

## Effects of the high pressure on the morphology of silica-based hybrid xerogels

SANDRA V. M. DE MORAES<sup>†</sup>, CELSO C. MORO<sup>†</sup>, TANIA M. H. COSTA<sup>†</sup>,  
MARCIA R. GALLAS<sup>‡</sup> and EDILSON V. BENVENUTTI<sup>\*†</sup>

<sup>†</sup>LSS, Instituto de Química, UFRGS, CP 15003, 91501-970 Porto Alegre, RS, Brazil

<sup>‡</sup>LAPMA, Instituto de Física, UFRGS, CP 15051, 91501-970 Porto Alegre, RS, Brazil

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The hybrid biphenylaminepropylsilica (bPhe/SiO<sub>2</sub>) and biphenylaminepropylsilicatitania xerogels were obtained by the sol-gel synthesis. The bPhe/SiO<sub>2</sub> material showed higher porosity and higher thermal stability of the organic component. These materials were submitted to high-pressure processing (3.5 and 6.0 GPa) and the changes in their morphological properties were investigated by using scanning electron microscopy, N<sub>2</sub> adsorption-desorption isotherms and infrared spectroscopy. The high-pressure processing produces changes in the morphological structure of hybrid materials caused by the compaction of the aggregated particles and the blocking of the pores with the entrapment of organics through the cold sintering process. However, when the organics are covalently bonded to the surface, this mechanism can be partially inhibited.

*Keywords:* Amorphous materials; Sol-gel chemistry; Microstructure

### 1. Introduction

The sol-gel method is an attractive route to prepare several hybrid materials with interesting properties, which allows their potential application as sorbents, sensors, catalysts, optical and electrochemical devices [1–5]. This method presents many advantages when compared with the classical procedure, as grafting reactions over inorganic powders, because the materials properties such as porosity, organic content and surface area can be controlled starting from the choice of the experimental conditions [6–9]. Furthermore, the synthesis can be performed at room temperature. Glasses of different oxides, binary and ternary systems, have also been obtained by the sol-gel method [10–12].

In previous papers, an efficient procedure was presented to obtain appropriate organic alkoxides as precursor reagent for the sol-gel synthesis of hybrid anilinepropylsilica and *p*-anisidinepropylsilica [8, 13]. The resulting nanometric powders were thermally stable up to 300 °C. The study of the synthesis of hybrid materials, similar to that cited above and

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\*Corresponding author. Tel.: +55 51 3316 7209; Fax: +55 51 3316 7304; Email: benvenuti@iq.ufrgs.br

containing binary Si/Ti oxide phases, can bring about materials with interesting properties. It was reported that the use of the binary oxides systems silica/titania, instead of pure silica, could serve to increase the surface selectivity in the adsorption process [14] and can be used to reduce the thermal expansion coefficient of silica [15].

The high-pressure technique at near 5.0 GPa (49,000 a.t.m.) has been used to compact nanometric inorganic powders to improve mechanical and optical properties of processed materials [16, 17]. A cold sintering mechanism was proposed for this compaction, at high pressure and room temperature. In this process, a reduction occurs in the surface area because of the formation of a microstructure with closed pores [17]. Afterwards, our group has proposed to apply this model on encapsulation of organic species in inorganic matrices, obtaining a new process to produce doped compact starting from hybrid sol-gel materials [18, 19]. This procedure is performed at room temperature without damage to the chemical and physical properties of organic species; however, high organic concentration can partially hinder the cold sintering process [19].

Aiming to explore the preparation of new hybrid materials and to make further investigation on mechanism of cold sintering for hybrid systems, in the present work, we have used the sol-gel method and the high-pressure technique, up to 6.0 GPa (59,200 a.t.m.), in the preparation and processing of new hybrid xerogels. The hybrids were obtained by using biphenylamine as organic precursor and two inorganic components, silica and titania:silica (1:9). The effect of high pressure in the morphology of the xerogels, mainly in their porosity, was investigated. The hybrid materials, before and after the high-pressure process, were characterized by using infrared spectroscopy, elemental analysis, scanning electron microscopy (SEM) and nitrogen adsorption-desorption isotherms.

## 2. Experimental

### 2.1 Syntheses of the hybrid materials

Biphenylamine ( $C_6H_5$ )<sub>2</sub>NH was first activated using sodium hydride in 10 ml of a mixture of aprotic solvent (toluene:thf) (1:1) for 30 min and then 3-chloropropyltrimethoxysilane (CPTMS) was added. The quantities used were stoichiometric (8 mmol) for biphenylamine, CPTMS and NaH, according to equations (1) and (2). The mixture was stirred under argon at solvent-reflux temperature for a period of 10 h. The resulting solution was centrifuged to eliminate the byproduct sodium chloride. The product of reaction, biphenylaminepropyltrimethoxysilane (bPAPS), was then used as organic sol-gel precursor reagent. The bPAPS was added to the inorganic precursor solution mixture, containing 5 ml of tetraethylorthosilicate (TEOS), 5 ml of ethanol, 1.6 ml of water and 0.1 ml of HF (40%), stirred for 20 min and stored for 1 week, just covered without sealing, for gelation. The resulting material was designated as bPhe/SiO<sub>2</sub>. For the hybrid containing 10% of titania, it was made by a previous hydrolysis of the TEOS for 20 min and after a titanium isopropoxide (TIPOT) solution (0.55 ml) was added. The mixture was stirred for 20 min and the obtained xerogel material was designated as biphenylaminepropylsilica (bPhe/SiO<sub>2</sub>/TiO<sub>2</sub>). The hybrid materials were then comminuted (lower than 250 mesh), washed extensively with various solvents and finally dried for 1 h, in an oven, at 100 °C.

### 2.2 Elemental analysis

The organic phase content was analysed using a CHN Perkin Elmer M CHNS/O Analyzer, model 2400. The analysis was performed in triplicate, after heating the materials at 100 °C, under vacuum, for 1 h.

### 2.3 Infrared measurements

Self-supporting discs, prepared by the compaction of pure powdered samples at near 55 MPa, with an area of 5 cm<sup>2</sup>, weighing ~100 mg, were prepared. The disc thickness should be sufficiently small to allow the use of the transmission technique. The discs were heated with a heat rate of 3 °C min<sup>-1</sup>, at 100, 200, 300, 400 and 450 °C, under vacuum (1 Pa), remaining 1 h in each temperature, using an IR cell [20]. The self-supporting discs were analysed at room temperature in the infrared region using a Shimadzu FTIR, model 8300. The spectra were obtained with a resolution of 4 cm<sup>-1</sup>, with a minimum of 100 scans.

### 2.4 Scanning electron microscopy

The materials were analysed by SEM in a Jeol equipment, model JSM 5800, with 20 kV and a maximum magnification of 30,000×.

### 2.5 EDS elemental analysis

The EDS analysis was made using a Noran detector in a Jeol equipment, model JSM 5800, with 20 kV, with an acquisition time of 100 s and magnification of 100×.

### 2.6 X-ray diffraction

The xerogel samples were submitted to XRD analysis using Cu K $\alpha$  radiation as source. The equipment was a Siemens Diffractometer D500.

### 2.7 N<sub>2</sub>-isotherms

The nitrogen adsorption–desorption isotherms of previous degassed solids, at 150 °C, were determined at liquid nitrogen boiling point in a homemade volumetric apparatus, with a vacuum line system employing a turbo molecular Edward vacuum pump. The pressure measurements were made using capillary Hg barometer and an active Pirani gauge. The apparatus was frequently checked with an alumina Aldrich standard reference (150 mesh, 5.8 nm and 155 m<sup>2</sup> g<sup>-1</sup>). The specific surface areas of the hybrid materials were determined from the BET (Brunauer, Emmett and Teller) [21] multipoint method and the pore size distribution curves were obtained using BJH (Barret, Joyner and Halenda) method [22].

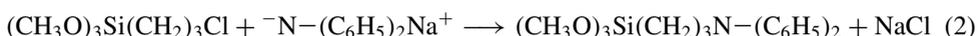
### 2.8 High-pressure experiments

For the high-pressure experiments, the xerogel powders were initially precompacted in a piston–cylinder type die to ~0.1 GPa. The volume of precompacted samples was ~0.35 cm<sup>3</sup> (diameter of 8 mm and height of 7 mm). The samples were then placed in a Pb container which acted as a pressure transmitting medium. The high-pressure processing was accomplished in a toroidal-type chamber at 3.5 GPa (34,500 a.t.m.) and 6.0 GPa (59,200 a.t.m.), at room temperature [23].

### 3. Results and discussion

#### 3.1 Synthesis of hybrid materials

The synthesis procedure of the organic precursor (bPAPS), used in this work, was recently described for similar systems [14]. In the reaction of biphenylamine with CPTMS, first the biphenylamine was activated with sodium hydride in aprotic solvent mixture, as illustrated in equations (1) and (2). The use of NaH as base activator results in reduction in the reaction time [24]. Furthermore, the insoluble byproduct NaCl can be easily separated from the organic medium by centrifugation. In the absence of NaH, there is a formation of HCl, which reacts with the biphenylamine, resulting in the organic salt, which is more difficult to separate from the organic medium [20].



The organic precursor obtained in equation (2) (bPAPS) was then added to the inorganic precursor solution containing TEOS or TEOS and TIPOT, to gelation. The resulting hybrid materials were assigned as bPhe/SiO<sub>2</sub> and bPhe/SiO<sub>2</sub>/TiO<sub>2</sub>, respectively. In the bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> case, the Ti/Si atomic ratio, determined by using EDS analysis, was 0.11 (table 1). This relation ensures an amorphous material with the titanium dispersed atomically in the tetrahedral silica structure, substituting the Si sites [25, 26], and considering that X-ray diffraction analysis did not show any titania or silica crystalline phase.

The idealized gelation step for bPhe/SiO<sub>2</sub> material is illustrated by equation (3).

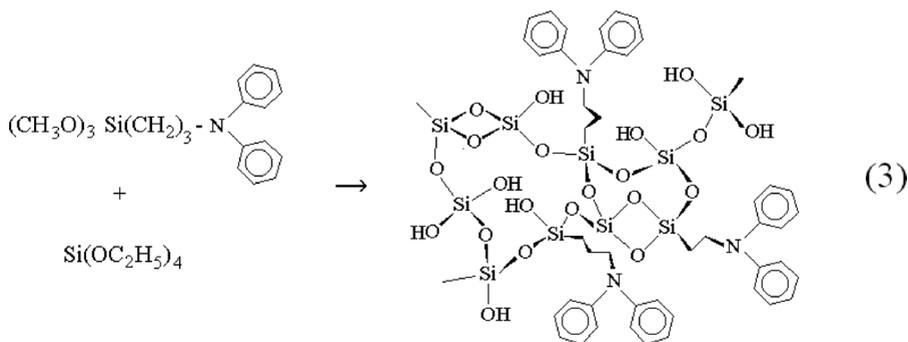


Table 1. Elemental composition and morphological data.

Material	Sample (GPa)	Organic content (mmol g <sup>-1</sup> ) <sup>†</sup>	Atomic ratio Ti/Si <sup>‡</sup>	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (ml g <sup>-1</sup> )
bPhe/SiO <sub>2</sub>	Powdered	1.42 ± 0.05	0.11 ± 0.02	112 ± 7	0.26 ± 0.02
	Pressed 3.5			46 ± 5	0.05 ± 0.02
	Pressed 6.0			40 ± 5	0.04 ± 0.02
bPhe/SiO <sub>2</sub> /TiO <sub>2</sub>	Powdered	1.46 ± 0.05	0.11 ± 0.02	38 ± 5	0.04 ± 0.02
	Pressed 3.5			<3	<0.01
	Pressed 6.0			<3	<0.01

<sup>†</sup>mmol of organic groups per gram of xerogel.

<sup>‡</sup>obtained from the EDS analysis.

The organic incorporation values obtained by using the CHN elemental analysis were 1.42 and  $1.46 \pm 0.05$  mmol of organic groups per gram of xerogel, for bPhe/SiO<sub>2</sub> and bPhe/SiO<sub>2</sub>/TiO<sub>2</sub>, respectively (table 1).

### 3.2 SEM analysis

The SEM analyses show different images for the bPhe/SiO<sub>2</sub> and bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> materials, as can be seen in figures 1 and 2, respectively. The bPhe/SiO<sub>2</sub> powdered sample has a mesoporous structure (figure 1a and b), whereas, in the powdered bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> sample, the nanoparticles are very close in the agglomerates, and thus it was observed only macropores (figures 2a and b). From figures 1c and 2c, it is evident that the pressed samples at 3.5 GPa are more compact and their pore structures are not visible in this scale. The application of higher pressure (6 GPa) causes no significant changes in the bPhe/SiO<sub>2</sub> (figure 1d); however, in the bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> case, it results in a fractured microstructure (figure 2d).

### 3.3 Infrared analysis

Figures 3 and 4 show the infrared spectra of the powdered and pressed samples of the hybrid materials, bPhe/SiO<sub>2</sub> and bPhe/SiO<sub>2</sub>/TiO<sub>2</sub>, respectively, obtained at room temperature, in

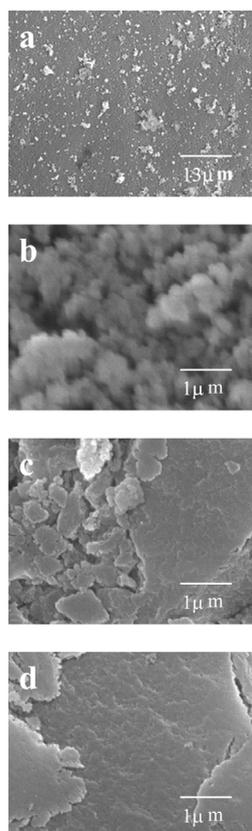


Figure 1. SEM images of bPhe/SiO<sub>2</sub> hybrid xerogel. (a and b) Powdered sample; (c) pressed at 3.5 GPa; (d) pressed at 6.0 GPa. The magnification was 2000 $\times$  for image (a) and 30,000 $\times$  for images (b, c and d).

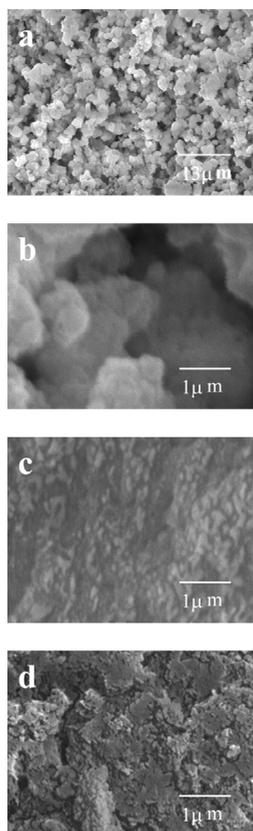


Figure 2. SEM images of bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> hybrid xerogel. (a and b) Powdered sample; (c) pressed at 3.5 GPa; (d) pressed at 6.0 GPa. The magnification was 2000× for image (a) and 30,000× for images (b, c and d).

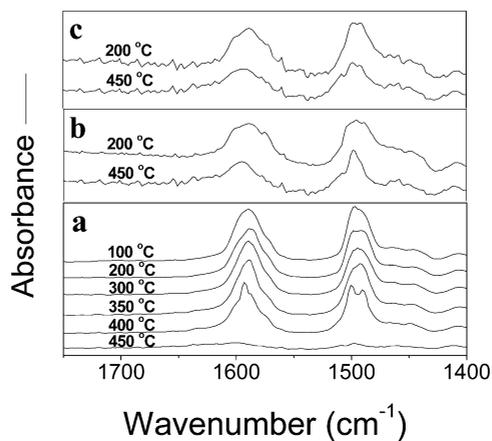


Figure 3. FTIR absorbance spectra of the bPhe/SiO<sub>2</sub> xerogel, obtained at room temperature, after heating in vacuum to temperatures ranging from 100 to 450 °C. (a) Powdered sample; (b) pressed at 3.5 GPa; (c) pressed at 6.0 GPa. The bar value is 2 for (a) and 0.6 for (b and c).

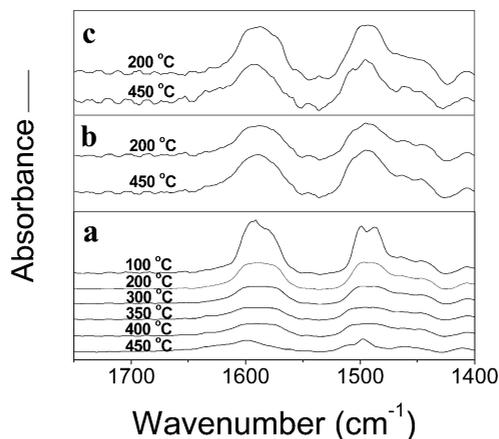


Figure 4. FTIR absorbance spectra of the xerogel bPhe/SiO<sub>2</sub>/TiO<sub>2</sub>, obtained at room temperature, after heating in vacuum to temperatures ranging from 100 to 450 °C. (a) Powdered sample; (b) pressed at 3.5 GPa; (c) pressed at 6.0 GPa. The bar value is 2 for (a) and 0.5 for (b and c).

vacuum. The aromatic ring modes at  $\sim 1590$  and  $1495\text{ cm}^{-1}$  are very strong in the spectra; therefore, the band area of these absorption modes can be used to estimate the thermal stability of the organics [27]. The infrared band areas of the organics, obtained for the samples heat treated from 100 to 450 °C, are presented in the table 2. The overtone band of silica at  $\sim 1870\text{ cm}^{-1}$  was used as a reference band. This normalization was necessary, considering the heterogeneity in disc thickness and for taking into account the position changes of the infrared beam.

It was observed in figure 3a that the organic phase of the powdered bPhe/SiO<sub>2</sub> sample is thermally stable because the infrared band areas of the organics are almost constant up to 400 °C (table 2). This high thermal stability is an indication that the organic groups are strongly

Table 2. Infrared band areas of aromatic phenyl group, obtained from the spectra of materials heated under vacuum.

Material	Sample (GPa)	Thermal treatment (°C)	IR band area ( $\text{cm}^{-1}\text{ abs}$ ) <sup>†</sup>
bPhe/SiO <sub>2</sub>	Powdered	100	3.1
		200	3.4
		300	3.1
		350	3.0
		400	2.7
		450	0.56
	Pressed at 3.5	200	3.0
		450	1.1
	Pressed at 6.0	200	3.3
		450	1.6
bPhe/SiO <sub>2</sub> /TiO <sub>2</sub>	Powdered	100	3.5
		200	2.4
		300	1.9
		350	1.6
		400	1.4
		450	1.1
	Pressed at 3.5	200	2.6
		450	2.7
	Pressed at 6.0	200	2.6
		450	2.0

<sup>†</sup>band area of phenyl ring at  $1590\text{ cm}^{-1}$ /silica overtone band area at  $1870\text{ cm}^{-1}$ .

bonded to the surface of the hybrid bPhe/SiO<sub>2</sub> material. Further thermal treatment (450 °C) results in a decrease in the band area, indicating that at this temperature the chemical bond was disrupted and the organic groups were desorbed from the surface [27]. However, for the powdered bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> sample, the increase in the temperature produces a progressive decrease in the infrared band area (figure 4a and table 2), indicating a lower thermal stability than that observed for the bPhe/SiO<sub>2</sub> material. Therefore, for the bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> sample, we propose that a fraction of the organic groups is not directly bonded to the surface of the silica/titania matrix, but some of the organosilane precursors are linked to each other forming oligomeric species which were gradually desorbed with the increasing temperature up to 200 °C. Nevertheless, a considerable organic band is present in the spectrum of the powdered bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> sample, even after heating up to 300 °C (table 2), and this band is related to organics chemically bonded to the silica/titania matrix. In addition, we can consider that the remained band after heating up to 450 °C can be explained by the retention of the organics in closed pores formed during the polycondensation and drying process [27, 28].

Considering now the spectra of the pressed samples, for the bPhe/SiO<sub>2</sub> material, in the spectra obtained after thermal treatment from 200 to 450 °C, a decrease in the organic band area was observed (table 2), indicating a considerable amount of open pores, even after applying 6 GPa of pressure (figure 3c). However, it is worth to observe a remaining band area (of 1.1 at 3.5 GPa and 1.6 at 6.0 GPa), higher than the powdered samples (0.56), heated at the same temperature. Considering the previous discussion, the high-pressure processing produced the partial closing of the pores and consequently the entrapment of the organics. For the bPhe/SiO<sub>2</sub>/TiO<sub>2</sub>, the infrared band area of the organics remains constant for samples pressed at 3.5 GPa, after thermal treatment up to 450 °C (figure 4b and table 2). On the other hand, when the bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> material was pressed at 6 GPa, the infrared spectrum of the sample heat treated up to 450 °C showed a slight band area reduction. This could be explained by the formation of cracks during the high-pressure compaction as evidenced by SEM image shown in figure 2d. These cracks allow the liberation of organics, which as shown in table 2 are not so strongly bonded when compared with the bPhe/SiO<sub>2</sub> material.

### 3.4 N<sub>2</sub> isotherms

The N<sub>2</sub> adsorption–desorption results are shown in table 1. The bPhe/SiO<sub>2</sub> sample has a BET surface area nearly three times larger than that obtained for the powdered bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> sample, according to the previous results reported for similar systems containing titania crystalline phase and silica [29]. However, in the present work, the lower porosity of the bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> when compared with the bPhe/SiO<sub>2</sub> material could not be explained by this same way because the samples did not show titania or silica crystalline phases. In both samples, the high-pressure processing produces a decrease in the BET surface area as well as in the pore volume.

The mesopore size distribution curves of the bPhe/SiO<sub>2</sub> and bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> materials, obtained by using the BJH method [22], are shown in figures 5 and 6, respectively. It was possible to observe that the porosity is higher for powdered samples than in the pressed ones. In the bPhe/SiO<sub>2</sub> case, the powdered sample presents two distinct mesopore diameter regions: (1) small pores with diameter <8 nm and (2) larger pores with average diameter of ~37 nm (figure 5). The powdered bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> sample has mainly mesopores with 5 nm diameter, however, with a lower amount of small pores in relation to bPhe/SiO<sub>2</sub> powdered sample (see the scales of figures 5 and 6). After applying pressure, the pores of the bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> material were not detected by the used technique (figure 6).

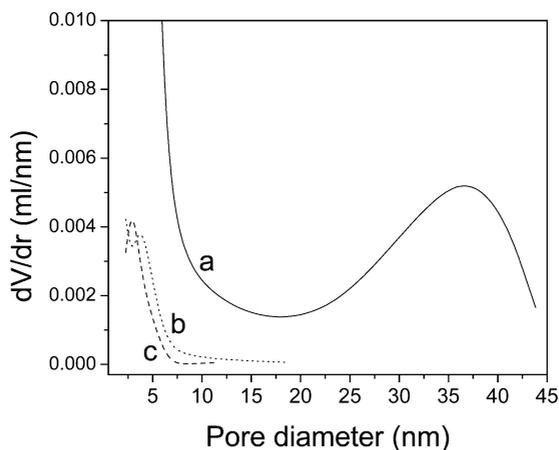


Figure 5. Pore size distribution of the bPhe/SiO<sub>2</sub> xerogel, obtained by the BJH method. (a) Powdered sample; (b) pressed at 3.5 GPa; (c) pressed at 6.0 GPa.

### 3.5 Further discussion

It was recently reported that high-pressure processing (up to 0.52 GPa) produces some decrease in the silica surface area, which was accompanied by a decrease in the pore volume [30]. These effects were attributed mainly to the decrease in the external surface area owing to the aggregation of particles, as the diameter of the main pores remains almost constant. In the present work, the pressure applied was nearly 10 times higher and the effects were more impressive, including closing of the pores containing organics. However, in the sample bPhe/SiO<sub>2</sub>, surprisingly, a considerable amount of small open pores with diameter <5 nm is still observed, even after applying pressures of 6 GPa (figure 5 and table 1). This fact can also be confirmed by the reduction in the infrared band area of organics in the pressed sample, after the thermal treatment up to 450 °C (table 2), which means an organic desorption. These results can be interpreted by taking into account the presence of the surface pendant organic groups that prevent the complete reaction between silanol groups hindering the cold sintering process [17, 19].

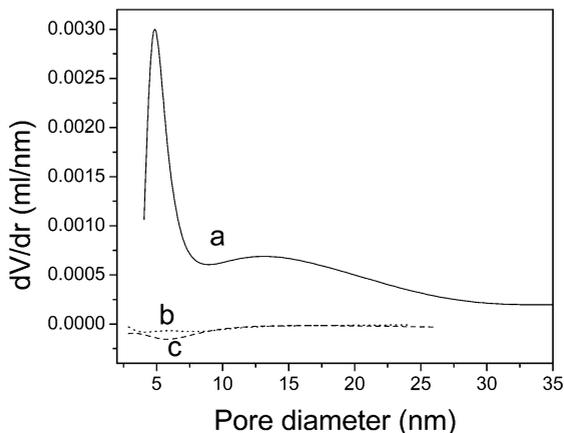


Figure 6. Pore size distribution of the bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> xerogel, obtained by the BJH method. (a) Powdered sample; (b) pressed at 3.5 GPa; (c) pressed at 6.0 GPa.

For the pressed bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> sample at 3.5 GPa, no opened pores were observed. This compaction was evident from the pore size distribution curves of figure 6, from the porosity data of the table 1 and also from the band area data showed in the table 2, where all organics remained trapped in the matrix. In this case, we proposed that there is no inhibition of cold sintering because the organics, in the oligomeric form, have higher mobility to accommodate during the compaction. However, after applying 6.0 GPa, the bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> sample shows a slight infrared band area reduction after thermal treatment. This could be caused by liberation of organics through the cracks formed in the microstructure during the compaction as observed in the SEM images (figure 2d and discussed earlier). These cracks were caused by the energy dissipation during the high-pressure compaction that was already observed in materials with low porosity [19].

#### 4. Conclusions

In this work, the combination of the sol-gel method and a high-pressure technique was successful in the preparation and processing of new hybrid xerogels. The organic phase of the powdered bPhe/SiO<sub>2</sub> sample was thermally stable up to 400 °C, indicating that the organics are covalently bonded to the surface. For the bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> material, the thermal treatment produces a progressive desorption of the organics, because in this sample, the organics are in oligomeric form. From the SEM and N<sub>2</sub>-isotherms, we conclude that the powdered bPhe/SiO<sub>2</sub> sample has a higher porosity than the powdered bPhe/SiO<sub>2</sub>/TiO<sub>2</sub>. The high-pressure processing produces a remarkable reduction in the surface area and pore volume. These effects are due to the compaction of the aggregated particles and also to the blocking of the pores. The closing of the pores results in organics entrapment, and this was more evident in the bPhe/SiO<sub>2</sub>/TiO<sub>2</sub> material. In the bPhe/SiO<sub>2</sub> material, the cold sintering was partially hindered, possibly by the presence of organics bonded on the silica surface. This study helped us to improve our understanding about the mechanisms of compaction of hybrid materials at high pressure. The high pressure processing can be used as a complementary tool to promote the encapsulation of organic species in inorganic solid media, enabling the preparation of a lot of new hybrid sol-gel-based materials.

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