

# Sol-gel synthesis, characterization and bioactivity of polycaprolactone/SiO<sub>2</sub> hybrid material

M. CATAURO, M. G. RAUCCI, F. DE GAETANO, A. MAROTTA

*Department of Materials and Production Engineering, University of Naples "Federico II,"  
Piazzale Tecchio, 80125 Naples, Italy*

*E-mail: albmarot@unina.it*

A novel organic/inorganic hybrid material was synthesized by sol-gel method from a multicomponent solution containing tetramethylorthosilicate (TMOS), polycaprolactone (PCL), water, and methylethylketone (MEK). The interpenetrating network structure is realized by hydrogen bonds between Si–OH group (H donor) in the sol-gel intermediate species and carboxylic group (H-acceptor) in the repeating units of the polymer. The presence of hydrogen bonds between organic/inorganic components of the hybrid material was proved by FTIR analysis. The morphology of the hybrid material was studied by scanning electron microscope (SEM). The structure of a molecular level dispersion has been disclosed by atomic force microscope (AFM), pore size distribution and surface measurements. The bioactivity of the synthesized hybrid material has been showed by the formation of a layer of hydroxyapatite on the surface of PCL/SiO<sub>2</sub> samples soaked in a fluid simulating the composition of the human blood plasma.

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## 1. Introduction

The sol-gel process has proved to be versatile and has been widely used in the preparation of organic/inorganic hybrid materials, [1–3] non-linear optical materials [4], and mesomorphous materials [5]. The sol-gel chemistry is based on the hydrolysis and polycondensation of metal alkoxides M(OR)<sub>x</sub>, where M = Si, Sn, Ti, Al, Mo, V, W, Ce and so forth. The following sequence of reactivity is usually found (OR)<sub>4</sub> ≪ Sn(OR)<sub>4</sub> = Ti(OR)<sub>4</sub> < Zr(OR)<sub>4</sub> = Ce(OR)<sub>4</sub> [3]. Because silicon alkoxides are not very reactive, the sol-gel process of the silicon alkoxides is slow and easy to control in order to produce a transparent gel. There is considerable interest in organic-inorganic hybrid/composite materials prepared via the sol-gel process. A variety of organic polymers have been introduced into inorganic networks to afford the hybrid or composite materials with or without covalent bonds between the polymer and inorganic, components, respectively. The sol-gel reactions are known to be affected by many synthetic parameters such as structure and concentration of the reactants, solvents, and catalysts as well as reaction temperature and rate of removal of by-products and solvents [6, 7]. In particular the presence of organic components modifies the morphology and physical properties of the sol-gel products. For example, the base-catalyzed sol-gel reaction usually results in translucent or opaque products with visible organic-inorganic phase separation. Under acid catalysis and carefully controlled reaction conditions, transparent and monolithic hybrid/composite materials can be obtained.

Recently, a family of monolithic and transparent hybrid materials have been synthesized via the acid- or photo-acid-catalyzed sol-gel reactions of inorganic precursor such as tetraethyl orthosilicate (TEOS) with polymer precursors that contain reactive alkoxy silyl groups [8–11]. A key issue that remains unresolved in these organic-modified materials is the degree of mixing of the organic-inorganic components, i.e., the phase homogeneity. The high optical transparency to visible light indicates that the organic-inorganic phase separation, if any, is on a scale of ≤400 nm. Many conventional methods for analyzing composite materials have not proved to be effective. For example, the changes in and disappearance of well-defined glass transition of the polymer component as measured by differential scanning calorimeter (DSC) or dynamic mechanical analysis (DMS) suggests the diminution of phase separation but offer little quantitative information [12, 13]. Transmission electron microscopy (TEM) often fails to provide useful morphological data because of weak contrast [12]. Recently, there have been several reports with encouraging examples of applying atomic force microscopy (AFM) in the analysis of sol-gel materials [12, 14].

Recently, the study of organic-inorganic nanocomposites networks and gel became an expanding field of investigation [15, 16]. At first glance, these materials are considered as biphasic materials, where the organic and inorganic phase is mixed at the nanometre to sub-micro scales. Nevertheless, it is obvious that the properties of these materials are not just the sum of the individual contributions from both phases; the

role of the inner interfaces could be predominant. The nature of the interface has been used recently to divide these materials into two distinct classes [17]. In class I, organic and inorganic compounds are embedded and only weak bonds (hydrogen, van der Waals or ionic bonds) give the cohesion to the whole structure. They result from much research work emerging from sol-gel and polymer chemists and these materials will present a large diversity in their structures and final properties. In class II materials, the phases are linked together through strong chemical bond (covalent or ionic-covalent bonds).

It is known that SiO<sub>2</sub> glass is bioactive, i.e., it is able to bond to living bone [18]. As reported in the literature [18, 19], the essential condition for glasses and glasses-ceramics to bond to living bone is the formation of a bone-like apatite layer on the surfaces. *In vitro* studies are performed [18, 19] by soaking the glasses in a simulated body fluid (SBF) to study hydroxyapatite formation on the surface.

In this paper a polycaprolactone/SiO<sub>2</sub> hybrid material class I has been prepared via sol-gel process. The existence of the hydrogen bonds between organic/inorganic hybrid and the formation of a hydroxyapatite layer on the surface has been proved by FTIR analysis. The phase homogeneity was also studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

## 2. Experimental procedure

A hybrid inorganic/organic material was prepared by means of sol-gel process from analytical reagent grade tetraethyl orthosilicate (TMOS) and polycaprolactone (PLC). Fig. 1 shows the flow chart of hybrid synthesis by the sol gel method. The molar ratio of the starting materials is indicated in the figure. After gelation the gel was dried by microwaves. Monolithic small pieces were obtained as shown in Fig. 2.

The microstructure of the synthesized gel has been studied by a scanning electron microscopy (SEM) Cambridge model S-240 on samples previously coated with a tin Au film and by a Digital Instruments Multimode atomic force microscopy (AFM) in contact mode in air.

In order to study their bioactivity, samples of the studied hybrid materials were soaked in a simulated body fluid (SBF) with ion concentrations, as reported elsewhere [19], nearly equal to those of the human blood plasma. During soaking the temperature was kept fixed at 37°C. The ability to form an apatite layer was studied by submitting reacted samples to IR spectroscopy. Powers (170 + 230 mesh) were soaked in SBF and analyzed in IR spectroscopy. Taking into account that [20, 21] the ratio of the exposed surface to the volume solution influences the reaction, a constant ratio was maintained of 50 m<sup>-1</sup> of solution, as in [20]. Fourier transform infrared (FTIR) transmittance spectra were recorded in the 400–1200 cm<sup>-1</sup> region using a Mattson 5020 system, equipped with a DTGS KBr (Deuterated Tryglycine Sulphate with potassium bromide windows) detector, with resolution of 2 cm<sup>-1</sup> (20 scans). KBr pelletized disks containing 2 mg of sample and 200 mg

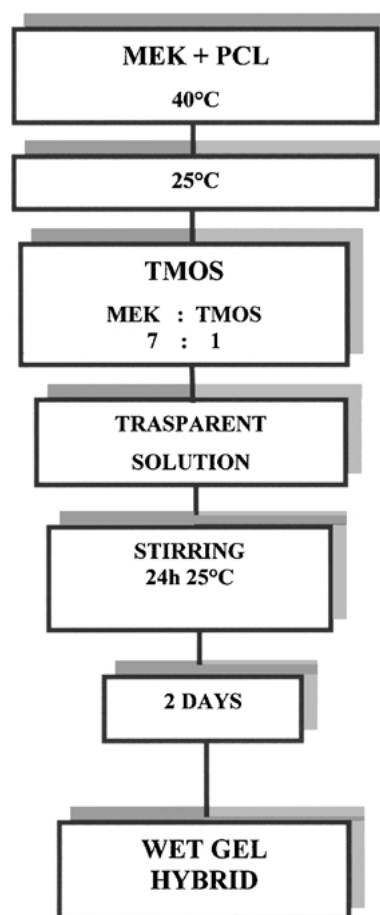
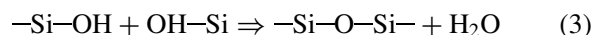
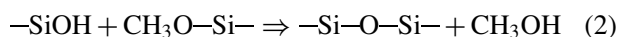
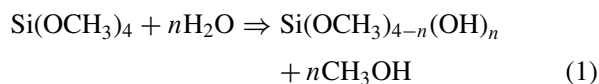


Figure 1 Flow chart of PCL/SiO<sub>2</sub> gel synthesis.

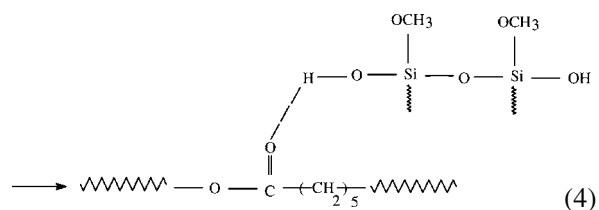
KBr were made. The FTIR spectra have been analysed by Mattson software (FTIR Macros).

## 3. Results and discussion

Gelation is the result of hydrolysis and condensation reactions according to the following reactions



The reaction mechanism is not known in much detail; however, it is generally accepted that they proceed through a second order nucleofic substitution [22].



Reaction 4 shows the formation of a hydrogen bond between the carboxylic group of the organic polymer and the hydroxyl group of the inorganic matrix.

The existence of hydrogen bonds was proved by FTIR measurements. Fig. 3 shows the infrared spectrum of (a) the SiO<sub>2</sub> gel and (b) the PCL/SiO<sub>2</sub> gel. In Fig. 3a the bands at 3400 and 1600 cm<sup>-1</sup> are attributed

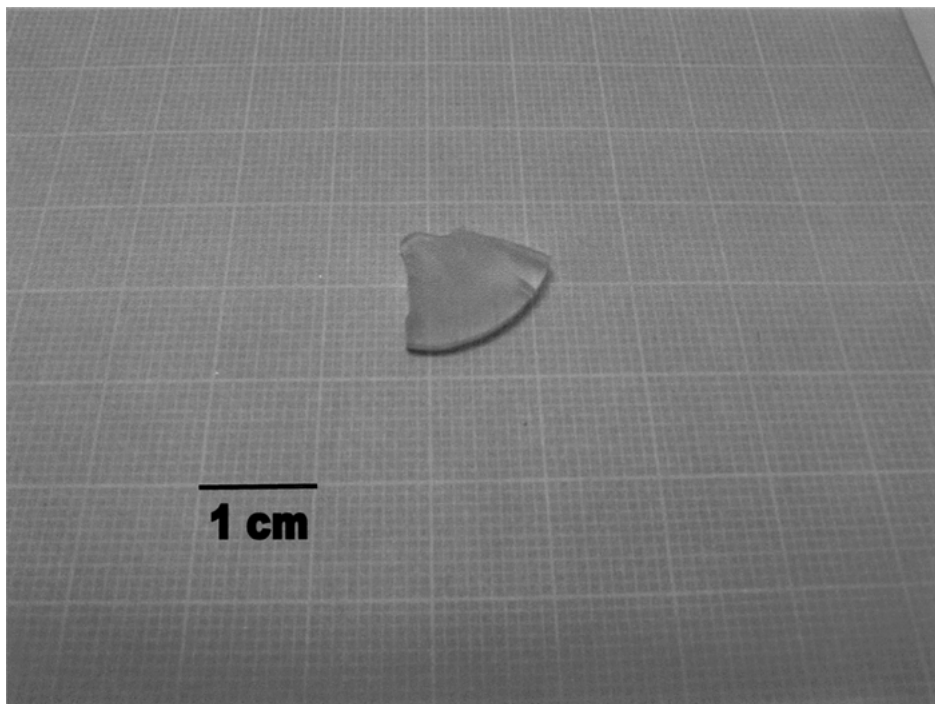


Figure 2 PCL/SiO<sub>2</sub> gel after drying in microwave apparatus.

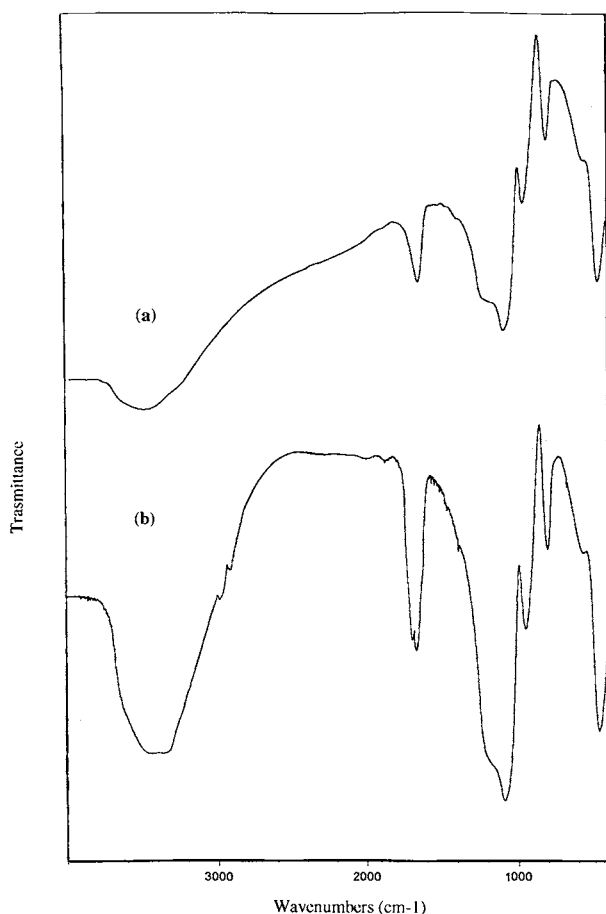


Figure 3 FTIR of (a) SiO<sub>2</sub> gel and (b) PCL/SiO<sub>2</sub> gel.

to water [23, 24]. The bands at 1080 and 470 cm<sup>-1</sup> are due to the stretching and bending modes of SiO<sub>4</sub> tetrahedra [25, 26]. In the Fig. 3b the bands at 2950 and 2853 cm<sup>-1</sup> are attributed to the symmetric stretching of —CH<sub>2</sub>— of polycaprolactone. The band at 1715 cm<sup>-1</sup> is due to the characteristic carboxylic group shifted to

low wave numbers, the broad band at 3200 cm<sup>-1</sup> is the characteristic O—H group of hydrogen bonds.

The microstructure of the PLC/SiO<sub>2</sub> hybrid material has been studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

SEM micrographs of a SiO<sub>2</sub> gel sample and of PCL/SiO<sub>2</sub> gel sample are shown in Figs 4 and 5. A marked difference between the morphology of the two crystalline materials can be observed. This result indicates that PCL plays an essential role in the crystallization of the SiO<sub>2</sub> system; the nature of the crystallizing phase is strongly affected by the presence of the polymeric component. Moreover this result according with those obtained by FTIR measurements suggests the formation of links (hydrogen bonds) between the polymeric component and the growing SiO<sub>2</sub> nuclei during the sol-gel synthesis.

The degree of mixing of the organic-inorganic components, i.e., the phase homogeneity has been ascertained applying the atomic force microscopy (AFM) in the analysis of the sol-gel hybrid material.

The AFM contact mode image can be measured in the height mode or in the force mode. Force images (z range in nN) have the advantage that they appear sharper and richer in contrast and that the contours of the nanostructure elements are clearer. In contrast, height images (z range in nm) show a more exact reproduction of the height itself [27]. In this work the height mode has been adopted to evaluate the homogeneity degree of the hybrid material. The AFM topographic image of PCL/SiO<sub>2</sub> gel samples is shown in Fig. 6. As can be observed the average domain size is less than 130 nm. This result confirms that the PCL/SiO<sub>2</sub> gel synthesized can be considered an organic/inorganic hybrid material as suggested by literature data [28].

The hybrid material was soaked in SBF, as indicated in [24] for *in vitro* bioactivity tests. The FTIR spectra

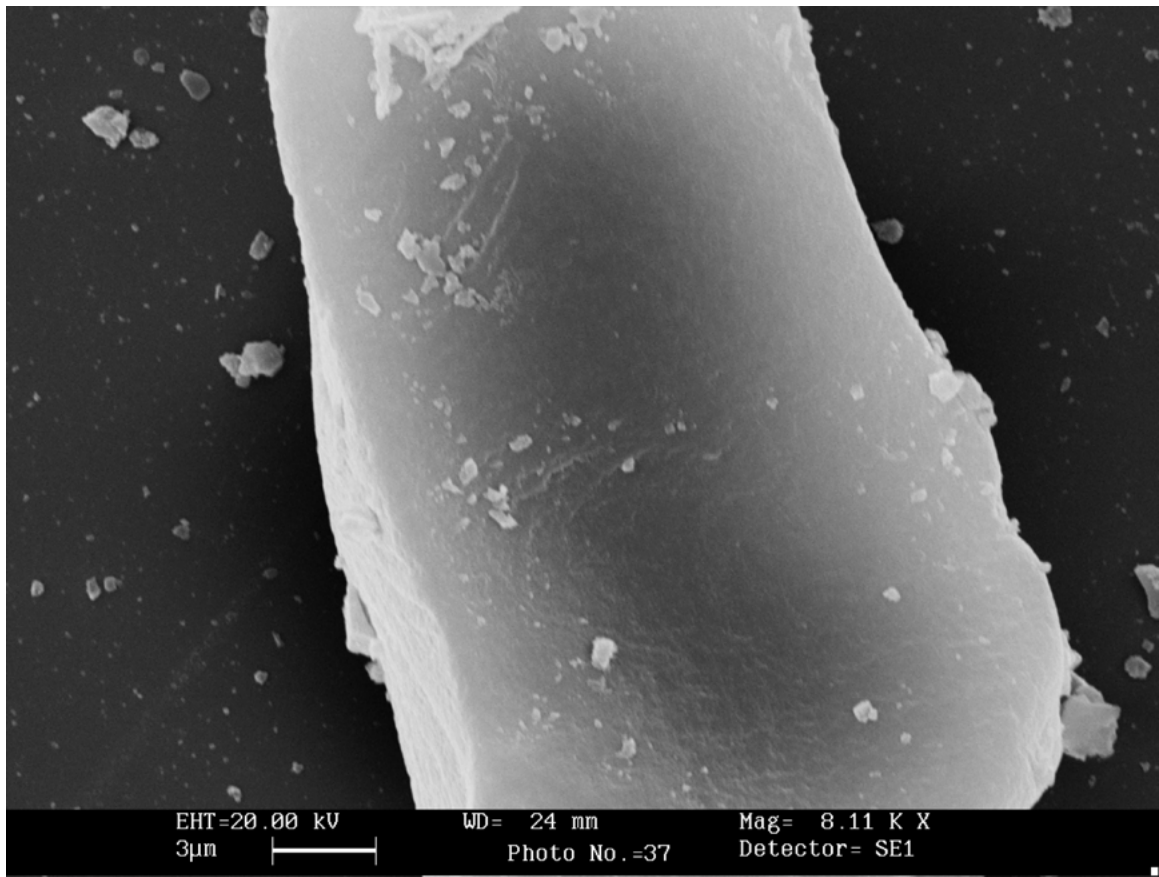


Figure 4 SEM micrograph of SiO<sub>2</sub> gel.

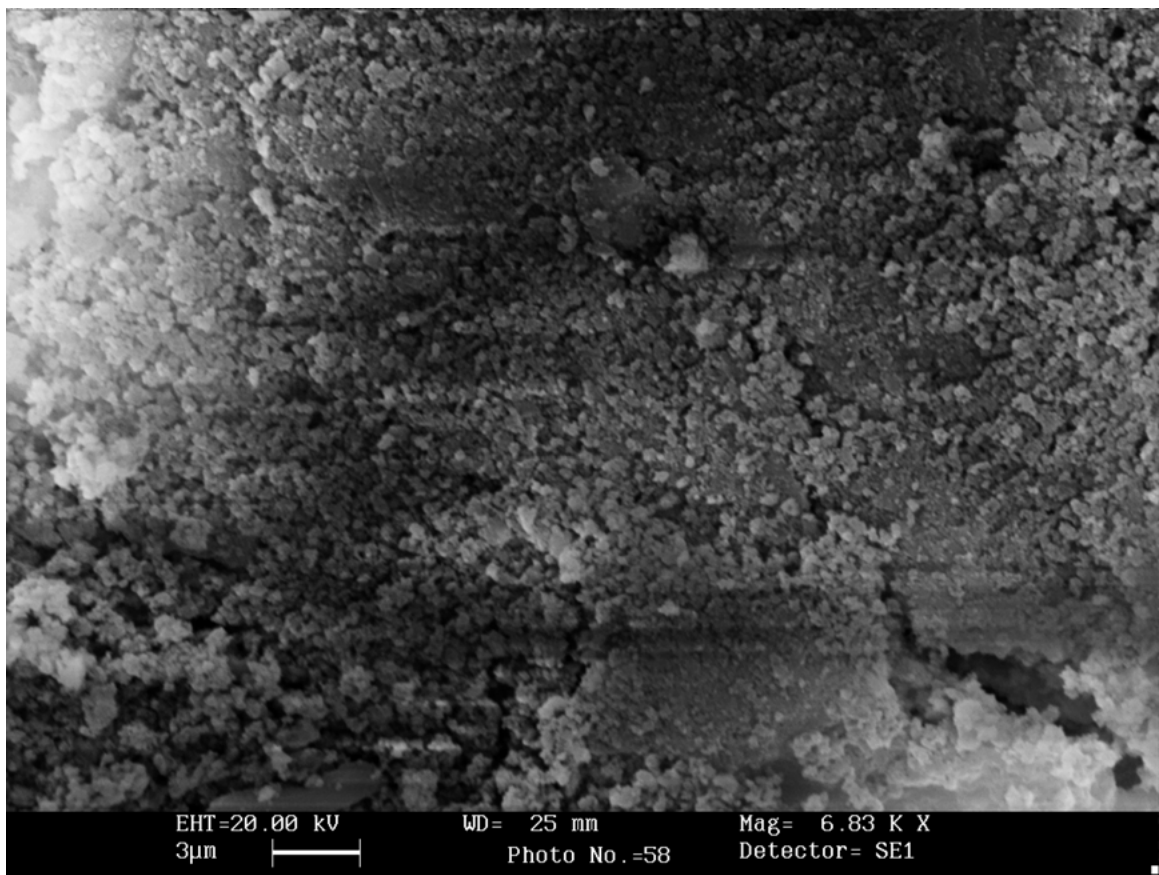


Figure 5 SEM micrograph of PCL/SiO<sub>2</sub> gel.

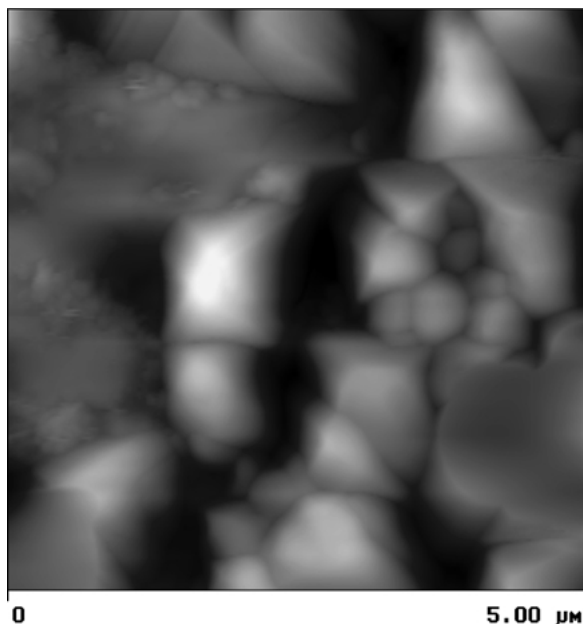


Figure 6 AFM image showing the microstructure of PCL/SiO<sub>2</sub> gel.

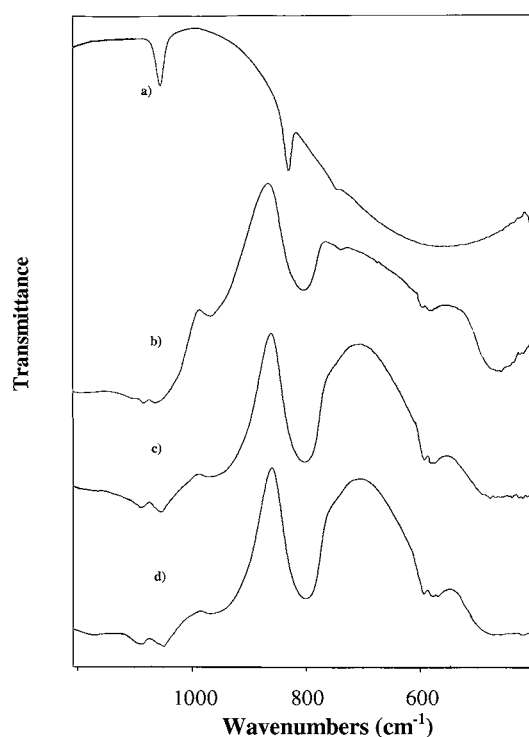


Figure 7 FTIR spectra of PCL/SiO<sub>2</sub> gel samples after different times of exposed to SBF: (a) not exposed, (b) 7 days, (c) 14 days, and (d) 21 days.

after different exposures to SBF, of 7, 14 and 21 days, are shown in Fig. 7. Evidence of formation of an hydroxyapatite layer is given by the appearance of the 1116 and 1035 cm<sup>-1</sup> bands, usually assigned to P—O stretching [26], and of the 580 cm<sup>-1</sup> band usually assigned to the P—O bending mode [26]. The splitting, after already 7 days soaking, of the 580 cm<sup>-1</sup> band into two others at 610 and at 570 cm<sup>-1</sup> can be attributed to formation of crystalline hydroxyapatite [24]. Finally the band at 800 cm<sup>-1</sup> can be assigned to the Si—O—Si band vibration between two adjacent tetrahedra characteristic of silica gel [26]. This supports the hypothesis that a surface layer of silica gel forms as supposed in

the mechanism proposed in the literature for hydroxyapatite deposition [29, 30].

#### 4. Conclusions

The polycaprolactone/silica (PCL/SiO<sub>2</sub>) material, prepared via sol-gel process, was found to be an organic/inorganic hybrid material.

The polymer (PCL) was incorporated into the network by hydrogen bonds between the carboxylic groups of the organic polymer and the hydroxyl groups of the inorganic matrix. The formation of hydrogen bonds was ascertained by FTIR measurements. Moreover the AFM and SEM analysis confirm that the PCL/SiO<sub>2</sub> can be considered a homogenous organic/inorganic hybrid material because the average domains are less than 400 nm in size.

Finally the formation of a layer of hydroxyapatite on the surface when samples of the PCL/SiO<sub>2</sub> were soaked in SBF (fluid simulating body), showed by FTIR spectra, indicates that the PCL/SiO<sub>2</sub> can be considered a bioactive material.

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