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Synthesis and study of the properties of filled sulfocation

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Abstract

The purpose of this work is to obtain new ion-exchange materials with improved sorption and mechanical properties. To achieve this task, we obtained a polymer composition based on polystyrene waste, modified with polyvinyl chloride and filled with red mud. Next, the resulting polymer composition was sulfonated with concentrated sulfuric acid (93.6%) in the presence of anhydrous $AlCl_3$. The main indicators of the synthesized sulfonic cation exchanger were studied, such as static and dynamic exchange capacity (COE and DOE), swelling coefficient, mechanical strength, and it was shown that a polymer-based sulfonic cation exchanger sample with a content of 4% (wt.) filler had static exchange capacity have improved results: COE for NaOH - 6.67 mg-eq/g and COE for $CaCl_2$ - 6.0 mg-eq/g.

Keywords: polystyrene waste, polyvinyl chloride, capillary viscometry, exchange capacity, mechanical strength.

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1. Introduction

One of the promising areas in the chemistry of macromolecular compounds is the preparation, synthesis, and application of new ion-exchange materials with a set of properties that help solve important scientific and technical problems in various industries [1–3].

A large number of studies carried out with the aim of synthesizing insoluble ion exchangers have shown the possibility of achieving high degrees of chemical transformations by introducing various ionogenic groups into polymers and co-polymers having a network structure of macromolecules. The transfer of the results of these studies to the chemical transformations of linear polymers and co-polymers requires, in each individual case, the selection of conditions that determine the nature of the intermolecular interaction in the polymer [4–8].

Considering the above, we carried out the synthesis of ion-exchange materials by sulfonation of the finished polymer framework. As a frame, household waste polystyrene modified with polyvinyl chloride was used [9].

The method of modifying polymers or oligomers with small additives was based on the concept of a significant effect of the supramolecular structure, as well as the conditions for the occurrence of relaxation processes, on the properties of polymers. In this case, a complex effect of additives on the structure and properties of polymers is observed [10–11].

2. Experiments

A study of the properties of the melt of polystyrene waste containing 1-5% (mass) of polyvinyl chloride showed that the introduction of PVC at a tempera-ture of 140-150ºC reduces the effective viscosity of the melt, which leads to an improvement in the processability of the material during the extrusion process and makes it possible to introduce fillers [12].

So, having carried out the mechano-chemical modification of polystyrene waste with polyvinyl chloride, polymer compositions were obtained (different ra-tios of the initial components), and then on the basis of these compositions, by sulfonation, we synthesized ion-exchange materials - sulfonic cation exchangers.

The main characteristics of the synthesized sulfonic cation exchangers, such as static and dynamic exchange capacity, swelling coefficient, and mechanical strength, were studied [13–18].

In order to improve a number of properties of synthesized sulfonic cation exchangers, we proposed the idea of adding a mineral filler with a small specific surface to the composition of the modified polymer mixture.

The use of fillers makes it possible to obtain a number of materials with dif-ferent properties on the same polymer base, while the filler can affect the proper-ties characteristic of the polymer base, in our case, the COE, DOE and density of the synthesized sulfonic cation exchangers, as well as the cost of the final prod-uct.

As a filler, we used the sludge of six washings - the residue of the processing of alunite from the Ganja plant "Azeraluminium". The sludge has the following composition, %: – 82; – 10; – 5,4; – 0,30; – 0,30 and others. The main characteristics of the sludge are given in table 1.

№	The name of indicators	Indicators
1	pH (aqueous suspension)	7
2	Density, кg/m^3	3960
3	Specific surface area, m^2/g	32
4	Particle size, мкм	3-12
5	Particle shape	Round

Table 1. Characteristics of the filler – sludge

The filler was introduced into the composition during thermomechanical modification in the molten state in the amount of 2÷10%(mass) of the polystyrene mass.

Interaction criteria in polymer mixtures were determined by the well-known method of G.V. Vinogradov [19].

Next, the granules of pre-swollen samples of the copolymer were subjected to sulfonation

After the completion 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 until neutral and left in distilled water for 24 hours. The granules of sulfonic cation exchangers washed in this way were filtered and dried in air at a temperature of 50–60°C, and then in a vacuum cabinet at a temperature of 40°C to constant weight [20, 21].

3. Results and discussion

As mentioned above, we carried out a mechano-chemical modification of polystyrene waste with suspension polyvinyl chloride. As household waste, we used the inner lining of the ORSK refrigerator, manufactured in 1979. First, household polymer waste was thoroughly cleaned, dried, and crushed. Then some properties of the polymer were determined, such as density, molecular weight, solubility, swelling, and an IR spectrum was taken. These studies have confirmed that the object of study is polystyrene. Further, on the basis of a polymer composition modified and filled with red mud by sulfonation with sulfuric acid, we synthesized an ion exchanger - a sulfonic cation exchanger.

To confirm the course of the sulfonation reaction and obtain sulfonic cation exchangers, the infrared spectrum of the sulfonated sample was taken and ab-sorption bands were found in the spectrum of the sulfonic cation exchanger in the region =460-470 cm^{-1} (aryl sulfides), =1180-1200 cm^{-1} (sulfo groups), =1310-1335 cm^{-1} (alkyl sulfones) corresponding to the structure of sulfo groups and confirming the formation of sulfocation exchanger (Figure 1).

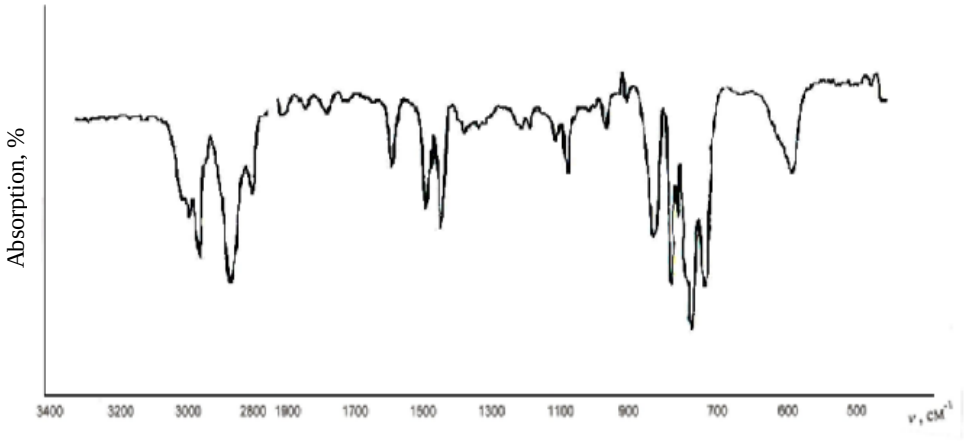

Figure 1. IR spectrum of sulfonic cation exchangers synthesized based on modified mixture OPS:PVC:filler. PVC content - 2% (wt.); filler 4% (wt.)

Further, the main characteristics of sulfocation exchangers based on a mixture of OPS:PVC:filler, such as static and dynamic exchange capacity, mechanical capacity, and swelling coefficient were determined (Table 2).

№	Sulfonic cationite based, % (mass)		K_{nab} in the water	COE for NaOH, mg-eq/g	SOE for $CaCl_2$, mg-eq/g	DOE for $CaCl_2$, mg-eq/g	Mechanical strength after 10 hours of shaking, %
	OPS: PVX 2%(mass)	Sludge					
1	100	-	1,23	6,0	5,8	0,82	100
2	98	2	1,23	6,31	6,0	0,81	100
3	96	4	1,22	6,67	6,0	0,80	100
4	94	6	1,21	6,66	5,9	0,80	100
5	92	8	1,18	6,32	5,7	0,79	100
6	90	10	1,15	5,99	5,4	0,72	98

Table 2. Main characteristics of sulfonic cation exchangers based on OPS: PVC mixture filled with red mud

As can be seen from the data in Table 1, with the introduction of sludge into the composition of the OPS: PVC mixture, in an amount of 2 to 10% (wt.), the swelling coefficient of sulfonic cation exchangers in water slightly decreases, and the static exchange capacity increases, although the DEC indicators deteriorate compared to the sample containing no filler.

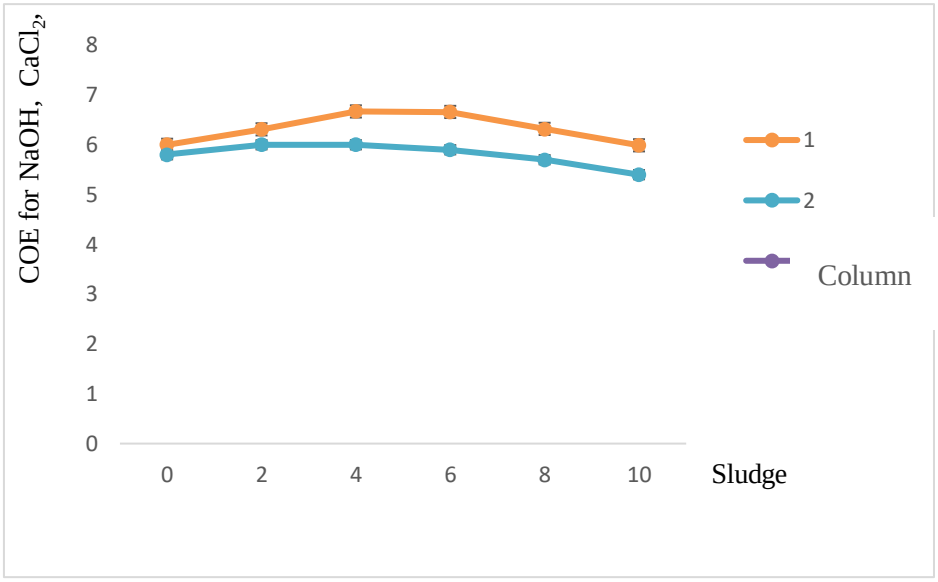

Figure 2. Dependence of COE min depending on the amount of filler contained in the composition
1- COE for NaOH, mg-eq/g
2- SOE for $CaCl_2$, mg-eq/g

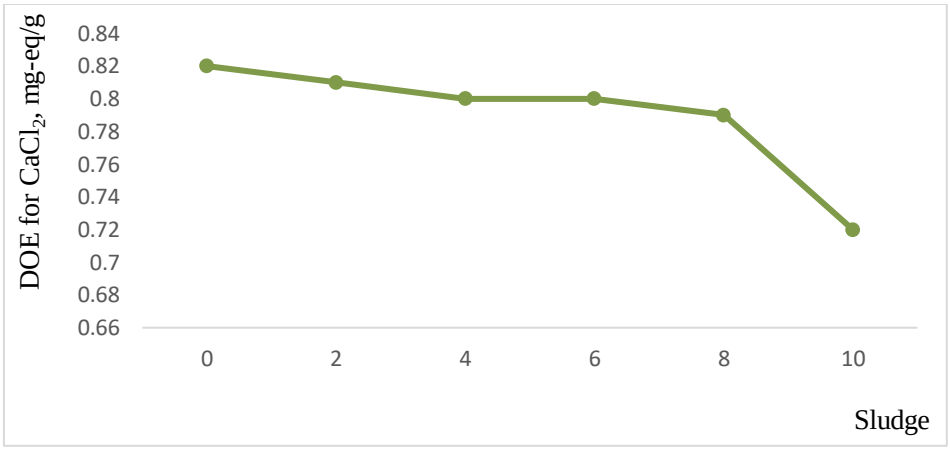

Figure 3. Dependence of DOE depending on the price of the filler

Analyzing the data in Table 1, we can conclude that the sulfonic cation exchangers obtained on the basis of a polymer mixture filled with sludge in an amount of 4% (mass) have the best static exchange capacity index compared to a sample that does not contain a filler. It is shown that when a filler is introduced into the composition of the OPS: PVC polymer mixture, the COE index of cation exchangers increases by 1.17 times, i. e. from 6.0 to 6.7 mg-eq/g (by 0.1N NaOH). By introducing more than 6% (mass) of the sludge into the polymer mixture, a more rigid system is formed, the filler blocks sulfo groups to a greater extent, the swelling coefficient decreases, as a result of which the sorption parameters of sulfocation exchangers obtained on their basis worsen [22, 23].

4. Conclusion

In order to increase the impact strength of polystyrene waste and sulfonic cationites obtained on its basis, the OPS was modified with polyvinyl chloride (1-5% (wt.)) and filled with red mud. The process of modification and filling was carried out by the extrusion method at a temperature of 140-150°C. The filler was introduced into the composition in the amount of 2÷10% (mass) of the polymer mass. Further, to obtain an ion exchange resin, the polymer composition was sulfonated with concentrated sulfuric acid.

To confirm the course of the sulfonation reaction and obtain sulfonated cation exchangers, the infrared spectrum of the sulfonated sample was taken and absorption bands corresponding to the structure of sulfo groups were found in the spectrum of the sulfonated cation exchanger.

The main characteristics of sulfonic cation exchangers synthesized on the basis of a filled polymer composition were studied and it was shown that modification with polyvinyl chloride and filling with red mud leads to an improvement in exchange characteristics and contributes to an increase in mechanical strength, as well as a reduction in the cost of the cost of synthesized ion exchangers. It is shown that sulfonic cation exchangers containing 4% (wt.) filler have more satisfactory sorption and mechanical properties.

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