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Organically modified silica (ORMOSIL) bearing imidazolium – Based ionic liquid prepared by hydrolysis/co-condensation of silane precursors: Synthesis, characterization and use in epoxy networks

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ABSTRACT

Organically modified silica (ORMOSIL) bearing N-methyl imidazolium ionic liquid covalently attached to the silica particle was prepared by one pot sol-gel route through the hydrolysis/co-condensation of 1-(3-trimethoxysilylpropyl)-3-methyl imidazolium chloride (IL-TMOS) with tetraethoxy-silane (TEOS), catalyzed by ammonium hydroxide. The presence of IL-TMOS precursor favors the gel formation with a very short time (around 5 min for IL-TMOS/TEOS molar ratio of 0.05). The gelation time, surface area and morphology were significantly affected by the amount of IL-TMOS during the sol-gel synthesis. Higher amount of the silylated ionic liquid precursor resulted in silica structure with decreased average surface area and pore volume probably because of the co-condensation interparticles. The ionogel-based ORMOSIL (IL-ORMOSIL) was compounded with epoxy prepolymer, whose dispersion was influenced by the amount of the ionic liquid tethered on the silica nanoparticles as observed by rheological properties of the uncured dispersions and by transmission electron microscopy of the cured epoxy networks. The addition of the IL-ORMOSIL resulted in a decrease in glass transition temperature without affecting the storage modulus, as indicated by dynamic-mechanical measurements.

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1. Introduction

Ionic liquids (IL), classified as a subclass of molten salts, are salts with melting point below 100 °C, constituted by a bulky organic cation and a weakly coordinated organic or inorganic anion [1]. Because of their unique properties, such as excellent thermal stability, low volatility, low flammability and good ionic conductivity, they have appeared as versatile materials for a range of interesting applications, which include solvent for green chemical reactions [2] and polymerizations [3], plasticizers [4], solid polymer electrolytes [5], curing agent for epoxy resin [6–11], tailoring lubricants [12], catalysis [13], etc. In the field of inorganic synthesis, ILs have been also extensively used on the development of different inorganic particles [13,14]. In this

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context, silica has been prepared by the sol gel process using silicon alkoxide in the presence of different ILs, giving rise to porous silica materials with controlled morphology [13,15–18] and ionogel-type silica where the IL is confined within the silica particles [14,19–23]. Such materials have been found potential applications as supported catalysts [21], electrorheological fluids [24,25], etc. These ionogel-type silica particles have been also employed as reinforcing additive for epoxy – based nanocomposites. For example, imidazolium-based ILs were employed to prepare silica-epoxy nanocomposites by performing the hydrolysis – condensation of tetraethoxy silane (TEOS) [26] or the mixture between TEOS and 3-glycidoxypropyl-trimethoxy silane (GTMS) [27] in the presence of ILs, within the epoxy matrix, through an in situ sol-gel route. Also ethyl-methyl imidazolium dicyandiamide IL was used to improve the dispersion of silica nanoparticle in the epoxy resin and also as curing agent [11]. The ionogel-type silica employed in these nanocomposites has been prepared by trapping the IL in the silica scaffold whose interactions are physical in nature. An interesting approach for improving the interaction between epoxy matrix and silica particles was reported by Donato et al. [28]. They have used carboxylic-functionalized task-imidazolium ILs which induces the in situ covalent bonding with the epoxy matrix. By using solvent-free nonaqueous sol-gel process, the authors observed better silica dispersion in the presence of functionalized IL.

Recently, a new class of hybrid silica-based ionogels has been developed where IL is immobilized within silica network through covalent link [29]. This procedure involves the preparation of IL bearing silane group (silylated IL) followed by the coupling reaction on the surface of pre-formed silica nanoparticle. These kind of ionic liquid- based organically modified silica (IL-ORMOSIL) have been employed as sorbents for the solid-phase extraction [30], as electrochemical sensors [31], as catalyst [32–34], and as carrier for papain immobilization [35].

Another procedure to introduce covalently linked surface functionality on the silica particle is by one-pot route involving the co-condensation of tetraalkoxy-silane and a functionalized trialkoxy-silane [36]. This route was used to prepare hybrid ionogel containing bis-silylated imidazolium compound [37,38].

Thus, the present paper describes the one pot sol-gel synthesis of organic modified silica bearing covalent bonded imidazolium-based ionic liquid (IL-Ormosil) with tuned morphology by performing the hydrolysis /co-condensation of the TEOS and mono-silylated ionic liquid in different proportions, using basic catalyst. Both precursors were simultaneously added to the mixture containing methanol, de-ionized water and ammonium hydroxide. The effect of the amount of the silylated ionic liquid precursor on the sol-gel characteristics, as gel time and specific surface area of the corresponding IL-ORMOSIL particles, was addressed. The IL-ORMOSIL was also dispersed in epoxy matrix to prepare epoxy- diamine nanocomposites. In this case, the IL should act as a filler – matrix coupling agent characterized by a covalent bonding at the silica surface and physical interaction with the epoxy matrix. Thus, the influence of such IL-ORMOSIL on the main features of epoxy networks was also considered for the first time.

2. Experimental

2.1. Materials

1-Methylimidazole, 3-chloropropyl-trimethoxysilane and tetraethoxysilane (TEOS) were purchased from Sigma-Aldrich, and used without further purification. Methyl alcohol (CH₃OH) and ammonium hydroxide (NH₄OH) (analytical grade) were purchased from Merck and used as received. Diglycidyl ether of bisphenol A (DGEBA) – based epoxy prepolymer (EPON 828) was purchased by Shell Chemicals do Brasil. Poly (propylene glycol) bis (2-aminopropyl ether) (Jeffamine D230) used as hardener was supplied by Hunstman. Both epoxy resin (ER) and the hardener were previously dried under vacuum at 70 °C during 4 h.

2.2. Synthesis of 1-(3-trimethoxysilylpropyl)-3-methyl-imidazolium chloride IL (IL-TMOS)

The synthesis of the silylated imidazolium-based ionic liquid (IL-TMOS) was performed according to the literature [39]. In a typical procedure, 3.0 g of 1-methylimidazole and 7.26 g of 3-chloropropyl-trimethoxysilane were mixed and heated at 95 °C during 24 h under N₂ atmosphere with stirring. After heating, a light yellow viscous oil was obtained and used immediately in the next step. The spectral data were in accordance with the literature data [39–41]: ¹H NMR (CDCl₃, 300 MHz, room temperature, δ ppm) δ = 0.71 (t, J = 7.7 Hz, 2H, H4 – [Si–CH₂]), 1.98–2.14 (m, 2H, H5 – [CH₂CH₂CH₂]), 3.34 (s, 9H, H1,H2,H3 – [3(O–CH₃)]), 3.97 (s, 3H, H10 – [N–CH₃]), 4.29–4.40 (t, J = 7.6 Hz, 2H, H6 – [N–CH₂]), 6.94–7.04 (m,1H), 7.60 (s,1H, H7 – [N–CH–CH]), 7.74 (s,1H, H8 – [N–CH–CH]), 10.5 (s,1H, H9 – [N–CH–N]); ¹³C NMR (CDCl₃, 75 MHz, room temperature, δ ppm) δ = 9.91–10.61 (C4 – [Si-CH₂]), 25.39 (C5 – [CH₂CH₂CH₂]), 36.69 (C10 – [N–CH₃]), 52.85 (C1,C2,C3 – [N–CH₂CH₂CH₂CH₃]), 76.13 (C6 – [N–CH]), 123.74–124.95 (C8, C7 – [N–CH]), 137.30–138.02 (C9 – [N–C–N]).

2.3. Preparation of silica and IL-modified silica (IL-ORMOSIL) by sol-gel method

The preparations of the silica and the IL- ORMOSIL were performed by Stöbe method using the sol-gel method [42]. For the silica preparation, TEOS was slowly added to a stirred mixture containing methanol, de-ionized water and ammonium hydroxide and the medium was kept under stirring at room temperature for 4 h. It was employed a H₂O/TEOS/CH₃OH/NH₄-OH molar ratio corresponding to 4/1/12/1.2 followed by magnetic stirring for 4 h. After that, the obtained suspension of silica

particles was centrifuged, washed with water and methanol and dried at 60 °C for 12 h and then, 120 °C for 4 h. After drying, the product was macerated in a mortar, passed on 150 mesh sieve and stored for later use in the dispersions of epoxy resin.

Similar procedure was used to prepare the ionogel-based ORMOSILs (IL-ORMOSIL), by using different amounts of the IL-TMOS. However, the presence of the IL resulted in the formation of a gel in short time and the stirring could not be continued. After gelation, the particles were directly dried at 60 °C for 12 h and then, 120 °C for 4 h.

2.4. Preparation of epoxy-based composites

Different amounts of silica (Si) or the ionogel-based ORMOSIL (IL-ORMOSIL) were dispersed into the epoxy prepolymer (ER) at 110 °C, using an Ultra Turrax high shear homogenizer for 10 min at 17,500 rpm, followed by an ultrasonication for 20 min and 45 W. After obtaining a homogeneous dispersion, the mixture was degassed under vacuum for 30 min and a stoichiometric amount of Jeffamine® D230 as the curing agent was added. The mixture was casted into silicone molds and cured at room temperature for 24 h and post cured at 125 °C for 3 h.

2.5. Characterizations

Thermogravimetric analysis (TGA) were performed on a Q50 thermobalance from TA Instruments Inc. The samples with average mass of 8–12 mg were heated from 30 to 800 °C, at a heating rate of 20 °C/min, under nitrogen flow.

Fourier transform infrared spectra (FTIR) were recorded from KBr pressed discs in a Nicolet Thermo Scientific, model iS-50 spectrometer in the range of 4000–400 cm^{-1} with 32 scans and resolution of 4 cm^{-1} . The samples and KBr were ground together in an agate mortar until the sample is well blended.

The morphology of the silica and ORMOSIL particles were evaluated by Field Emission Scanning Electron Microscopy (FEG-SEM) using a Quanta FEG 450 equipment operating at 10 kV. A powder of each sample was placed on a sample holder, covered with a carbon to obtain the images using a secondary electron detector.

BET surface area, average pore volume, and average pore diameter of the silica and ORMOSIL were measured by physisorption of N_2 at 78 K over a Micromeritics ASAP 2010. Before measurement, the samples were degassed at 80 °C for 10 h to remove the moisture and adsorbed gases. The isotherms were elaborated according to the BET (Brunauer, Emmett and Teller) method for surface area calculation, and pore size distribution curves derived from the desorption branches for the porous silica gel materials with BJH (Barrett–Joyner–Halenda) methods.

^{29}Si Cross polarization/Magic Angle Spinning (CP/MAS) solid state nuclear magnetic resonance spectra (^{29}Si CP/MAS NMR) of the silica and the ionogel-based ORMOSIL were recorded on an Agilent Model 500/54 DD2 (7.5 T) spectrometer, using a pulse interval of 60 s, 512 scans, relaxation time of 5 s, cross-polarization period of 16 ms and repetition delay of 5 s.

Dynamic light scattering (DLS) measurements were performed on a Zetasizer NanoZs from Malvern Instruments. Diluted dispersions of the samples (silica and ORMOSIL) were prepared in acetone at concentrations of 0.025% (w/v), with the aid of a tip sonicator, operating at 45 W for 5 min.

Transmission electron microscopy (TEM) of the epoxy composites was carried out on a Tecnai Spirit from FEI Company, operating at 120 kV. The samples were ultramicrotomed in a RMC ultramicrotome, in order to obtain 70–80 nm ultrathin sections.

Dynamic mechanical analysis (DMA) was performed on a DMA Q800, from TA Instruments Inc, from 25 °C to 160 °C, at a heating rate 3 °C/min and frequency of 1 Hz, using single cantilever clamp.

Differential scanning calorimetry was carried out on a DSC 204 F1 Phoenix DSC from Netzsch, operating in dynamic mode at 10 °C/min, from 25 to 200 °C under nitrogen atmosphere (50 mL/min).

The rheology of the dispersions was carried out on an Anton Paar rheometer – model Physica MCR-302, equipped with parallel plate geometry (25 mm) with a distance of 0.5 mm between the plates. The measurements were performed in an oscillatory mode at a frequency range from 1 to 100 Hz and amplitude of 1%.

3. Results and discussion

3.1. Synthesis and characterization of the ionic liquid-based ORMOSIL (IL-ORMOSIL)

The scheme for the preparation of ORMOSIL bearing ionic liquid covalently linked to the silica particles is illustrated in Fig. 1. The reaction was performed by hydrolysis/co-condensation of the silylated IL (IL-TMOS) and TEOS as the sol-gel precursors. The main characteristics of the synthesized IL-ORMOSIL are summarized in Table 1. The sol-gel process in absence of IL-TMOS takes place as reported in the literature for the basic-catalyzed reaction [42], resulting in the formation of a white dispersion of silica particles after 4 h of reaction. The presence of a small amount of IL-TMOS (IL-ORMOSIL1) results in a significant decrease in gelation time. After 5 min of reaction, a white gel is formed, completely blocking the stirring process. Fig. 2 illustrates the aspect of the formed gels. It is important to point out that the pH of the medium remained around 7 during the sol-gel process of the TEOS/IL-TMOS mixture. These results confirm that the IL covalently linked to the silane precursor is effective in accelerating the gelation process. As stated in the literature, imidazolium-based ILs can act as organogelator, which should solidify organic solvents via physically bonds such as van der Waals forces, hydrogen bonding, π -

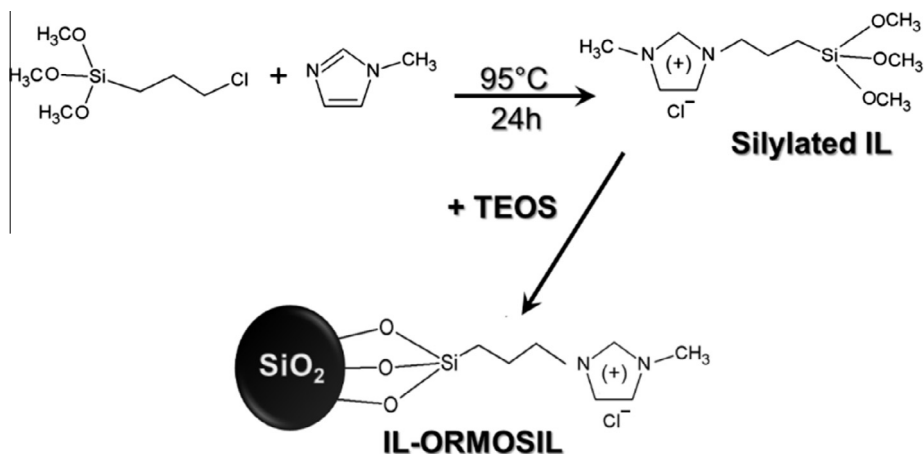


Fig. 1. Scheme for the synthesis of the IL-ORMOSIL.

Table 1
Main characteristics of the IL-ORMOSIL.

Sample code	$\eta_{\text{IL}}/\eta_{\text{TEOS}}$ molar ratio	Gelation time (min)	N_2 adsorption		Average particle/aggregate size (nm)
			S_{BET} (m^2/g)	V_p (cm^3/g)	
Silica	0	240	260	0.49	207 ± 64
IL-ORMOSIL1	0.05	5	366	0.76	271 ± 46
IL-ORMOSIL2	0.10	23	245	0.28	561 ± 80
IL-ORMOSIL3	0.20	50	7.5	0.02	635 ± 79

S_{BET} = surface area calculated by BET; V_p = pore volume; average particle size determined from DLS experiments.



Fig. 2. Visual aspect of the IL-ORMOSILs prepared by the one-pot sol-gel route.

cation and π - π bond stacking, leading to the formation of noncovalent network, which explain the stable gel [43]. For example, different authors have demonstrated that small molecules such as 12-hydroxystearic acid can be used as organo-gelator of water, organic solvent and ionic liquids [44–46]. Similar behavior has been reported by other authors for the acidic catalyzed sol-gel reaction of alkoxy-silane in the presence of conventional imidazolium – based IL (non silylated IL) [19,23,47]. Also the formation of silica networks instead of nanoparticles has been reported by Litschauer and Neouze [38] when performed the one-pot sol-gel process of bis-silylated imidazolium ionic liquid together with TEOS in basic medium.

Increasing the amount of IL-TMOS molar ratio, an increase of the gelation time is observed, but the values are still significantly lower than that one for the sol-gel reaction of the pure TEOS. Karout and Pierre [48] have also observed similar trend by using imidazolium- based ionic liquid containing BF_4^- of Cl^- as the anion, without catalyst. They have attributed to an increase of the viscosity of the system, resulting in slower diffusion of the silica oligomer [48]. In our system, the IL moiety is covalently linked to the silane. Thus, increasing the amount of this organo-silane should increase the steric hindrance which should retard the condensation. In fact, we have tried to perform the sol-gel process with only the IL-TMOS precursor but we have not succeeded.

The presence of silylated IL also influences the textural properties and the morphologies of the corresponding IL-ORMOSILs. The IL-ORMOSIL prepared with lower amount of IL-TMOS (IL-ORMOSIL1) displays higher surface area and higher pore volume compared with pure silica prepared at similar conditions (see Table 1). In contrast, increasing the amount of IL-TMOS, a decrease of both surface area and average pore volume is observed. This behavior suggests that IL-TMOS should promote the interparticle co-condensation, which should decrease the surface area of the particles. Moreover, the ionic liquid at the particle surface may interact with the silanol contributing for the formation of such structures.

The BET results are in agreement with the morphological behavior. Fig. 3 illustrates the FEG-SEM micrographs of the pure silica and the corresponding IL-ORMOSIL. The morphology of pure silica is characterized by the presence of aggregates constituted by primary spherical particles with size in the range from 80 to 130 nm. In contrast, the IL-ORMOSIL prepared with low amount of IL-TMOS (IL-ORMOSIL1) exhibits larger aggregates surrounded by porous clusters constituted by particles with very small size (around 18 nm), thus forming a hierarchical structure extending from micrometer to nanometer scale, as also observed in previous work regarding mercapto-modified ORMOSIL [49]. This feature is in agreement with the larger surface area found in BET analysis. Increasing the amount of IL-TMOS, denser aggregates are observed, which is in agreement with the BET analysis and confirm the interparticle co-condensation promoted by the silylated IL.

The size of the particles/aggregates was evaluated by DLS measurements and the results are also summarized in Table 1. Pure silica presents aggregates with size in the range of 207 ± 64 nm. The presence of IL-TMOS during the sol-gel synthesis resulted in an increase of the average aggregate size of the corresponding ORMOSILs. This characteristics is more pronounced

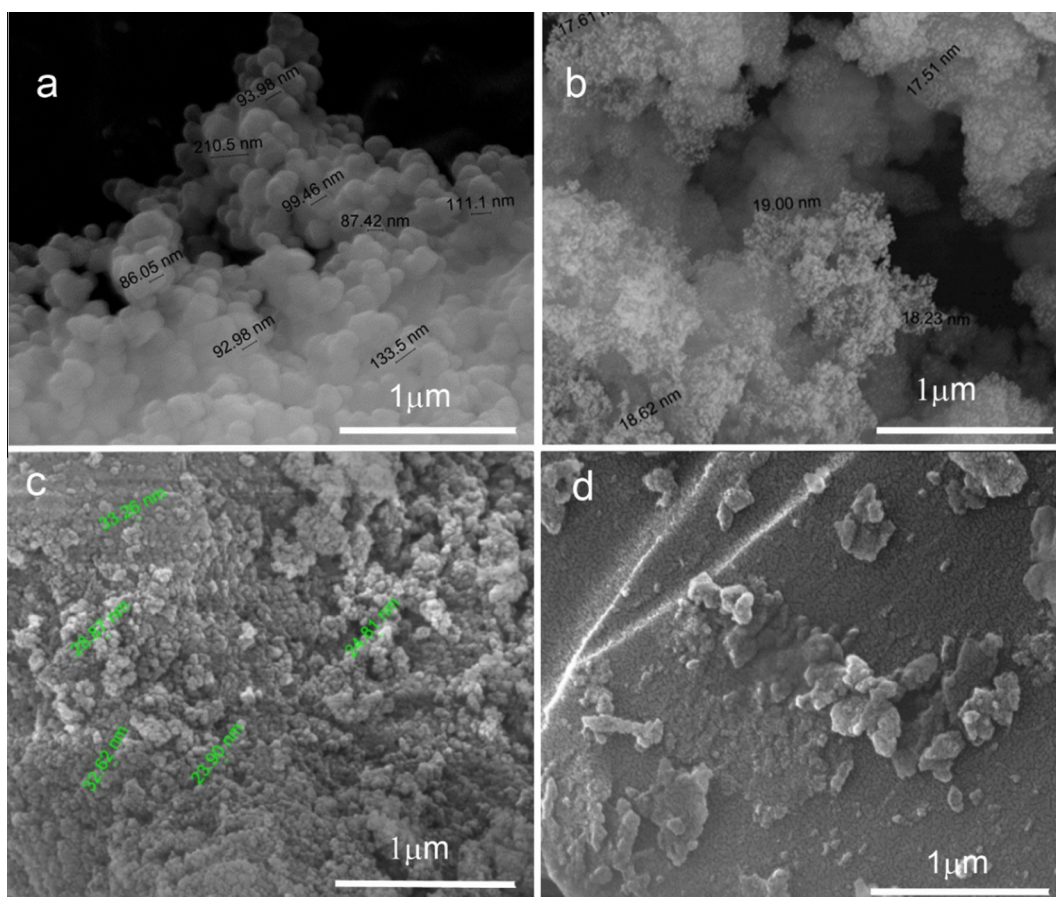


Fig. 3. FEG-SEM micrographs of (a) silica; and the IL-modified ORMOSIL; (b) IL-ORMOSIL1; (c) IL-ORMOSIL2; (d) IL-ORMOSIL3.

as the amount of silylated IL precursor increases suggesting strong interparticle interactions between IL moiety and the silanol groups at the silica surface.

The presence of silylated IL covalently linked to the IL-ORMOSIL is confirmed by FTIR spectroscopy. Fig. 4 presents the FTIR spectra of silica and the IL-ORMOSILs. The strong absorption at around 1100 cm^{-1} (peak a) in the spectrum of silica is assigned to the Si-O-Si stretching vibration. Considering the IL-ORMOSIL samples, this absorption is shifted to lower wave number. Also the presence of a shoulder at around 1165 cm^{-1} (peak b) may be attributed to the changes in Si-O-Si bonding angles due to the presence of the silsesquioxane moiety [50]. The presence of silylated IL linked to the silica surface is confirmed by the absorption bands at 1575 cm^{-1} (peak c), assigned to the imidazolium ring and at 2960 cm^{-1} (peak d) and 1466 cm^{-1} (peak e) due to the stretching and bending vibrations of the C-H bonds.

The IL-ORMOSIL samples were analyzed by TGA in order to estimate the amount of silylated IL in the sample. Fig. 5 compares the TGA and DTG profiles of pure IL-TMOS and the different IL-ORMOSILs. All IL-ORMOSIL samples and the IL-TMOS precursor display three main decomposition steps. The first one, below $200\text{ }^{\circ}\text{C}$, is assigned to the water and other volatile compounds present in the systems. The second and third decomposition stages refer to the decomposition of the IL moiety attached to the silica particles, as compared with the pure IL-TMOS precursor. The maximum temperature corresponding to the second decomposition step is $320\text{ }^{\circ}\text{C}$ for the pure IL-TMOS precursor. This event occurs at higher temperatures for the IL-ORMOSILs, indicating that the IL attached to the silica particle is thermally more stable.

The amount of IL moiety in the IL-ORMOSIL was estimated from the difference of the mass loss of silica and the IL-ORMOSIL between 200 and $700\text{ }^{\circ}\text{C}$. As indicated in Table 2 the addition of increased amount of IL-TMOS during the sol-gel process resulted in higher portion of the IL incorporated into the IL-ORMOSIL, confirming the co-condensation.

The ^{29}Si NMR analysis was used to estimate the structure of the silicon species in the IL-ORMOSIL samples. Fig. 6 presents the ^{29}Si NMR spectra, where it is possible to identify the two main regions of chemical shifts corresponding to the trifunctional Si-O units (Q^n) and tetrafunctional Si-O units (Q^n) [51,52], resulting from the hydrolysis/condensation of IL-TMOS and TEOS precursors, respectively. The signals at -111 ppm and -102 ppm are assigned to the Q^4 (SiO_4) and Q^3 [$\text{SiO}_3(\text{OH})$] species resulted from the hydrolysis/condensation of the TEOS precursor, indicating a high degree of condensation [53]. The small peaks at around -67 ppm and -60 ppm are related to the T^3 [$\text{RSi}(\text{OSi})_3$] and T^2 [$\text{RSi}(\text{OSi})_2\text{OH}$] species, respectively, resulted from the hydrolysis/condensation of the IL-TMOS precursor [54], confirming the condensation of both silane compounds.

3.2. Blends of epoxy resin and IL-ORMOSIL

3.2.1. Effect of the IL-ORMOSIL composition

The effect of the IL-ORMOSIL composition on the rheology of the epoxy dispersion and morphology of the epoxy networks was first studied by employing 2.5 phr (part per hundred parts of resin) of IL-ORMOSIL. The dispersion of IL-ORMOSIL2 and IL-ORMOSIL3, prepared with higher amount of IL-TMOS, resulted in unstable dispersion. The particles were deposited after three days. In the opposite, the dispersion of the IL-ORMOSIL1 (prepared with an IL-TMOS/TEOS = 0.05) remained stable after the same period.

Rheological behavior is an important tool for evaluating the dispersion of nanocomposites. Fig. 7 illustrates the dependence of complex viscosity, η^* , with frequency for ER/silica and ER/IL-ORMOSIL dispersions, as a function of the IL-ORMOSIL composition. The addition of 2.5 phr of silica results in slight increase of the viscosity. The presence of the silylated IL covalently bonded at the silica surface leads to a significant increase of the viscosity of the epoxy dispersion suggesting an improvement of the filler-matrix interaction due to the presence of the IL at the silica surface. This behavior is observed for

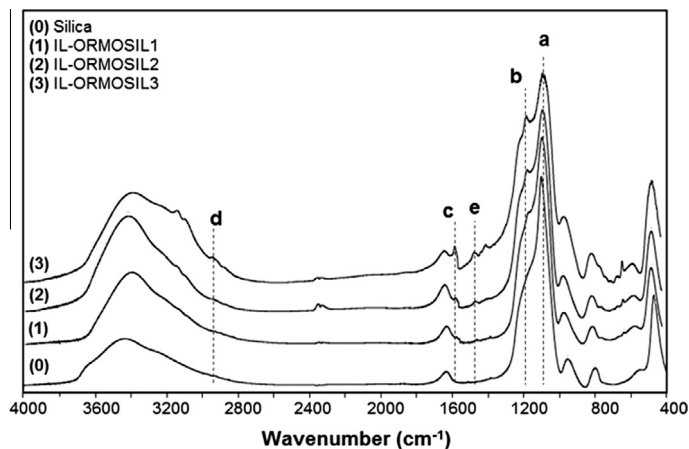


Fig. 4. FTIR spectra of silica and the IL-ORMOSIL.

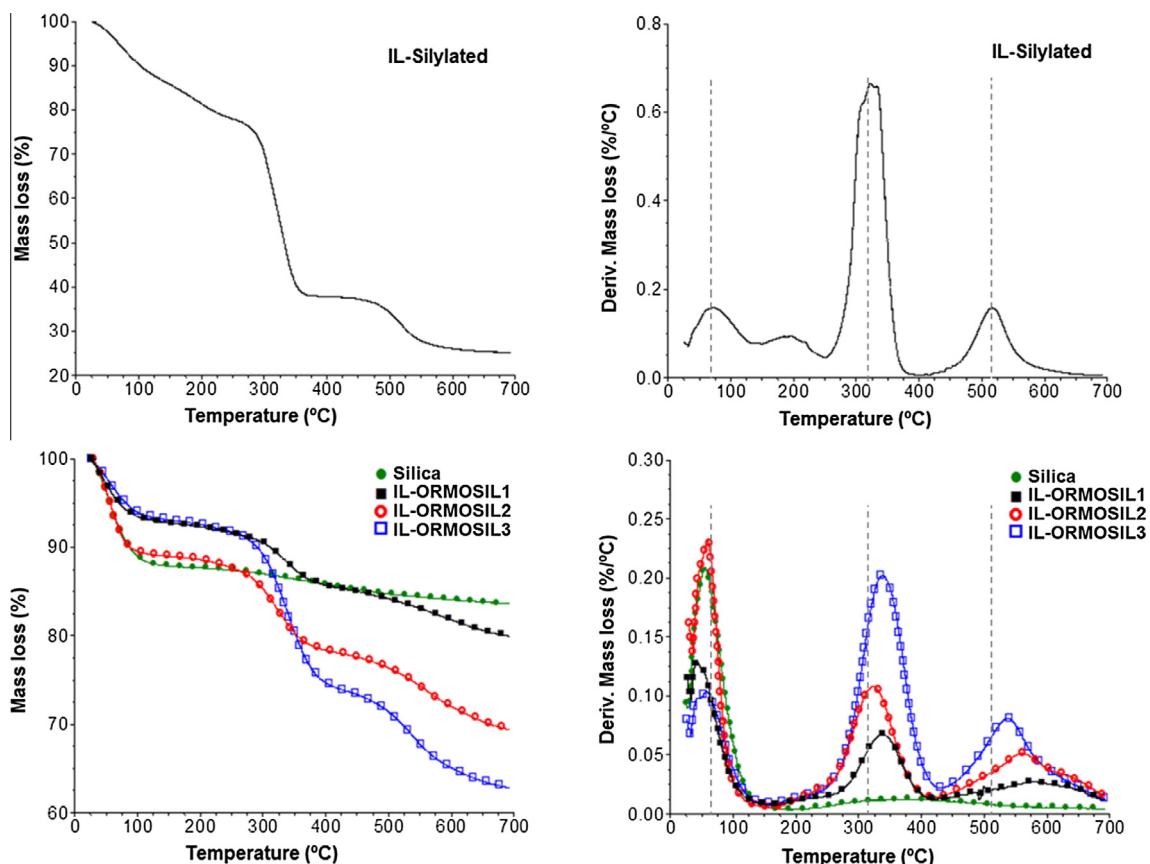


Fig. 5. Thermograms of (a, b) silylated imidazolium-based ionic liquid and (c, d) the IL-ORMOSIL samples as a function of the amount of IL-TMOS during the sol-gel synthesis.

Table 2

Amount of IL in the IL-ORMOSIL particles estimated from TGA analysis.

Sample code	IL/TEOS molar ratio	Mass loss at 200 °C (A) (%)	Mass loss at 700 °C (B) (%)	(B)–(A) (%)	Estimated amount of IL (wt%)
Silica		12	16	4	0
IL-ORMOSIL1	0.05	8	20	12	8
IL-ORMOSIL2	0.1	12	31	19	15
IL-ORMOSIL3	0.2	7	37	30	26

the systems containing up to 15 wt% of IL (IL-ORMOSIL2). The ER/IL-ORMOSIL3 dispersion presents viscosity value lower than that containing silica due to the poor and unstable dispersion of this sample within the epoxy matrix.

TEM micrographs of the cured epoxy networks containing 2.5 phr of silica and different IL-ORMOSILs are illustrated in Fig. 8. Silica is not well dispersed within the epoxy matrix and presents large aggregates. Contrarily, the systems with IL-ORMOSIL1 and IL-ORMOSIL2 displayed much smaller aggregates indicating that the IL moiety at the silica surface can better interact with the epoxy matrix thus forming better dispersion. In the case of epoxy system modified with IL-ORMOSIL 1 (Fig. 8b), the morphology is characterized by the presence of very small particles and some aggregates (see insert of Fig. 8b). The compatibilization between silica particle and epoxy network cured with Jeffamine D230 with ionic liquid was also reported by Donato et al. [28] by using different approach based on the in situ sol-gel process within the epoxy matrix.

The system prepared with IL-ORMOSIL3 presents a heterogeneous morphology characterized by the presence of compacted aggregates.

3.2.2. Effect of the amount of filler

As IL-ORMOSIL1 result in more stable dispersion within epoxy matrix, this sample was used for the further studies involving the effect of the filler content. The viscosity behaviors of the epoxy dispersion containing different amounts of silica or IL-ORMOSIL1 are compared in Fig. 9. The presence of IL-ORMOSIL results in a significant increase in viscosity, suggesting a bet-

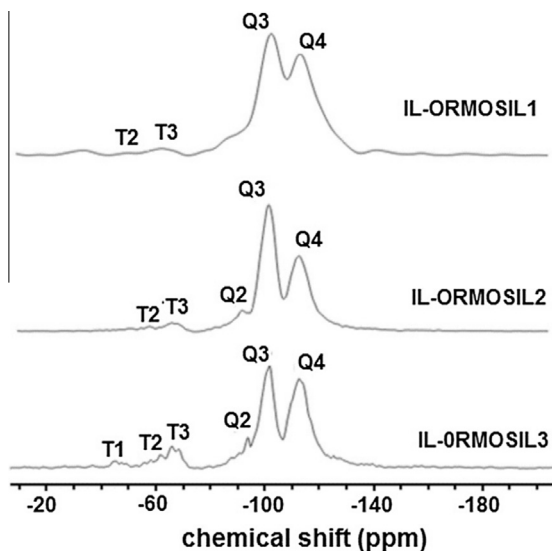


Fig. 6. ^{29}Si NMR spectra of IL-ORMOSIL samples as a function of the amount of IL-TMOS used during the synthesis.

ter dispersion of the filler promoted by effective interaction between the filler and matrix imparted by the ionic liquid moiety in the silica particles.

The effect of the silica and IL-ORMOSIL on the curing process of the epoxy system with Jeffamine D230 was investigated by DSC under dynamic mode, whose main results are summarized in Table 3. Both silica and IL-ORMOSIL result in a decrease of the maximum curing temperature indicating an accelerating effect of these fillers. This effect is more pronounced for the IL-ORMOSIL – filled epoxy system, as expected, because the IL moiety in the IL-ORMOSIL is known to catalyze the curing of epoxy systems or even participate on the curing process [55].

The effect of silica and IL-ORMOSIL on the dynamic-mechanical properties of epoxy networks was evaluated. Table 4 presents the main properties obtained from the DMA analysis. The glass transition temperature (T_g) was taken from the maximum of the tan delta peak. The addition of up to 5 phr of silica or IL-ORMOSIL1 does not significantly affect the storage modulus before the T_g . Also, the presence of silica does not exert great influence on the T_g values of the composites. However, the addition of IL-ORMOSIL brings on a decrease of T_g , mainly for the system containing 2.5 phr of the filler. It is well known that IL acts as plasticizer for several polymer system [1,3,4]. Thus, the IL moiety at the silica surface plays the role of interfacial agent and acts as plasticizer, contributing for an increase of the mobility of the polymer chain at the filler-matrix interface, thus decreasing the T_g . Moreover, the presence of the porous nanostructure of the IL-ORMOSIL1 aggregates (see Fig. 3) may contribute for a loosening of molecular packing, resulting in an increase in free volume and consequently a decrease in T_g . The composite containing 5 phr of IL-ORMOSIL1 presents higher T_g than the other composites, probably because at this composition the reinforcing effect of the silica particles starts to exert some influence on the T_g . At this composition, the modulus is also slightly higher, confirming the reinforcing effect.

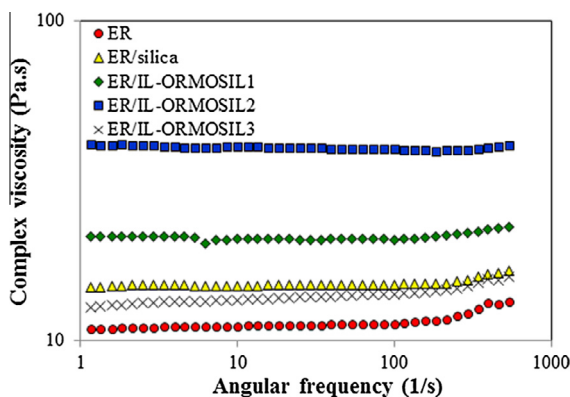


Fig. 7. Dependence of the complex viscosity with frequency for the ER dispersion containing 2.5 phr of silica or IL-ORMOSIL.

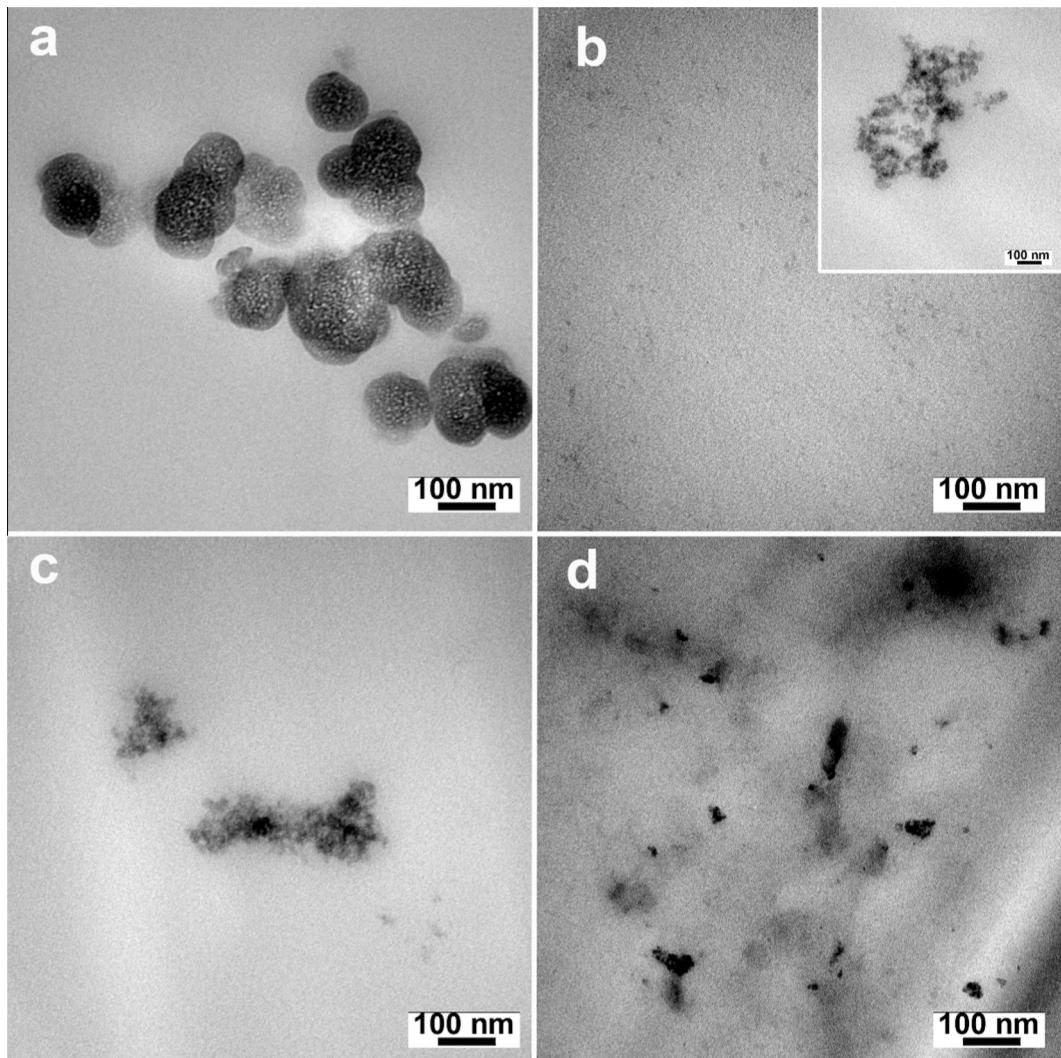


Fig. 8. TEM images of epoxy networks containing 2.5 phr of (a) silica (b) IL-ORMOSIL1, (c) IL-ORMOSIL2 and (d) IL-ORMOSIL3.

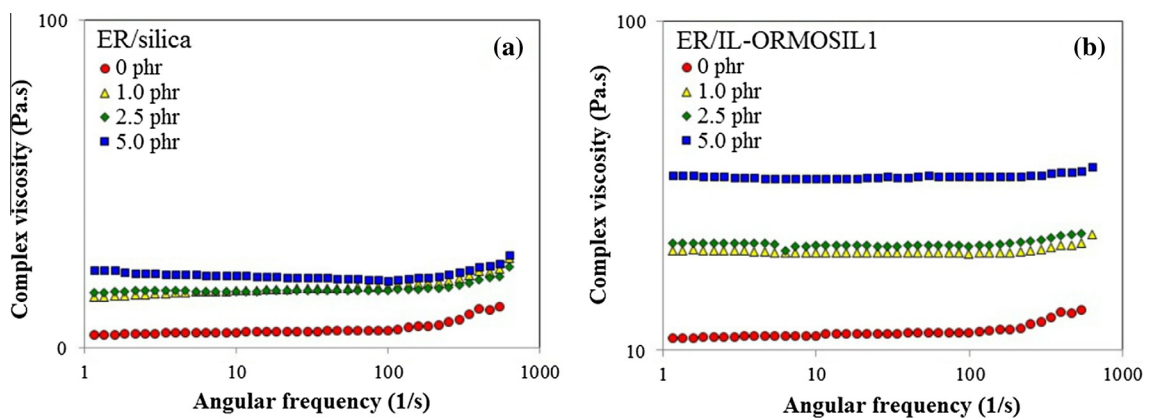


Fig. 9. Dependence of viscosity with frequency for the (a) ER/silica and (b) ER/IL-ORMOSIL1 dispersions as a function of the filler content.

Table 3

Maximum curing temperature taken from the DSC measurements, for the epoxy composites containing silica or IL-ORMOSIL1.

Amount of filler (phr)	Maximum curing temperature (°C)	
	Silica	IL-ORMOSIL1
0	130	130
1.0	127	126
2.5	126	122
5.0	125	119

Table 4

Dynamic-mechanical properties of epoxy networks filled with silica or IL-ORMOSIL1.

Amount of filler (phr)	Storage modulus (GPa)		Glass transition temperature (°C)	
	Silica	IL-ORMOSIL1	Silica	IL-ORMOSIL1
0	2.1	2.1	94	94
1.0	1.9	2.0	93	91
2.5	2.1	2.1	93	78
5.0	1.9	2.2	94	85

4. Conclusions

In this work, the synthesis of ionogel-based ORMOSIL by hydrolysis/co-condensation of a silylated imidazolium-based ionic liquid (IL-TMOS) combined with TEOS was successfully performed using ammonium hydroxide as catalyst. The presence of IL-TMOS resulted in a substantial decreasing of the gelation time, as compared to the sol-gel process of pure TEOS at the same conditions. The addition of low amount of IL-TMOS leads to IL-ORMOSIL particles with higher average surface area and higher pore volume compared with pure silica prepared at the same conditions. These features is confirmed by FEG-SEM microscopy, characterized by the presence of large aggregates surrounded by porous clusters constituted by particles with very small size. Increasing the amount of IL-TMOS leads to particles with smaller average surface area and less porous structure probably due to the interparticle co-condensation and also due to the interactions between the IL moiety and the silanols.

The presence of the IL covalently attached to the silica surface increases the interaction of the IL-ORMOSIL particles with epoxy prepolymer as indicated by the increasing of the viscosity of the corresponding dispersion. The best value was observed for the dispersion containing IL-ORMOSIL2. The good dispersion of IL-ORMOSIL1 and IL-ORMOSIL2 within the epoxy matrix was confirmed by TEM images. The presence of the IL-ORMOSIL1 results in a decrease of Tg of the epoxy networks probably because of the plasticizing effect of the IL located at the silica surface and also due to an increase of the free volume imparted by the structure of this particles. Finally, the system reported in this work opens new possibilities of developing epoxy systems with outstanding electrical properties without leaching of the ionic liquid. Such studies involving electrical properties as well as the studies related to the effect of different anions attached to these silylated ionic liquid are in progress and will be the issue of forthcoming papers.

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