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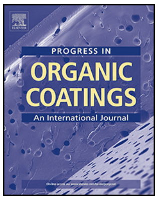

# Polymerization of hybrid organic–inorganic materials from several silicon compounds followed by TGA/DTA, FTIR and NMR techniques

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ABSTRACT

Hybrid organic–inorganic films have been prepared by hydrolysis and condensation of several silicon compounds: 3-methacryloxypropyltrimethoxysilane (MPTS) or methyltriethoxysilane (MTES) and tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) precursors using four [TEOS] or [TMOS]/[MPTS] or [MTES] molar ratios: 0, 0.5, 1 and 2.

The progress on the organic and inorganic polymerizations was followed employing thermogravimetric analysis (TGA), differential thermal analysis (DTA), Fourier transform infrared spectroscopy (FTIR), $^{13}$C and $^{29}$Si nuclear magnetic resonance (NMR). These techniques have provided information about the hybrid network formation inside films. The formation of the hybrids prepared from [TEOS]/[MPTS] and [TMOS]/[MPTS] mixtures was accomplished through the reaction of Si—OR groups, via condensation of silanols (inorganic condensation), and opening of the C=C double bond in MPTS (organic polymerization). The formation of the hybrids prepared from [TEOS]/[MTES] and [TMOS]/[MTES] mixtures was mainly accomplished through the reaction of Si—OR groups.

The increment of TEOS or TMOS in MPTS mixtures favored the inorganic ($Q^3$ and $Q^4$ units) condensation. Total degrees of condensation for hybrids synthetized with [TEOS] or [TMOS]/[MTES] were higher than those obtained with [TEOS] or [TMOS]/[MPTS], so MTES favored the formation of hybrids with branched organic structures.

## 1. Introduction

The study of hybrid organic–inorganic Si polymers is a very active field of the sol–gel process [1]. The importance of these compounds derives from the possibility of obtaining novel materials in optics, electronics, mechanics and electrochemistry fields [2]. One of the most diffused commercial application is their use as coating films [3–6]. These hybrid films combine properties of organic polymers and ceramics materials [7]. The inorganic components improve durability, scratch resistance, and adhesion to the metal substrates, while the organic components increase flexibility, density, and functional compatibility with organic polymer paint systems [8].

The sol–gel process is mainly based on hydrolysis and condensation reactions of metal alkoxides ($M(OR)_n$). During the hydrolysis (first stage), the replacement of alkoxide groups (—OR) by hydroxyl groups (—OH) occurs during interaction of alkoxide molecules with water. The second stage consists on the condensation of two —OH groups or of a —OH with a —OR group, which produces M—O—M bonds [9]. The resulting oxide materials vary from nanoparticulate sols to continuous polymer gels depending on the rate of reactions and drying and processing steps. The hybrid organic–inorganic sol–gel materials can be constituted by stable organic and inorganic groups linked by stable chemical bonds or by organic components embedded into an inorganic material, or vice versa [9].

Following the classification of Sanchez et al. [1], hybrids of class II are those exhibiting covalent bonding between organic and inorganic components. The organic groups can be directly connected to the inorganic network and their role can behave as network modifiers. A peculiar group of class II hybrids is characterized by the presence of polymerizable vinyl, acrylate, or epoxy groups. They can be partially or completely polymerized directly in the sol depending on synthesis conditions and photo or thermal curing [10].

The polymerization of organic and inorganic precursors may be carried out sequentially or simultaneously [11,12]. When the organic polymerization is performed first, linear polymers or copolymers are formed, which are functionalized with inorganic

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polymer precursors, present either in the polymer backbone or at chain ends [13,14]. When the inorganic polymerization is first started in the sol stage, the coating is formed and both organic and inorganic polymerizations are produced in the coated material. In general, it is difficult to achieve high conversion degrees in both organic and inorganic networks.

The final physicochemical properties of the hybrid organic–inorganic materials depend on the extent of the hydrolysis–condensation reactions, the branching degree of the polymers and the gel homogeneity [15].

The aim of this study was to investigate the local structure of hybrid polysiloxane materials prepared from polymerization of Si compounds containing different alkoxide groups. This will permit the future design of new metal coatings that enhance stability of reinforced concrete structures (RCS) against corrosion caused by chloride ions or carbon dioxide.

## 2. Experimental

The reagents used in this work 3-methacryloxypropyltrimethoxysilane ($CH_2=C(CH_3)COO(CH_2)_3Si(OCH_3)_3$, MPTS, Sigma–Aldrich), methyltriethoxysilane ($(CH_3)Si(OCH_2CH_3)_3$, MTES, Sigma–Aldrich), tetraethyl orthosilicate ($Si(OCH_2CH_3)_4$, TEOS, Sigma–Aldrich), tetramethyl orthosilicate ($Si(OCH_3)_4$, TMOS, Sigma–Aldrich) and benzoyl peroxide (BPO, VWR International Eurolab) were laboratory grade.

Sol–gel coatings were prepared from condensation and polymerization of TEOS and MPTS, TEOS and MTES, TMOS and MPTS or TMOS and MTES. Sol–gel reactions were achieved by mixing 5 g of MPTS or MTES with the TEOS or TMOS amounts required to obtain the four molar ratios: 0, 0.5, 1 and 2. Afterwards, $HNO_3$-acidified water (pH = 1 and $[H_2O]/[Si] = 3.5$) was added. All reagents were stirred (700 rpm) for 1 h at 60 °C, using ethanol as solvent ($[\text{ethanol}]/[H_2O] = 1$). At the same time, the thermal initiator of polymerization (BPO) was added to the mixtures ([BPO]/[MPTS] or [MTES] = 0.01).

The films were prepared by drying sols in a Petri dish at 65 °C for 24 h. After curing at 160 °C for 3 h, films were detached from the dish and analyzed by TGA/DTA, FTIR and MAS-NMR techniques.

The TGA/DTA curves of hybrid films were recorded using a SDT Q600 TA Instruments, with nitrogen as purge gas at a flow rate of 100 ml $min^{-1}$. Samples were heated from 25 to 600 °C at a rate of 10 °C $min^{-1}$.

FTIR spectra (4000–250 $cm^{-1}$) were recorded in two spectrophotometers: a Nicolet 20 SXC for liquid samples (pure reagents) and a Bruker IFS 66V/S was used for solid samples (synthetized films). In both apparatus the spectral resolution was 2 $cm^{-1}$. The KBr pellet method was used to prepare solid samples.

Solid-state $^{29}$Si MAS and $^{13}$C CPMAS-NMR spectra were recorded using a Bruker Avance-400 pulse spectrometer. Spectra were recorded after irradiation of samples with a $\pi/2$ (5-μs) pulse. The resonance frequencies used were 79.5 and 100.63 MHz (9.4 T magnetic field). In order to avoid saturation effects, the recycle delay time used was 10 s. The spinning rate used in MAS-NMR experiments was 10 kHz. A contact time of 2 ms and a recycle delay of 5 s were used in $^{13}$C CPMAS-NMR experiments. All measurements were taken at room temperature with TMS (tetramethylsilane) as external standard. The error in chemical shift values was estimated to be lower than 0.5 ppm. NMR spectra deconvolutions were performed by using the DMFIT software [16]. Chemical shift (position of the line), intensity (integrated area), width (width at half height) and line shape (Lorentzian or Gaussian) of components were deduced.

## 3. Results and discussion

### 3.1. TGA/DTA analysis of the films

In order to understand the thermal behavior of the hybrid organic–inorganic materials, thermogravimetric (TGA) and differential thermal analysis (DTA) were carried out.

The TGA curves of Fig. 1a indicate the existence of three different weight losses. The first loss, visible in the temperature range 25–125 °C (was comprised between 1.3 and 1.9%), was associated with evaporation of solvent, specifically ethanol and/or water [17]. The sample mass remained essentially invariable until 300 °C. Above this temperature, a second degradation was detected with weight losses of 40.5, 31.5, 27.7 and 20.0% for R0, R0.5, R1 and R2 ratios, respectively. This second step can be attributed to random scissions within the polymer chains [6,18]. The last loss took place from 470 °C to 600 °C, displaying 16.8, 14.7, 13.8 and 12.0% weight losses for R0, R0.5, R1 and R2 ratios, respectively. This loss was attributed to the dehydration of silanol groups present in the $SiO_2$ network [18].

The DTA curves of Fig. 1b show three minima at about 47–63 °C, 386–402 °C and 479–550 °C, attributed to three detected stages. The three weight losses presented an endothermic character. Finally, two other minima were observed in R0, R1 samples at about 340–350 °C, that were ascribed to scissions of chains produced at the terminal vinylidene groups [6,18].

The TGA curves of Fig. 1c show a small weight loss (0.13–4.46%) below 160 °C, assigned to the evaporation of residual small molecules, such as water, alcohol, and ethanol [17]. The amount of water and ethanol lost in this series of hybrids is higher than that added in the synthesis hybrids formed from TEOS and MPTS. In the temperature range 160–440 °C (minimum peak around 340 °C in absence of TEOS and around 240 °C in presence of TEOS), a new degradation was observed, see Fig. 1c. This could be assigned to volatile compounds produced in condensation of Si—OH and Si—OR groups [19]. The weight loss was between 3.2 and 5.1%. The last loss should result from the oxidation and degradation of methyl groups of MTES, that probably cause the formation of Si—C—Si bonds at 536 °C [20,21]. The associated weight loss was between 2.6 and 5.6%.

DTA curves of Fig. 1d shows three minima between 38–62 °C (first stage), 229–339 °C (second stage) and 527–548 °C (third stage). The three peaks display an endothermic character. As the [TEOS]/[MTES] ratios and temperatures increases, suggesting a higher thermal stability of formed hybrids.

Thermograms of the hybrid polysiloxanes synthetized from TMOS and MPTS (see Fig. 2a) are very similar to those obtained for hybrid polysiloxanes prepared by mixing TEOS and MPTS (see Fig. 1a). In these thermograms, three degradation stages were detected; the first visible below 110 °C, due to the evaporation of ethanol and water [17], with weight losses between 1.3 and 1.5%. The second stage, produced between 110 °C and 470 °C, attributed to scission within the polymer chains [6,18], with weight losses of 40.5, 31.5, 26.4 and 19.5% for R0, R0.5, R1 and R2. Finally, the third stage produced between 470 and 600 °C, ascribed to the dehydration of silanol groups present in $SiO_2$ networks [18], with weight losses between 13.1 and 16.8%. The DTA curves of this family of hybrids (see Fig. 2b) are also similar to those obtained for the hybrid polysiloxanes synthetized from TEOS and MPTS (see Fig. 1b), which presented three minima at 47–50 °C, 390–402 °C and 479–527 °C for three weight losses. Finally it should be highlighted the presence of an additional endothermic peak between 197 and 209 °C for R1 and R2 ratios, associated to the scissions of head-to-head linkages in the polymethylmethacrylate homopolymer [18].

The temperatures corresponding to each degradation stage were similar for the hybrid polysiloxanes synthetized from TEOS