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Hybrid composites from poly[(4-vinylbenzyl)trimethylammonium chloride]–metal oxide using simultaneous radical polymerization/sol–gel synthesis

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ABSTRACT

This communication reports the preparation and characterization of poly(4-vinylbenzyl)trimethylammonium chloride (PClVBTA)–3-(trimethoxysilyl)propylmethacrylate (TMPM)–M_xO_y (M: Al, Ti or Zr) composites using a radical polymerization/sol–gel synthesis route. The results indicate that all of the materials form interpenetrating networks (IPNs) and that TMPM forms a bridge between the organic and inorganic networks. The polymer phase yield, with respect to the oxide, occurred in the following order: $Al_2O_3 > TiO_2 > ZrO_2$. The physico-chemical properties of the materials were dependent on the nature of the metal oxide that was incorporated in the network. All materials exhibited good thermal stability and morphologies that were typical for non-porous materials.

1. Introduction

Polymer composite systems have recently received extensive attention due to their high potential for various applications. Filler surface properties and polymer–filler interactions have dominant influences on the viscoelastic and mechanical properties of these systems [1,2]. Organic–inorganic hybrid materials have been regarded as a new class of multifaceted materials. Despite many advantages it is difficult to obtain well-dispersed organic–inorganic hybrid materials due to their strong aggregation tendencies with inorganic phases, which may depress the physico-chemical properties of composites [3–5]. The sol–gel synthesis is mainly based on inorganic polymerization reactions and is a chemical synthesis method that was initially used for the preparation of inorganic materials, such as glasses and ceramics [4–6]. For our purposes, the use of simultaneous synthesis methods provides a unique opportunity to obtain pure and well-controlled organic/inorganic hybrid materials by incorporating low molecular weight and oligomeric/polymeric organic molecules into appropriate inorganic moieties at temperatures that the organics can survive (350–370 K) [7–9]. In addition, hybrid networks can be formed by interpenetrating networks and the simultaneous formation of inorganic and organic phases. By using combined routes to promote the formation of polymeric networks (with a radical initiator) and the inorganic oxide matrix (hydrolysis/condensation of the inorganic precursor), we can prepare simultaneous interpenetrating networks (SIPNs) [4,5].

The aim of this study was to investigate the fundamental properties of simultaneous interpenetrating networks (SIPNs) using polyelectrolytes as polymer phase. In the last decade, polymeric quaternary ammonium compounds have been studied because they represent a class of polyelectrolytes that derive unique properties from the density and distribution of positive charges along their macromolecular backbone [10–12].

The novelty of this research is the use of a cationic polymer, poly[(4-vinylbenzyl)trimethylammoniumchloride] (P[ClVBTA]), and different metal oxides in the presence of a coupling agent (CA) [13–15]. In our case, 3-(trimethoxysilyl)propylmethacrylate (TMPM) was used to improve the solubility by chemical bonds that were formed between the metal oxide phases and alkoxysilane groups. The polymer phase of P[ClVBTA] acted as a functional cationic polymer, and the metal oxides that were used to study the influence of the inorganic phases on the thermal and porous properties of this hybrid material included Al_2O_3, TiO_2 and ZrO_2.

2. Experimental section

Composite materials synthesis: All air-sensitive reactions were performed in a polymerization flask using an inert N_2 atmosphere. An appropriate amount of inorganic precursor (aluminum

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trisec-butoxide, 97%; tetraisopropyl ortho titanate, 98%; or zirconium (IV) butoxide, 80 wt% solution in 1-butanol) (0.03 mol) was dissolved in 2-butanol. The mixture was heated at 353 K before adding acetylacetonate (acac) and TMPM at molar ratio of inorganic precursor:acac:TMPM = 1:1.33:1. The monomer, 4-(vinylbenzyl)trimethyl ammonium chloride (ClVBTA; 1.27 g, 0.02 mol), and potassium persulfate ($K_2S_2O_8$; 0.48 g, 0.002 mol) were added to the reaction mixture while continuously stirring at molar ratio of inorganic precursor:ClVBTA:$K_2S_2O_8$ = 1.5:1:0.1. Once all of the reagents were dissolved, the solutions were polymerized at 358 K. After 1 h, the solution was cooled at room temperature and deionized water was added as a hydrolyzing agent. Subsequently, the mixture was stirred mechanically up to formation of uniform gel. The hybrid gel remained at room temperature for 8 h. Then, each material was dried at 353 K in a vacuum oven. The resulting composites were washed in water, stirred for 12 h, and then filtered and dried at 373 K. A random copolymer blank P(TMPM-*co*-ClVBTA) was synthesized at the same conditions and molar ratio as prepared for the composites, but in the absence of inorganic precursor for comparing thermal properties.

Characterization: The morphological and structural characteristics of the composites were determined with XRD (RigakuD/max-2500 diffractometer with Cu Kα radiation at 40 kV and 100 mA), FT-IR spectroscopy (Nicolet 400D in a KBr matrix and between 4000 and 400 cm^{-1}), SEM (JEOL JSM-6380 LV) and thermal analysis TGA (Netzsch STA 409 PC/PG [STA] at temperatures of 300–873 K and a heating rate of 10 K/min in a N_2 atmosphere). Solid-state ^{29}Si cross-polarization (CP) MAS NMR spectra were recorded at 100.6 and 79.49 MHz, with a Bruker AV 400 WB spectrometer. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. N_2-BET surface areas and pore volumes were determined using a Micromeritics ASAP 2010 apparatus at 77 K.

3. Results and discussion

All of the synthesized P[ClVBTA]/TMPM/M_xO_y composites were solids and had similar physical aspects. The metal oxides gave different properties to the hybrids, which were related to the interactions between the inorganic material surface and the polymer chains. The hybrids were synthesized in the presence of the TMPM reagent to improve the solubility of the phases. The washing procedure was conducted to remove the unreacted monomer and material impurities. The observed loss of mass was attributed to polymer chains of low molecular weight that were slightly bound with the hybrid matrix. After washing, the hybrid composite yields were as follows: ZrO_2 (87.4%) > TiO_2 (84.2) > Al_2O_3 (74.8%). These results can be explained by considering that solid oxides are generally electrically charged in aqueous suspensions and have a pH dependent surface charge, which is called the isoelectric point (IEP) or point of zero charge (ZPC) [16]. For the hybrids in this study, the IEPs were 8.0, 6.7, and 6.2 for Al_2O_3, ZrO_2, and TiO_2, respectively. Consequently, during the washing process (at pH 7.0), the TiO_2 and ZrO_2 phases have a negative surface charge and theAl_2O_3 phase has a positive charge. This phenomenon promotes the coulombic interactions between the polycations and the oxide surfaces. Although the composites lost mass during the washing procedure the yields remained > 70%, which suggested that the polymeric material and inorganic phases of TMPM were mediated by covalent bonding.

Nitrogen isotherms showed that specific surface area determined by BET method was around 10 $m^2 g^{-1}$ for all the hybrids, while the pore volumes were 1.8, 0.74, and 0.15 for Al_2O_3, TiO_2, and ZrO_2 based hybrid, respectively. These results indicate that hybrids can be considered as non-porous materials.

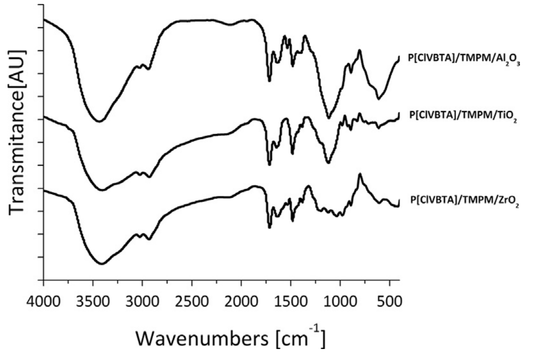

Fig. 1. Fourier transformation infrared (FT-IR) spectra of P[ClVBTA]/TMPM/M_xO_y composites materials.

Infrared spectroscopy: Fig. 1 contains the FT-IR spectra of the P[ClVBTA]/TMPM/M_xO_y hybrid materials. The spectra that show bands at 3436 cm^{-1}were attributed to OH bond vibrations in the inorganic phase. In addition, it was possible to observe vibrations associated with the polymeric phase. For example, bands between 3200 and 2870 cm^{-1} corresponded to CH_2 from the backbone, bands at 1641 and 1482 cm^{-1} corresponded with flexion of the C–C bonds in the aromatic rings and the band at 1483 cm^{-1} was attributed to the quaternary ammonium groups. The band at 1720 $cm^{-1}$was characteristic of the C–O ester band in TMPM. Other bands attributed to CA included the M–O–Si–C band at 1100–1000 cm^{-1}. Regarding P[ClVBTA]/TMPM/Al_2O_3, the expected alumino-silicate bands were observed at 1113 cm^{-1} (C–Si–O, st). The hybrid P[ClVBTA]/TMPM/TiO_2 has two bands in this zone. The band at 1115 cm^{-1} corresponds to the TMPM linkage on the TiO_2 surface and the band at 981 cm^{-1}corresponds to the Si vibrations. In this case CA can form different linkages, as reported by El-Nahal et al. [17]. The bands between 1130 and 980 cm^{-1}were attributed to vibrations from the unreactive silicon alkoxides (Si–OCH_3) or silicon hydroxyls (Si–OH). For the hybrid P[ClVBTA]/TMPMP/ZrO_2, many bands are observed in the Si bond region. Despite the similar reactivities of ZrO_2 and Al_2O_3 [4], the spectrum does not show an intense absorption band at 1100 cm^{-1}like the other hybrids. Instead, ZrO_2 and Al_2O_3 show many weak intensity bands between 1190 and 900 cm^{-1}. This result can be explained by the acid–base nature of ZrO_2 [18]. The Zr atom can be mono- or multi-coordinated by unreactive free hydroxyls or the TMPM methoxy groups.

^{29}Si (CP) MAS NMR: Fig. 2 shows the ^{29}Si CP MAS NMR results from the P[ClVBTA]/TMPM/M_xO_y materials. In all the hybrids, residual non-converted TMPM was not detected because no peak was observed between 0 and −50 ppm (TMPM should have a signal at −43.1 ppm) [19]. For the P[ClVBTA]/TMPM/Al_2O_3 hybrid, three types of anchoring were expected in the inorganic matrix [19,20]. However only two types were detected at −56.8 and −67.8 ppm, which corresponded to T^2 and T^3 anchorages, respectively. The signal at −100.7 (Q^3) is generally assigned to free silanol from TMPM. Regarding P[ClVBTA]/TMPM/TiO_2 the same group signals were observed, but with a different intensity between the T and Q signals. The anchorage was detected at −58.0 and −64.5 ppm, which corresponded to the T^2 and T^3. In addition, the two Q^3 signals that were attributed to free silanols occurred at −101.5 and −108.3 ppm in different chemical environments. TiO_2 is an amphoteric metal oxide with acid–base pairs of Ti^{4+} (Lewis acid) and O^{2-} (Lewis base) ions on its surface [21]. These acid–base pairs can interact with the remaining free silanol groups and cause the signals to exhibit a chemical shift. This interaction is very strong. Consequently, we assumed that the signal at −108.3 ppm corresponded to the free silanol group and the signal at −101.5 ppm corresponded to the strong interaction with the inorganic phase. Similarly, P

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