

Polyvinylphosphonic acid used in synthesis of organic inorganic hybrids by sol-gel method

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Organophosphorus coupling molecules are much less widespread than organosilicon compounds, but they are finding increasing applications. In this paper we present the use of polyvinylphosphonic acid as precursor in synthesis of new organic-inorganic hybrids with interpenetrated network, using sol-gel method, under ultrasound conditions. The interpenetrated network is a results of two networks coupled through covalent bonds. The covalent bonds are produced by polycondensation between M-OH and P-OH groups from alkoxide and polyvinylphosphonic acid respectively. The obtained hybrids were investigated using FTIR, SEM, and AFM.

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1. Introduction

Hybrid materials or even nanotechnology is not an invention of the last decade but was developed a long time ago. In ancient world mixing organic and inorganic components was a manner for new materials. However, it was only at the end of the 20th and the beginning of the 21st century that it was realized by scientists, in particular because of the availability of novel physical-chemical characterization methods, the field of nanoscience opened many perspectives for approaches to new materials [1]. The most wide-ranging definition is the following: a hybrid material is a material that includes two moieties blended on the molecular scale. Commonly one of these compounds is inorganic and the other one organic in nature. A more detailed definition distinguishes between the possible interactions connecting the inorganic and organic species. Class I hybrid materials are those that show weak interactions between the two phases, such as van der Waals, hydrogen bonding or weak electrostatic interactions. Class II hybrid materials are those that show strong chemical interactions between the components [2].

The coupling of organic and inorganic moieties is most often implemented by sol-gel processing [3]. By far the best known coupling molecules are organosilicon compounds, usually organoalkoxysilanes or organochlorosilanes [4,5]. Indeed, Si-C bonds are stable toward hydrolysis, and the linkage between the organic and inorganic moieties involves the formation of M-O-Si-C bonds. Organophosphorus coupling molecules are much less widespread, but they are finding increasing applications. Actually, both P-C and P-O-C bonds are quite stable toward hydrolysis, and the linkage to the inorganic network involves the formation of M-O-P-C or M-O-P-O-C bonds [6].

Hydrolytic sol-gel process has been studied extensively over the last 25 years as a facile route to organic-inorganic hybrids, [7-9] it is only in the last 15 years that the corresponding non-hydrolytic sol-gel process has been recognized as a useful route to [10-12] Synthesis of organic-inorganic hybrids by sol-gel processing offers many possibilities: control of the organic content, of the surface area and porosity, and shaping of the final material before the liquid-to-gel transition (film coating for instance). A few years ago, the incorporation of organophosphorus groups within zirconium, titanium and aluminium oxides by a two step sol-gel process has been reported [13-15].

The metal alkoxide precursor was first mixed with a solution of a phosphonic or phosphinic acid in an organic solvent. P-O-M bonds form at this stage, in the absence of water, by heterocondensation between P-OH and M-OR' groups, with release of alcohol. In the second step water (neutral) was added, leading to the formation of the M-O-M bonds of the oxide network by hydrolysis/condensation of the residual alkoxide groups.

Works have demonstrated that hybrid materials can be easily formed by using organic polymers [16,17]. Therefore, the polymer must contain reactive functional groups such as vinyl, hydroxyl, etc., to react with silanol groups belonging to the hydrolysis of TEOS or be able to react with the hydroxyl groups coming from metallic alkoxides (e.g. Ti, Al, Zr) [18-20]. In fact, metallic alkoxides used in the synthesis of hybrid materials promote the crosslinking of the inorganic network and catalyze the hydrolysis-condensation reactions. Thus, the final properties of the hybrid materials are strongly dependent on the type and concentration of the metallic alkoxide as well as the amount of catalyst, the hydrolysis ratio, the reaction temperature and also the molecular

weight of the organic polymer plays an important role in the synthesis [21].

In this paper we present the use of polyvinylphosphonic acid as precursor in synthesis of new organic-inorganic hybrids with interpenetrated network, using sol-gel method, under ultrasound conditions, not mentioned in the studied literature by our knowledge. The network is formed by polycondensation of metal alkoxide with P-OH groups resulting P-O-M- linkages.

2. Experimental

Ti(OEt)₄, Zr(On-Bu)₄ 80% in Butanol, polyvinylphosphonic acid were purchased from Aldrich and used without purification. Ethanol was also purchased from Aldrich.

2.1 General procedure

Polyvinylphosphonic acid was dissolved under ultrasound condition (20 min) in absolute ethanol (1molL⁻¹). Metal alkoxide is dissolved in absolute ethanol(1molL⁻¹) and is added dropwise under ultrasound to the first solution. Then the mixture is kept 15 min under ultrasound. After this period, the mixture is kept two days for ageing at ambient temperature. Then water is added and the mixture was kept another day at ambient

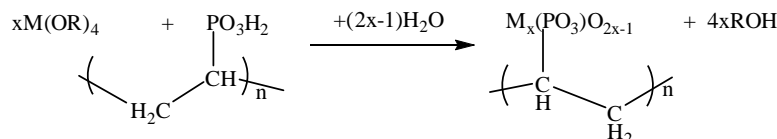
temperature. The resulting mixture is dried at 100°C for 5 hours.

It was used an ultrasound apparatus MRC D80H with operating frequency 43 KHz.

The obtained hybrids were investigated using FTIR, SEM, AFM. The IR absorption spectra were recorded with a Jasco 430 spectrometer (spectral range 4000-400 cm⁻¹, 256 scans, and resolution 2 cm⁻¹) using KBr pellets. The SEM images and EDAX were obtained using Inspect S microscope. AFM images were obtained with Nanosurf Easy Scan 2 Advanced Research AFM.

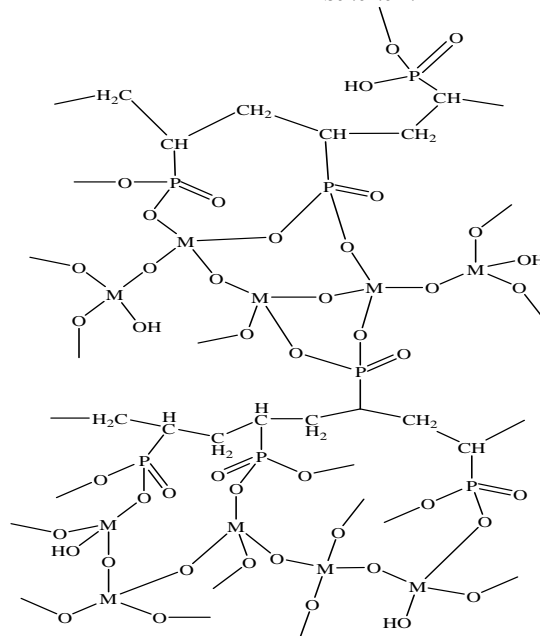
3. Results and discussion

In our paper we present the results obtained in synthesis of hybrid material having an interpenetrated network, by sol-gel technique, under ultrasound conditions (Scheme 1 and 2). The interpenetrated network is a results of two networks coupled through covalent bonds. The covalent bonds are produced by polycondensation between M-OH and P-OH groups from alkoxide and polyvinylphosphonic acid respectively. Usually the reaction results in a three-dimensional (3-D) crosslinked network. Polyvinylphosphonic acid was used with two reasons: as polymer and in the same time as „coupling agent”.



M=Ti, Zr

Scheme 1.

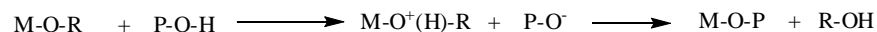


M=Ti, Zr.
Scheme 2.

In sol-gel technique the main reactions involved are hydrolysis and condensation reactions. Heterocondensation between the metal alkoxide and phosphonic coupling molecules leads to the formation of P-O-M (M=Ti; Zr) bonds, while homocondensation between two metal alkoxide molecules leads to the formation of M-O-M bonds. Accordingly, the structure of hybrids based on phosphonic coupling molecules is governed by the competition between heterocondensation and homocondensation reactions. Phosphorus derivatives

are much less sensitive to nucleophilic substitution than the titanium or zirconium parent derivatives, with two important consequences: P-O-C bonds are quite stable toward hydrolysis, and homocondensation of P-O-H bonds with formation of P-O-P bonds takes place only under high temperature dehydrating conditions[6].

The formation of M-O-P bonds by heterocondensation is kinetically favored, due to the protonation of the leaving alkoxy group by the acidic P-OH groups (Scheme 3):



Scheme 3.

The reactivity of organophosphorus acids is quite different from that of organosilicon coupling molecules, leading to different structures and stabilities for the hybrid materials. The main difference in terms of reactivity is the absence of homocondensation between P-OH groups. Thus, the use of organophosphorus coupling molecules in sol-gel processing is very attractive for the preparation of highly homogeneous hybrid materials.

Furthermore, transition metals often show several stable coordination environments. While the negatively charged alkoxides balance the charge of the metal cation

they generally cannot completely saturate the coordination sphere of the metals, which leads to the formation of oligomers via alkoxide or alcohol bridges and/or the saturation of the coordination environment by additional coordination of alcohol molecules, which also has an impact on the reactivity of the metal alkoxides. Titanium oxide (zirconium oxide)/polyvinylphosphonate hybrids with different Ti (Zr)/P ratios were prepared from Ti(OEt)₄ or Zr(OnBu)₄ 80% in BuOH and polyvinylphosphonic acid (PVPA) precursors. In Table 1 the molar ratios for synthesized hybrid are presented.

Table 1. Molar ratio for synthesized hybrids.

Code	Ti(OEt) ₄ , mmol	Zr(OnBu) ₄ , mmol	PVPA, mmol repeat unit	Water, mmol	Aspect
SGP1	10	-	20	50	White opaque gel
SGP2	-	10	20	50	White opaque gel
SGP3	20	-	10	100	White opaque gel
SGP4	-	20	10	100	White opaque gel

The FT-IR spectra of hybrids shows strong bands at 1040-910 cm⁻¹ and 1150cm⁻¹ due to (P-O)H and P = O stretching respectively, characteristic to homopolymer structure. The phosphonic acid group gives an additional band in the region of 1700-1630 cm⁻¹. The broad band at 3300-2850 cm⁻¹ belongs to -OH stretching of the same group. After polycondensation, the intensity of (P-O)H stretching at 1040-910 cm⁻¹ and the OH band at 3408 cm⁻¹ of the acid group, decreases with increasing of polycondensation degree. The decrease or absence of these bands is a measure of polycondensation.

In the case of SGP1 and SGP3 the absence of peaks at 1097 and 1125 cm⁻¹ which can be assignable to the Ti-OEt groups and presence of broad peak at 1130 cm⁻¹ is assignable to the Ti-O-P group, indicates that sol-gel polycondensation proceeds successfully.

The absence of C-H stretching bands at 2984, 2932, 2905, and 2871 cm⁻¹ from the OEt groups confirms the complete cleavage of the M-OEt groups.

SEM images of hybrid materials are shown in Figs. 1 and 2. The microstructure of all samples showed a same morphology, composed of aggregates with irregular size.

The chemical compositions of these organic-inorganic hybrid materials have been determined by energy dispersive analysis of X-rays (EDAX). The collected EDAX data Fig. 3 indicated that the Ti and Zr existed in the porous structure. EDAX also indicated that the element C, O, P and Cl existed. The appeared C and P element by EDAX analysis indicated that the materials contain organophosphorus moiety and therefore, were considered as an organic-inorganic hybrid materials.

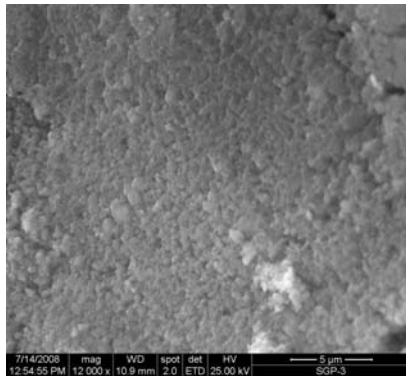


Fig. 1. SEM image of SGP3.

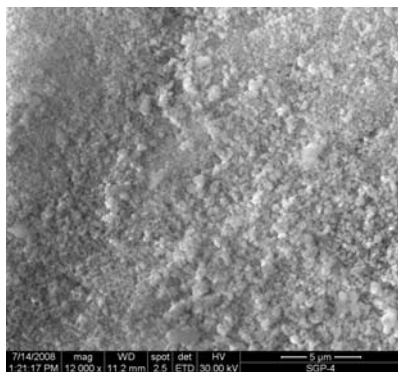
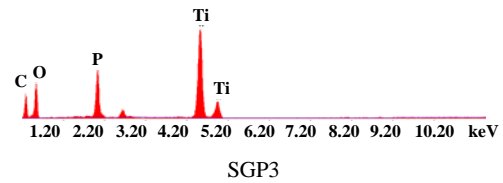


Fig. 2. SEM image SGP4.

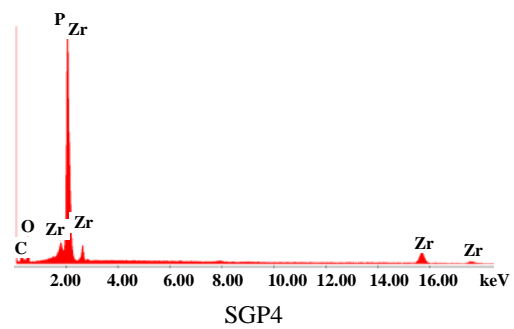


Fig. 3. Energy dispersive analysis of X-rays (EDAX).

The AFM images also exhibit structures representing aggregates, as illustrated in Fig. 4 (a) and (b) and Fig. 5 (a-c). This aggregation occurs on the sample surface.

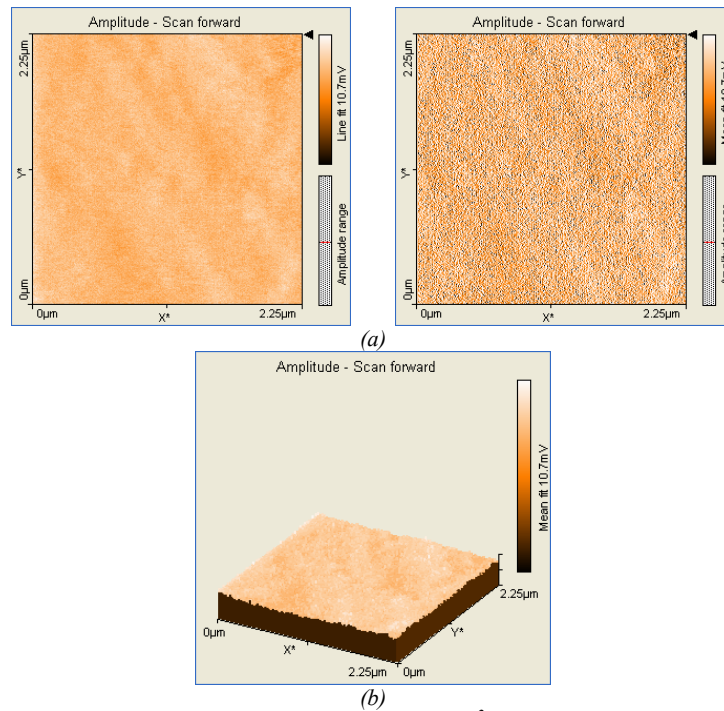


Fig. 4. (a). Bidimensional representation of SGP3. Surface area : $2.3\mu\text{m}^2$. Color map; (b). Bidimensional representation of SGP3. 3D map.

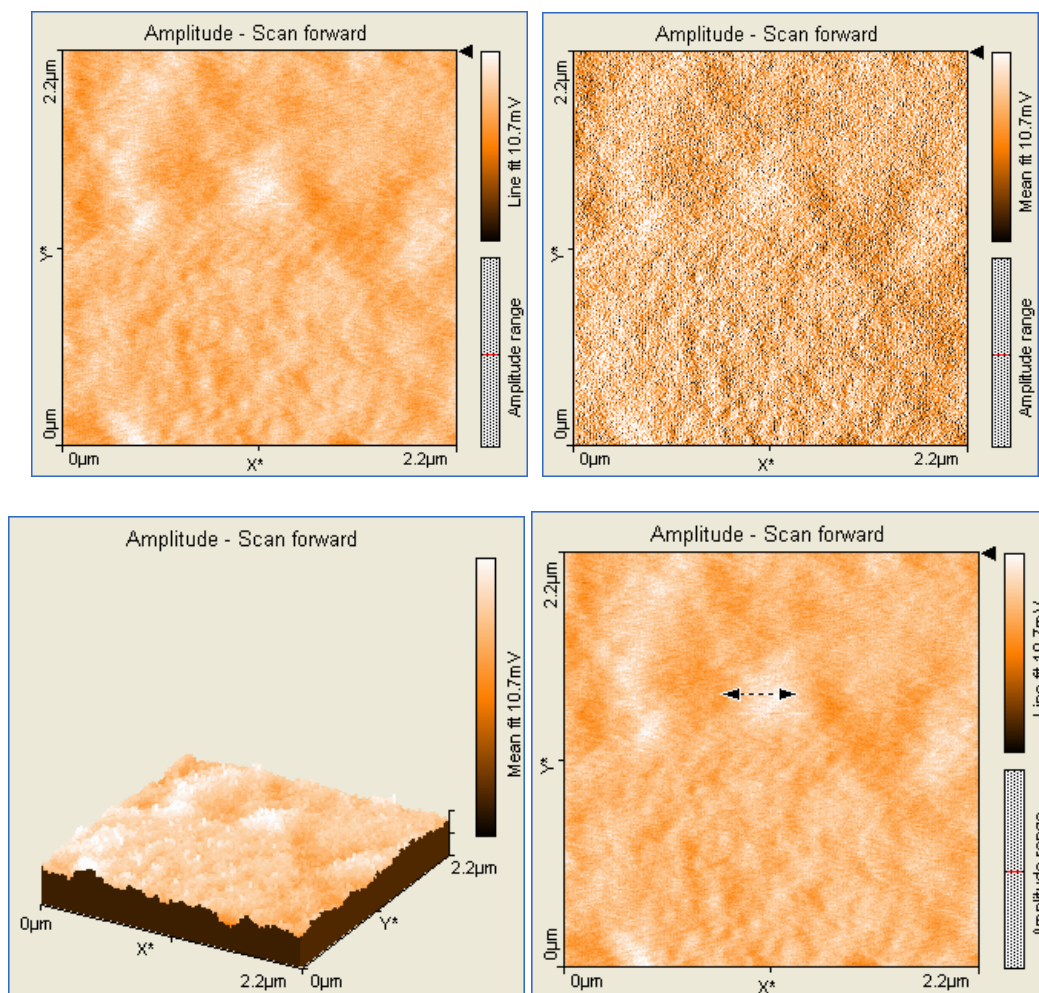


Fig.5. (a). Bidimensional representation of SGP4. Surface area : $2.3\mu\text{m}^2$. Color map: (b). Bidimensional representation of SGP4. 3D map; (c). 3D map; (d). 2D representation of studied surface: the diameter of particle is 412 nm.

4. Conclusions

Polyvinylphosphonic acid can be considered a precursor in synthesis of some new organic-inorganic hybrids with interpenetrated network, using sol-gel method. These hybrids presents the same morphology, composed of aggregates with irregular size.

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