

<https://doi.org/10.29013/AJT-22-7.8-16-21>

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DRILLING MIXES TO CREATE NEW COMPOSITIONS AND RESEARCH PROPERTIES

Abstract. In the article, the structure of modified starch obtained in different proportions was studied by means of IR-spectroscopy, SEM analysis, and its physical and chemical properties were analyzed. The resulting modified starch, which forms the basis of new compositions, allows the use of drilling mixtures at different pressures and temperatures in oil and gas wells.

Keywords: phosphorus, mineral powder (calcium carbonate), modified starch, IR-spectroscopy, electron microscope analysis, drilling mixtures.

Introduction. Today, the production of modified starch is increasing year by year worldwide. In 2016–2017 alone, production was expected to reach 9.36 billion US dollars, and according to experts, it is predicted to grow by 5.7% by 2025. In the global market for the production and consumption of modified starch, the leading countries such as the USA, China, Europe and Russia have achieved large production and are widely used in food, pharmaceutical, oil and gas well drilling [1].

Exploration of hydrocarbon products and drilling in high temperature and pressure conditions are becoming more difficult. This situation can be attributed to the decrease of reserves of oil and gas products, changes in pressure and temperature during drilling, inefficiency of the rheological properties of the drilling fluids, pollution of the interstices of the underground layer or deterioration of the geological parameters of the rocks, deterioration of the pipelines, changes in the shale layers and high technologi-

cal pressure. complicated the processes. In order to overcome these problems, the fact that, as a result of the use of modified starch-based drilling fluids, has properties such as pressure, normalization of aquifers, and control of the mixture density, there is an opportunity for scientific research and the development of effective technologies in this field [2; 3; 4].

Some properties of modified starch, such as molar mass, chemical structure, and solubility, as well as their effects on reservoir corrosion and oil refining efficiency, are widely studied by researchers [5; 6]. Based on research on the modification of starch derivatives obtained from various raw materials, several methods of synthesis have been developed, the result of the analysis of the optimal conditions of the reaction, the degree of modification and the physico-chemical properties of the derivatives are being studied [7; 8].

In order to obtain and widely use the modified starch offered by us in drilling, which is necessary

in the production of local raw materials – the starch contained in rice husks, the production enterprises of «Uzkimyosanoat» JSC focus on the preparation of mixtures consisting of compounds containing metal, phosphorus, and nitrogen.

Polymer composite mixtures widely used in drilling oil and gas wells have high stabilization properties, they form a dispersed system in cold water and provide an opportunity to control moisture during the drilling process. In the implementation of these goals, it is possible to obtain modified starches with the help of a reactor under the influence of tempera-

ture with dehydrated starch products, ammonium polyphosphate and mineral powder (calcium carbonate) reagents.

Starch, ammonium polyphosphate and mineral powder (calcium carbonate) (3:0.5:1), (3:2:2), (2:2:2) and (3:1:1) reagents were prepared using a reactor under the influence of temperature. MKPM brand modified starch was obtained in different proportions and their proportions are as follows:

Starch	100–150
Ammonium polyphosphate	10–15
Mineral powder (calcium carbonate)	30–50

Table 1.– Properties of modified phosphorus-retaining malleable starch composites

MKPM modified starch	proportions	Properties of the drilling mixture				water loss, cm ³ /30 min
		Conditional viscoelasticity	rotational viscometer rotation speed, rpm			
			600	300	3	
Starch, ammonium polyphosphate and mineral powder (calcium carbonate)	3:0,5:1	39	148	137	280	7
	3:2:2	44	146	133	274	6
	2:2:2	45	133	124	241	5
	3:1:1	41	149	135	276	6

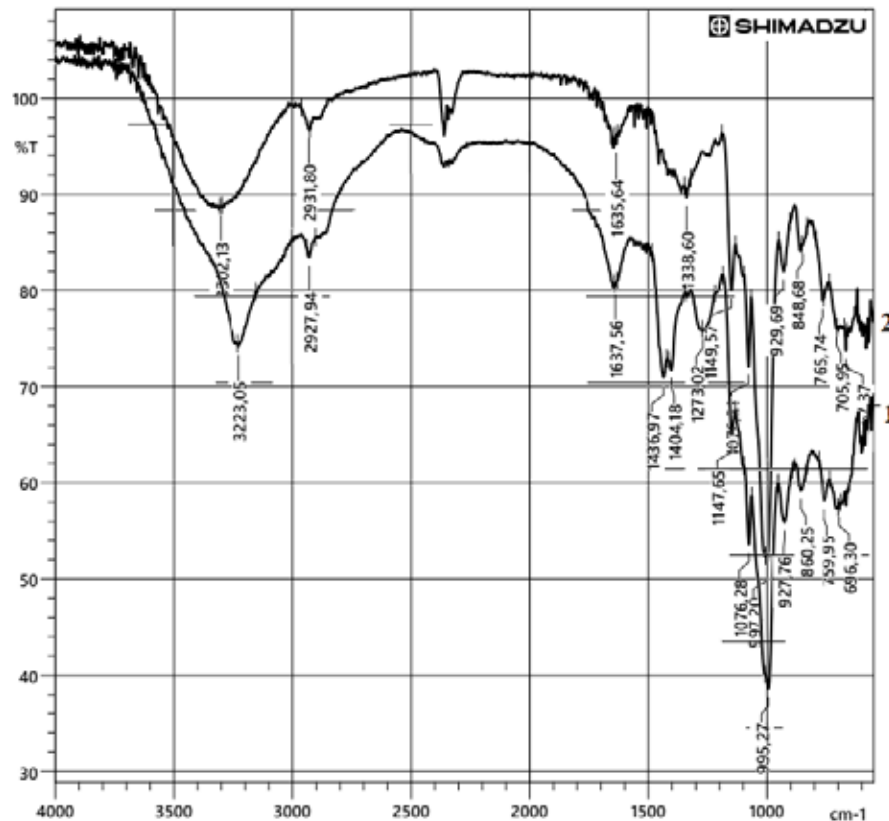


Figure 1. IK spectrum: 1 – starch; 2 – modified phosphorus-containing starch

In the course of research, changes in characteristic bonds were analyzed by IR spectroscopy of MKPM (starch, ammonium polyphosphate and mineral powder) brand modified starch. Accordingly, IR spectroscopy was performed using a Varian 3100 FT-IR spectrometer with a sampling range of $4000\text{--}400\text{ cm}^{-1}$. The IR spectra show that when the IR spectra of the modified starch etherification products we offer are compared with unmodified starch (Fig. 1), new absorption lines appear: R–O groups at 504 cm^{-1} deformation vibrations, R–ON at 936 cm^{-1} – valence vibrations groups, 1718 cm^{-1} asymmetric valence vibrations – C=O carboxylate groups and 1190 cm^{-1} – R=O groups. (Figure 1). 1019 cm^{-1} in the absorption range, characteristic of the IR spectrum characterizing the original starch, it can be shifted to the high frequency region up to 1024 cm^{-1} with a simultaneous increase in its intensity.

The formation of a composite structure, morphological changes of processes, and mixing of substances with each other have been studied through scanning electron microscope SEM analysis of modified phosphorus-containing starch. In these studies, modified starch particles ranging in size from $10\text{ }\mu\text{m}$ to $100\text{ }\mu\text{m}$ were investigated. It was investigated that the composition of the composites formed irregularly shaped granules with a polygonal shape. In addition, in the samples presented in the pictures, the composites obtained on the basis of different proportions of starch, ammonium polyphosphate and mineral powder (calcium carbonate) chemical reagents were studied (a) (2:2:2); (b) (3:0.5:1); (c) (3:2:2), and (d) (3:1:1) modified starch composite samples obtained on the basis of the ratios (b) and (d) in these ratios have the feature of a completely smooth surface (c) and (a) it is possible to analyze whether it formed a good mixture compared to composites. (Figure 2).

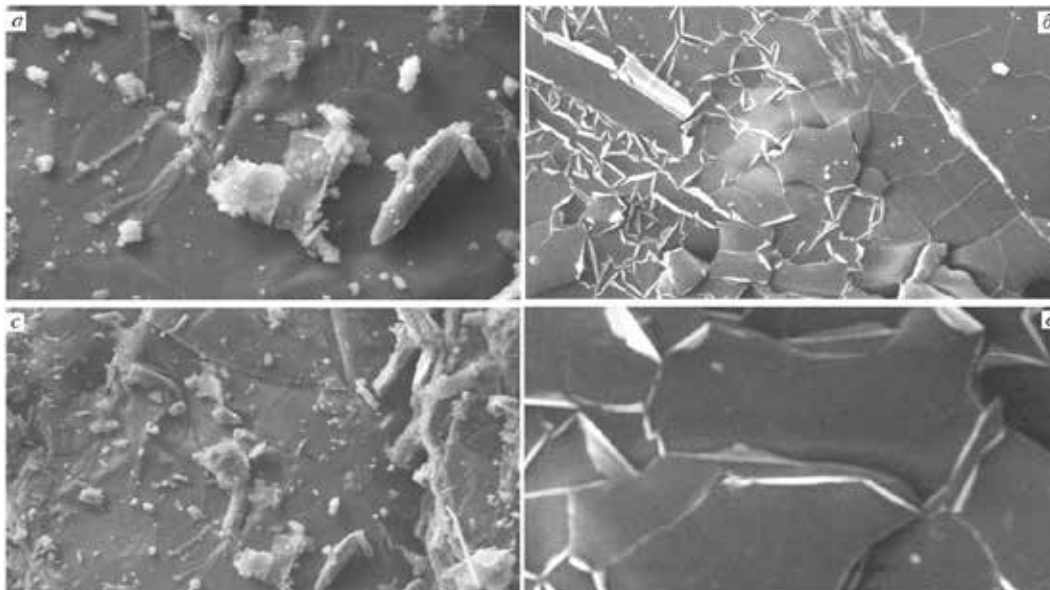


Figure 2. SEM Analysis: Starch, Ammonium Polyphosphate and Mineral Powder (Calcium Carbonate) Chemical Reagent Ratios; (a) (2:2:2); (b) (3:0.5:1); (c) (3:2:2), and (d) (3:1:1)

(b) In this paper, the extraction process of carboxymethyl starch is also researched, this starch has the properties of forming a sticky paste in cold water, and the extraction process consists of simple technology. This modified starch is one of the economically and ecologically effective products that are stable to

heat and biological effects. Carboxymethyl starch was obtained as a result of the reaction of etherification of hydroxyl groups with monochlorous acid or its sodium salts in an alkaline environment. In the first stage of the reaction, an equal amount of NaOH reacts with the hydroxyl groups of starch.

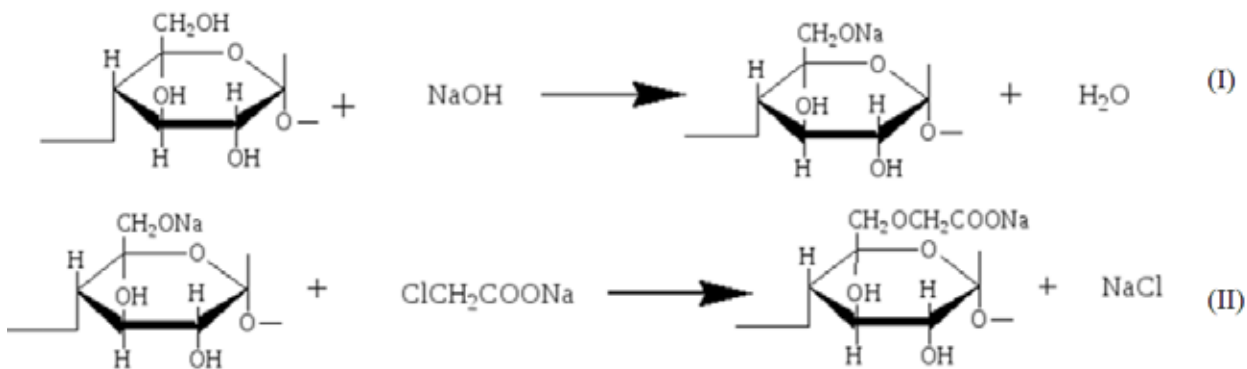


Figure 2.7. Reaction of carboxymethyl starch sodium salt

In the second step, the reaction process continues by replacing sodium monochloroacetate with a carboxymethyl group.

KMK-Na (sodium – carboxymethylstarch) are biopolymers with a high level of viscoelasticity, which can be analyzed with characteristic frequencies under IR spectroscopy.

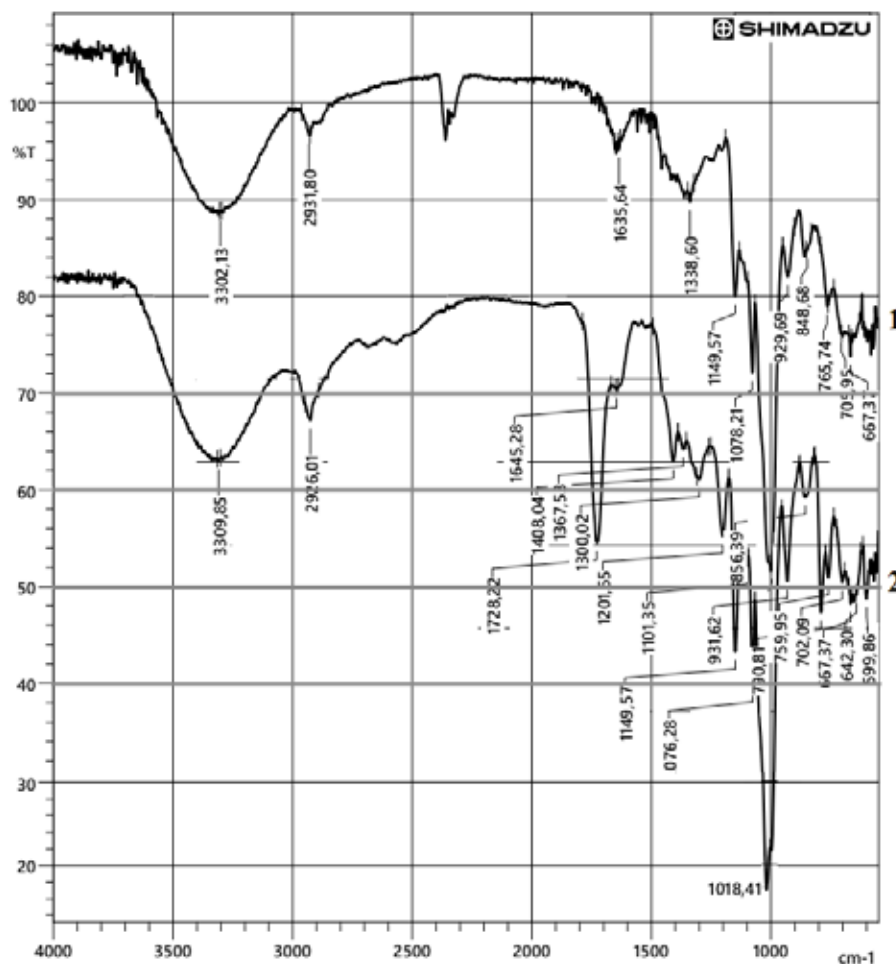


Figure 3. IR spectrum starch (1) and modified starch (2)

Figure 3 shows the IR spectroscopy of starch, and mainly hydroxyl groups have peaks in the re-

gion of 3365 cm^{-1} . In addition, frequencies related to the S-N group were observed in the range of

2950–2900 cm^{-1} . It can be seen that the frequency in the region of 1100–1000 cm^{-1} is characteristic of the SN2-O-SN2 group, showing valence and valence strains. IR spectroscopy of sodium carboxymethylstarch and starch revealed frequencies in several different regions. According to it, it was studied that the hydroxyl group in the region of 3300 cm^{-1} and two new peaks at 1600–1400 cm^{-1} belong to the SOO-group in sodium carboxymethyl starch. There is also an absorption band at 1750–1700 cm^{-1} corresponding to the vibrations of the carboxyl group.

In addition, the physico-chemical properties of polyelectrolyte solutions differ from other types (in the case of electrolyte) of polymers. In polyelectrolytes, the formation of ionic bonds in the polymer structure greatly affects the viscosity of the solution, regardless of whether the solution is concentrated or diluted. In this process, the ionization structure causes a significant change in the conformation of the polymer in solution.

As a result, the viscous flow of polymers deviates from the straight line depending on the concentration of the solution $\eta_{sp}/c = f(c)$. Figure 4 shows the dependence of the decrease in the viscosity of aqueous solutions of the sodium salt of carboxymethyl starch on the polymer concentration. It can be analyzed that this feature is characteristic of polyelectrolytes and differs sharply from starch.

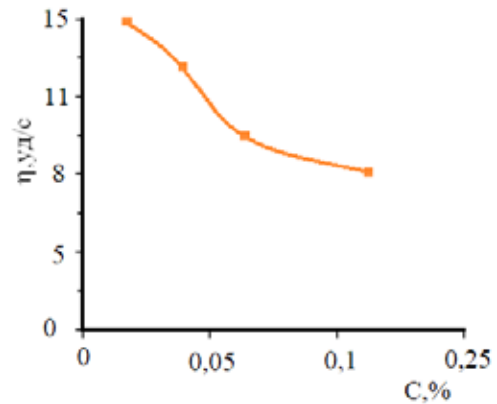


Figure 4. Dependence of the concentration of the viscosity of aqueous solutions of the sodium salt of carboxymethyl starch

Carboxymethyl starch-based drilling compounds allow the use of various temperatures in oil and gas wells. Drilling mixtures containing carboxymethyl starch (KMK) are stable to mineralization and temperature, and their proportions are based on their composition, mass.%.

Carboxymethyl starch (KMK)	3.0–3.5
Sodium hydroxide	0.02–0.03
Sodium carbonate	0.02–0.05
Sodium chloride	30–33
mineral powder (calcium carbonate)	10–12
copolymer based on acrylic starch	1–2
bentonite	7–10
water is normal	

The properties and characteristics of the proposed drilling mix are studied and the results are presented in (Table 2).

Table 2. – Properties of drilling compound based on carboxymethyl starch (KMK)

№ r/p	The name of Indicators	Unground mixture	Ground mixture
1	appearance	powder	powder
2	colour	Pale yellow	Pale yellow
3	the smell	odorless	odorless
4	density	10.8	10.8
5	environment, pH	7.5–8.0	7.5–8.0
6	solubility, 22°C	soluble in water	

Thus, chemical reagents based on starch, ammonium polyphosphate and mineral powder (calcium carbonate) (3:0.5:1), (3:2:2), (2:2:2) and (3:1:1) Mineralization of drilling mixtures containing

MKPM modified starch and carboxymethyl starch (KMK) with the help of ammonium polyphosphate and mineral powder (calcium carbonate) under the influence of temperature using a reactor allows creat-

ing new compositions of temperature-stable drilling mixtures.

In conclusion, we can say that the current process of globalization is affecting the oil and gas industry as well as other industries. Therefore, it is one of the most important problems to study and analyze the chemical components and reagents used in oil and

gas wells. As a result of studies, the concentration dependence of the viscosity of aqueous solutions of mineralized drilling mixtures with the help of modified MKPM and KMK ammonium polyphosphate and mineral powder (calcium carbonate) makes it possible to use them in oil and gas wells at different temperatures.

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