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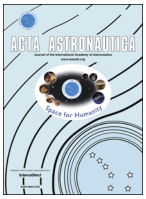

Sol–gel hybrid materials for aerospace applications: Chemical characterization and comparative investigation of the magnetic properties

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ABSTRACT

In the material science field, weightless conditions can be successfully used to understand the relationship between manufacturing process, structure and properties of the obtained materials. Aerogels with controlled microstructure could be obtained by sol–gel methods in microgravity environment, simulated using magnetic levitation if they are diamagnetic. In the present work, a sol–gel route was used to synthesize class I, organic–inorganic nanocomposite materials. Two different formulations were prepared: the former consisted in a SiO_2 matrix in which different percentages of polyethylene glycol (PEG) were incorporated, the latter was a ZrO_2 matrix entrapping different amounts of poly (ε-caprolactone) (PCL). Fourier Transform Infrared Spectroscopy (FT-IR) detected that the organic and the inorganic components in both the formulation interact by means of hydrogen bonds. X-ray diffraction (XRD) analysis highlighted the amorphous nature of the synthesized materials and Scanning Electron Microscope (SEM) showed that they have homogeneous morphology and are nanocomposites.

Superconducting Quantum Interference Device (SQUID) magnetometry confirmed the expected diamagnetic character of those hybrid systems. The obtained results were compared to those achieved in previous studies regarding the influence of the polymer amount on the magnetic properties of SiO_2/PCL and ZiO_2/PEG hybrids, in order to understand how the diamagnetic susceptibility is influenced by variation of both the inorganic matrix and organic component.

1. Introduction

There is a growing interest towards magnetic gravity compensation in science and technology [1]. Studies in many areas (materials science, fluid physics and combustion, biology and biotechnology) showed that gravity-free environments may be used to improve many industrial processes [2]. In the material science field, in particular, low gravity conditions are required to identify and understand the cause–effect relationship between processing, structure and properties of materials. The investigations include studies of directional solidification, semiconductor and zeolite crystal growth, diffusion in liquid metals, container-less processing of corrosive materials, formation of metal foams, special alloys, composites, special glasses, ceramics and polymers [3,4].

A synthesis method affected by the gravity force is the sol–gel technique, a method to make ceramic and glassy materials at a relatively low temperature [5]. The increasing attention to this method was due to its versatility which

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derives from the various special shapes obtained directly from the gel state (e.g. monoliths [6–9], film [10–15], fibers [16–18], and monosized powders), the composition and microstructural control and low processing temperatures which allow to entrap thermolabile molecules (polymers [19–21], drugs [22–26], biomolecules [27], etc.) in the inorganic glassy matrix to modify its properties [5,28].

During a sol–gel synthesis, the transition from a colloidal solution (the 'sol') into a solid 'gel' phase occurs through hydrolysis and polycondensation reactions of one (or more) metal alkoxide precursor(s). By drying the obtained wet gel, it is possible to prepare xerogels (by exposure to low temperatures) or aerogels (by solvent extraction under supercritical conditions) [5].

The last ones are microstructured, open-pore materials with many properties, such as lightness, high thermal resistance, very low refractive index and sound velocity, and high surface area. For this reason they are used in a wide range of applications, including thermal and acoustical insulation, kinetic energy absorption, electronics, optics, chemistry, biomedicine and aerospace industry [29]. Zirconia aerogel prepared via a sol–gel route was successfully proposed to prepare thermal barrier coatings (TBCs) on superalloys in aircraft engines [30,31]. Silica aerogel, because of its optical transparency in the visible spectrum, high surface area, low thermal conductivity, bulk density, refractive index, dielectric constant and sound velocity, was proposed as hypervelocity particle capture medium, thermal insulator and cryogenic fluid containment [29].

The low processing temperature combined with the high sol homogeneity, due to mixing on the molecular scale, makes the sol–gel method an ideal technology to manufacture organic–inorganic hybrid materials by entrapping various organic polymers in a glassy matrix. Those materials are biphasic systems in which the organic and inorganic components are connected on a nanometric scale. The leading idea in their development is to take advantage of the best properties of each component which forms the hybrid, trying to decrease or eliminate its drawbacks, thus achieving a synergic effect which results in the generation of a new material with new properties.

Organic–inorganic hybrid coatings, prepared by mixing zirconium tetrapropoxide and methacrilic acid to a siloxane sol, were proposed for corrosion protection of AA7075-TS aluminum alloy under aircraft conditions [32].

Studies curried out using Ground-based facilities for simulation of microgravity [33–39] proved that the final microstructure of the gels obtained via the sol–gel route is affected by gravity. In particular, a low gravity induces branched siloxane groups formation, instead of the usual silanol ones. Therefore, microgravity environment allows to obtain rigid gels with a larger pore size, surface area and pore volume than the ones obtained in normal gravity and could be suitable to control final gel microstructure [33]. To simulate long-lasting weightlessness conditions, which are necessary to allow the transition from sol to gel, magnetic levitation technique can be used [40–44]. However, only samples diamagnetic can levitate [40–45], since they receive an upward repulsive force when are appropriately placed at an off-center position of a magnetic vertical field which can be strong enough to exceed the force due to the gravity. The analysis of the magnetic properties of sol–gel materials, thus, deserves investigations. In previous works [46,47], the Authors synthesized organic–inorganic hybrid materials consisting of a SiO_2 or ZrO_2 matrix in which poly (ε-caprolactone) (PCL) and polyethylene glycol (PEG) were added respectively; the materials emerged as diamagnetic with a diamagnetic susceptibility independent of temperature and which increases with the polymer amount.

The present work describes the preparation, by means of a sol–gel method, and the chemical–physical characterization of two new formulations of organic–inorganic hybrid materials: The former consists of silica (SiO_2) as inorganic phase and PEG 400 as organic component, and the latter consists of zirconia (ZrO_2) and PCL. Their physicochemical properties were compared with the published SiO_2/PCL and ZrO_2/PEG hybrids ones in order to study the influence of both phases (organic and inorganic) in the hybrids properties. To allow a homogenous comparison between the hybrid systems, the oxide/polymer ratios used in the previous works have been kept constant in the samples synthesis.

In the hybrids preparation diamagnetic substances were used and the polymers were incorporated in different percentages (0, 6, 12, 24, 50 wt%), as a particular attention has been devoted to investigate the magnetic properties of the obtained materials as a function of the polymer amount by means of SQUID magnetometry to verify and quantify their diamagnetic character.

2. Experimental study

2.1. Sol–gel synthesis

Both the formulations of organic–inorganic hybrid materials were synthesized by means of a sol–gel process. To prepare the SiO_2-based formulation, pure tetraethyl orthosilicate (SigmaAldrich) was used as precursor material and added to a mixture of ethanol, water and nitric acid ($\geq$65.0%, SigmaAldrich) with molar ratio $TEOS:HNO_3:EtOH:H_2O=1:0.6:6:2$. The nitric acid was used to catalyze the hydrolytic activity of the precursor. Successively, polyethylene glycol (PEG 400, SigmaAldrich), previously dissolved in ethanol, was added to the solution under vigorous stirring to obtain a uniform and homogeneous sol. Five hybrid systems were obtained by entrapping different PEG percentages (0, 6, 12, 24, 50 wt%) in the silica matrix (see Table 1).

The ZrO_2-based hybrids, containing PCL 0, 6, 12, 24, and 50 wt% (see Table 1), were synthesized using a Zirconium(IV) propoxide solution ($Zr(OC_3H_7)_4$ 70 wt% in *n*-propanol, SigmaAldrich) as precursor of the inorganic matrix and poly(ε-caprolactone) (PCL Mw=65000, SigmaAldrich) dissolved in chloroform as organic component. Zirconium(IV) propoxide was added to a solution of water, acetylacetone and ethanol, with molar ratio $Zr(OC_3H_7)_4:H_2O:AcAc=1:1:0.3$. Acetylacetone (AcAc) was used in the process as chelating agent to control and decrease the hydrolytic activity of zirconium alkoxide [48,49].