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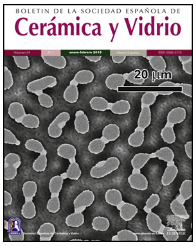

FT-IR study of the hydrolysis and condensation of 3-(2-amino-ethylamino)propyl-trimethoxy silane

Juan Rubio[a], *Maria Alejandra Mazo*[a], *Araceli Martín-Ilana*[b], *Aitana Tamayo*[a,*]

[a] *Ceramics and Glass Institute, CSIC, Madrid, Spain*
[b] *Dept. of Pharmaceutical Technology, Faculty of Pharmacy, Complutense University of Madrid, Madrid, Spain*

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ABSTRACT

The hydrolysis and self-condensation reactions of 3-(2-amino-ethylamino)propyl-trimethoxy silane have been studied by means FT-IR spectroscopy for different water and ethanol concentrations. The hydrolysis of 3-(2-amino-ethylamino)propyl-trimethoxy silane occurs at a high rate and depends if the water concentration is lower or higher than the stoichiometric one for hydrolysing all the hydrolysable groups. The presence of ethanol delays the hydrolysis reaction. The hydrolysis of 3-(2-amino-ethylamino)propyl-trimethoxy silane gives hydroxyl groups (Si–OH) that self-condense to form Si–O–Si bonds in linear and cyclic structures. For high water and low ethanol concentrations not all Si–OH groups self-condense, whereas for low water or high ethanol concentrations the major part of the Si–OH groups self-condense and tends to disappear in the gel state.

Estudio FT-IR de la hidrólisis y condensación del 3-(2-amino-etilamino)propil-trimetoxi silano

Palabras clave:
3-(2-amino-etilamino)propil-trimetoxi silano
Espectroscopía FT-IR
Cinética de reacción
Hidrólisis
Autocondensación

RESUMEN

Las reacciones de hidrólisis y autocondensación del 3-(2-amino-etilamino)propil-trimetoxi silano han sido estudiadas mediante espectroscopía FT-IR para concentraciones diferentes de agua y etanol. La hidrólisis del 3-(2-amino-etilamino)propil-trimetoxi silano tiene lugar a alta velocidad y depende de si la concentración de agua es menor o mayor que la requerida estequiométricamente para hidrolizar todos los grupos hidrolizables. La presencia de etanol retrasa la reacción de hidrólisis. La hidrólisis del 3-(2-amino-etilamino)propil-trimetoxi silano proporciona grupos hidroxilo (Si-OH) que auto-condensan para formar enlaces Si-O-Si en estructuras lineales y cíclicas. Para concentraciones de agua elevadas y bajas de etanol,

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* *Corresponding author.*
E-mail address: aitanath@icv.csic.es (A. Tamayo).

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no todos los grupos Si-OH auto-condensan, mientras que para concentraciones bajas de agua y altas de etanol, parte de estos grupos Si-OH auto-condensan y tienden a desaparecer en el estado de gel.

Introduction

Functional organosilanes, commonly known as silane coupling agents, have been studied and used in many different applications for decades [1–3]. In the last century, functional organosilanes were extensively used in the fabrication of lightweight composite in transportation, principally. The most common materials of this kind are fibre reinforced plastic composites (FRPC) where high resistance inorganic fibres are mixed with organic matrices. The improvement of the mechanical properties in FRPC is only reached when it exist a chemical compatibility between the matrix and the reinforcements. The use of silane coupling agents promotes interfacial adhesion and thus, the mechanical properties of the composite materials are strengthened. Since then, multiple and important applications for silanes have been reported in the literature, being most of them related to surface modification of support materials for biomolecule transport [4,5], enzyme [6] and bioactive substances immobilization [7] or smart drug delivery systems [8]. In the field of composite materials, we also find a wide variability of applications such as the surface modification of natural organic or inorganic fibres [9] and particles [10], the modification of synthetic carbon nanofibers [11,12] or as promoters of the adhesion between carbon nanotubes and glass fibres [13,14]. Silanes can be also used in the preparation of proton—conducting membranes obtained by the sol–gel method [15], in the synthesis of organic–inorganic hybrids [16] and in the preparation of temperature-resistant silicon oxycarbonitride ceramics [17].

In a typical silane structure, one silicon atom is bonded to three hydrolysable alkoxy groups and to one non-hydrolysable organic moiety. The hydrolysable groups form Si–OH terminations which are able to interact with active hydroxyl groups existing on the solid surface subjected to condensation reactions [1,18] or some other adjacent molecules. The hydrolysis rate and the formation of these Si–OH termination depend upon the number of carbon atoms of the hydrolysable alkoxy group as well as some other factors such as pH, H_2O concentration, nature of the solvent, etc. [19]. Silane condensation reactions, either with Si–OH groups existing on the solid surface, with other hydrolysed silanes (polycondensation reactions) or with other hydrolysed molecules of the same silane (self-condensation), also depend upon the pH of the solution, silane concentration, catalysts, type of solvent, steric and inductive effects, etc. [20]. The chemical nature of the un-hydrolysable organic moiety is selected according to the required functionality. Silanes containing amino groups ($-NH_2$) in the organic chain have been, by far, the most extensively used in many of the above referred applications, and the position of the amino group within the organic chain provides different molecular conformations of the silane when it is attached to the solid surface [11,21–23]. Hydrolysis and condensation reactions of aminosilanes have been reported in the literature [1,24,25], standing out the systematic studies carried out by Belgacem et al. [19,26,27]. In a previous work, we also detailed the different steps involved in the hydrolysis and condensation of 3-aminopropyltriethoxysilane (APS) [25]. For these studies, we selected the FT-IR spectroscopy as the preferred characterization technique since it requires a minimum volume and the results can be obtained in just a few seconds. In a similar way as we did before, we now focus our attention on the hydrolysis and condensation reactions occurring in solutions containing N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (DAMO) since it accomplishes a necessary step in the functionalization process of solid surfaces. In this work, we report on the competitiveness of the H_2O and EtOH molecules against the hydrolysis and condensation reaction of DAMO silane. In the presence of large amounts of H_2O, hydrolysis occurs fast but self-condensation reactions are delayed and many Si–OH groups remain un-condensed. Increasing EtOH ratios lead to a delay in the hydrolysis rate.

Experimental

3-(2-aminoethyl)-3-aminopropyltrimethoxysilane (DAMO, Gelest, 98%), ethanol (EtOH, Merck 99%) and distilled-deionized H_2O were the reactants used. DAMO and H_2O were thermosthated into two different vessels in a silicone bath at 25 °C for 30 min. If used, the total amount of EtOH was divided in two and added equally to the two different vessels. After temperature stabilization, both solutions were then mixed and maintained under vigorous stirring for reaction. After the condensation reactions finished and once gelling was achieved, white solid materials were obtained and dried in an oven at 50 °C. Two reactions sets were studied: In the first set, no EtOH was used and the amount of H_2O was fixed to 1 or 3 moles respect to 1 mole of DAMO (samples named DH1 and DH3, respectively) and, in the second reaction set, the molar ratio DAMO/H_2O/EtOH was 1/3/2, 1/3/4, 1/3/8 and 1/3/16. The samples corresponding to this set are labelled as DH3E (number of EtOH molecules).

The FT-IR spectra were collected in the attenuated total reflectance mode (FTIR-ATR) by dropping 1 μl solution over the diamond crystal which was rapidly covered with a glass plate to avoid evaporation. It was considered that the extraction of 1 μl from a 100 ml solution does not affect the reaction kinetics. Solution aliquots were taken at different reaction times starting from 1 min intervals to several hours. The spectra were obtained by a Perkin–Elmer FT-IR instrument X-spectrum model in the 4000–600 cm^{-1} spectral range and 2 cm^{-1} resolution. 16 scans were recorded for each spectrum and background was subtracted in all cases. Methanol (MeOH, Merck 99.9%) was used for FT-IR calibration.

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