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Synthesis and Characterization of Functional Chemically Modified Silica Fillers

Valentin Tertykh, Victor Yanishpolskii, Yulia Bol'bukh*

Institute of Surface Chemistry, National Academy of Sciences of Ukraine,
Gen. Naumov Str. 17, 03680 Kyiv-164, Ukraine

Summary: Elaborated methods of synthesis of chemically modified silicas with grafted silicon hydride and amino groups are analyzed. Experimental results on use of modified silicas with bonded amino groups as fillers of carboxyl-containing rubbers and epoxy resins are reported. It was shown that modified silica fillers with grafted silicon hydride groups could be applied for carrying out processes of catalytic solid-phase hydrosilylation of 2-hydroxyethylmethacrylate and some other functional olefins.

Introduction

As known, in some cases essential strengthening of a filled polymer system can be achieved when active sites of a filler surface have the property of chemical interaction with the functional groups of polymer macromolecules[1]. In this respect the dispersed silicas containing grafted amino and silicon hydride groups represent the important class of chemically active fillers of appropriate polymers. In this paper the accumulated experience in preparation and characterization of silica fillers with chemically grafted amino and silicon hydride groups is analyzed. New experimental results on application of amino-containing silicas as fillers of carboxyl-containing rubbers and epoxy resins and on use of silicas with $\equiv$SiH groups in catalytic hydrosilylation of 2-hydroxyethylmethacrylate are reported.

Synthesis and some applications of amine-containing silica fillers

The modification by amino-containing organosilanes, etherification reactions of structural silanols, alcoholysis reactions of preliminarily chlorinated silica surface, reactions of electrophilic addition of nitrogen-containing heterocycles are the most-used

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methods of the aminoorganosilicas synthesis[2, 3]. The simplest method of the introduction of amino groups into surface modifying layer consists in modification of a hydroxylated silica surface by amino alcohols:

$$\equiv SiOH + HORNH_2 \xrightarrow[-H_2O]{} \equiv SiORNH_2$$

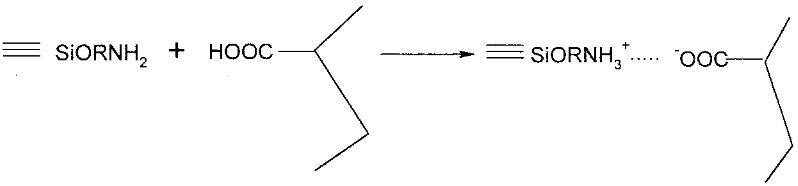
Amino alcohols appear more active modifying reagents as compared with appropriate alcohol analogues. So, if etherification of structural silanols of a silica surface at interaction with ethanol vapors proceeds only above 250°C, the reaction of $\equiv SiOH$ groups with 2-aminoethanol vapors occurs already at 70°C. As it follows from IR spectroscopy data, after contact of fumed silica with 2-aminoethanol vapors at 70°C and subsequent desorption in vacuum 2 hrs at 200°C the significant reduction of intensity of a free hydroxyls (3750 cm^{-1}) band is observed in the spectrum. Simultaneously, there are the intensive absorptions in the region of frequencies of stretching vibrations of N-H (3390 and 3330 cm^{-1}) and C-H (2800-3000 cm^{-1}) bonds. The bands 3390 and 3330 cm^{-1} correspond to asymmetric and symmetric vibrations N-H in primary amino groups of surface chemical compounds ($\equiv SiOCH_2CH_2NH_2$). Increase of reaction temperature up to 120°C results in greater reduction of 3750 cm^{-1} band intensity. It corresponds to the increase of chemisorbed amino alcohol molecules contents in these conditions. Contact of silica with 2-aminoethanol vapors at 200°C results in decrease of the silanol groups concentration also. However this decrease was less than at 70 and 120°C. The softer conditions of 2-aminoethanol chemisorption in comparison with ethanol are certainly connected with catalytic influence of amino groups. In a like manner 3-aminoprophanol reacts with structural silanol groups of a silica surface in much softer conditions, than 1-butanol does.

Two-site adsorption of monoethanolamine on dispersed silica proceeds as a two-stage process with participation of both functional groups. As it follows from quantum-chemical simulation[4], the bonding is mainly affected owing to proton-accepting properties of amine groups. Two main directions of the marked catalytic influence are possible. First of all, the chemisorption of a certain amino alcohol molecule, which is proceeding in result of an attack by alcohol hydroxyl at a surface silicon atom, is accelerated owing to the assistance of another modifying reagent molecule. Amino group of this second molecule for account of acceptor properties in relation to proton of alcohol hydroxyl in the chemisorbing molecule can essentially increase the nucleophility of oxygen atom in $-CH_2OH$ group. The similar explanation will be agreed with the proposed for alcohol chemisorption mechanism of nucleophilic substitution at silicon atom of the silica surface2). From this standpoint the reduction rate for the reaction of silica silanol groups with 2-aminoethanol at increase of temperature up to 200°C may be explained. At the same time for investigated system on the basis of available spectral data rather difficulty to allocate which of protons of two interacting partners ($\equiv SiOH$ or $\equiv COH$) resides in the stronger influence of an amino group. As is known, ammonia and its organic derivatives can form with hydroxyl groups of silica surface rather strong hydrogen bonds. Therefore it is necessary to take into account also strong interaction of atom of nitrogen in molecule modifying reagent with protons of structural silanol groups of silica surface. Is not excluded, however, that in case of chemisorption of 2-aminoethanol and other amino alcohols the catalytic influence of amino groups is carried out simultaneously on two indicated directions. Of particular interest in this respect is the experimental fact that the reetherification reaction of the grafted ethoxy groups under 2-aminoethanol action proceeds only at temperatures above 250°C:

$$\equiv SiOC_2H_5 + HORNH_2 \xrightarrow[-C_2H_5OH]{} \equiv SiORNH_2$$

Taking into account of a feature of the ethylene imine structure, which results in occurrence of a ring tension, but also the presence of =NH groups, acting as proton acceptor, and the high sensitivity of a molecule to action of nucleophilic reagents, it was natural be for assuming that interaction with silanol groups of the silica surface will proceed in soft conditions. Really, the interaction of isolated hydroxyl groups of the silica surface with ethylene imine occurs at room temperature. Reaction electrophylic addition of ethylene imine with formation of grafted aminoethoxysilyl groups is in this case carried out.

State and properties of attached amino groups in the grafted layer, peculiarities of interaction of such sites with electron-donating molecules, reactions of formation of salt-like surface compounds by interaction with acid adsorbates were investigated by adsorption and spectral methods[2). It was shown also that the amino-containing organosilica fillers could considerably strengthen (in 1.3-1.5 times) physicomechanical properties of the filled carboxyl-containing rubbers. It can be connected with chemical interaction of active sites of the filler surface with the functional groups of the polymers with the formation of crosswise chemical polymer-filler bonds:

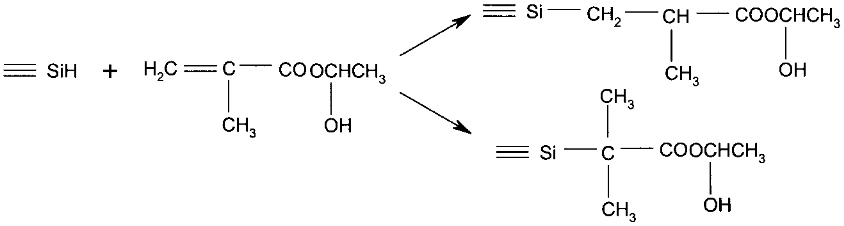


Aminoorganosilicas possess by organophilic properties and they may provide with the considerable life times of the filled epoxide resins at usual temperatures of its storage (up to 2 months). At the same time the complexes with H-bonds are disrupted at 150°C, and the fast system structurization takes place at these conditions. As it follows from IR spectra the grafted amino groups interact chemically with epoxy groups of resin and accelerate the hardening of epoxide resins by anhydride hardeners. In IR-spectrum of aminoethoxysilica after interaction with glycidyl phenyl ether during 2 h at 120°C the absorption bands with the frequencies 3350 and 3280 cm^{-1} are not displayed and there are the absorption bands, characteristic for grafted residues of glycidyl phenyl ether. Observable increase of mechanical strength and waterproof properties of the epoxy-composition, filled by aminoethoxysilica, in comparison with similar system, filled unmodified fumed silica, confirms the proceeding of reaction surface amino groups and epoxy groups of the resin. The large lifetime of the composition in an uncured state (more than 1.5 months) confirms availability strong hydrogen bonds between anchored amino groups and other surface sites, preventing the curing of epoxide resins at room temperature. Experimental data about the essential improving of mechanical strength, thermal deformation and water-resistance of the polymeric compounds filled by aminoorganosilicas were received.

Silicon hydride-containing silicas and hydrosilylation reactions of some olefin monomers

Fillers with attached silicon hydride groups can be produced as a result hydrolysis and polycondensation of trichloro-and triethoxysilane in surface layer, during chemical modification of silica with various organosilanes containing Si-H bonds, by the reaction between inorganic hydrides and ≡SiCl groups of the chlorinated silica surface or as a result of the thermal destruction of methoxysilica. Of late years it was shown5) that matrices with grafted silicon hydride groups can be successfully applied for carrying out processes of catalytic solid-phase hydrosilylation of simple terminal and functional olefins. In particular, catalytic additions of styrene, acetyl acetone, vinyl acetate, acrylamide were executed.

Be of special interest is to investigate interaction of silicon hydride-containing silicas with derivatives of methacrylic acid. For preparation of a matrix with attached ≡SiH groups the weighed portion of fumed silica with specific surface area 300 m^2/g was processed by a solution of triethoxysilane in ethanol at room temperature for 24 hrs with following solvent removal on water bath. The concentration of bonded ≡SiH groups was about $5.0 \cdot 10^{-4}$ mol/g. We have studied an opportunity proceeding of solid-phase hydrosilylation reaction with 2-hydroxyethylmethacrylate (Fluka). Grafting of this modifier to silica may provide both hydrophobic and hydrophilic properties of the filler surface. The reaction was conducted in an excess of the monomer for 3 hrs at 60°C with use of the Speier catalyst (0.01 M $H_2PtCl_6 \cdot 6H_2O$ solution in isopropanol). Process was carried out in open test tubes at mixing. Upon termination of reaction a mixture was cooled, washed by ethanol and then dried for 24 hrs on air. 2-hydroxyethylmethacrylate is rather slowly dissolved in ethanol, therefore there are both chemically bonded and adsorbed monomer molecules on the surface of modified silica. We investigated an opportunity of application of bromide-bromate method and iodometry for determination of concentration of silicon hydride and vinyl groups on the silica surface before and after interaction with 2-hydroxyethylmethacrylate. Both these methods are based on bromine or iodine ions interaction with ≡SiH and vinyl groups with subsequent titration of unreacted halogen by thiosulfate. As it follows from results obtained, bromine ions interact both with silicon hydride and vinyl groups, but iodine ions react with silicon hydride groups only. It permits with iodometry use to conduct determination of unreacted ≡SiH groups in the presence of adsorbed monomer. According to the iodometry data up to 90% of ≡SiH groups react with 2-hydroxyethylmethacrylate in these conditions (after reaction the contents of residual ≡SiH groups on the silica surface was $0.5 \cdot 10^{-4}$ mol/g). The data obtained confirm an opportunity of solid-phase hydrosilylation reaction proceeding with 2-hydroxyethylmethacrylate in accordance with the probable scheme:



As this takes place, there is some amount of adsorbed monomer in the surface layer of modified silica (up to $4.0 \cdot 10^{-4}$ mol/g).

Conclusion

The dispersed silicas containing grafted amino and silicon hydride groups can be applied as chemically active fillers of some polymers. Catalytic addition of 2-hydroxyethylmethacrylate to Si-H groups on the silica surface is proceeding with the tolerable yield (up to 90%).

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