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Preparation of silica-poly(2-hydroxyethyl methacrylate) hybrids modified with 3-methacryloxypropyltrimethoxysilane

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Abstract

In this work we successfully prepared sol–gel derived organic–inorganic hybrids by the incorporation of poly(2-hydroxyethyl methacrylate) and 3-methacryloxypropyltrimethoxysilane into a silica matrix. The obtained samples were examined by Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG), differential scanning calorimetry (DSC), Nitrogen adsorption tests, and Vickers microhardness measurements. The incorporation of PHEMA and P(HEMA-co-MPS) into silica gave rise to samples with smaller specific surface areas and pore volumes when compared to pure silica. It was observed that materials prepared with polymer additions above 40 wt% were virtually non-porous. These findings may be related to the blockage of silica pores by polymer chains in the hybrid materials. It seems that the initial addition of either PHEMA or P(HEMA-co-MPS) to silica caused a partial filling of its pore structure, leading to an increase of its microhardness. On the other hand, when these polymers are incorporated at concentrations above 20 wt% it may occur a partial rupture of the silica framework, which decreases the microhardness of the processed materials. In addition, the increase of the polymer loading led to large polymer domains in the prepared samples. However, this behavior was less pronounced for hybrids modified with MPS.

Keywords: A. Sol–gel processes; B. Composites; C. Hardness; D. SiO_2

1. Introduction

Organic–inorganic hybrid materials have received great attention over the past years due to their outstanding properties, which arise from the synergy between their organic and inorganic components [1,2]. The possibility of incorporating the chemical functionality of an organic component into a thermally and mechanically reliable inorganic framework is of interest in many fields [3]. The sol–gel process stands out among the synthesis techniques generally used in the preparation of these materials. This chemical route enables to obtain hybrid materials with tailored properties, including composition, surface chemistry, and pore structure [4]. Another convenient feature of this technology is related to the fact that sol–gel samples can be obtained as bulks, thin films or powders [5].

Silica-based organic–inorganic hybrids have been widely used in a range of applications, including catalysis [6–8], membranes [9–11], water treatment [12–14], and sensing [15–17]. A variety of polymers have been used for obtaining these materials, i.e. polyetherimide [18], polyurea [19], polymethylsiloxane [20], poly(tetramethylene oxide) [21], and poly(2-hydroxyethyl methacrylate) (PHEMA) [22]. PHEMA is an attractive choice because it exhibits a significant solubility in water-alcohol mixtures commonly used in the sol–gel process. In addition, PHEMA shows a significant biocompatibility

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[23–25]. Although several works deal with the use of PHEMA for preparing silica-based hybrids, they rarely compare the properties of materials obtained with and without the addition of bonding agents. It is well established that the use of bonding agents may inhibit the macrophase separation in hybrid materials [26,27].

In this work we prepared sol–gel derived silica-PHEMA hybrids. 3-methacryloxypropyltrimethoxysilane (MPS) was eventually used as bonding agent, which gave rise to silica-P(HEMA-co-MPS) hybrids. The obtained samples were examined by Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG), differential scanning calorimetry (DSC), Nitrogen adsorption tests, and Vickers microhardness measurements. On the basis of the findings obtained in this study, we discuss the effect of PHEMA and P(HEMA-co-MPS) on the properties of the prepared organic–inorganic hybrids.

2. Experimental

2.1. Synthesis

PHEMA was obtained as follows. First, 2-hydroxyethyl methacrylate (HEMA – Polysciences – 99% – $M_W = 200{,}000$) was dissolved at room temperature and under N_2 flow in a mixture of ethanol (EtOH – Merck – 99.8%) and 2,2′-azobis (isobutyronitrile) (AIBN – Polysciences – 98%). The concentration of HEMA in the as-prepared solution was adjusted to 20 wt%, whereas the AIBN loading was kept at 0.5 wt% of the HEMA amount. Subsequently, this solution was heated at 70 °C for 6 h. The obtained PHEMA solution was then allowed to cool down to room temperature. Silica-PHEMA hybrids were prepared by adding tetramethyl orthosilicate (TMOS – Aldrich – 98%), deionized water, and EtOH to the as-prepared PHEMA solution. The TMOS: PHEMA molar ratio ranged from 50 to 1, which gave rise to samples with PHEMA loadings from 5 to 93 wt%. The TMOS: water mass ratio was kept at 2, which corresponds to a TMOS: water molar ratio of about 0.24. After gelation the obtained solutions were aged in air at room temperature for 4 days, and at 50 and 65 °C for additional 30 and 20 h, respectively. Next, they were dried in air at 80 °C for 30 h.

PHEMA was also copolymerized with MPS (Polysciences – 99% – $M_W = 248$) and the obtained copolymer was denoted as P(HEMA-co-MPS). This copolymer was obtained by a procedure slightly different from that used for preparing PHEMA. Briefly, HEMA and MPS were dissolved at room temperature and under N_2 flow in a solution of EtOH, AIBN, and TMOS. The MPS loading was kept at 20 wt% of the PHEMA concentration. When this methodology is compared to that used for preparing PHEMA, about 50 vol% of EtOH was replaced by TMOS. This strategy was used in order to inhibit the premature hydrolysis of MPS when in contact with EtOH. Next, the as-prepared solution was heated at 70 °C for 6 h and then allowed to cool down to room temperature. Silica-P(HEMA-co-MPS) hybrids were prepared by adding TMOS and H_2O to the as-obtained P(HEMA-co-MPS) solution. EtOH was subsequently added in amounts sufficient to promote the dissolution of the reactants. The processed samples were then aged and dried using procedure similar to that used for the silica-PHEMA hybrids. Fig. 1 depicts the methodology used for the preparation of hybrid materials in this work. SiO_2-PHEMA and SiO_2-P(HEMA-co-MPS) hybrids were denoted as SP and SPM, respectively.

A fraction of the obtained samples was subsequently heat treated at 450 °C for 1 h for further examination. This step was performed using a Lindberg Blue furnace at a heating rate of 10 °C min^{-1}. The heat treated silica, SiO_2-PHEMA, and SiO_2-P(HEMA-co-MPS) samples were denoted as HT-silica, HT-SP, and HT-SPM, respectively.

2.2. Characterization

FTIR (Fourier transform infrared spectroscopy) was performed using a PERKIN-ELMER Spectrum 1000 spectrometer. The spectra were taken from 4000 to 500 cm^{-1}, with a resolution of 4 cm^{-1} and 64 scans. Pure silica and organic–inorganic hybrid samples were examined with a diffuse reflectance attachment available in the spectrometer. PHEMA and P(HEMA-co-MPS) were tested with an attenuated total reflectance (ATR) accessory and using a zinc selenide (ZnSe) crystal as reflection element. TG (thermogravimetry) and DSC (differential scanning calorimetry) were conducted using SHIMADZU TG-50 and DSC-50 apparatus, respectively. These tests were carried out under N_2 flow (20 ml min^{-1}) at a heating rate of 10 °C min^{-1}. The glass transition temperature of the prepared samples was evaluated by DSC. N_2 sorption tests were performed in a QUANTACHROME Autosorb apparatus. Samples used in these tests were previously degassed at 110 °C for at least 12 h under vacuum. Specific surface areas and pore size distributions were assessed by the BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) methods, respectively. The mean pore size (S) of the prepared samples was evaluated by assuming a cylindrical pore geometry and taking into account Eq. (1) [28]:

$$S = \frac{2\mathrm{PV}}{\mathrm{SA}} \qquad (1)$$

where PV and SA represent the specific pore volume and surface area, respectively. Vickers microhardness tests were conducted with a FUTURE-TECH FM-1 apparatus using disk-shaped samples with 1.2 cm in diameter and 2.5 cm thick.

3. Results and discussion

Fig. 2 shows the FTIR spectra of PHEMA, P(HEMA-co-MPS), and hybrid materials prepared in this work. The spectrum of a pure silica sample is also exhibited for comparison purposes. The bands at 820 and 2840 cm^{-1} clearly observed in the spectrum of P(HEMA-co-MPS) are ascribed to Si–C and C–H bonds, respectively [28,29]. The feature at 1070 cm^{-1} has been related to the Si-O-C bending mode [30]. The bands at 1450 and 2945 cm^{-1} are associated with CH_2 groups, whereas the