ample opportunities to use them in different practice areas, including pharmacy.

Macromolecular complexes based on sodium carboxymethylcellulose (Na-CMC) (polyanion) and synthetic urea–formaldehyde oligomers (UFOs) and

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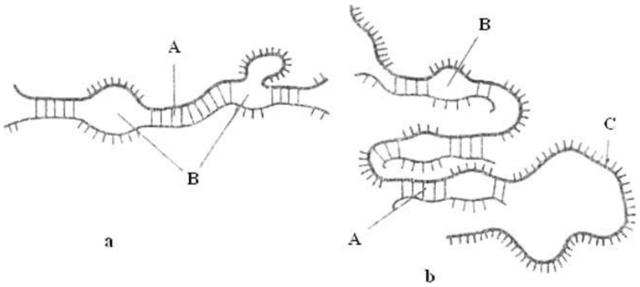


Scheme 1 Schematic representation of the structure SIPC (a) and NIPC (b).

linear cyclochain structure (polycations) are very interesting and promising in this aspect.

In this regard, this work studied the structure and properties of the IPC obtained on the basis of Na-CMC with UFOs of different structures by varying the ratio of interacting components and depending on the pH of the medium.

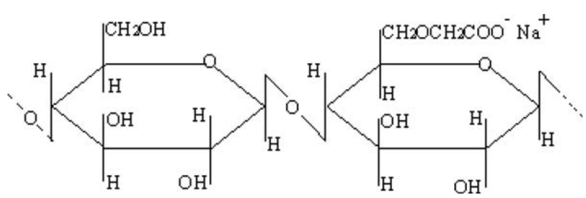
The research of the IPC films' physical and mechanical properties is of great interest as they are directly related to the structure of the polymer body and the possibility of their use.[7] Such a study is an independent scientific value and practical significance, since the structure of IPC Na-CMC-UFO can be varied by changing the structure of the UFO, and the mechanical properties directly depend on the structure of the initial components. The structure of the IPC pretty much defines the area of their possible use in the economics. Research in this area in the literature are scarce, and the interest in the physical and mechanical properties of films IPC Na-CMC-UFOs is due to the possibility of obtaining new polymeric materials with desired mechanical properties and their deliberate use as a basis for flexible dosage forms in pharmacy[6,13] and as soil conditioners in agriculture.[14–16]

EXPERIMENTAL

Materials

Sodium carboxymethylcellulose

The main material of the study is a purified Na-CMC of Namangan chemical plant, which is obtained by heterogenic solid-phase esterification of sulfite wood pulp monochloroacetic acid (MHCA) with the following structure:



with the degree of substitution (DS) 70 and the degree of polymerization (DP) 450, according to GOST 5.588-79. Na-CMC was repurified from low molecular salts by the method described in Ref. 12.

Na-CMC is a weak polyacid; the dissociation constant of it depends on the DS. The dissociation constant changes from 5.25×10^{-7} to 5×10^{-5} when the DS is changed from 10 to 80. Na-CMC is a white or slightly yellowish powder or fibrous product; it is odorless with a bulk weight of 400–800 kg/m^3 and density of 1.59 $g/sm.^3$ Its refractive index is 1.515. Softening temperature of Na-CMC is 170°C, and at a higher temperature it decomposes. Na-CMC is soluble in cold and hot water, and it forms a highly viscous aqueous solutions. In aqueous solutions, it is a polyelectrolyte. Na-CMC is approved for widespread use in medicine and pharmacy.[17,18]

Urea

It has been used urea grade pure for analysis (P.F.A.) without further purification, Gost 6691-77.

Formaldehyde

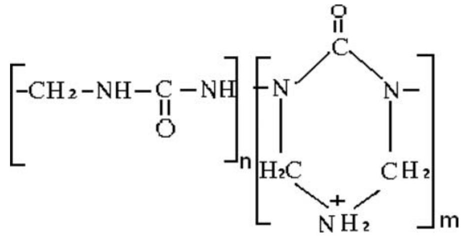
It has been used formalin of type "FM" (30–40% solution of formaldehyde in water, methanol content 7–12%); the concentration of formaldehyde in the solution was determined by oxime titration method.[12]

Urea–formaldehyde oligomer

There were used industrial UFOs of brand carbamide–formaldehyde low-toxic resin (CFLTR) and carbamide–formaldehyde vitality resin (CFVR), representing a 60–70% solution containing the condensation products of urea and formaldehyde. Product complies with GOST 14231–78.

Characterization and receive CFLTR-30

The carbamide–formaldehyde resin was used with low-toxic cyclochain structure marks CFLTR-30, which along with the usual linear fragments have triazinon cyclic structure comprising amino groups:



Relation between different types of units (*n*—linear range of links and *m*—area links with triazinon cycles) can vary within wide limits by changing the pH and composition of the reaction mixture or the ratio of urea, formaldehyde, and ammonia. We have used CFLTR-30 obtained by polycondensation of urea, formaldehyde, and ammonia taken in molar ratios of 1 : 2 : 0,3. The composition and structure of oligomers is established by NMR, infrared spectroscopy, and potentiometry.[12,19] The presence of amino groups in triazinon cycles gives properties of polyelectrolytes to oligomers UFOs and CFLTR-30.[12,20] Further, in this work, UFOs with linear structures are marked as UFOl, UFOs with triazinon cycles containing cycles of 15% as UFOt, and containing 35% of cycles as CFLTR-30.

Synthesis of interpolymer complexes based on Na-CMC with urea–formaldehyde oligomers

The reaction between urea and formaldehyde was carried out in the pH range from 3.3 to 8.8 by introducing urea and formaldehyde at a molar ratio 1 : 1,3 –2, respectively. To do this, ammonia (NH_4CH, 0,1–0,3 mol for urea) to a solution of formaldehyde (pH 3.3) was added to a value of 6 pH, urea was added at 35–40°C.

Using solutions of Na-CMC in distilled water, the concentration from 0.01 to 0.1 mol/L. The reaction mixtures of required concentrations were prepared by mixing reagent solutions in the respective proportions at room temperature and pH of 7.5–7.8. Under these conditions, polycondensation of urea and formaldehyde in the presence of Na-CMC is not observed for a long time. At the same time, by adding low molecular weight acids, such as phosphoric or hydrochloric acid, at a pH of 2–3, IPC is formed.

Getting IPC films

Films of IPC were prepared by mixing aqueous solutions of the components Na-CMC and UFO at a equinormal ratios for different components content and pH. Solution was poured onto a substrate of optical glass and evaporated at room temperature. Solid dry films were washed with distilled water to neutral pH and then dried at room temperature. Mechanical properties of films of IPC are figured out in an air-dry state.

Mechanical properties research

Mechanical properties of films of polycomplexes were determined by stretching at a constant rate of motion of the lower clamp (50 mm/min) on automatic dynamometer "Instron-1100" (England) at room temperature.[21] Samples of the films are prepared in the form of blades with a working section of 5 × 50 mm and a thickness of 0.07 mm. Measurement of samples was carried out in air-dry state preconditioned at a certain humidity. Breaking stress, $_p$ (MPa), under uniaxial tension was calculated by the formula:

$$\sigma_p = \frac{P}{S_0} \tag{1}$$

where P is the breaking force acting on the sample and S_0 is the initial cross-sectional sample.

Elongation was calculated by the formula:

$$\varepsilon = \frac{l - l_0}{l_0} \times 100\% \tag{2}$$

where l_0 and l are the length of the original and the stretched samples, respectively.

Initial modulus of elasticity was calculated on the straight sections of the initial stress–strain curves using the formula:

$$E_0 = \frac{\sigma}{\varepsilon} \tag{3}$$

Viscosimetric properties

Viscosity of solutions of IPCs was determined on Ubbellode viscometer ($d = 2$ mm) at different temperatures in a thermostatically controlled conditions, and the expiration time of the solution was determined from the capillary. The solutions' viscosity determination methods are detailed in Refs. 12 and 13.

Electron microscopic studies

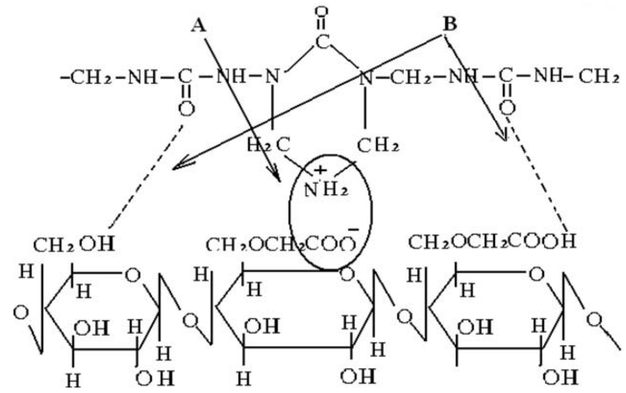
Electron microscopy studies of surfaces and cleavages (ends) of the IPC films were performed on scanning electron microscope "Hitachi–520" (Japan) with a resolution of 60 é. Samples were prepared by brittle cleavages at liquid nitrogen temperature.[22] The research results were recorded in electron micrographs.

RESULTS AND DISCUSSION

By mixing aqueous solutions of Na-CMC and UFOs in acidic environments, IPCs stabilized by ionic bonds between carboxylate anions of Na-CMC and amino groups of triazinon fragment of UFO [Scheme 2(A)] and hydrogen bonds between hydroxyl groups of Na-CMC and carbonyl groups of UFOs [Scheme 2(B)] are formed[12]:

To investigate the physical and mechanical properties and structure of the samples, IPC Na-CMC-UFO is obtained in the form of films from aqueous solutions by evaporating the solvent with subsequent washing of the films to neutral (pH > 5).

Typical curves of uniaxial tension of the films IPC Na-CMC-UFO with different structures are shown in Figure 1, where the abscissa is the relative strain ε (%) and the ordinate axis is the stress σ (MPa) calculated on the initial cross-sectional sample. Figure 1 shows that the film Na-CMC and IPC have small



Scheme 2 Formation of ionic (A) and hydrogen (B) bonds between the components of IPC.

values of deformation and consists mainly of the elastic region. From the literature,[18,23] it is known that the cellulose ethers, including Na-CMC in air-dry at room temperature, are in the glassy state, which is reflected in the diagram of uniaxial tension (Fig. 1). Comparisons of the deformation–strength curves of Na-CMC and IPC show (Fig. 1) that they have the same type, and this suggests that they are in the same physical state, i.e., glassy.

Graph dilations due to small values of the strain do not provide complete information about the structure of the objects under study, given that they are in the glassy state. Therefore, to evaluate the structure of the IPC films of different structure and relationships, it is necessary to determine the elastic modulus (Fig. 2), since the latter is determined by the structure and frequency of interchain macromolecular interactions.[12,21,24]

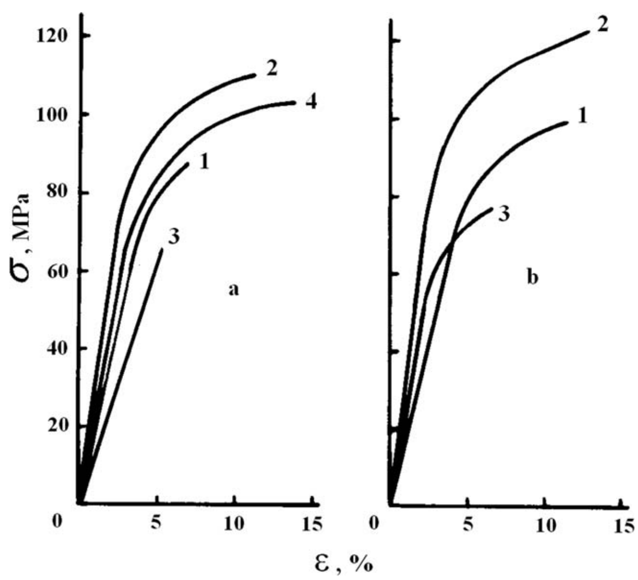


Figure 1 Deformation–strength curves of films based on IPC Na-CMC-UFO at 25°C in air-dry state at a ratio of components Na-CMC-UFOs: 1-0.4; 2-0.8; 3-1.6 and 4 - Na-CMC; a-UFOl, b-UFOt (15% triazinon cycles).

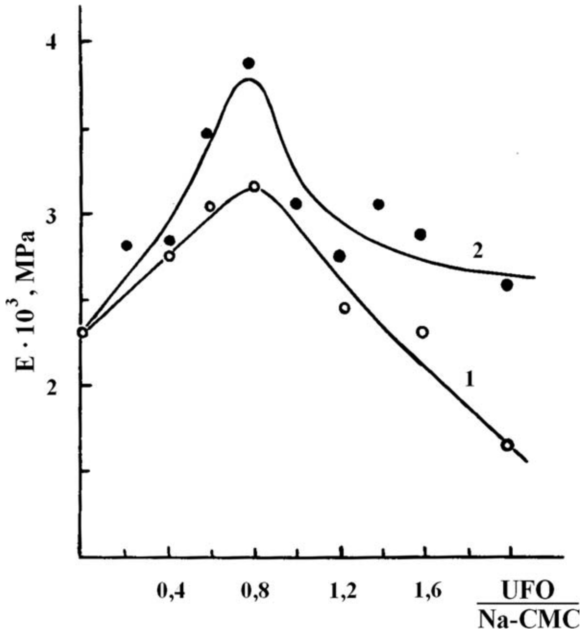


Figure 2 The dependence of the elastic modulus E of the films products polycondensation Na-CMC with UFOl (1) and UFOt (2) from mixing ratio at 25°C.

It is known[7,21,24] that any interaction on the polymer system, leading to a lowering of kinetic flexibility of macromolecules, causes an increase in the elastic properties of the system. With increasing content of UFOs in IPC Na-CMC-UFOs to equimolar composition increases the intermolecular interaction between the Na-CMC and UFOs, and the kinetic flexibility of the macromolecules decreases Na-CMC. This is reflected in enhancing the elastic properties of polycomplex films, as confirmed by the growth of the elastic modulus (Fig. 2). With a further increase in the number of UFOs, and thus, the volume fraction of dispersed phase, the elastic modulus decreases, which is associated with a decrease in the frequency of intermolecular bonds. In addition, the decrease in elastic modulus IPC with an excess of Na-CMC or UFO is associated with the formation of heterogeneous structures, which is evident from electron microscopic images (Fig. 3). Fibrillar structure of Na-CMC with the introduction of the UFO is undergoing changes, accompanied by the formation of extended ball-shaped structures corresponding to the product of the interaction of several tens of macromolecules. Ball-shaped structure of the IPC can be explained by the strong water repellent product of interaction of Na-CMC because of the screening of hydrophilic groups. As a result of this interaction, the complex formed double strands fold into a compact formation. The average particle size depends on the type of forces between the interacting components, and it can be seen from a comparison of micrographs of the films IPC Na-CMC-UFOl and

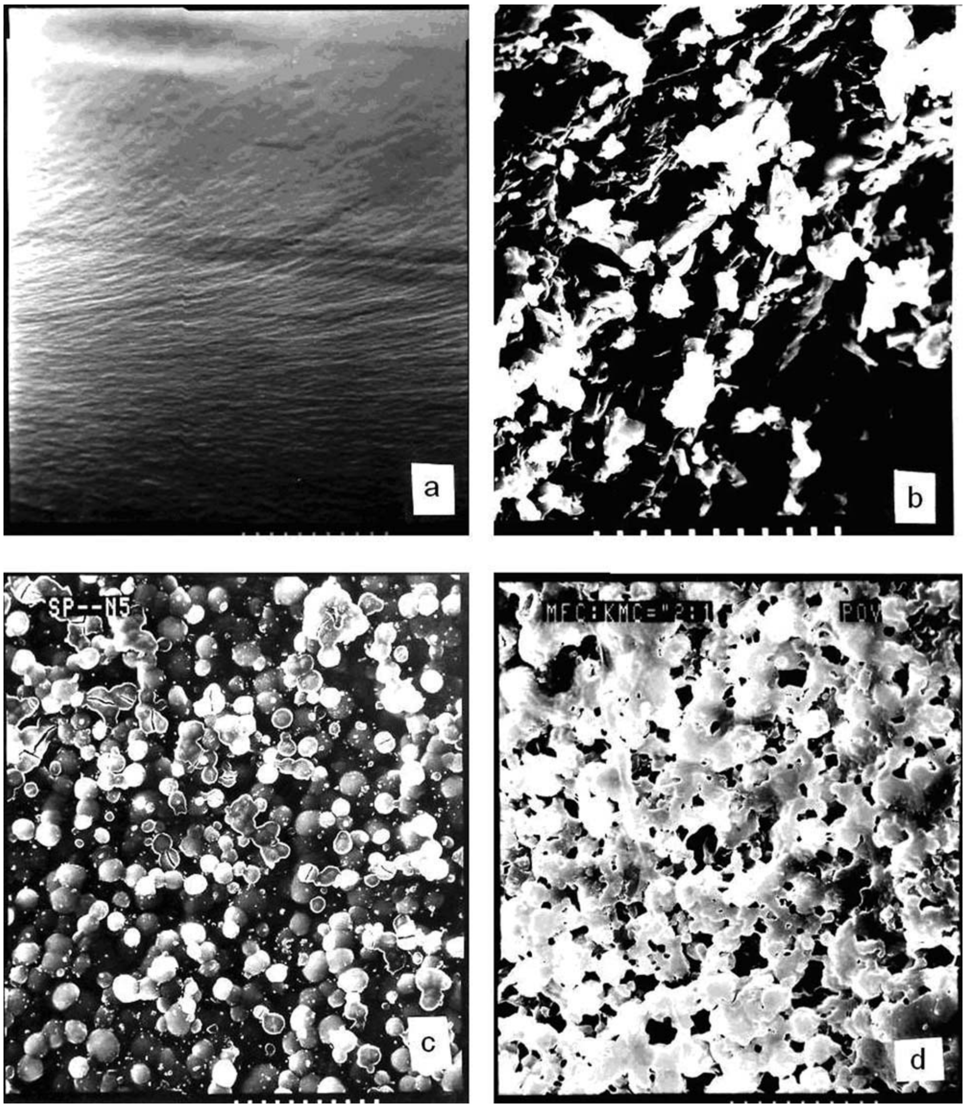


Figure 3 Electron microscopic images of the surface films Na-CMC (a), UFOl [(b), used in powder form] and the interpolymer complexes at a molar ratio UFOl : Na-CMC = 0.8 : 1 (c), 2 : 1 (d).

Na-CMC-UFOt equimolar composition, particle diameter of which increases with the number of triazinon cycles in the chain of UFO [Fig. 4(a,b)]. Increasing the number of triazinon fragments up to 35% in the initial CFLTR-30 leads to a much more homogeneous structure, as shown in Figure 4(c). This reflects a much greater affinity for Na-CMC and CFLTR-30 to each other because of the intense interpolymer electrostatic interaction, indicating a more homogeneous structure of the IPC. A further increase of UFO in IPC leads to the formation of heterogeneous structures, indicating the formation of two phases of IPC and the UFO [Fig. 3(d)].

The results of the study of deformation–strength properties of the films show the complexity of IPC change the value of fracture stress σ_p with a change in the ratio of interacting components (Fig. 5, cr.1). Initial addition of UFOl in the Na-CMC reduces the mechanical strength of the films. At equimolar composition of the interacting components, maximum value of mechanical strength is observed. A further increase in UFOl in films leads to a decrease in fracture stress.

As it is known,[7,23] the formation of an IPC is a conformational change in macromolecular components of the polymer–polymer complexes. Apparently, adding a solution UFOl to solutions of Na-CMC is a similar process to folding polycomplexes particles, which leads to a decrease in the viscosity solutions of Na-CMC-MFOl, which is observed experimentally (Fig. 6, cr.1). If IPC presents in solution an excess amount of Na-CMC, the films from such solutions have heterogeneous supramolecular structure because of the fact that the particles form a single IPC domain, and the unreacted Na-CMC macromolecules—the second, as Na-CMC

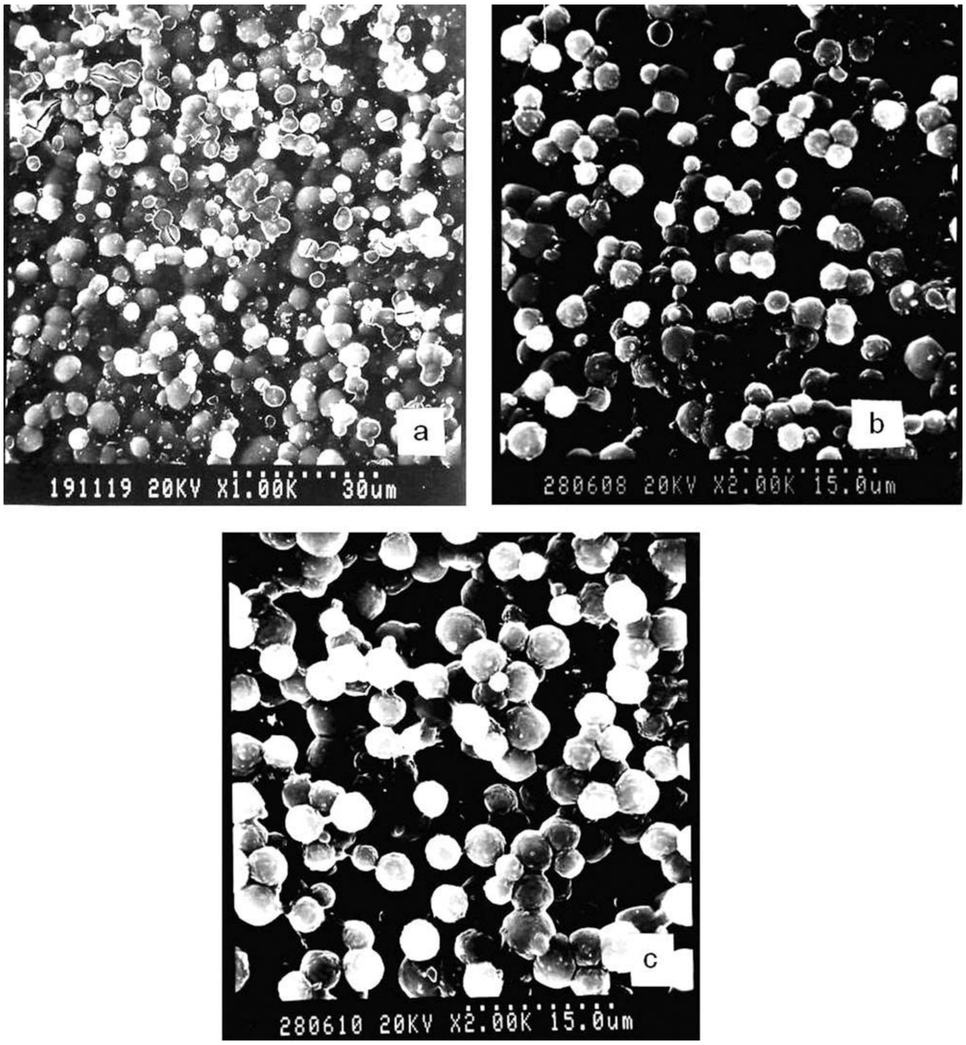


Figure 4 Electron microscopic images of the surface of polymer films complexes of equimolar compositions obtained at pH 2.5: (a) Na-CMC-UFOl; (b) Na-CMC-UFOt, 15% triazinon cycles; (c) Na-CMC-CFLTR-30, 35% triazinon cycles.

macromolecules in obtaining IPC (pH 2–3) are in a state of static coil.[7,23] The result is two areas, the first of which is saturated with particles of an IPC and the second an excessive number of coils Na-CMC.[12,23] Obtained from such solutions, the films have a relatively lower mechanical strength (Fig. 5, cr.1) because of the presence of different IPC domains in films in which there are different types of interaction between molecules[7,12]: chemical forces between the atoms acting along chain, intramolecular interactions Na-CMC, as well as ionic and hydrogen bonds between the macromolecules of Na-CMC and the UFO, which leads to very heterogeneous distribution of mechanical stresses in these areas. At equimolar ratio of interacting components observed maximum mechanical strength of films UFO (Fig. 5, cr.1) and the minimum value of viscosity solutions (Fig. 6, cr.1). Changing the mechanical strength of this character was observed in the study of polyelectrolyte complexes based on polycarboxylic acids with a flexible chain polyamines.[7] This is due to the formation of a homogeneous molecular structure IPC stabilized as ionic and hydrogen bonds. In these films, the mechanical stress is distributed evenly in terms of IPC, which leads to an increase in fracture stress.

Further increase in the proportion UFOl leads to the formation of a heterogeneous structure consisting of an IPC and an excess of the UFO. Formed two areas, the first of them, as was said above, filled with particles of an IPC and the second crosslinked macromolecules UFOl. Therefore, the mechanical stress is distributed inhomogeneously, which leads to a decrease in fracture stress.

Results of the study, depending on the structure of the UFO, showed that the change in the structure of UFOs in the IPC, the increase of triazinon cycles in the chain of IPC, is directly proportional function of the concentration cycles in the chain of UFO (Fig. 7, cr.1). This dependence is also observed when

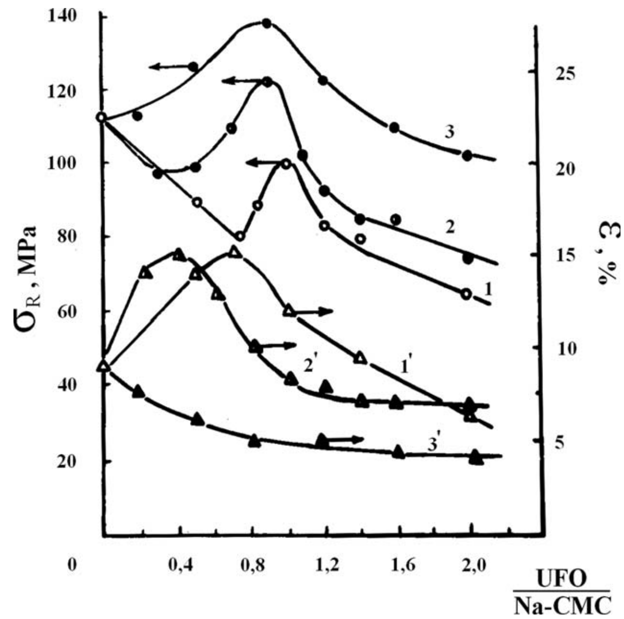


Figure 5 Depending on deformative stress σ_p (1,2,3) and elongation at break ε (1*, 2*, 3*) on the ratio of Na-CMC with UFOl (1,1*), UFOt (2,2*), and CFLTR-30 (3,3*) at a temperature of 25°C.

comparing the viscosity IPC Na-CMC-UFOl (0.16 Pa s) and Na-CMC-UFOt (0.20 Pa s) (Fig. 6, cr.1, 2) that apparently due to increased intermolecular interactions[12,25] due to triazinon cycles in the chain UFO, entering into complex formation. Elongation at

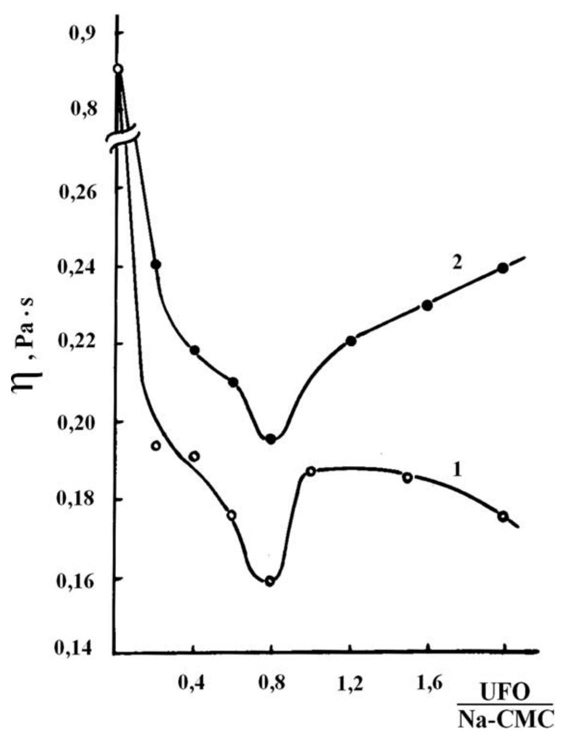


Figure 6 Dependence of viscosity of IPC Na-CMC-UFOl (1) and Na-CMC-UFOt (2) the ratio of interacting component concentration Co = 0.1 osn.mol/L at 25°C.

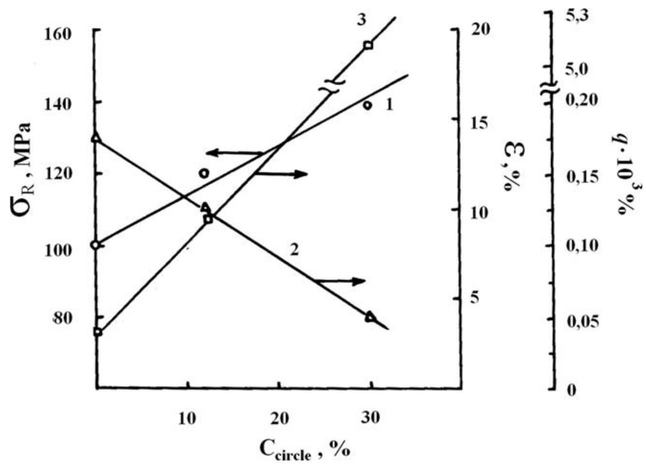


Figure 7 Change in fracture stress σ_p (1), elongation at breaking ε (2), and the degree of swelling θ (3) films on the content of IPC "C" triazinon cycles.

break, depending on the content of UFO films Na-CMC-UFOl and Na-CMC-UFOt, expressed maximum (Fig. 5, cr.1, 2). Polycomplex composite films in the Na-CMC-IPC and IPC-UFO correspond relatively lower values of strain at break. Definitely, these results are currently impossible to explain, but we can assume that the deformation properties of polymers are determined by intermacromolecular bonds (between the particles of IPC). It is known[7] that the film of IPC in the investigated temperature range is in the glassy state, so increasing the deformation properties of IPC is a manifestation of maximal intermolecular interactions (Fig. 5, cr.1, 2). In samples of IPC-UFO the decrease of deformation properties is associated with the formation of cross-linked regions containing an excess of the UFO. With increasing content triazinon cycles in the chain, UFO elongation at break decreases because of the

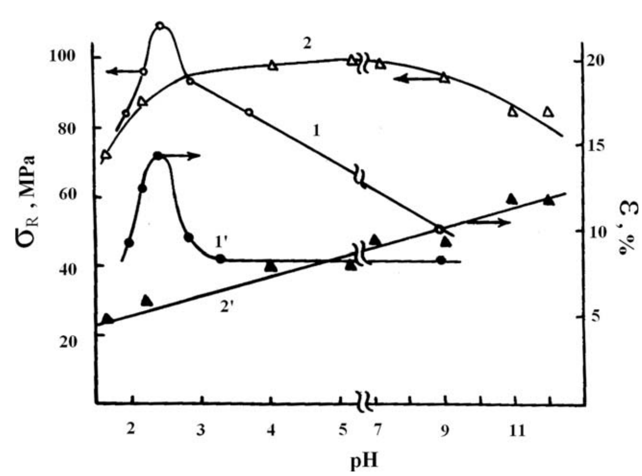


Figure 8 Dependence of tensile strength σ_p (1,2) and elongation at break ε (1′,2′) Na-CMC films (1,1′) and IPC-Na-CMC UFOl (2,2′) on the pH environment of film at 25°C.

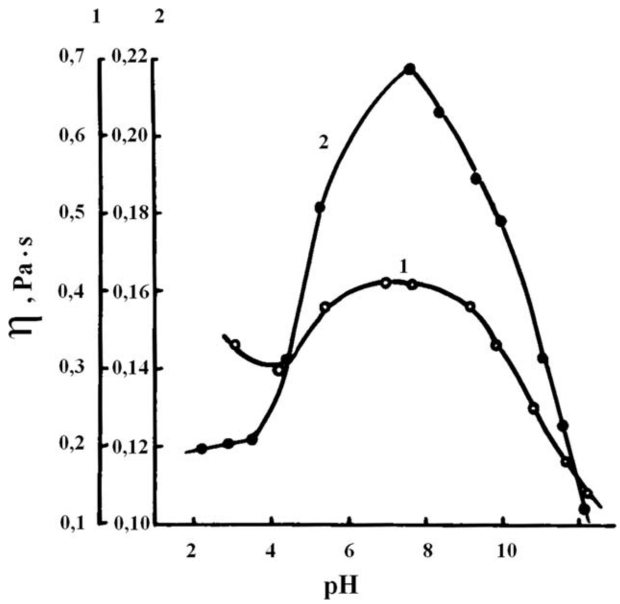


Figure 9 Changing the viscosity of aqueous solutions of Na-CMC (1) and interpolymer complex Na-CMC-UFOl (2), the pH of the medium at 25°C, the concentration of solutions is osn.mol 0.015 per liter.

decrease in the frequency crosslinks between the constituent components of IPCs (Fig. 7, cr.2).

Thus, on the basis of the earlier data, we suggest that the strain–strength properties of IPCs depend on the nature and frequency of intermolecular bonds and the heterogeneity of supramolecular structures.

As it is known,[12,18,23] with a change in pH of the environment during complex changes dissociated number of functional groups and the nature of relationships between interacting components. Therefore, we studied the deformation–strength properties of films obtained at different pH environments. Studies have shown that the strain–strength properties of films of equimolar composition obtained for different values of pH are consistent with the earlier experimental data. Figure 8 shows that the highest strain–strength values are observed at pH 2.5. It is known[12,26] that at pH 2.5, an IPC is formed with the maximum number of ionic and hydrogen bonds. With further increase of pH in the obtaining the IPC films, the deformation and strength characteristics fall, indicating a decrease in strength of intermolecular interactions. Since at high pH, the ionization of Na-CMC[18,23], results in rupture of hydrogen and then ionic bonds stabilize the IPC. At this point, we change the values of viscosity of Na-CMC of the pH of the medium (Fig. 9), where the viscosity of Na-CMC solution has a maximum at pH 6–9. With further increase of the pH effect is observed collapse of the coil macromolecules Na-CMC because of the weakening of electrostatic forces between like charges.

Fall in viscosity with the acidification of Na-CMC solution due to the conversion of salt form-COO^-Na^+ in less-dissociated carbonyl group —COOH, which lead to the association by interchain hydrogen bonds and the subsequent deposition of polymer from solution.[12,27,28] Change the value of the viscosity of solutions of mixtures of Na-CMC with UFO equimolar composition shows the formation of IPC in the limit of pH 2–3, with further increase in pH Na-CMC in dissociated state (Fig. 9, cr.2).

CONCLUSIONS

Thus, the identified relationship between the structure of the UFO and the structure formed by their interaction with Na-CMC IPC pattern shows the changing nature of relationships, which is due to the emergence of new electrostatic or hydrogen bonds between macromolecules, providing additional stability to the grid membranes. In this case, we can assume that ionic bonds determine the mechanical strength of the systems to a greater extent. From the above, we can conclude that the IPCs based on Na-CMC and UFO with high-strength properties can be obtained from the solutions of the components taken in equimolar ratio and at pH 2.0–3.0, and the changing structure of the interacting components and conditions of the complexation can significantly alter the structure and properties of the resulting products. It can serve a means of controlling the structure and properties of IPCs of Na-CMC and UFO.

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