

# Journal of Advanced Zoology

ISSN: 0253-7214 Volume 44 Issue S-5 Year 2023 Page 439:448

# Hydrogels Based on Rice Starch, Acrylic - and N, N'-Methylenbi Sacrylamide, Metacrylamides and Their Use in Agriculture

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Article History	Abstract
Received: 06 June 2023 Revised: 05 Sept 2023 Accepted: 14 Oct 2023	Hydrogels containing soil and atmospheric moisture with hydrogel characteristics were synthesized by polymerizing polymers with acrylamide and methacrylamide, N,N-methylene-bis-acrylamide, and their physical and chemical properties were studied. The effects of temperature, the amount of oxidizing agent - N,N-methylene-bis-acrylamide in the reaction mixture, initiator concentration, and various solvents (water, ethyl alcohol, etc.) on the solubility of the obtained polymers in water were studied. The synthesized spatially structured polymers have been studied to form highly swelling hydrogels depending on the reaction conditions. Based on the samples obtained as a result of the research, the scientific basis for obtaining hydrogels that absorb moisture from the soil and atmosphere at a high level was developed. By modifying polymers with natural compounds, the possibility of obtaining hydrogels with a positive effect on the growth of cultivated plants in agriculture was investigated.
CC License CC-BY-NC-SA 4.0	<b>Keywords:</b> Acrylamide, Methacrylamides, N,N - Methylene - Bis- Acrylamide, Hydrogel, Polymer, Hydrophilic, Hydrophobic Graft Copolymer, Methacrylic Acid

# 1. Introduction

Plants and products based on them form the basis of all human needs. Water is the main factor for plant growth and healthy crops, and the increasing concentration of various gases in the atmosphere leads to rapid evaporation of water. Synthesis of polymer hydrogels that absorb moisture from soil and air remains one of the urgent problems. The purpose and tasks of the work: the fused polymers of acrylic and methacrylamides have strong hydrogel properties, they consist in synthesizing swelling hydrogels due to moisture in the soil and atmosphere and studying their physicochemical properties. In times of water scarcity in recent years, we should value every drop of water and use it effectively. To date, a number of scientific results of world importance have been created and are being used in practice regarding water-saving and resource-saving technologies. After the soil dries out, water is retained by water-swollen hydrogels. This process can last up to 4-5 years. (2). Hydrogels that have expired during this time are absorbed directly into the soil as fertilizer. SEM images and IR spectrum of the obtained hydrogel were analyzed. The importance of hydrogels in agricultural plants was studied.

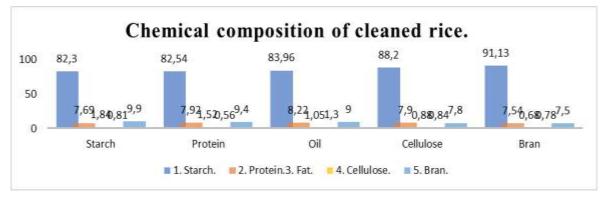
# Chemical composition of cleaned rice

Composition of rice. Fully	Fully dried starch				
dried starch	1	2	3	4	5
Starch	82,30	82,54	83,96	88,2	91,13
Protein	7,69	7,92	8.22	7,90	7,54
fat	1,84	1,52	1,05	0,88	0,68

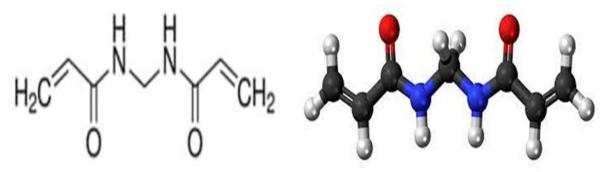
Tabla I

Hydrogels Based on Rice Star	ch, Acrylic -	and N, N'-Me	thylenbi Sa	crylamide,
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Cellulose	0.81	0.56	13	0.84

Cellulose	0,81	0,56	1,3	0,84	0,78
Bran	9,9	9,4	9,0	7,8	7,5



Currently, the creation of synthetic materials that can satisfy all the requirements of some sectors of the national economy is one of the urgent tasks of polymer chemistry. It is important to create watersoluble or highly soluble polymers (hydrogels) obtained from local raw materials and finding their place in practice in certain sectors of the national economy. In this regard, the synthesis of fused hydrophilic polymers based on acryl- and methacrylamides and their derivatives and the study of physico-chemical properties of hydrogels based on them have great prospects. Polymer hydrogels, which are highly water-swellable, elastic, and compatible with various submolecular compounds, are attracting great interest from researchers. Such a hydrogel can be widely used in biology, medicine, wastewater treatment, oil production, as well as in the national economy, agriculture and other fields. However, the range of these highly flexible polymer hydrogels is quite limited, so the search for new multifunctional polymers and their creation remains an important current task. Hydrogels with different structures can be obtained by polymerization and copolymerization methods in the presence of bifunctional monomers as a blocking agent of hydrophilic monomers. When persulfate is heated with oxygen and alkali, sulfate anion radicals react with water to form free radicals. free radicals combine hydrogen from starch hydroxyl groups. Then oxygen binds to acrylamide and free polymerization radicals between starch and acrylamide. Methylene-bis-acrylamide is added to the reaction to cross-link the high molecular weight composition that cross-links the polymer chains that define the hydrogel.



#### N-N, Methylenebisacrylamide

A characteristic feature is that for ON groups of kaolin, starch and  $\text{CONH}_2$  amide group, if the absorbance changes after the copolymerization reaction, this reaction is assumed to be positive. A chain reaction occurs between the ON groups of kaolin, starch and acrylamide  $\text{CONH}_2$ , which leads to the formation of a network structure and a water absorption group. According to the binding mechanism, it is suggested that starch reacts with hydroxyl groups functional groups based on the catalyst - and -CHO and COH n copolymerization occurs between them. The cross-linking reaction leads to the formation of three-dimensional networks of polymer chains and kaolin particles, as well - 440 -

as cross-linking based on the cross-linking agent ). ( $CH_2=CH_2$ - CO-NH-CH<sub>2</sub>-NH-CO-CH=CH<sub>2</sub>). As a result of the reaction, a water-swellable hydrogel is formed by the copolymerization of starch, acrylamide and mineral ultrafine powder. Since the ability of the hydrogel to absorb water depends on the amount of kaolin, it can be assumed that the kaolin particles are chemically bonded to the polymer in the form of cross-linking points.

Such synthetic hydrogels are obtained by synthesizing copolymers based on hydrophilic and hydrophobic monomers. The absorption of liquids, including water, by hydrogels depends on the chemical structure of the polymer, the amount of interlocking bridges, temperature, ionic strength of the medium, and other factors. For example, in order to obtain strong hydrogels, amphiphilic graft copolymers were synthesized using the macromonomer method [3]. The hydrophilic part of these graft copolymers consists of methacrylic acid, and the hydrophobic part consists of polystyrene chains of the same molecular weight. The condition of the obtained hydrogels in boiling and the ability to pass oxygen were studied. These hydrogels were highly swollen and stable at temperatures below the glass transition temperature of polystyrene. E.E. Skorikova [4] studied water vapor sorption of polyelectrolyte complexes (PEK) hydrogels of different composition at different relative humidity. The water vapor absorption isotherm of polyelectrolyte complex gels with different composition is characterized by two areas of, which differ in the dependence of the absorption coefficient on the composition of the polyelectrolyte complex. Extreme dependence of water content and conductivity on polyelectrolyte complex hydrogel composition was noted. Polyelectrolyte complex gel containing double excess polyacrylic acid 0.01 n. The strength of polyelectrolyte complex hydrogels impermeable to NaCI and urea solutions decreased with increasing polyacrylic acid content.

Copolymers based on acrylic acid, methacrylic acid, 2-hydroxypropyl methacrylate, Nvinylpyrrolidone, methyl methacrylate and ethylene glycol dimethyl methacrylate formed hydrogels with 30-90% water retention. Mechanical and surface properties, oxygen permeability and protein absorption of membranes made of these hydrogels have been studied [5]. It has been shown that the compositional dependence of copolymer properties is close to additivity in the case of weak interaction between pairs of monomers. Spanish scientists [6] have shown the acrylic monomers used in the production of hydrogels, the methods of polymerization of these monomers, the main physicochemical properties of gels and their fields of use in medicine. To obtain gels, mainly hydrophilic or water-soluble monomers and polymers are used. In some works, mixtures of N-vinylpyrrolidone, polyvinyl alcohol, acrylamide with monomers containing acrylic acid salts were used to

obtain gels. For example, in order to obtain highly hydrophilic polymer systems, Shibalovich et al. [7] studied the copolymerization of acrylic acid and its alkaline salts with acrylamide in the presence of manganese (III+) mixed-ligand complexes in an aqueous medium at 20 in an air oxygen atmosphere, depending on the nature and concentration of the monomers of the initiator and coagulation agent. The effect of the nature and concentration of ionogenic groups, the nature of the etching agent and the degree of etching on the water absorption and water retention capacity of the copolymer was studied. It has been shown that the nature and concentration of ionogenic groups and the degree of crosslinking are the main factors responsible for the rate and degree of water absorption of the copolymer.

Optimum conditions for obtaining polyelnectrolite hydrogel, which can absorb 40 g of water per 1 g of dry polymer, have been determined. In order to study the thermodynamics of strong swelling hydrogels, K.S. Kazansky et al. [8] studied swelling patterns of hydrogels obtained by radiation welding of acrylamide (70-90 mol %) sodium acrylate or acrylic acid copolymer. A very large amount of solvent can induce spatial transitions in swollen gels. This leads to displacement of the solvent from the gel into the external solution due to increased friction between the mesh links under certain conditions. As a result, the gel volume decreases hundreds of times [9]. A sharp decrease in the volume of the gel with a slight change in external conditions is called collapse [10]. The attractive forces that cause this are usually due to hydrophobic interactions or hydrogen bonds in aqueous solution. A change in any of the external factors (for example, temperature, solvent composition, pH, etc.) will increase the attraction forces and the collapse of the gel will inevitably occur. [11].

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Thus, a polymer gel on the verge of collapse can reversibly change its volume dramatically in response to very small changes in environmental parameters. Therefore, such gels are called sensitive or "smart" materials [12]. Currently, the creation of new synthetic materials that can meet the very high and all requirements of some sectors of the national economy with complex properties is one of the main tasks of polymer chemistry. Water-soluble or highly soluble polymers (hydrogels), which are obtained from cheap local raw materials and find their place in practice in certain sectors of the national economy, are becoming important. In this regard, the synthesis of fused hydrophilic polymers based on acryl- and methacrylamides and their derivatives and the research of physicochemical properties of hydrogels have great prospects. [13]. Therefore, in recent years special attention has been paid to the detailed and in-depth study of specific aspects of acrylic and methacrylamide polymerization processes. The polymerization reaction of acryl- and methacrylamides has been studied mainly in aqueous solutions, because monomers and polymers are well soluble in water and the reaction proceeds in homogeneous conditions. [14]. Polymerization of acrylamide in the presence of MBA Polymerization of acrylamide in aqueous solution was carried out in the presence of MBA under the influence of dinitrile of azoisomoic acid (DAK) and potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>). Polymerization was carried out at different amounts of the occlusive agent (0.005-5.0%) until the polymer was formed in high yield. Separation of obtained polyacrylamide (PAA) samples into sol-gel fractions by washing in distilled water showed that the yield of the sol fraction in the samples decreases with the increase in the amount of oxidizing agent in the initial reaction mixture. [15]. The dependence of the formation of polyacrylamide hydrogels on the amount of the oxidizing agent N,N'-methylene-bis-acrylamide in the reaction mixture is presented in Table II. Dependence of the formation of polyacrylamide hydrogels on the amount of caustic agent (N,N'methylene-bis-acrylamide) in the reaction mixture (reaction time 240 minutes, temperature 42, initiator [ K2S2O8]=0.1%).

AA	MBA.	Productivity%.	Gel fraction%.	Zol%.	Stiffness rate%.
94,0	6,0	90,2	84,0	15,46	7,9
94,5	5,5	90,4	84,11	15,30	8,2
95,0	5,0	90,6	84,24	15,10	8,5
95,5	4,5	89,5	83,99	15,01	8,7
96,0	4,0	88,4	83,96	16,02	9,5
97	3,5	88,2	83,96	16,33	11,4
97,5	3,0	88,0	83,61	16,12	12,4
98,0	2,0	90,1	87,42	12,50	14,6
99,5	1,0	91,2	86,73	13,30	20,2
99,95	0,05	95,1	88,81	11,11	25,4
99,99	0,01	88,5	66,40	33,5	32,8

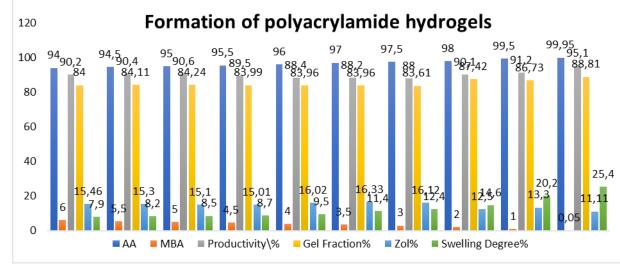


Table 2

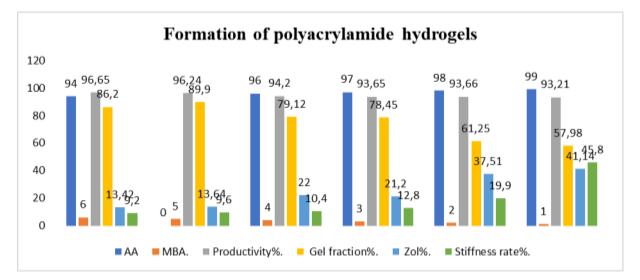
From the data presented in Table 1, it can be seen that the experiments made it possible to produce fused polymers with high productivity. An increase in the amount of the coagulation agent MBA in the reaction mixture led to an increase in the gel fraction. The degree of swelling of the obtained samples decreases with the increase of MBA in the reaction mixture, which is explained by the increase in the density of macromolecular junctions. Table II shows the composition of the precipitated polyacrylamide formed by the action of azo-isoamino acid dinitrile on the polymerization of a mixture of acrylamide and MBA in aqueous solution. Table II

Dependence of the formation of polyacrylamide hydrogels on the amount of scavenging agent (MBA) in the reaction mixture. (Reaction time 120 minutes, [DAK]=0.5%; temperature 70, N2 O=30%).

Table 3

AA	MBA.	Productivity%.	Gel fraction%.	Zol%.	Stiffness rate%.
94,0	6,0	96,65	86,2	13,42	9,2
95.0	5,0	96,24	89,9	13,64	9,6
96,0	4,0	94,20	79,12	22,0	10,4
97,0	3,0	93,65	78,45	21,20	12,8
98,0	2,0	93,66	61,25	37,51	19,9
99,0	1,0	93,21	57,98	41,14	45,8

#### Formation of polyacrylamide hydrogels

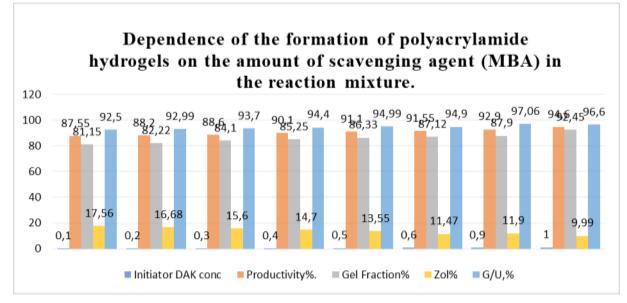


As can be seen from Table 2, the yield of polymers obtained with the presence of DAK is almost the same as that of polymers obtained under the influence of potassium persulfate, but it is distinguished by a slightly higher sol fraction. A preliminary study of the degree of swelling of the resulting polymers showed the possibility of obtaining hydrogels with a high degree of swelling with very small amounts of the etching agent. The effect of the concentration of the initiator - DAK on the polymerization of acrylamide in the presence of MBA was carried out in the range of 0.1-1.0% in the ratio of AA:MBA=95:5 at 70 temperature, with the addition of 30% water for 2 hours. The results of the experiment are presented in Table 3. The results presented in Table 3 show that an increase in initiator concentration from 0.1 to 1.0% increases the amount of AA and MBA carbonized polymer produced by the reaction from 94% to 99%. At the same time, the amount of the gel fraction increased from 57.98% to 86.0%, and the sol decreased from 41.14% to 13.42%. Dependence of the formation of polyacrylamide hydrogels on the amount of scavenging agent (MBA) in the reaction mixture.

Table 4					
Initiator DAK conc	Productivity%.	Gel Fraction%	Zol%	G/U,%	
0,1	87,55	81,15	17,56	92,50	

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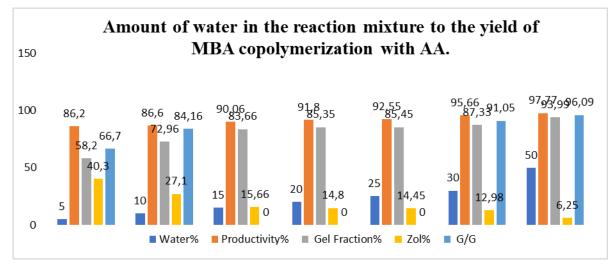
interact y fullinges and		tui t			
0,2	88,20	82,22	16,68	92,99	
0,3	88,60	84,10	15,60	93,70	
0,4	90,10	85,25	14,70	94,40	
0,5	91,10	86,33	13,55	94,99	
0,6	91,55	87,12	11,47	94,90	
0,9	92,90	87,90	11,90	97,06	
1,0	94,60	92,45	9,99	96,60	



So, from the polymerization of AA in the presence of MBA, it is possible to obtain sintered polymers with a high yield (96.60%), in which the yield of sintered products is 92.5%. Importantly, even at very low concentrations of the initiator (0.1%), the yield of the gel fraction in the reaction product is 81.15%. It is known that the properties of polymer hydrogels, in particular, the permeability to various substances and gases, hydrophilicity, transparency in the broken state, etc., can be controlled by carrying out the polymerization reaction in different solvents. In Table 4. The results of the study of the effect of the amount of water in the reaction mixture on the yield of MBA copolymerization with AA are presented. The reaction was carried out for 2 hours at a temperature of 75 °C in the presence of 0.5% DAK in the ratio of AA:MBA=96:6 mol%. Amount of water in the reaction mixture to the yield of MBA copolymerization with AA.

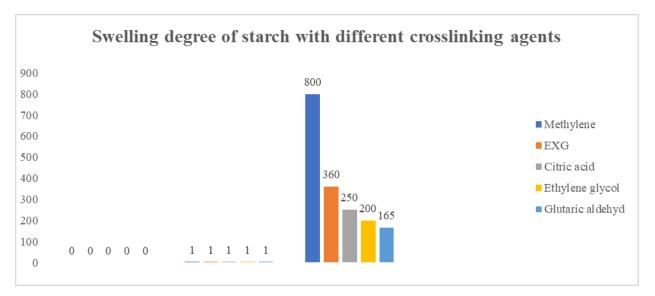
		Tuble 5		
Water%	Productivity%	Gel Fraction%	Zol%	G/G
5	86,20	58,20	40,30	66,70
10	86,60	72,96	27,10	84,16
15	90,06	83,66	15,66	93.75
20	91,80	85,35	14,80	93.05
25	92,55	85,45	14,45	93.44
30	95,66	87,33	12,98	91,05
50	97,77	93,99	6,25	96,09

Table 5
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Study and description of the synthesis of superabsorbent hydrogel based on starch, acrylamide and kaolin When persulfate is heated, sulfate anion radicals react with water to form free radicals. free radicals combine hydrogen from starch hydroxyl groups. Then oxygen binds to acrylamide and free polymerization radicals between starch and acrylamide. Methylene-bis-acrylamide is added to the reaction to cross-link the high molecular weight composition that binds the polymer chains that define the hydrogel. The degree of swelling of hydrogels based on starch copolymers with different cross-linking agents.

		Table 6	5		
Starch/AA/B	1	2	3	4	5
The name of the	Methylene	EXG	Citric	Ethylene	Glutaric
interconnector	bisacrylamide		acid	glycol	aldehyde
Percentageof crosslinker	One	1	1	1	1
The degree of swelling	800	360	250	200	165



Starting from the characteristic peak, if the absorbance for the ON groups of kaolin, starch and  $CONH_2$  amide group changed after the copolymerization reaction, it is assumed that the reaction is a chain reaction between the ON groups of kaolin, starch and acrylamide  $CONH_2$  group, which leads to the formation of a network structure, and the water absorption group . According to the binding mechanism, it is proposed that starch reacts with hydroxyl groups functional groups based on the catalyst - and -CHO and COOH, copolymerization between them occurs. The cross-linking reaction leads to the formation of three-dimensional networks of polymer chains and kaolin particles, as well as cross-linking based on the cross-linking agent ). ( $CH_2=CH_2$ - CO-NH-CH<sub>2</sub>-NH-CO-CH=CH<sub>2</sub>).).

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Hydrogel is formed as a result of the reaction copolymerization of starch, acrylamide and mineral ultrafine powder. Since the ability of the hydrogel to absorb water depends on the amount of kaolin, it can be assumed that the kaolin particles are chemically bonded to the polymer in the form of cross-linking points.

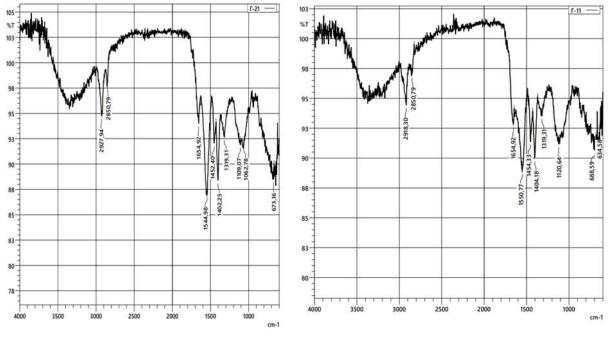


Table 7

#### **Corn starch**

#### **Rice starch**

According to the IR spectra, the obtained product corresponds to the peak observed at 2927 cm<sup>-1</sup> and 2850 cm<sup>-1</sup>. SO-N is a potassium salt of polyphosphoric acid and an extension of polyvinyl acetate, a C = O extension of the unit of potassium salt of polyphosphoric acid and polyvinyl acetate in the superabsorbent at 1654 cm<sup>-1</sup>. The absorption peak associated with the OH- group of polyvinyl acetate changed from 2927 cm<sup>-1</sup> and 2918 cm<sup>-1</sup> to 1654 cm<sup>-1</sup> after the reaction. The absorption peak at 1544 cm<sup>-1</sup> and 1550 cm<sup>-1</sup> associated with starch was shifted, indicating the change of OH group in starch during the reaction. The absorption peaks at 2918 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> belonging to the group of hydrogel obtained from the factory - CONH<sub>2</sub> and -SO<sub>2</sub> also change during the reaction. a new peak appears at 1550 cm<sup>-1</sup> belonging to the group The above results showed that the characteristic absorption peak of OH and –CONH<sub>2</sub> groups in starch changed after the copolymerization reaction. Hydrogel soaked in water and dry hydrogel.

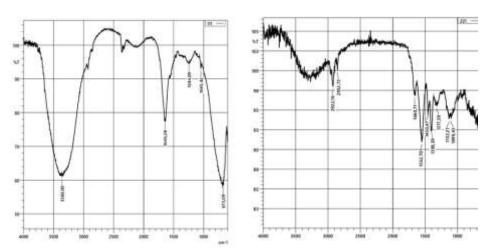
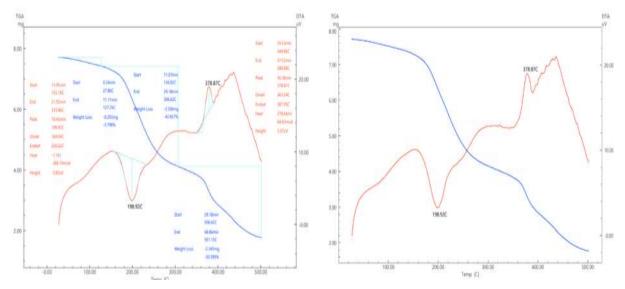


Table 8

According to the IR spectra of the dry and water-soluble hydrogel, the obtained product corresponds to the observed peak at 3336 cm<sup>-1</sup>. SO-N is the potassium salt of polyphosphoric acid and the = O extension of polyvinyl acetate, 2902 cm<sup>-1</sup> and polyvinyl acetate in superabsorbent. The absorption peak associated with OH- bentonite group changed from 3600 to 3400-3200 cm<sup>-1</sup> after the reaction. The absorption peak at 1190 cm<sup>-1</sup> associated with starch was shifted, indicating the change of the OH group in starch during the reaction. The absorption peaks at 3207, 2348 and 1026 cm<sup>-1</sup> of hydrogels wetted with water – CONH<sub>2</sub> and –SO<sub>2</sub> also change during the reaction. A new peak appears at 1403 cm<sup>-1</sup> belonging to the group The above results showed that the characteristic absorption peak of OH and –CONH<sub>2</sub> groups in starch changed after the copolymerization reaction. Differential scanning calorimetric.IX.



# 4. Conclusion

Differential scanning calorimetric. The absence of dramatic weight loss of the starch-based hydrogel was proven by differential scanning calorimetric analysis. Weight loss above 700 C begins in three stages. The first stage occurs at a temperature of  $70^{\circ}$  C  $-198^{\circ}$  C at a rate of 11.07%/min, the second stage at a rate of  $198^{\circ}$  C -3780 C at a rate of 8.28%/min and the third at a rate of -3200 C  $-378^{\circ}$  C at a rate of 3.71%/min. with decay. Tests have shown that weight loss at temperatures above  $70^{\circ}$ C occurs due to the low moisture content of the hydrogel. And at temperatures above  $378^{\circ}$  C - as a result of the decomposition of amino acids in the polymer. It can be seen that there are two weight losses, the first of which takes place at a temperature of  $70^{-1}98^{\circ}$ C at a rate of 12.11% min and the second stage at a temperature of  $378^{\circ}$ C - $500^{\circ}$ C. Very strong absorbent hydrogels - supersorbents deserve special attention. These are three-dimensional polymers with extremely high water absorption capacity, and 1 g of dry gel absorbs up to 1000 g of water. This, in turn, is of great interest due to the problems of moisture retention in the soil of regions with extreme heat and drought. [16].

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