Synthesis of Sulfocationites Based on Filled Polymer Mixtures

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***Abstract*—The purpose of the scientific publication is to consider the issue of the synthesis of sulfo-cationites with improved physical and mechanical properties on a polymer basis. Firstly, to achieve this task, the mechanical and chemical modification of polystyrene and polyvinyl chloride wastes was carried out with the introduction of a filler – red sludge. The optimal conditions of the process of mechanical and chemical modification, i.e. temperature and time, were determined. Further, sulfocationites were synthesized based on a polymer mixture filled with sludge by sulfonation. The main properties of ionites were studied and it was shown that they have satisfactory characteristics.**

***Keywords*—polystyrene waste, polyvinyl chloride, red sludge, mechanical and chemical modification, sulfonation, static and dynamic exchange capacity, swelling coefficient, density, mechanical strength**

I. INTRODUCTION

One of the promising directions in the chemistry of high-molecular compounds is the preparation, synthesis and application of new ion-exchange materials with a complex of properties that solve important scientific and technical problems in various industries.

İon-exchange materials are of paramount importance in chemical technology, in particular in the technology of obtaining biological products and medicinal substances. Ionites have found their application in the production of antibiotics, vitamins, insulin, blood preservation, extraction of toxic substances from the blood, softening and purification of water, in the production of iodine and bromine, as well as in the food industry for the purification of glucose, gelatin, glycerin, etc.

A large number of studies conducted for the synthesis of insoluble ionites have shown that it is possible to achieve high degrees of chemical transformations when introducing various ionogenic groups into polymers and copolymers with a mesh structure of macromolecules. The transfer of the results of these studies to the chemical transformations of linear polymers and copolymers requires, in each individual case, the selection of conditions that determine the nature of the intermolecular interaction in the polymer.

II Experimental part

We have conducted research in the field of synthesis of ion-exchange materials, in particular, the production of sulfocationites based on a polymer frame using household waste and a polymer containing a functional group [1-3]. Binary mixtures based on waste polystyrene and polyvinyl chloride were obtained by the method of mechanical and chemical modification (OPS:PVC) taken in different ratios. Further, on the basis of these mixtures, sulfocationites were obtained by sulfonation. The main characteristics of sulfocationites were studied, such as static and dynamic exchange capacity (SEC and DEC), swelling coefficient in water, mechanical strength, chemical resistance, density, etc. It was found that the density of the obtained ion-exchange materials is 906 kg/cm^3. Sulfocationites having a relatively low density compared to water create some difficulties when conducting tests to determine the dynamic exchange capacity, since ionites float to the surface of the test solution. In order to improve a number of properties of synthesized sulfocationites, in particular, to increase the density of ion-exchange materials, we proposed the idea of adding a mineral filler with a small specific surface area to their composition. Fillers are introduced into ion-exchange materials in order to improve their mechanical and operational characteristics, such as strength, stiffness, heat and heat resistance, as well as to increase their density and bulk volume. These indicators are directly related to the technology of operation of ion-exchange materials. In particular, the low density of polymer sulfocationites does not contribute to the effective use of industrial ion exchange devices. There, in order to increase the efficiency of industrial ion exchange plants, sulfocationites should have a density greater than, for example, the density of the treated water. As a filler to increase the density of the sulfocationites synthesized by us, we used a six-fold washing sludge-the residue of processing alunite from the Ganja Azeraluminium combine, with the following characteristics.

pH (water suspension)…….……7
Density, kg/m^3 3960
Specific surface area, m^2/g .....32 Particle
Size shape, microns.....3-12
Particle shape.....round

The sludge has the following composition, %: SiO_2 – 82; Al_2O_3 – 10; Fe_2O_3 – 5,4; K_2O – 0,30; Na_2O – 0,30, etc.

III Results and discussion

As mentioned earlier, the introduction of a filler into the polymer frame, in addition to changing the mechanical parameters of the obtained mixtures and giving them some special properties, for example, chemical resistance, also reduces the cost of the obtained ion-exchange materials, since fillers, as a rule, have a low cost, and in our case it is a waste of production. The introduction of the filler into the polymer frame was carried out during mechanical and chemical modification. Polystyrene waste, PVC and filler were mixed mechanically in the molten state and then loaded into a laboratory extruder for further modification and for uniform dispersion of the mixture components. The filled polymer mixtures were obtained at a temperature of 140-150^{0}C for 5 minutes. The filler was introduced in an amount of 2÷10% (wt.) from the mass of the polymer mixture of OPS:PVC. To obtain sulfocationites, polymer mixtures filled with sludge were sulfonated with concentrated sulfuric acid in the presence of anhydrous as a catalyst. Sulfonation was carried out for 4 hours at a temperature of 40-50^{0}C. After the end of the reaction, the sulfonated product was transferred to a glass filter and washed with sulfuric acid with a gradual decrease in the acid concentration from 75% to 5%. Then the sulfonated product was washed with distilled water to a neutral reaction and left in distilled water for 24 hours. The granules of sulfocationites washed in this way were filtered and dried in air, and then in a vacuum cabinet at a temperature of 40°C to a constant mass. The main characteristics of sulfocationites obtained on the basis of a mixture of OPS were determined:PVC filled with sludge (Table 1).

№	Composition of sulfocationite, %(wt)		$K_{наб}$ in the water	SEC according NaOH, meq / g	SEC according $CaCl_2$, meq / g	DEC according $CaCl_2$, meq / g	Mechanical strength after 10 hours of shaking, %
	OPS: PVC	Sludge					
1	100	-	1,22	6,0	5,8	0,82	100
2	98	2	1,23	6,34	5,9	0,80	100
3	96	4	1,22	6,67	6,0	0,80	100
4	94	6	1,20	6,67	5,9	0,80	100
5	92	8	1,15	6,32	5,4	0,78	98
6	90	10	1,14	5,99	5,1	0,75	98

TABLE 1. THE MAIN CHARACTERISTICS OF SULFOCATIONITES BASED ON A MIXTURE OF OPS:PVC FILLED WITH SLUDGE

As can be seen from Table 1 with the introduction of into the mixture OPS:PVC sludge, in an amount from 2 to 10% (wt.) the swelling coefficient of sulfocationites in water decreases slightly, and the static exchange capacity increases, although the indicators of DEC worsen compared to a sample that does not contain a filler.

Analyzing the data in Table 1, it can be concluded that in sulfocationites obtained on the basis of a polymer mixture filled with sludge in an amount of 4-6% (wt), the static exchange capacity indicator has better results compared to a sample that does not contain a filler. It is shown that with such an amount of introduced filler, the SOE index of cationites increases from 6.0 to 6.67 mg-eq/g (0,1N each), and at the same time, the indicator of the dynamic exchange capacity of this sample is better than that of others. By introducing sludge in an amount of more than 6%(by weight) into the polymer mixture, a more rigid system is formed, the filler blocks the sulfogroups to a greater extent, the swelling coefficient decreases, as a result of which the sorption parameters of sulfocationites obtained on their basis deteriorate.

There, the optimal amount of filler in the composition of sulfocationite is 4-6% (by weight). The improvement of the properties of cationites occurs, apparently, for two reasons. Firstly, sludge is a mineral filler, the particles of which are metal oxides that shield individual sections of the macromolecule and reduce the destructive effect of sulfuric acid on polystyrene. Secondly, we believe that the metal oxides that are part of the filler, such as, SiO_2, Al_2O_3 and Fe_2O_3 increase the rate of diffusion of sulfuric acid into the mass of the mixture.

IV Conclusions

Polymer mixtures of were obtained by the method of mechanical and chemical modification OPS:PVC:sludge. The mechanical and chemical modification was carried out on a laboratory extruder at a temperature of 140-150^{0}C for 5 minutes. The filler was introduced in an amount of 2 to 10% (wt.).

Further, sulfocationites were obtained based on a modified polymer mixture filled with sludge by sulfonation with concentrated sulfuric acid for 4 hours at a temperature of 40-50^{0}C.

The main indicators of ion-exchange materials filled with sludge were studied, such as SEC (according $NaOH$ and $CaCl_2$), DEC (according $CaCl_2$), swelling coefficient, etc. It is shown that sulfocationites with a sludge content in the amount of 4-6% (wt.) the indicators of static and dynamic exchange capacity have the best results.

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