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THE METHOD OF PRODUCING HYDROPHOBIC ORGANOSILICON POLYMERS BASED ON HYDROLYZED POLYACRYLONITRILE

Abstract. The article discusses the possibilities of obtaining hydrophobizators based on hydrolyzed polyacrylonitrile and tetraethoxysilanan. Studies have shown that the properties of the resulting composition depend on the temperature and the ratio of selected substances. The optimum temperature for obtaining the desired composition is the temperature range 10-50 °C. Samples were investigated by methods of differential thermal analysis, IR spectrometry. The resulting composition is not inferior to existing analogues in terms of its hydrophobic properties, and the cost of the materials developed is 10–15% lower compared to alkyl silicates.

Key words: polymer, hydrolyzed polyacrylonitrile, organosilicon compounds, viscosity, hydrophobization, solution.

Introduction. Hydrolyzed Polyacrylonitrile (HPAN), like other acrylic polymers, forms with clay particles strong polymer clay structures due to chelate bonds and polymer membranes, which partially prevent the hydration of rocks. Additive HPAN in fresh solutions at 30 °C is up to 0.15% (dry) or 1.0-1.5% of liquid, at 100-120 °C to 0.75%, at 150 °C to 2%. When using low-mineralized solutions, the consumption of HPAN increases several times, and the heat resistance is no more than 100 °C. HPAN exhibits an optimal protective effect at pH = 10-11, at larger and smaller values of which coagulation of clay particles occurs, especially in fresh solutions at elevated temperatures.

An aqueous solution with a concentration of 33% with a density of 1.2409 g/ml of yellowish color, is a viscous liquid mass that dissolves in water in any ratios [1].

HPAN is an interesting object from the point of view of theoretical and practical study as a crosslinking agent for the production of hydrophobic polymers. Because, organosilicon compounds have a peculiar property, i.e. Processed materials with these substances do not allow moisture and water to pass, forming a thin film, while the air permeability of the material is preserved. Such a film is resistant to temperature changes, chemically stable and has mechanical strength. In this regard, in recent years there has been an intense increase in interest in obtaining and researching the use of organosilicon compounds in various fields.

From the analysis of the known scientific literature, in our opinion, a convenient method for producing organosilicon compounds can be considered the method of crosslinking [2].

EXPERIMENTAL PART

Synthesis of HPAN.

Reagents: polyacrylonitrile 10 g, sodium hydroxide 8% solution 110 ml, methanol 250 ml.

Equipment: Round bottom flask, reflux refrigerator, glass, oil bath, capillary viscometers of the Ubbelohde type, NETZSCH STA-409 PG TG-DSC analyzer, IR-spectrometer, REM 250 adhesiometer.

In a 300 ml round-bottom flask, equipped with a reflux condenser, 110 ml (0.22 mol) of 8% sodium hydroxide solution are poured in and 10 g (0.2 mol) of finely ground polyacrylonitrile are poured. The mixture is heated on an oil bath to a boil (bath temperature is about 100-110 ° C) and held for about 13 hours. When the solution becomes colorless and transparent, the heating is stopped, the solution is cooled and poured into a 500 ml beaker, neutralized with 0–5 N hydrochloric acid to pH 8–8.2 according to a universal indicator.

Sodium polyacrylate is precipitated from the solution by adding 150 ml of methanol. The precipitate obtained is filtered on a Buchner funnel and washed with methanol until all the chlorides in the solution disappear. The purified sodium polyacrylate is air dried for 48 hours. The polymer yield is 15.6 g

Crosslinking of organosilicon compounds. In a flask equipped with a stirrer, a thermometer and a separating funnel, 10 ml of HPAN were placed and, keeping the temperature at about 15-60 °C with vigorous stirring, slowly, dropwise, was added (with emulsifier) tetraethoxysilane (TEOS). Then the solution was stirred for several hours at room temperature, after which a viscous polymer with a silicon content was obtained.

Reactions were carried out in the ratios of HPAN:TEOS 50: 1; 50: 2; 50: 3; 50: 4; 50: 5 moles and different temperatures by constant mixing.

DISCUSSION OF THE RESULTS

It was determined that even at low degrees of conversion, the polymer yield depends on the initial ratio of components and temperature. It was found that with initial conversions, the yield of the product increases linearly in accordance with the duration of the reaction.

In order to influence the temperature on the kinetics, the reaction was carried out at a temperature range of 10-50 °C with different ratios of the initial reagents (with an increase in the HPAN ratio from 10:1, a solid mass was obtained that did not dissolve in solvents, this is apparently due to the complete crosslinking of the substances). An increase in temperature led to an increase in the rate of the process, and to an increase in the yield of the polymer. An increase in temperature from 50 °C and further resulted in complete crosslinking and the formation of a solid mass. Note that at the same time the resulting product had a higher characteristic viscosity, which is clearly seen from figure 1.

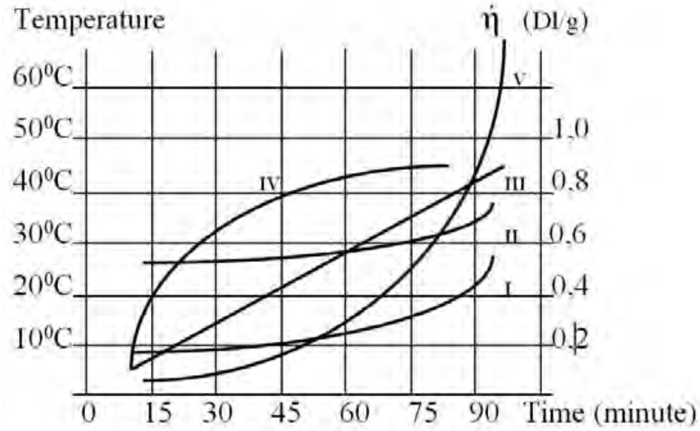

Figure 1 – Change in viscosity relative to time and temperature

The viscosity of (oligo)polymers in organic solvents was measured in capillary viscometers of the Ubbelohde type, which allow sequential dilutions of the sample under study in the viscometer itself. Viscosity was determined at 50 ± 0.1 °C by a known method.

As can be seen from the figure 1, with an increase in the ratio of TEOS reagent and temperature, an increase in viscosity is observed, which can be attributed to an increase in the degree of crosslinking. As the amount of TEOS and temperature increases, HPAN hardens. The obtained sample was studied by the method of IR-spectroscopy, and also, the differential thermal analysis (DTA) indices, which indicate crosslinking by carboxyl bonds, were investigated.

Thermoanalytical studies were conducted on a NETZSCH STA-409 PG TG-DSC analyzer, equipped with a K-type (Low RG Silver) thermocouple and using aluminum crucibles. The amount of sample was taken in the range of 5-6 mg.

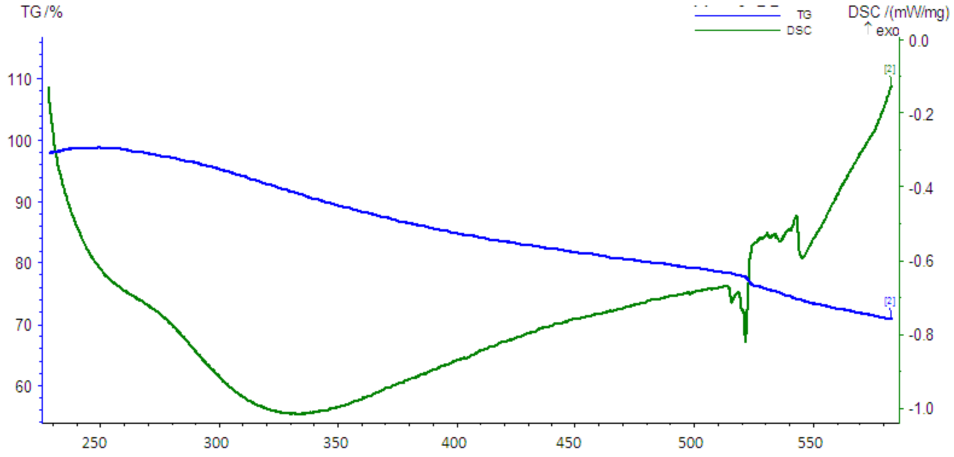

Figure 2 – Thermal examination of the sample

All measurements were carried out in an inert atmosphere of nitrogen with a purge rate of 50 ml/min. The temperature range of measurements was 20-600 °C at a heating rate of 10 K/min. The measuring system was calibrated using standard substances – indium, bismuth, tin, zinc, and cesium chloride.

From the data obtained, it can be concluded that thermal stability increases with an increase in the silicone bridges in the HPAN molecule. The decomposition temperature of HPAN 350 °C is known from the scientific literature.

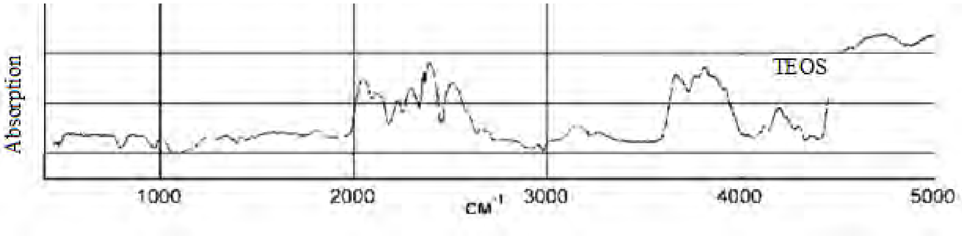

Figure 3 – Spectrum of TEOS

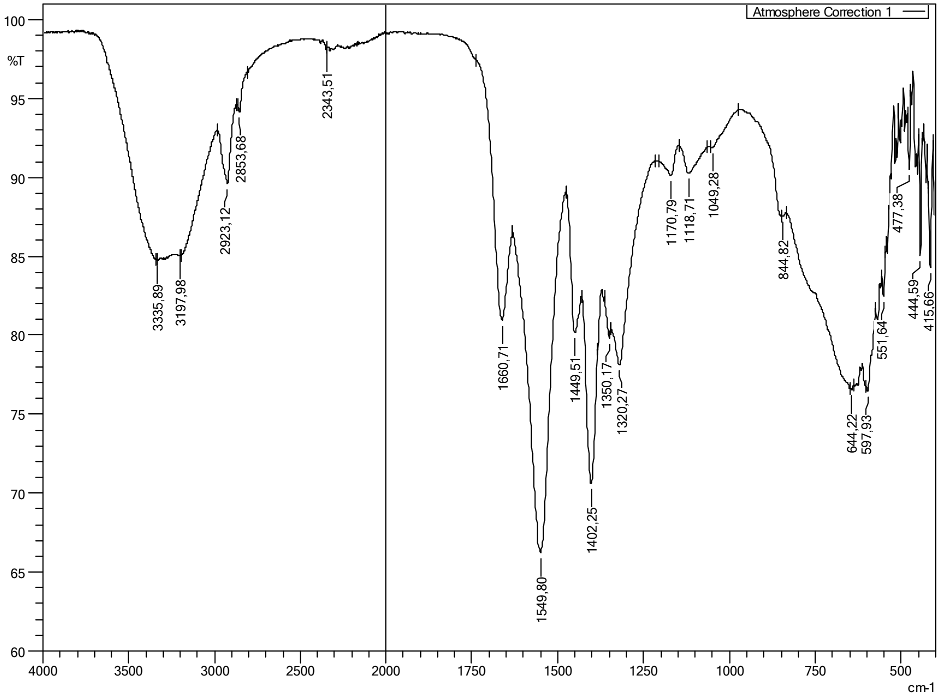

Figure 4 – IR spectrum of a polymer film crosslinked with TEOS

In figure 4 the absorption bands of the average intensity in the region of 1400, 1465, 1250 cm^{-1}, characterizing the stretching vibrations of a single C – C bond, are noted. The absorption bands of about 1025 and 1095 cm^{-1} of vibration frequencies indicate, respectively, the presence of Si-OH and Si-C bonds.

The characteristic bands of the valence vibrations of the multiple bond for the ethylene group (υ (C = C)) are found to be 1795, 1740, 1680 cm^{-1}. Such characteristic absorption band is also present in the spectra of a compound.

Based on the spectra shown in Figures 3,4 it can be concluded that the carboxyl groups in the composition of HPAN entered into the esterification reaction with the CH_3CH_2O-groups in TEOS.

On the basis of the obtained crosslinked TEOS polymer, compositions with different makeup were created and their hydrophobic properties were studied.

The study of the effect of hydrophobization was carried out on standard samples. Water repellency was carried out by immersing the samples for two minutes in a 5% solution of the studied polymer composition and their subsequent exposure to air for 28 days.

One of the conditions for long-term preservation of the beneficial properties of water-repellent coatings is the presence of sufficient adhesion between the protective polymer film and the building material. However, it is extremely difficult to determine the adhesion characteristics directly on the hydrophobic sample due to the fact that the cement material has a porous structure and, moreover, there is no continuous polymer film.

For the formation of a continuous film of sufficient thickness, a solution of a water-repellent agent with a higher concentration was used. Adhesive characteristics were determined on an REM 250 adhesiometer. The hydrophobic composition in the form of a 15% solution in alcohol was applied to the substrate using a pneumatic spray. After drying the material for 72 hours, steel bar were glued to the coating with acrylate glue and tests were carried out to determine the tensile strength at detachment.

This circumstance is apparently related to the porosity of the structure of these materials, which probably led to overestimated results in determining the tensile strength at separation. But, despite this, the tensile strength for separation for a solid substrate reaches a significant value - 3.8 MPa, and the control value is relatively smaller and amounts to - 2.9 MPa, but on the whole is at a fairly high level.

The dependence of the tensile strength at separation, regardless of the material of the substrate, is extreme. The maximum values of the tensile strength at separation are achieved at a TEOS concentration of 8–10%. To study the weather resistance of the hydrophobic coating, accelerated tests were carried out in a climatic chamber for 30 days of both the hydrophobised samples and coatings in the form of a film obtained similarly as in the case of determining the adhesive characteristics.

It is usually accepted that testing samples for 15 days in a climate chamber corresponds to one year of their stay in actual atmospheric conditions. Adding to the composition already 10% of TEOS increases the material's resistance to adverse technological conditions, and the modified coatings withstand the test without damage. The loss of the hydrophobic effect for compositions containing TEOS is extremely insignificant and, according to the test results, it can be assumed that the life expectancy of satisfactory hydrophobic properties during operation of structures treated with these compositions in real conditions will be at least five years. This is comparable with such commonly used water repellents as sodium silicates. According to preliminary calculations, the cost of the developed materials will be 10–15% lower compared to alkyl silicates, which, under the conditions of their mass use, can lead to a significant economic effect.

Use for the preparation of a hydrophobic composition based on HPAN as an adhesive – hydrophobic agent does not cause technological difficulties in its dosing and mixing with other components. High miscibility and aggregative stability of the composition in the form of a mixture, in an environment of organic solvents, and not stratified during storage indicates the effectiveness of the developed composition.

Hydrophobization of polymers leads to a long synthesis time, a decrease in the yield of the target product (especially in the workshop conditions) and complicates the transition to a continuous process. The filtering stage is particularly laborious, leading in particular to a more than one and a half time increase in the amount of solvent used. Large losses of volatile solvents at the stage of selection of the target product in the workshop conditions lead to environmental pollution.

The hydrophobic processing developed by the compositions was carried out using a laboratory unit according to the following procedure.

The installation was poured, the calculated amount of the developed hydrophobic composition was thoroughly mixed. The concentration of the resulting product depended on the type of material being processed, for cement it was 6 g/l, in all other cases - 4.0 g/l. The samples were impregnated for 8-10 min of cement rotation.

Then the sample was lightly dried between sheets of filter paper using a pad and dried at a temperature of 50-60 °C for 40-50 min in a drying cabinet. The consumption of the water-repellent composition in all cases did not exceed 5.3 g/kg of the material being processed.

The use of this composition provides an improvement in the quality of materials, by increasing the indicators of water-repellent properties, without deterioration as a result of the hydrophobization of their other indicators.

Conclusion. Thus, as a result of the research conducted, it was shown that it is possible in principle to use the composition under study as a water-repellent material for the surface treatment of building materials, and a trend has been revealed to develop new water-repellent agents with an unconventional chemical structure.

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Резюме

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ГИДРОЛИЗДЕНГЕН ПОЛИАКРИЛОНИТРИЛДІҢ НЕГІЗІНДЕГІ ГИДРОФОБТЫ КРЕМНИЙОРГАНИКАЛЫҚ ПОЛИМЕРЛЕРДІҢ АЛЫНУ ӘДІСІ

Мақалада гидролизденген полиакрилонитрил мен тетреэтоксисиланның негізіндегі гидрофобизаторды алудың мүмкіншіліктері қарастырылған. Зерттеулерде көрсетілгендей, алынған композицияның қасиеттері температура мен таңдалып алынған заттың қатынасына байланысты. Таңдалып алынған композицияның оптималды температура мәні 10-50^{o}C аралығы болып табылады. Үлгілер ИҚ-спектрометрия, дифференциалды термиялық анализ әдістерімен зерттелінді. Алынған композиция берілген аналогтан гидрофобты қасиеттері бойынша төмендемейді, ал өңделген материалдардың бағасы алкилсиликонаттармен салыстырғанда 10-15%-ға төмен.

Түйін сөздер: полимер, гидролизденген полиакрилонитрил, кремнийорганикалық қосылыс, тұтқырлық, гидрофобизация, ерітінді.

Резюме

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МЕТОД ПОЛУЧЕНИЯ ГИДРОФОБНЫХ КРЕМНИЙОРГАНИЧЕСКИХ ПОЛИМЕРОВ НА ОСНОВЕ ГИДРОЛИЗОВАННОГО ПОЛИАКРИЛОНИТРИЛА

В статье рассмотрены возможности получения гидрофобизаторов на основе гидролизованного полиакрилонитрила и тетраэтоксисиланана. Как показали исследования, свойства получаемой композиции зависят от температуры и соотношения выбранных веществ. Оптимальной температурой получения желаемой композиции является интервал температуры 10-50 °C. Образцы были исследованы методами дифференциально термического анализа, ИК-спектрометрии. Полученная композиция по гидрофобизирущим свойствам не уступает существующим аналогам, а стоимость разработанных материалов на 10–15 % ниже по сравнению с алкилсиликонатами.

Ключевые слова: полимер, гидролизованный полиакрилонитрил, кремнийорганические соединения, вязкость, гидрофобизация, раствор.