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Main Physicochemical and Structural Characteristics of Synthesized Polyelectrolytes

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ABSTRACT: The research focuses on the development of new reagents from industrial waste and natural materials for the stabilization of saline soils and sands. The work includes regulating the textural properties of adsorbents and structuring soil dispersions, thereby contributing to environmental protection and the implementation of environmentally friendly technologies. It was found that various conditions affect the hydrolysis process of polyacrylonitrile (OPAN). The methodology is based on standardized tests and analytical procedures to evaluate the characteristics of new reagents.

KEYWORDS: polyelectrolyte, polyacrylonitrile, pollutant, soil structurant, polyacrylamide, polyacrylonitrile waste, polymer.

I.INTRODUCTION

In our republic, scientific and practical research is developing to obtain new materials, including polyelectrolytes based on polymers [1]. In the third direction of the strategy for the development of new Uzbekistan, aimed at further development of the Republic of Uzbekistan, tasks were set to "Ensure the stability of the national economy and increase the overall domestic production of industrial products by 14 times." The use of polymers to stabilize moving sands is relevant in many countries. Their use opens up opportunities for environmental protection [1]. However, many studies have shown that modern polymer preparations are economically advantageous to use only for strengthening the surface layer of soil or in combination with other measures [2]. In this regard, it is of great scientific and practical importance to study the composition of polyacrylamide - a local product, to determine the optimal conditions for its hydrolysis with high efficiency, and to study hydrolyzed samples of polyacrylamide with the aim of forming a structure with sand and soil particles. The binding of polyelectrolytes with clay minerals depends on many factors. The degree of the aggregating effect of polyanions is strongly influenced by their quantity. This can be seen in the example of the coagulation of mud suspensions. Aggregation increases with the increase in the amount of linear polymers in them [3-5]. The processes of coagulation, peptization, and sedimentation show that the introduction of neutral salts or electrolytes of a certain concentration into the solution and bringing the pH value of the solution to the appropriate level can increase or decrease the overall level of polyanion impact. The use of distilled liquid as a hydrolyzing agent for PAN contributes to obtaining PE with good structuring properties. These polymers are effective in increasing water resistance and improving the physicochemical properties of sandy and soil suspensions [5-8].

II. SIGNIFICANCE OF THE SYSTEM

Synthesis and study of the physicochemical and structural characteristics of polyelectrolytes based on water-soluble polymers.

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III. METHODOLOGY

The physicochemical and structural characteristics of polyelectrolytes were investigated, and the possibility of using polyacrylonitrile (PAN) and hydrolyzing agents, including distilled liquid, for creating new types of structuring materials was assessed. Polyacrylonitrile waste produced by JSC "Navoiazot" was the main focus of our research in the development of structured crusts. This waste is usually in the form of fibers or twisted bundles of beige-brown color, although other colors may also be present. PAN is a linear polymer with a molecular weight of 30,000-50,000 and a density of 1.14-1.15 g/cm³ at 20°C. This material retains its properties up to a temperature of almost 220°C. Among its technical characteristics, notable are the strength properties comparable to kapron and a relative elongation of 10-15%, which is about twice less than technical PAN. The moisture absorption of PAN is 0.9-1.0% at 20°C and relative humidity of 41%. This material is resistant to the effects of common solvents, fats, and does not undergo atmospheric conditions and sunlight. PAN dissolves in dimethylformamide, dimethylacetamide, ethylene carbonate, as well as in concentrated aqueous solutions of LiBr, NaCNS, $ZnCl_2 + CaCl_2$, and concentrated HNO_3, H_2SO_4.

The study also considered traditional polymer reagents such as GIPAN and CMC, as well as a new hydrolyzed copolymer of acrylamide and maleic acid synthesized in our laboratory. Additionally, inorganic reagents were used, including liquid glass (Na_2SiO_3) known as liquid glass (JS).

For the experiments, bidistilled water was also used to prepare hydrolysis solutions, high-purity acetone to separate polyelectrolytes from solutions, hydrochloric acid with a density of 1.0251 g/cm³, and other reagents with corresponding characteristics.The pH of solutions of polymer-like transformations of the starting materials and their diluted solutions prepared withthe addition of water or 0.1н. KCl solution was measured using a standard method on a universal pH meter-ionomer EV-74 equipped with a silver-chloride and glass electrodes.

The composition of synthesized polymers and products of their polymer-like transformations was determined by determining the acid number and nitrogen content, as well as by analyzing IR spectra. The acid number (AN) of polymers and their hydrolysis products was determined by the reverse titration method. Based on the AN values, the change in the number of carboxyl groups in the process of hydrolysis of the original polymer waste was assessed. The nitrogen content in polymers was measured according to the standard Kjeldahl method [2,8]. IR spectra of synthesized materials and sand-polymer complexes obtained using hydrolyzed polymer were recorded on an Avatar 360 FT-IR Nicolet iS50 Thermo Fisher Scientific spectrometer with Fourier transformation in the frequency range of 400-4000 cm^$^{-1}$.

The viscosity of polymer sample solutions and filtrates of sand suspensions treated with polymer solutions was determined at 25°C using a VBR 2M viscometer. Solutions of various concentrations (0.50-0.01 g/dl) were prepared by dilution with water or 0.1н. KCl solution. The characteristic viscosity [η] of polymer solutions was determined graphically from the dependence of $\eta sp/C$ on the concentration (C). In studies of the influence of the pH of the medium on the viscosity of polymer solutions, solutions with different pH values were prepared by adding various volumes of 0.1н. HCl and KOH solutions to the initial 0.2 g/dl solution.

IV. EXPERIMENTAL RESULTS

Experimental results show that the macromolecules of hydrolyzed OPAN treated with various hydrolyzing agents contain different functional groups. By regulating process conditions such as temperature and duration, the ratio of hydrophilic groups can be changed, thereby purposefully influencing their structuring ability.

It is widely recognized that polymer materials containing hydroxyl, amide, carboxyl, and other functional groups have improved physicochemical and structural properties. The ionic strength of solutions, which depends on the type of hydrolyzing agent used, affects the degree of dissociation of polymers and the conformation of their macromolecules. These conformational changes can affect the performance characteristics of polymers. As a result of dissociation, the number of kinetic units, the concentration of ions, increases, which in turn affects the hydrodynamic properties of polymer solutions.

The original OPAN is not soluble in water; however, its hydrolyzed forms become significantly more soluble in water depending on the duration of the hydrolysis process, which also affects the change in the viscosity properties of their solutions. Observed changes in specific viscosity depending on the concentration of the solution of hydrolyzed polymers have a similar nature. However, in Ca-OPAN solutions at high concentrations, significant structuring occurs, which may be related to differences in molecular weight and structural characteristics of Ca^{2+} ions associated with carboxyl groups. The relationship between the specific viscosity, pH of solutions, and polymer concentration is presented in Table 1.

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Table 1.
Viscosity and pH of solutions depending on concentration

Sample	Concentration, %							
	0,01		0,05		0,1		0,5	
	η_{sp}	pH	η_{sp}	pH	η_{sp}	pH	η_{sp}	pH
Na-ОПАН	0,29	9,7	0,77	10,3	0,98	10,7	3,32	11,4
NaSi-ОПАН	0,16	7,6	0,71	8,8	0,87	9,02	3,03	10,01
NaC-ОПАН	0,12	9,4	0,61	10,2	0,83	10,6	2,92	11,07
Ca-ОПАН	0,20	7,8	0,73	8,9	0,90	9,3	3,14	10,09

As the table data show, an increase in concentration leads to an instant increase in viscosity values for all studied samples, which is especially noticeable in aqueous solutions of samples obtained by hydrolysis of NaOH and Na2SiO3. The presence of a viscosity anomaly is less pronounced for Ca-OPAN.

The viscosity of solutions of hydrolyzed forms of OPAN, with the exception of their NaSi forms, practically does not change during long-term storage. There is evidence that polymers hydrolyzed in liquid glass form a precipitate of silicic acid. This is probably the reason for this change.

The effect of temperature on the viscosity of solutions of hydrolyzed OPANS has been studied. The study showed that the temperature rise to 40-45 °C leads to a slight increase in the viscosity of Ca- and NaSi-based solutions. A further increase in temperature causes a sharp decrease in the value of the viscosity characteristics. For other studied objects, a similar dependence is not observed, but only an increase in temperature reduces the viscosity of solutions. The results of studying the changes in temperature and pH of solutions on its viscosity are shown in Fig. 1.

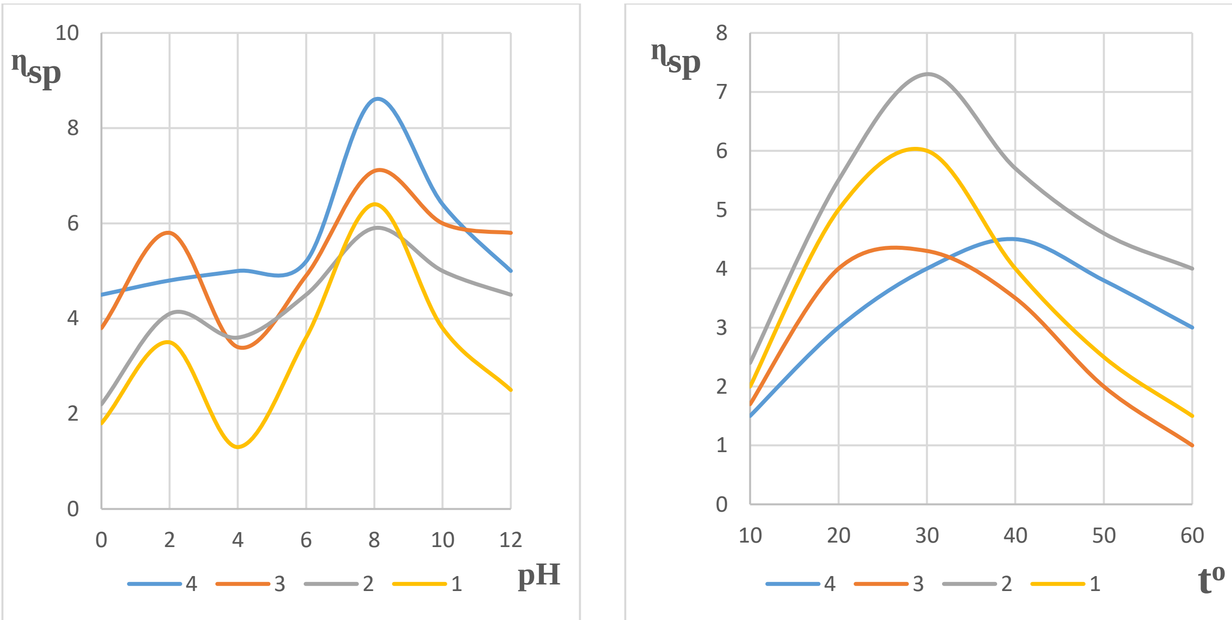

Figure 1. Dependence of the specific viscosity of solutions: 1) Na-OPAN; 2) NaSi-OPAN; 3) NaC-OPAN; 4) Ca-OPAN on a) temperature; b) pH.

According to the literature, it is known that at different pH values of the medium, macromolecules of water-soluble polymers have different structures. The experimental results show that the viscosity of solutions of polymer preparations at different pH values of the medium changes identically to the viscosity of known polymers (hypane). Thus, at pH > 10, straightening occurs due to the presence of carboxyl groups and dissociation of salt groups, due to which the viscosity increases sharply. As the curves of the figure show, in highly alkaline media, the viscosity characteristics of these PE do not differ from each other. Under strongly acidic conditions, these PE data differ slightly from each other.

With an increase in temperature to 30° C, an increase in the viscosity of the medium is observed, and a further increase in temperature contributes to a decrease in all polyelectrolytes. Consequently, changes in the viscosity of solutions of all PE are subject to general patterns.

To establish the composition and ratio of the functional groups of the obtained PE, the acid number and nitrogen content were determined (Table 2).

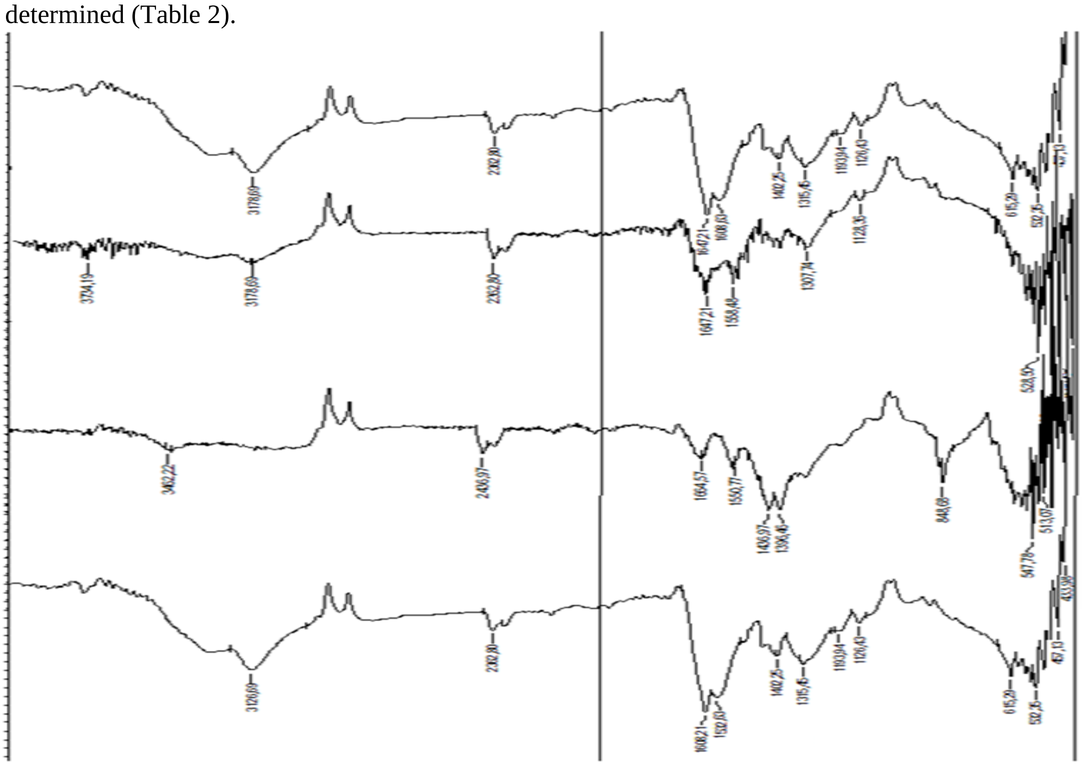

Figure 2. IR spectra of hydrolyzed polyesters: (from top to bottom) 1) Na-OPAN; 2) NaSi-OPAN; 3) NaC-OPAN; 4) Ca-OPAN.

The IR spectra of hydrolyzed polyelectrolytes (PE) differ in the presence of certain functional groups, depending on the hydrolysis conditions. All spectra contain lines in the range 3200-3600 cm^{-1} corresponding to hydroxyl groups. The absorption bands of carbonyl groups with a frequency of 1670-1675 cm^{-1} and symmetrical deformation vibrations of the NH2 amide group at 1510 cm^{-1} are present on the spectra of PE hydrolyzed with a solution of sodium hydroxide, indicating the presence of –CONH2. Absorption bands in the range of 2260-2240 cm^{-1}, characteristic of the –CN groups, are also observed. In the spectra of samples treated with sodium silicate, there is a peak in the region of 1100-930 cm^{-1}, characterizing the fluctuations of Si-O groups. OCa bonds are present in the reagent synthesized by the G method, which is confirmed by the detection of a high level of ash content and the appearance of new peaks in the range of 560-660 cm^{-1}, as shown in Fig. 3.

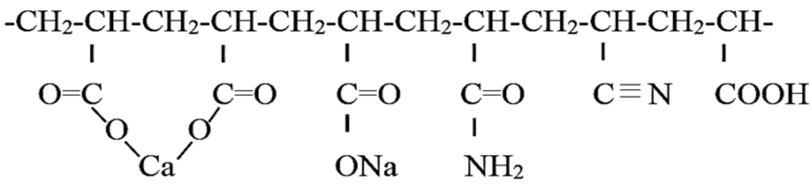

Figure 3. Possible functional groups in the composition of Ca-OPAN.

Strong absorption in the range of 1550-1554 cm^{-1} is detected on all IR spectra, which is associated with the appearance of carboxylate groups (-COO–), as well as absorption in the range of 1650-1700 cm^{-1}, indicating the presence of amide groups. Valence fluctuations of the carboxylate ion (-COO-) in samples after hydrolysis with NaOH are observed at about 1400 cm^{-1}, but in samples obtained using Na_2SiO_3, these bands shift to 1455 cm^{-1}.

Table 2
Characteristics of hydrolyzed polymers

Sample	Nitrogen content in the polymer, %.	Degree of hydrolysis, %	Acid number, мг/г
Na-OPAN	11,25	43,2	118,4
NaSi-OPAN	11,58	41,9	167,7
NaC-OPAN	14,38	31,1	141,7
Ca-OPAN	13,63	37,9	131,9

As the table data show, during hydrolysis with sodium hydroxide and silicate, the yields of the process have the highest values, thereby reducing the amount of nitrogen in the composition of polymers. At the same time, the values of HF have comparatively lower values, probably due to saponification and the formation of COONa groups [8].

Thus, the macromolecules of these polymers at pH values of the medium 3-4.5 pass from one form to another. The maximum structure formation for individual polymers lies in the range of 6.5-9 values.

The molecular weight of the obtained polymers (Infinitely better 1200 infinity series) was measured. The obtained results showed the possibility of changing the molecular weight of the polymer material as a result of hydrolysis. As it turned out, the conditions of hydrolysis and the nature of the hydrolyzing agent will affect the values of molecular weight and polymer yield. The results are shown in Table 3.

Table 3
Molecular weight of polymers and their composition

Sample	The molecular weight of the base substance and impurities	The content of the basic substance and impurities
OPAN	560000 5000 3000	80,7 9,8 9,5
Na-OPAN	1200000	99,8
NaSi-OPAN	1290000 1500	98,9 1,0
NaC-OPAN	920000 2200	99,0 1,0
Ca-OPAN	1000000 1500	99,0 1,0

V. CONCLUSION AND FUTURE WORK

Thus, the OPAN sample has the greatest diversity of molecular weights among the components: 560000, 5000 and 3000. The main substance makes up 80.7% of the total content, while the two impurities make up 9.8% and 9.5%. This indicates a relatively uneven chemical composition of OPAN.

In general, hydrolyzing agents play a key role in determining the structure-forming and strength properties of polymers obtained from PAN. The choice of a specific agent depends on the desired characteristics and the specific application of the PE.

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