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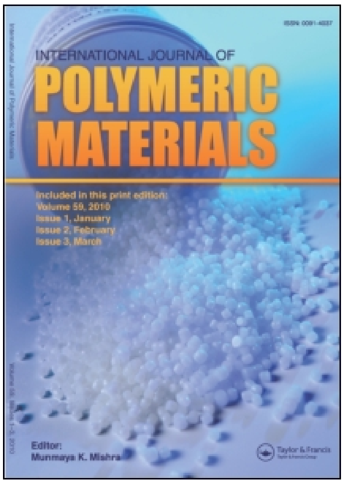

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Mendelovici, Efraim(1983) 'Organosilicon Derivatives of Silicates Including Clay Minerals', International Journal of Polymeric Materials, 10: 1, 77 — 82
To link to this Article: DOI: 10.1080/00914038308077991
URL: http://dx.doi.org/10.1080/00914038308077991

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Intern. J. Polymeric Mater., 1983, Vol. 10, pp. 77–82
0091–4037/83/1001–0077 $18.50/0

Printed in Great Britain

Organosilicon Derivatives of Silicates Including Clay Minerals

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(*Received June 14, 1982*)

The general mechanism for the preparation of organosilicon derivatives from clay minerals and inorganic silicates is described, on the basis of pioneer work made in this field. Functionality and nature of the coupling agents (organosilyl groups) as well as the structure of the mineral silicate, will determine the characteristics of the resulting products. When difunctional modifying agents are used, organosilicon sheet polymers may be derived from clay silicates, by an (acid) extraction-grafting process. The reaction of fibrous silicates in presence or absence of HCl, and on the other hand when organohalosilanes or organoalkoxysilanes are hydrolyzed is comparatively discussed. Surface properties, stability, methodology and potentialities of these organopolysiloxane materials are briefly explored.

INTRODUCTION

The modification of silicates—including clay minerals—by organosilicon compounds, is a topic which has deserved the attention of a number of investigators in the last two or three decades. The organomineral derivatives resulting from these modifications, may give important information for the study of the mineral's surface as well as for the mechanism of their interaction with the organosilicon compounds. Moreover, some of the resulting organosilicates may give origin to interesting applications.

Several procedures have been used for the preparation of organomineral compounds, which include grinding, the action of ultrasonic waves or coating of the minerals by dipping them in the organosilicon systems (oils, amines, etc). However, in order to obtain stable derivatives, a covalent bonding must be established between the surface's active OH groups of the mineral and the organosilyl groups (coupling agents) derived from the organosilicon compounds. The basic principle is related to the surface properties of the mineral as well as the ability of the modifying agents—the organosilicon compounds—to undergo hydrolysis under specific conditions.

COHYDROLYSIS

The mineral's active OH groups are generally Si—OH (silanols) which only seldom are detected on the surface of some unmodified silicates,[1] but are rather induced by HCl treatment, which causes the partial or total dissolution of the octahedral metallic layer of the mineral. Accordingly the following reaction takes place:

$$\equiv\mathrm{Si{-}O{-}M{-}OH} + 2\mathrm{H_3O^+} \xrightarrow{\text{iso-PrOH}} \equiv\mathrm{Si{-}OH} + \mathrm{M^{++}} + 3\mathrm{H_2O} \tag{I}$$

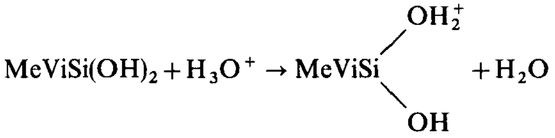
where M = metallic cation like Mg (isopropanol is a proton acceptor and reaction regulator).

Thus, upon cleavage of the Si—O—M bonds, acidic OH groups are created on the surface of the silicate. The distribution and population of these Si—OH groups will play a role in the probabilities of coupling with the organosilyl units. Beside, the functionality and nature of the modifying agents will determine the products of the acid hydrolysis. Thus, the hydrolysis of a linear siloxane may be represented by:

$$\mathrm{Me_3Si{-}O{-}SiMe_3} + \mathrm{H_3O^+} \rightarrow \mathrm{Me_3Si(OH)_2^+} + \mathrm{Me_3Si{-}OH} \tag{II}$$

whereas the hydrolysis of a difunctional chlorosilane by:

$$\mathrm{MeViSiCl_2} + \mathrm{H_2O} \rightarrow \mathrm{MeViSi(OH)_2} + 2\mathrm{HCl} \tag{III}$$



$$\mathrm{MeViSi(OH)_2} + \mathrm{H_3O^+} \rightarrow \mathrm{MeViSi}\begin{matrix} \diagup \mathrm{OH_2^+} \\ \diagdown \mathrm{OH} \end{matrix} + \mathrm{H_2O} \tag{IV}$$

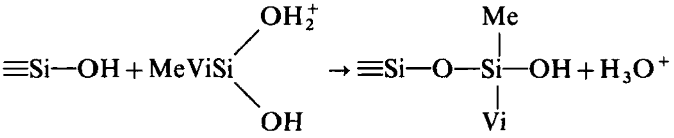
where Me = methyl and Vi = vinyl.

Then, upon controlled cohydrolysis (of the mineral and organosilicon compound) by 6N HCl (diluted by isopropanol) Si—OH sites are generated in both processes. The mechanism of condensation may be schematized as follows:

for the siloxane (II):

$$\equiv\mathrm{Si{-}OH} + \mathrm{Me_3Si{-}OH_2^+} \rightarrow \equiv\mathrm{Si{-}O{-}SiMe_3} + \mathrm{H_3O^+} \tag{V}$$

wwhereas for the silane (IV):



$$\equiv\mathrm{Si{-}OH} + \mathrm{MeViSi}\begin{matrix} \diagup \mathrm{OH_2^+} \\ \diagdown \mathrm{OH} \end{matrix} \rightarrow \equiv\mathrm{Si{-}O{-}}\overset{\mathrm{Me}}{\underset{\mathrm{Vi}}{\mathrm{Si}}}\mathrm{{-}OH} + \mathrm{H_3O^+} \tag{VI}$$

The repetition of the steps IV and VI allows the grafting of organopolysiloxanic chains on the solid as well as polycondensation in the liquid phase.

Two remarkable aspects must be emphasized from this procedure:

a) The controlled HCl leaching of the octahedral layer of the mineral as well as the concomitant grafting of organosilyl units on the siloxanic planes preserves the essential Si—O structure (the silicate backbone).

b) The new hydrophobic compounds which contain both portions of silicon, the "mineral" (from the original Si—O backbone) and the "organic" (from the Si—C bonding) are fairly stable. This is due to the formation of a ≡Si—O—Si—C covalent bonding.

Organic derivatives of e.g. montmorillonite clays, exhibiting Si—O—C and Si—NH—C bonds[2] are not stable because these bonds are labile and readily hydrolyzable.

COMPARATIVE MECHANISMS OF SILICATES MODIFICATION

A number of silicates have been modified by the method of cohydrolysis. The synthesis of methyl derivatives of silicate minerals ranging from ortho to tectosilicates, by a procedure involving hydrochloric acid and hexamethyldisiloxane as modifying agents, has been described by Lentz.[3] Side effects due to polymerization or depolymerization of silicate ions must be reckoned in this reaction. Following this procedure, organic derivatives of some phyllosilicates or layer-silicates (originally constituted by tetrahedral siloxanic sheets condensed with octahedral sheets containing hexacoordinated metallic cations) have been prepared.[4–6] As well, trimethylsilylation of a wide range of silicates structures, including lunar cryptocrystallites and glasses has been studied.[7–12]

Mendelovici[13] (1967) and then Zapata *et al.*[14] (1971) described the mechanism (above schematized) prevailing in the modification of chrysotile-asbestos (a magnesium fibrous silicate) by organochlorosilanes like methyl and vinyl chlorosilanes in acid medium, and showed that diffusion governs the kinetics of this process. The treatment of chrysotile by phenyl-bearing chlorosilanes has also been reported.[15]

On the other hand, attapulgite or palygorskite (a fibrous silicate, where chains of silica tetrahedrons are linked together by octahedral groups of oxygens and OH containing Al and Mg atoms in hexahedral coordination) has been reacted with methyl and phenyl alkoxysilanes in presence or absence of HCl,[16] the latter in non-aqueous phase. In the first case, organosilyl radicals—produced by the acid hydrolysis of the alkoxysilanes—are coupled with the acidic silanol groups on the surface of the mineral. In the absence of HCl, a different mechanism must be invoked for the incorporation of organosilyl groups on attapulgite. Water contained by this mineral as well as the nature of its surface must play a role in promoting the hydrolysis of i.e. dimethyldiethoxysilane. Sepiolite (a mineral akin to attapulgite) has been also modified recently by chlorosilanes, in presence or absence of HCl.[17,18] The low volatility, lack of corrosivity and other properties are some advantages of using organoalkoxysilanes instead of organochlorosilanes. The grafting of polysiloxane chains on some clays minerals, so that organosilicon sheet polymers may be derived from silicates by an extraction—grafting process, are discussed by Linsky *et al.*,[19] and by Ruiz-Hizky and Van Meerbek.[20] Reactions of chrysotile with γ-methachriloxipropyltrimethoxysilane and δ-aminobutilmethyldiethoxysilane have been reported by Mendelovici.[21]

The importance of synthetizing these organomineral derivatives is that silicates which in their natural state are inert, may be rendered reactive upon the aforementioned treatments. The properties of such sheet polymeric compounds may find useful applications as composite materials in the reinforcement of siloxane elastomers by silicates,[22,23] etc.

SURFACE PROPERTIES AND STABILITY OF ORGANOSILICATES

When the modification of some silicates is carried out by monofunctional silanes, as trimethylchlorosilane—and by hydrochloric acid—their surface area may steadily increase. This has been shown, i.e. for chrysotile-asbestos, whose surface area increases as much as 20 times,[4,13] due to the gradual extraction of the trioctahedral layer from this two sheets-silicate by a diffusion process. Otherwise, when difunctional silanes substitute the monofunctional monomer in this reaction, short, linear organopolysiloxanic chains result; such a polymerization pattern is impossible in the presence of trimethylsilyl groups. Part of these linear organopolysiloxane chains are grafted to the silicate surface through the silanol groups (steric and other effects must be taken in account when the end groups are other than CH_3) by a covalent bonding. Another part of the polysiloxane chains are not covalently bonded but just covering the modified surface of the silicate (these polymers are easily extracted by hot benzene). When these organopolysiloxanes are not extracted, the surface area of the modified silicates sensibly decreases. Nevertheless, such surface may become reactive for further copolymerization depending on the nature of the organic groups and the mineral substrate. In all of the above mentioned treatments the surface of the silicates becomes organophilic, but their stability to heat and acid attack is variable.

On the other hand, Mendelovici has prepared highly stable derivatives of chrysotile-asbestos[24] called "LCA" and of other minerals. The hydrophobic properties of such compounds are preserved after heating in air until ~ 525°C or shaking with N HCl for 72 hours at room temperature.

Methodology (Physico-chemical characterization and analysis of organosilicon derivatives of silicates)

In order to characterize the organosilicates which have been synthesized by the above described methods, IR absorption spectroscopy,[4,13,16,17,23] specific surface area determinations (BET),[4,13,17,18] X-ray diffraction,[9,16,17] electron microscopy,[4,13,19,25] chromatography,[3,6,7,10] DTA[4,11,12,13,24] and eventually other techniques have been used.

Total chemical analysis has been carried out by classic methods (gravimetrical, complexometrical[4,7]) and more recently by atomic absorption using a fluoboric-boric acid matrix (Mendelovici *et al.*[26]). A special technique (alternative to the Kjeldakl's wet chemistry) has been employed for the determination of nitrogen (present in form of primary-amine groups as $NH_2(CH_2)_3CH_3SiO$—), when the latters are incorporated in the silicates.[27] Microanalysis of nitrogen and carbon are also performed by specialized laboratories.

Summary

In this contribution, it is not possible to cover all the existing literature and ongoing works made on organosilicon derivatives of silicates, including clay minerals. There is an attempt, rather, to emphasize the pioneer work in this field, which has opened a far reaching potential for the development of new organomineral compounds, including organosilicon sheet polymers and highly stable hydrophobic or organophilic materials.

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