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Structure and magnetic properties of SiO_2/PCL novel sol–gel organic–inorganic hybrid materials

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ABSTRACT

Organic–inorganic nanocomposite materials have been synthesized via sol–gel. They consist of an inorganic SiO_2 matrix, in which different percentages of poly(ε-caprolactone) (PCL) have been incorporated. The formation of H-bonds among the carbonyl groups of the polymer chains and Si–OH group of the inorganic matrix has been proved by means of Fourier transform infrared spectroscopy (FT-IR) analysis and has been confirmed by solid-state nuclear magnetic resonance (NMR). X-Ray diffraction (XRD) analysis highlighted the amorphous nature of the synthesized materials. Scanning electron microscope (SEM) micrograph and atomic force microscope (AFM) topography showed their homogeneous morphology and nanostructure nature. Considering the opportunity to synthesize these hybrid materials under microgravity conditions by means of magnetic levitation, superconducting quantum interference device (SQUID) magnetometry has been used to quantify their magnetic susceptibility. This measure has shown that the SiO_2/PCL hybrid materials are diamagnetic and that their diamagnetic susceptibility is independent of temperature and increases with the PCL amount.

1. Introduction

Sol–gel process is the method of making ceramic and glassy materials at a relatively low temperature. The transition of a sol–gel system from a colloidal solution (the 'sol') into a solid 'gel' phase occurs through hydrolysis and polycondensation of a metal alkoxide precursor. By drying the obtained wet gel is possible to prepare xerogels (by exposure to low temperatures) or aerogel (by means of supercritical conditions) [1]. The low processing temperature of sol–gel technology combined with the high sol homogeneity, due to mixing on the molecular scale, make it an ideal technology for the fabrication of organic–inorganic hybrid materials by entrapping various organic polymers in a glassy matrix. Generally the properties (thermal behavior, mechanical properties, stability, *etc.*) of each single phase are held constant in the hybrid and the nature of the bonds present between them has an impact on the properties of the materials. Judenstein et al. [2] proposed a classification of the hybrid materials based on the interactions between the phases. They defined those materials as first class hybrids, if they were characterized by weak bonds (hydrogen bond, Van der Waals forces, *etc.*) between the two phases, or second class hybrids, if strong bonds (covalent bond or ionic-covalent bond) occurred.

The microstructure and shaping process of gelling precursors was found to be influenced by surface tension and convective mass transport effects; hence, a microgravity environment would be suitable, in sol–gel experiments, to produce shaped rigid gels with a controlled microstructure [3]. In literature [3–9], studies carried out by using parabolic flights, drop toward or International Space Station (ISS) are reported. Those experiments showed that reduced gravity affects the final microstructure of xerogels and aerogels because it helps both a rapid hydrolysis and the condensation reactions which result in the formation of siloxane groups. Those groups oppose capillary stress and a sol–gel structure with large pore sizes and surface areas is formed. On the contrary, the normal gravity limits the condensation reactions and favours the formation of silanol groups. These phenomena and the dominance of surface tension effects would result in a microporous structure.

Magnetic levitation is another technique usefully adopted to create microgravity conditions for materials synthesis. For example, different kinds of crystals have been grown, with improved qualities, by levitating droplets or aqueous solutions [10,11] and different levitating materials have been melt without contamination due to the crucible, even for synthesis purposes [10,12]. The crucial property which a material must have to undergo conventional stable magnetic levitation is to be diamagnetic [10,13–16]. A diamagnetic sample experiences a force acting upwards if it is

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appropriately placed at an off-center position of a magnetic vertical field. Levitation occurs when the magnetic force is higher than that due to gravity: suitable values of sample susceptibility and of magnetic field intensity and gradient are indeed requested for this goal [10].

In this study, SiO_2/PCL(PCL 0, 6, 12, 24, 50 %wt) hybrid materials were prepared by sol–gel methods and their nature has been tested by several techniques, including FT-IR and solid-state ^{13}C NMR. These techniques allowed to identify the nature of the bonds present between the organic and inorganic phases in the synthesized hybrid materials. Indeed, solid-state nuclear magnetic resonance (NMR) is a well-suited technique to study inter- and intrachains interactions, as well as both short and long range dynamics in polymers [17]. This technique has been applied to poly(ε-caprolactone). 1-D and 2-D ^{13}C NMR analyses on PCL crystallized from the melt were reported by Kaji and Horii [18]. The formation of hydrogen bonds between the hydroxyl groups of poly(4-vinylphenol) and the PCL carbonyl was characterized by ^{13}C NMR [19]. The structure and dynamics of PCL-clay nanocomposites were investigated by ^{31}P and ^{13}C NMR [20]. Finally, both static and CPMAS ^{13}C NMR were used to investigate PCL-$CaCO_3$ composites [21]. Moreover, the author recently prepared several PCL-based hybrids for drug delivery by means of sol–gel methods, using different oxides, CaO and/or SiO_2 [22–25], TiO_2 [26], and ZrO_2 [27] and composite substrates for tissue engineering consisting of a poly(ε-caprolactone) matrix reinforced with sol–gel synthesized PCL/TiO_2 or PCL/ZrO_2 hybrid fillers [28]. In all the examined cases, Fourier transform infrared spectroscopy (FT-IR) measurements gave circumstantial evidence of the formation of class I hybrids, characterized by the presence of hydrogen bonds among the carbonyl groups of the polymer and the OH– groups of the inorganic phase.

Considering the opportunity to synthesize SiO_2/PCL hybrid materials under microgravity conditions, the magnetic character of our samples has been tested by means of SQUID magnetometry and the value of their magnetic susceptibility as a function of PCL amount has been determined.

2. Experimental study

2.1. Sol–gel synthesis

The SiO_2/PCL (PCL 0, 6, 12, 24, 50 %wt) organic–inorganic hybrid materials were prepared by means of the sol–gel process starting from an analytical reagent grade of tetraethyl orthosilicate (TEOS), used as a precursor material, in a mixture of ethanol, water and nitric acid (HNO_3 65%) as catalyst. Poly(ε-caprolactone) (PCL Mw=65,000), previously dissolved in chloroform ($CHCl_3$), was added to the solution under vigorous stirring to obtain an uniform and homogeneous sol. Fig. 1 shows the flowchart of the (SiO_2/PCL) hybrid synthesis by the sol–gel method.

The gelification time depends on the amount of PCL, as shown in Table 1. After gelification the wet gels were air dried at 50 °C for 48 h to remove the residual solvent; glassy pieces were obtained (Fig. 2). They were crushed in a mortar and the resulting fine (<125 μm) glassy powder was used to characterize the obtained materials.

2.2. Sol–gel materials characterization

The kind of the bonds between organic and inorganic components in the hybrid materials was verified by FT-IR analysis. FT-IR transmittance spectra were recorded in the 400–4000 cm^{-1} region using a Prestige 21 Shimatzu system, equipped with a DTGS KBr (deuterated tryglycine sulfate with potassium bromide windows)

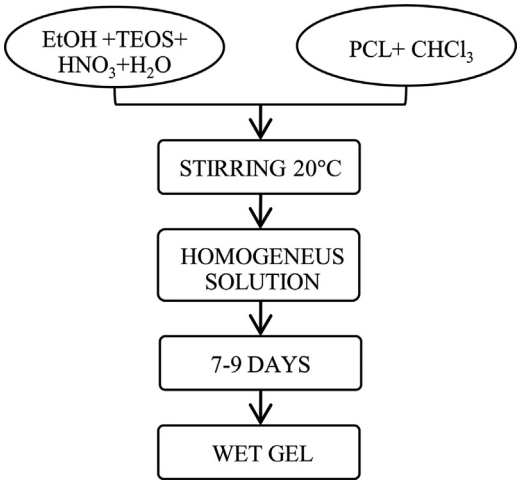

Fig. 1. Flow chart of SiO_2/PCL gels synthesis.

Table 1
Prepared materials gelification time.

System	Gelification time (days)
SiO_2	9
SiO_2+PCL 6 wt%	8
SiO_2+PCL 12 wt%	8
SiO_2+PCL 24 wt%	8
SiO_2+PCL 50 wt%	7

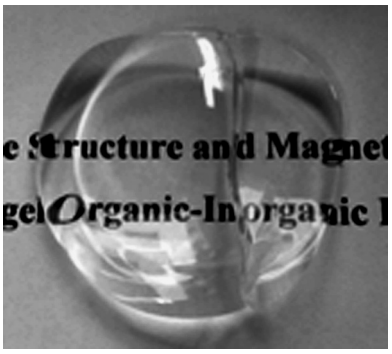

Fig. 2. Photograph of a representative gel sample.

detector, with a resolution of 2 cm^{-1} (45 scans). KBr pelletised disks containing 2 mg of sample and 200 mg KBr were made. The FT-IR spectra were elaborated by IR solution software.

^1H MAS and ^1H–^{13}C CPMAS NMR spectra were obtained on a 400 MHz spectrometer (Avance III, Bruker) equipped with a 4 mm MAS probe. ^1H spectra were obtained by single-pulse and Hahn-echo sequences, by spinning the sample at 4 kHz, with a 90° pulse of 4.5 μs, and a delay time of 4 s. ^1H–^{13}C CPMAS spectra were obtained by spinning the sample at 4 kHz, with a delay time of 4 s, and a contact time of 2 ms. The spectra were analyzed with the Topspin package (Bruker).

The nature of SiO_2 gel, poly(ε-caprolactone) (PCL) and SiO_2/PCL hybrid materials was established by X-ray diffraction (XRD) analysis using a Philips diffractometer. Powder samples were scanned from $2\Theta=5°$ to 60° using Cu$K\alpha$ radiation.

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