

Investigation of the structure and morphology of modified materials based on polyvinyl chloride

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Abstract. The use of polyvinyl chloride in practice is associated with many difficulties due to the hydrophobic nature of the polymer surface. This can lead to great adverse consequences when used in technological processes of the chemical industry and hydrometallurgy. Due to its high hydrophobicity and low surface free energy, PVC has a low degree of wettability with water, resulting in low ion sorption capacity, as well as undesirable protein absorption and bacterial adhesion. The aim of the work was to increase the hydrophilicity of the surface of industrially produced powdered PVC by modifying it with various organic amines and, as a result, hydrophilic ion-exchange materials of various structures and morphology will be obtained on its basis. The course of the reactions was studied by potentiometric titration, IR spectroscopy, and diffractionometry. The correlation between the morphology and chemical properties of the products obtained in the studied reactions and the formation of new covalent bonds in the structure of the polymer matrix was investigated using IR spectroscopy and diffractionometry. The influence of the nature of the modifying reagent, solvent and temperature on the modification process has been established.

1 Introduction

In the world, polyvinyl chloride (PVC) is the fourth widely used synthetic polymer in terms of accounting for consumption for global production (46 million tons per year). A significant amount of it is used mainly in the construction field over 55% , electrical engineering 15.0% , transport - 10.0%, consumer goods – 10.0% and other industries 10.0% [1].

It is known that interactions among various materials take place on their surface. In the case of polymer materials, in addition to environmental factors such as pressure, pH and temperature, these interactions can be significantly influenced by changes in the

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hydrophilicity, topography and chemical composition of their surface. This implies that by manipulating the surface characteristics from the point of view of physico-chemical aspects, it is possible to change the interaction in the desired direction. Because of this, the surface modification of polymers has become a very relevant area of research for many scientists. To this end, many scientific works have been carried out using various methods: from simple - physical and mechanical surface treatment of polymers to complex - adsorption of various substances and chemical modifications [2]. The obtained scientific conclusions indicate the possibility of using chemical modification methods to solve this problem with a very slight change in most properties of PVC [3,4].

The presence of labile chlorine atoms in polyvinyl chloride is considered to be the main source of its negative properties, which leads to some violations of intermacromolecular interactions and, consequently, PVC products have the above disadvantages [5]. Such unstable or irregular chlorine atoms, which from a chemical point of view belong to allylic and tertiary chlorides, can easily be converted into other functional groups. These tertiary and allyl chlorine atoms have been subjected to numerous chemical modifications by various researchers [6]. In particular, a chemical modification of PVC was proposed aimed at obtaining ion-exchange materials of various types (fibers, films, granules), ion-selective electrode membranes, membrane sensors and products for biomedical devices [7,8].

2 Materials and methods

To obtain various types of ion-exchange materials, PVC powder obtained by the industrial suspension method (S 70 grades) was used as an object of research, and thiourea, guanidine and aminoguanidine (H.H. grades) were used as modifying reagents. Sorbent samples were synthesized in autoclaves with a volume of 50 ml, where PVC powder was placed and poured in calculated volumes an aqueous solution of modifying reagents of various concentrations. The autoclave was sealed and heated in a LABWIT thermostat for a certain time at a set temperature. After completion of the modification reaction, the autoclave was cooled to room temperature, the product was removed from the autoclave and the product was separated from the solution by filtration. The non-reacting reagents were removed by rinsing the resulting product with water. Next, the product was dried in air and the static exchange capacity (SOE) was determined by reverse titration.

Potentiometric titration was performed on an I-130 ionomer with a glass electrode with a measurement accuracy of 0.02 pH units at 298 K. The ionomer was pre-calibrated with buffer solutions.

IR spectroscopic studies of the synthesized sorbents were carried out on a Fourier infrared spectrometer Nicolet iS50 (Thermo Fisher Scientific) in the range of 400-4000 cm^{-1} .

The morphology of the particles of the obtained sorbents was studied using an Imperial Series 2 diffractometer, as well as a Series Scanning Electron Microscope at various magnifications.

3 Results and discussion

PVC is a chemically resistant polymer with good mechanical strength and impact resistance; on the other hand, it has a very low water absorbency [6]. Usually, for the completeness of polymerological reactions, the location of macromolecules in space and the availability of polymer functional groups for modifying reagents play an important role [9]. Table presents the conditions for the synthesis of the developed ion-exchange materials.

Table 1. Dependence of synthesis conditions and values of static exchange capacities of modified PVC samples (the reaction time is 6 hours, the bath module is 1:20).

№	Sample number	Solvent	Modifying reagent concentration	T, °C	HC COE1, mg-eq/g
1	Sample 1	water	20 % thiourea	140	0.988
2	Sample 3	water-ethanol (70 %)	23 % thiourea	140	1.26
3	Sample 4	water-ethanol (70 %)	22% thiourea	140	1.14
4	Sample 21	water-dioxane (20 %)	15 % thiourea	160	1.66
5	Sample 22	water	15 % thiourea	160	1.58
6	Sample 23	water-dioxane (20 %)	15 % thiourea	165	1.80
7	Sample 24	water	15 % thiourea	165	1.65
8	Sample 25	water-dioxane (20 %)	20% thiourea	165	3.17
9	Sample 26	water-ethanol (70 %)	20% thiourea	165	2.21
10	Sample 27	water-glycerin (32 %)	20 % thiourea	165	1.92
11	Sample 28	water	20 % thiourea	165	2.24
12	Sample 29	water	19 % thiourea	165	2.12
13	Sample 30	water	20 % guanidine	165	2.31
14	Sample 18	water	10 % aminoguanidine	120	1.14
15	Sample 20	water	15 % aminoguanidine	125	1.82
16	Sample 38	water	20% aminoguanidine	140	2.30
17	Sample 35	water	25% aminoguanidine	160	2.58

As expected, in the studied reactions of PVC modification with amines, the product yield was influenced by the temperature of the process, the concentration and nature of the modifying reagent, as well as the nature of the solvent, which predetermined the morphology of the materials obtained. As a characteristic of the completeness of the studied reactions, we selected the SOE of the obtained samples.

In the IR spectrum of the initial PVC (Figure 1) and its modifications, three absorption regions are observed (Figure 2-5): in the range of 600-700 cm^{-1} characteristic of the C-Cl bond; in the range of 900-1200 cm^{-1} characteristic of the C-C bond; the third region extending - 1250-2970 cm^{-1} characteristic of numerous modes of C-H PVC [10]. It can be seen from Figure 2 that when using guanidine as a modifying reagent, it shifts to 1713.5 cm^{-1} , and a new peak appears in the region of 1601.14 cm^{-1} , characteristic of deformation vibrations [11]. When used as a modifying reagent of thiourea, it shifts to 1735.17 cm^{-1} (Figure 3), which indicates the influence of the nature of the modifying reagent on the modification process.

Another strongly influencing factor in the polymer modification process is the solvent. A comparison of the spectra of samples modified with amines in water with the spectrum of the initial polymer shows their very close similarity (Figure 1-3), which is apparently explained by the high hydrophobicity of PVC and the very low moisture permeability of this polymer. With an increase in the solvent capacity of the solvents of the polymer under study in the order: water < ethanol < glycerin < dioxane, a significant increase in the COE of the products obtained is observed, which indicates a positive effect of the solvent on the course of the reaction in the above order (table) [12].

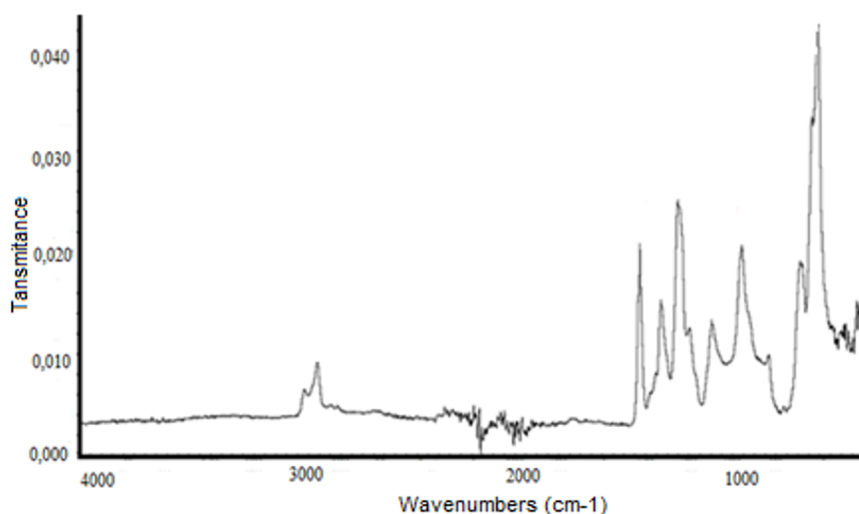


Fig. 1. The IR spectrum of the original PVC.

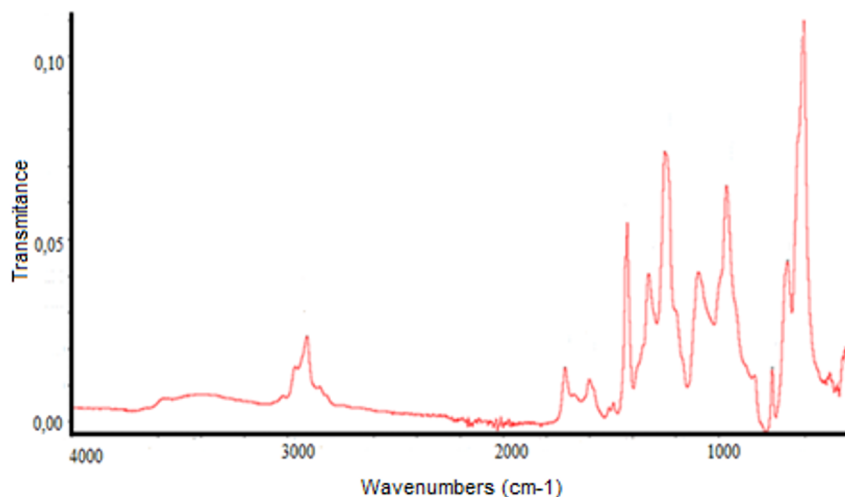


Fig. 2. IR spectrum of modified PVC with guanidine (sample No. 30).

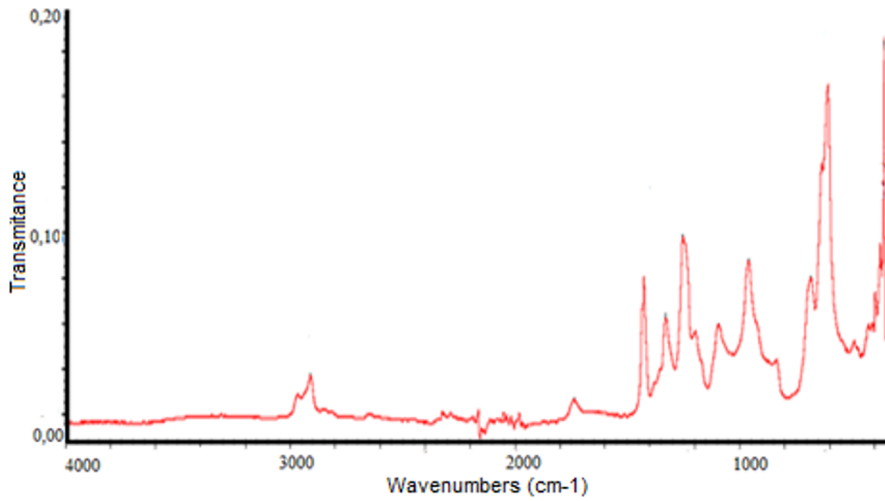


Fig. 3. IR spectrum of modified PVC with aminoguanidine (sample No. 20).

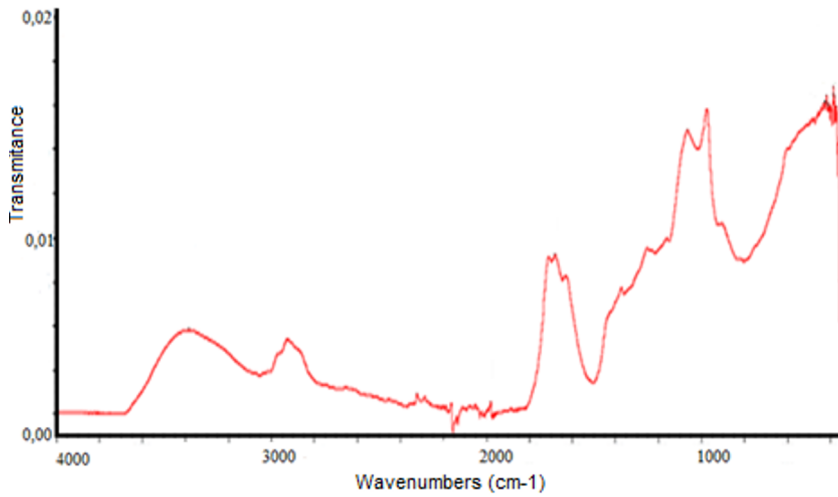


Fig. 4. IR spectrum of modified PVC with thiourea (sample No. 3).

In the IR spectra of samples obtained in aqueous organic solvents, an expansion of the absorption regions and the appearance of new absorption signals observed (Figure 4, 5) [13]. For example, deformation fluctuations of the secondary amino group are manifested in the absorption region of 3383.55 cm^{-1} (Figure 4). The same situation was observed in IR spectra obtained in solutions: water-glycerine and water-dioxane (Figure 5). It was interesting to compare the IR spectra of samples obtained by modification of aminoguanidine PVC with previously presented. It can be seen from Figure 6 that the signal related to the valence oscillations of the secondary amino group in the region of 3290.02 cm^{-1} , and especially in the region of 2919.26 cm^{-1} , is even more pronounced [14].

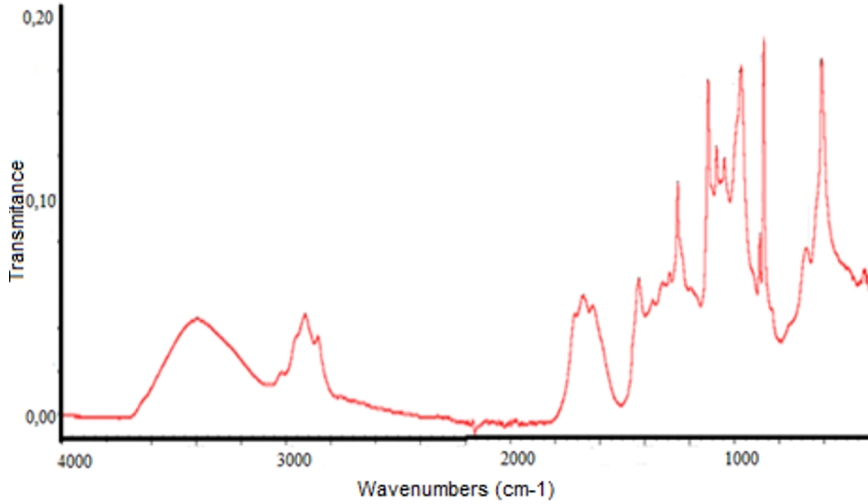


Fig. 5. IR spectrum of modified PVC with thiourea (sample No. 25).

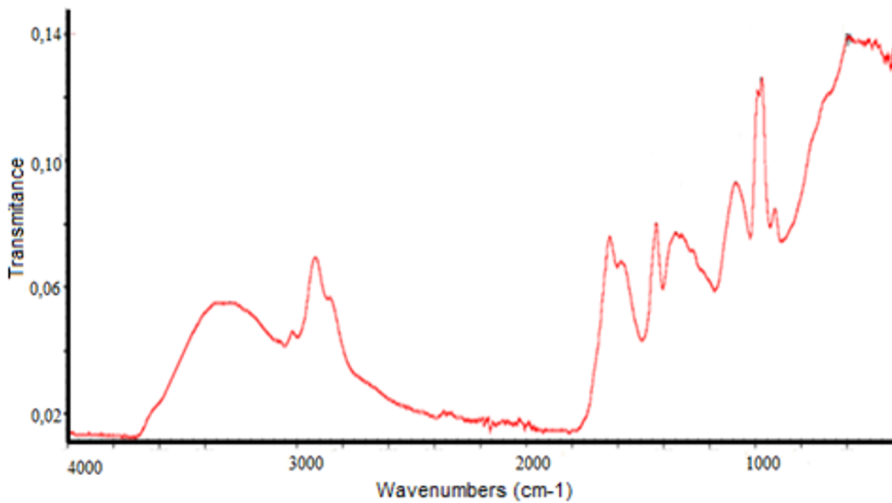


Fig. 6. IR spectrum of modified PVC with aminoguanidine (sample No. 18).

It is known that the morphology and structure of polymers strongly affects its sorption and technological characteristics [15-18]. Therefore, it was important to investigate the change in the morphology and particle structure of the sorbents obtained in the studied PVC modification reactions. PVC itself has a low X-ray diffraction intensity, which cannot be detected by standard diffraction methods. The intensity of a commercial PVC sample is only five times higher than the background values. The improvement of the experimental diffractometer technique made it possible to overcome such low PVC diffraction. The following factors are the reason for the very low X-ray diffraction intensity of PVC [12-20]:

- 1) Only syndiotactic isomers of polymers can have crystalline regions. Isotactic and atactic isomers have an amorphous structure and the diffraction intensity is overestimated only by the amount of the syndiotactic isomer in the sample, the proportion of which in the commercially produced polymer is very insignificant.

2) Theoretically, the diffraction of a sample of a syndiotactic polymer isomer is based on the two-axial ordering of macromolecules, although three-dimensional ordering would lead to an increase in the reflectivity of the planes.

3) Probably the molding conditions in industrial conditions also make the PVC structure more amorphous.

4) The main criterion for optimal diffraction ability of an unknown sample is an arbitrarily oriented crystallinity in such a way that X-rays can be reflected repeatedly in the aisles of each crystal. This requirement cannot be fully satisfied by any organic polymer, although in fact, small crystalline areas can contribute to the expansion of lines or, in extreme cases, to an amorphous background.

In our work, we used a method based on the averaging principle of recording the diffraction of samples. The only diffraction trace obtained on the diffractometer and the band diagram of the recorder did not always show one diffraction peak, which stood out quite clearly, but recorded repeating traces superimposed on the original curve and gave out as averaged for this sample. A comparison of radiographs of the original polymer and modified PVC forms shows that all samples have a mostly amorphous structure, since the radiographs are located below 1000 units of X-ray signal intensity. However, the high resolution and sensitivity of the Imperial Series 2 diffractometer made it possible to fix some ordered areas in the particles of the polymer under study (Figure 7), which are consistent with the literature data [4,16,17,21].

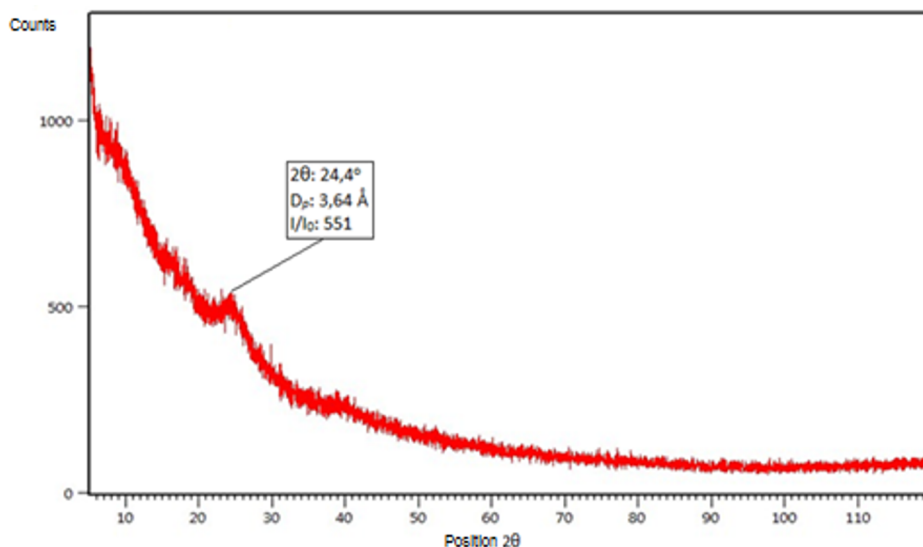


Fig. 7. X-ray of the initial polyvinyl chloride.

It is expected that the reactions of PVC modifications with various reagents affect the morphology of the initial polymer. When comparing radiographs modified with different PVC amines under the same conditions (Figure 8), a difference is found, which indicates the influence of the nature of the modifying reagent on the morphology of the sorbent obtained. Apparently, the small chemical structure of thiourea is more convenient for partial ordering of macromolecules, which leads to an increase in such sites (Figure 8). As expected, the results of the conducted studies showed a strong influence of the solvent on the morphology of the sorbents obtained. When comparing radiographs of PVC modified with thiourea in water and in various aqueous organic solvents, a significant difference is found, which indicates the influence of the nature of the solvent on the morphology of the samples obtained (Figure 8-10). It can be seen that with an approximately close number of

modified groups in the product, an increase in the content of organic matter (ethanol) in the solvent favors an increase in ordered areas. And the presence of a "good" solvent for PVC dioxane in the system, even in smaller quantities, allows you to obtain a sorbent with a higher SOE content (table, sample No. 25). It should also be noted that the highest value of the diffraction peak is observed in this sample.

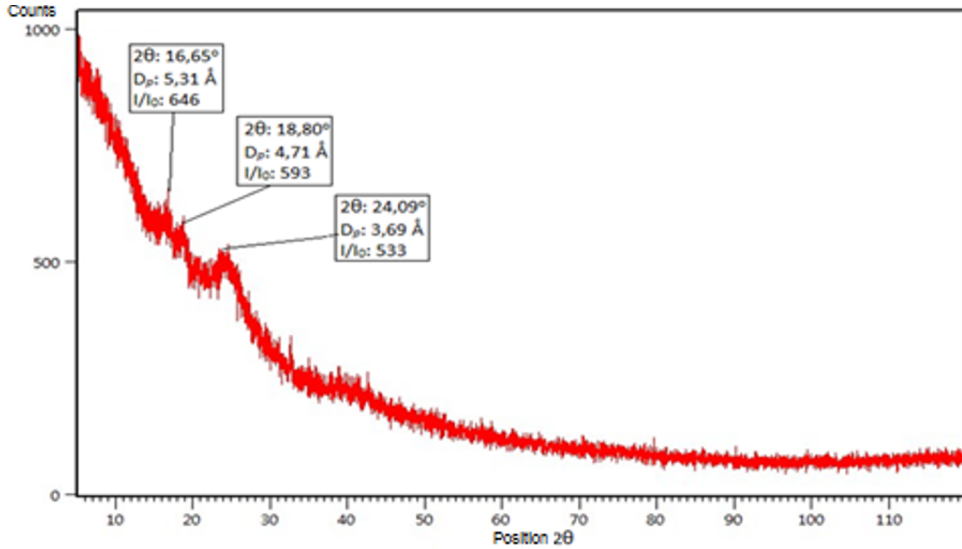


Fig. 8. Radiograph of PVC modified with thiourea in water (sample No. 28).

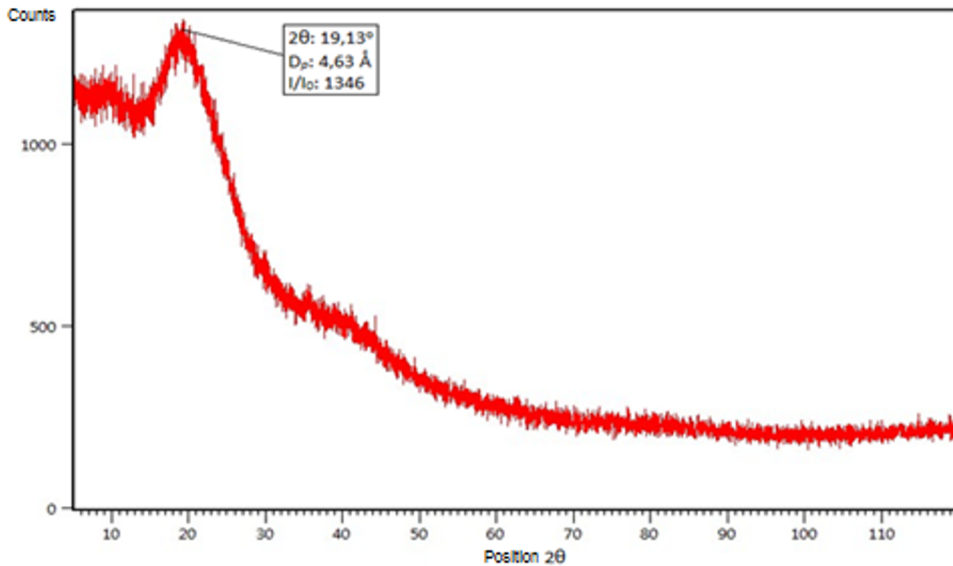


Fig. 9. Radiograph of PVC modified with thiourea in an aqueous alcohol solvent (sample No. 26).

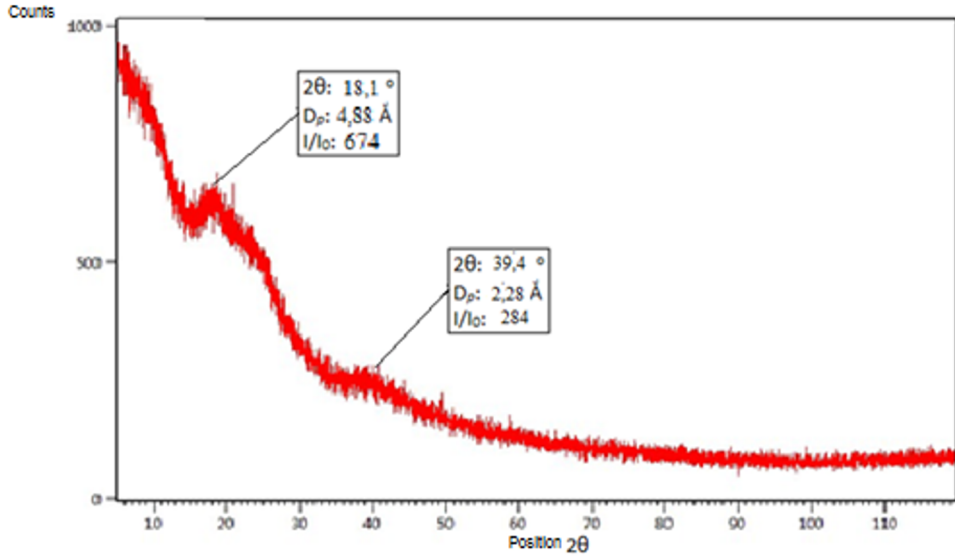


Fig. 10. Radiograph of PVC modified with thiourea in an aqueous dioxane solvent (sample No. 25).

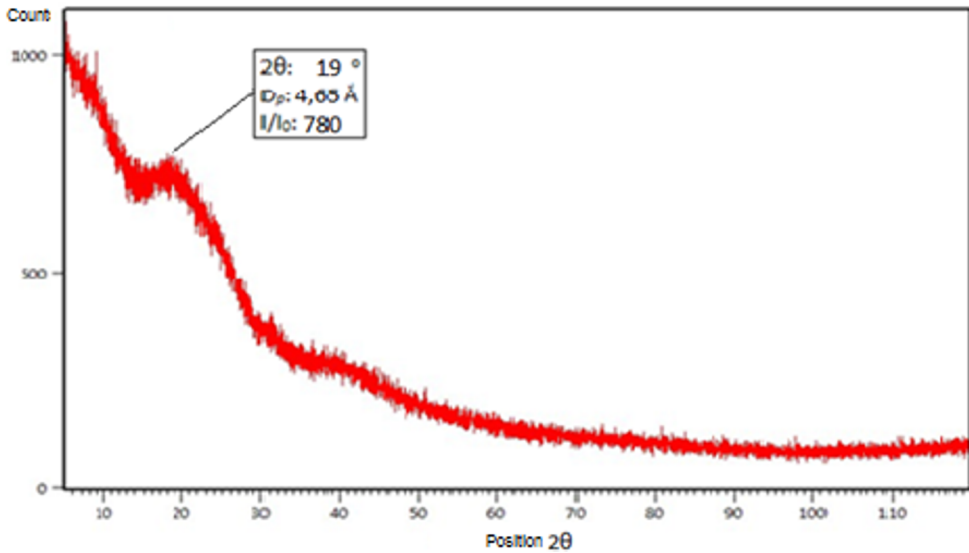


Fig. 11. Radiograph of PVC modified with aminoguanidine (sample No. 20).

It was interesting to compare the X-ray images of PVC samples modified with aminoguanidine with different contents of amino groups in the polymer matrix. The results showed that an increase in ESR, that is, amino groups in the sorbent, leads to an increase in ordered sites on polymer particles. Apparently, in this case, partial crosslinking of macromolecules occurs, as well as various sections of the macromolecules themselves are more likely, which can increase the number of ordered sections in the polymer (Figure 6). It can be seen that an increase in the value of SOE from 1.14 to 2.58 mg.eq/g leads to a twofold increase in the ordered areas in the sorbent particles.

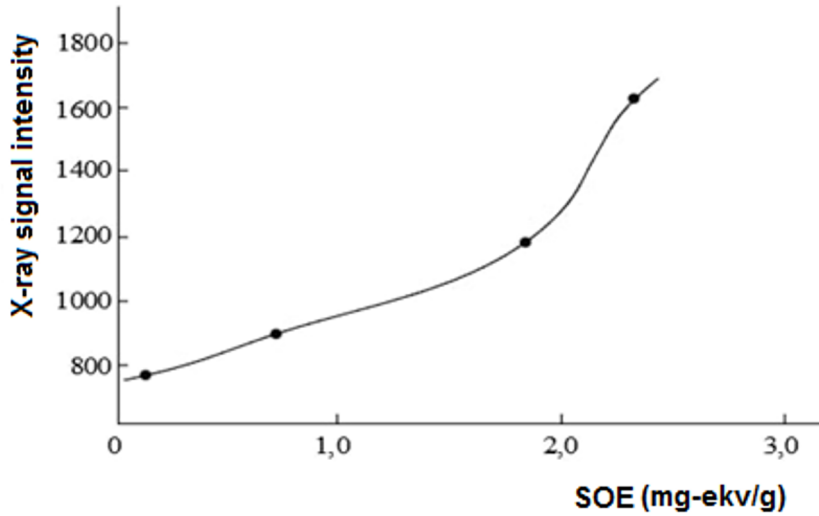


Fig. 12. Dependence of the intensity of Bragg peaks on the SOE of a PVC sample modified with aminoguanidine.

Studies of the structure of the obtained modified PVC samples on the ZEISS EVO MA Series Scanning Electron Microscope device at various magnifications showed that under the conditions of surveys, the dispersion of the particles of the original PVC did not affect the roughness of the topographic surface, and all of them have a sufficiently porous structure (Figure 13).

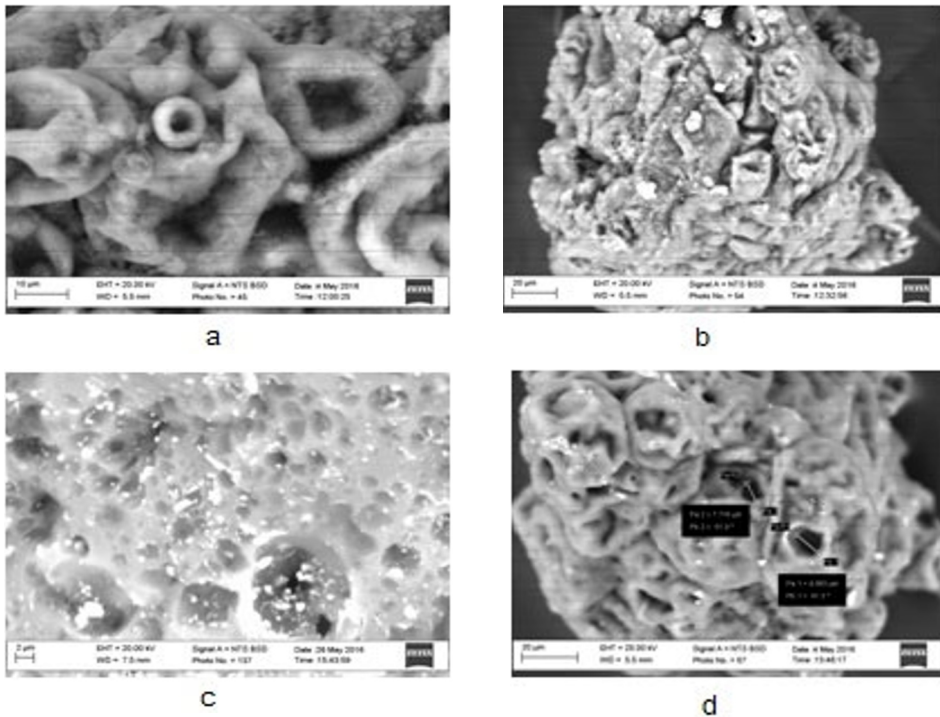


Fig. 13. Micrography: a) the original PVC, b) PVC modified with thiourea in alcohol, c) PVC modified with thiourea in dioxane, d) PVC modified with aminoguanidine in water.

The similarity of structures in samples synthesized in water and aqueous alcohol solvents with the initial polymer, as noted above, can be explained by the small water absorption capacity of PVC. It also follows from the obtained images that the fragments of particles have smooth spherical shapes and depressions. Experimentally, a decrease in particle size was found in all cases of polymer modification.

4 Conclusion

The synthesis of PVC-based ion exchange materials has been investigated and the chemical structure and chemical properties of the products obtained have been determined, which depends on the nature of the modifying reagents. In all the studied reactions, crosslinked structures are formed due to the crosslinking reactions of macromolecules with the used multifunctional organic molecules.

All the reaction products obtained have ion-exchange properties due to the inclusion of functional groups ionizing in water in their structures, the number of which strongly depends on temperature and on the nature of the solvent. It was found that the used solvents are arranged in the following row according to their activity: water < ethanol < glycerin < dioxane.

The surfaces of ion-exchange materials have been studied, which have a sufficiently porous structure and topographic roughness, particle fragments have smooth spherical shapes and depressions. A correlation has been established between the morphology and chemical properties of ion-exchange materials.

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