K. Yu. Ivanova, Kuzmin M. V., N. I. Kol'tsov
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Synthesis and research of polyfunctional silicon-containing amines — new promoters of adhesion

K. Yu. Ivanova*, M. V. Kuzmin, N. I. Kol'tsov

Chuvash State University named after I. N. Ulyanov
15 Moskovskii pr., Cheboksary, 428015, Russia
**email: cool.karakyrt@ya.ru*

Abstract. Currently, in order to obtain high-tech hybrid products, modern adhesives have high requirements for creating strong joints between dissimilar materials. It is known that adhesion depends on the compatibility of the adhesives with the surfaces of the materials. Amine compounds are the main hardeners for epoxy compositions. That is why, in this article, we synthesized silicon-containing amines based on polyfunctional aminoalkoxysiloxanes for epoxy compositions. Aminoalkoxysiloxanes were prepared by the interaction of 3-aminopropyltriethoxysilane with monoethanolamine in nitrogen at atmospheric pressure in the presence of a binary antioxidant and catalytic amounts of an alkali metal alcoholate. During the reaction in a homogeneous phase, the reaction mixture was heated to a temperature of 100–110 °C and distilled off to 90% of ethanol from the theoretically calculated amount. Further, the reaction was carried out at a reduced temperature of 10–20 mmHg pressure until the release of alcohol stops. At the same time, gravimetric control was carried out and the refractive index of the reaction mixture was measured. As a result, aminoalkoxysilanes were obtained in the form of light-yellow oily liquids. The structure of the obtained compounds was investigated by IR spectroscopy on an FSM-1202 Fourier spectrophotometer and ^{1}H NMR spectroscopy on a high-resolution BrukerWM-250 NMR spectrometer. It was found that under the selected synthesis conditions, aminopropyltri-(2-aminoethoxy)silane is obtained with the highest yield of 97.6% at a molar ratio of 3-aminopropyltriethoxysilane AGM-9 with monoethanolamine 1:3.

Keywords: 3-aminopropyltriethoxysilane; aminoalkoxysiloxanes; adhesion promoters

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Introduction

Various types of aminosiloxanes are used to improve the adhesion characteristics of coatings, since silicon-containing compounds can significantly improve the adhesion of polymer resins to substrates such as glass, silica, aluminum oxide and active metals [1, 2]. The advantage of epoxy compounds is their high adhesion capacity, low shrinkage, the possibility of curing in a wide temperature range [3]. However, epoxy compositions have a number of disadvantages: high brittleness, low heat resistance, which manifests itself in a decrease in strength and stiffness at elevated temperatures. An increase in temperature at the moment of formation of the adhesive

contact leads to a decrease in viscosity and contributes to the achievement of the highest adhesion strength. The chemical nature of the adhesive plays a decisive role in the adhesion of the polymer to the metal. It is not the number of polar groups that is important, but the ability to enter into intense interaction with the surface groups of the substrate and the ability to act as electron donors. The more clearly expressed the electron-donor properties of functional groups, the higher their adhesion to metal [4].

Experimental

It is known that organosilicon compounds are biodegradable; they can increase the intensity of biological processes of oxidation of organic pollution of wastewater and thereby reduce the anthropogenic load on the environment [5–7]. For this, we synthesized organosilicon compounds — aminosiloxanes — as adhesion promoters, which can significantly increase the adhesive strength and water resistance of the adhesive bonds of epoxyamine coatings on various metal surfaces.

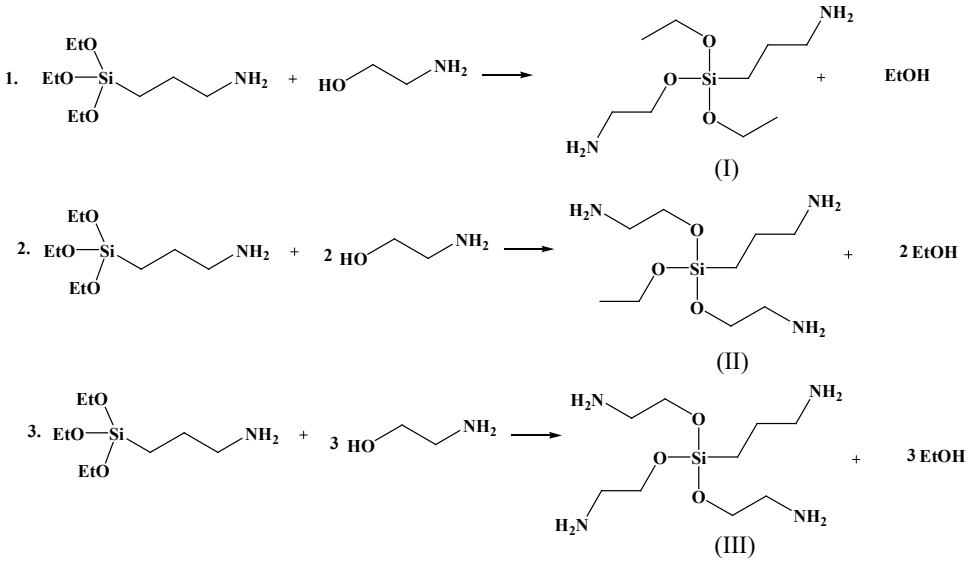
Aminoalkoxysilanes I–III were obtained by the interaction of 3-aminopropyltriethoxysilane with monoethanolamine at different molar ratios in the presence of a binary antioxidant and an alkali metal alcoholate. To do this, (ν_1, mol) 3-aminopropyltriethoxysilane, (ν_2, mol) pre-distilled monoethanolamine are loaded into a reactor equipped with a stirrer, the reaction is carried out in the presence of an antioxidant and an alkali metal alcoholate, the mixture is kept at room temperature for 10 minutes, then evacuated at temperature up to 100 °C for 10–20 minutes, until the alcohol is completely removed. The process was monitored by IR spectroscopy on an FSM-1202 Fourier spectrophotometer. The structure of the obtained compounds was confirmed by the data of NMR spectroscopy, ^{1}H NMR — high resolution spectra were obtained on a Bruker WM-250 spectrometer in DMSO-d_6, the internal standard was hexamethylenedisiloxane.

Results and discussion

In this work, we have studied for the first time the process of obtaining silicon-containing amines by addition of alkanolamines to ethoxy-substituted derivatives, for example, to aminopropyltriethoxysilane.

Aminoalkoxysilanes I–III were obtained at different molar ratios of 3-aminopropyltriethoxysilane with monoethanolamine. For this, the calculated amount of reagents was loaded into an Arbuzov flask and heated in a nitrogen flow. The reaction begins in a heterogeneous phase, when a certain temperature is reached, the reaction mixture is homogenized (for example, at a ratio of 1:4, the homogenization temperature of the mixture is 104 °C). With a further increase in temperature, distillation of ethyl alcohol begins. With a slow increase in temperature, 80–90% of the theoretically calculated amount of alcohol (ethanol) was distilled off. Then, at a reduced pressure of 10–20 mmHg completed the reaction until the release of alcohol ceases. At the end of the process were performed gravimetric control and measurement of the refractive index of the reaction mixture. As a result, aminoalkoxysilanes were obtained in the form of a light-yellow oily liquid.

Reactions of 3-aminopropyltriethoxysilane with monoethanolamine in various mole ratios are presented below:



Data on the synthesis of aminosiloxanes are given in Table. 1.

Aminoalkoxysiloxanes were obtained as clear to light yellow oily liquids. In the IR spectra of the obtained products, there are intense absorption bands at 1081–1085 cm^{-1}, which are typical for Si-O-C bonds. The absorption bands of the hydroxyl group directly bonded to the silicon atom are absent, and the bands corresponding to the NH_2 group are observed at 3275–3373 cm^{-1}.

In ^1H NMR spectra of compounds I–III the signals related to the CH_2Si were obsereved at 0.563 ppm, and signals of amino groups protons were observed at 2.50 ppm. In ^1H NMR spectra of compounds I, II there were signals related to the vibrations of the Si-O-CH_2 bond of 2-aminoethoxy and ethoxy groups at 3.33 ppm and 3.44 ppm, respectively. In the spectrum

Table 1

The structure and properties of aminosiloxanes

№	Name	ν_1:ν_2	Reaction yield, %	n_D^{20}	IR spectroscopy, ν, cm^{-1}:	NMR spectroscopy, d, ppm
1	3-aminopropyl-(2-aminoethoxy) diethoxysilane (I)	1:1	89.7	1.4440	3373, 3294 (NH_2), 2974, 2927, 2883 (CH_3, CH_2), 1083 (Si-O-C)	0.563 s (2H, CH_2Si), 1.058 t (6H, $2CH_3$), 2.50 s (4H, $2NH_2$), 2.546 m (2H, $CH_2\underline{CH_2}CH_2$), 2.547 t (4H, $2NH_2\underline{CH_2}$), 3.334 t (2H, $2H_2NCH_2\underline{CH_2}O$), 3.443 (4H, 2 $CH_3\underline{CH_2}O$). M 236.373

End of Table 1

№	Name	ν_1:ν_2	Reaction yield, %	n_D^{20}	IR spectroscopy, ν, cm^{-1}:	NMR spectroscopy, d, ppm
2	3-aminopropyl-di-(2-aminoethoxy) ethoxysilane (II)	2:1	95.7	1.4521	3366, 3293 (NH_2), 2971, 2927, 2875 (CH_3, CH_2), 1081 (Si-O-C)	0.56 s (2H, CH_2Si), 1.06 t (3H, CH_3), 2.50 s (6H, $3NH_2$), 2.335 t (4H, $2H_2NCH_2\underline{CH_2}O$), 2.544 m (2H, $CH_2\underline{CH_2}CH_2$), 2.546 t (6H, $3NH_2\underline{CH_2}$), 3.334 (2H, $CH_3\underline{CH_2}O$). M 251.388
3	3-aminopropyl-tri-(2-aminoethoxy) silane (III)	3:1	97.6	1.4650	1590 (Si-O-C); 3362, 3293 (NH_2); 1083–1020 (Si-O)	0.57 s (2H, CH_2Si), 2.50 s (8H, $4NH_2$), 2.544 m (2H, $CH_2\underline{CH_2}CH_2$), 2.546 t (8H, $4NH_2\underline{CH_2}$), 3.333 t (6H, $3H_2NCH_2\underline{CH_2}O$). M 270.384

of compound III there were no vibrations of the protons of the OCH_2CH_3 groups, which indicates the complete replacement of the ethoxy groups in 3-aminopropyltriethoxysilane by 2-aminoethoxy groups.

Conclusions

To sum up, aminoalkoxysiloxanes — polyfunctional silicon-containing amines — have been synthesized, the structure of which was confirmed by IR and ^1H NMR spectroscopy. These aminoalkoxysiloxanes are recommended for use as adhesion promoters.

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