

EVALUATION OF ORDERED MESOPOROUS SILICA SBA-15 DISPERSED IN EPOXY RESIN

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ABSTRACT

To obtain the mesoporous nanostructured SBA-15 silica particles, a chemical reaction was performed using a template – a triblock copolymer (Pluronic 123®) - and a silica source - the tetraethyl orthosilicate - in acid medium. These silica particles were obtained by classical chemical reaction method and irradiation process (gamma rays from ⁶⁰Co-Gammacell) at absorbed dose values of 0.5 kGy, 10 kGy and 25 kGy. Then, these silica particles were dispersed in epoxy resin Araldite® GY260 (diglycidyl ether of bisphenol A - DGEBA) and a cure agent. The particles dispersion was evaluated by two methodologies: a) Melt blending mode, where silica particles are dispersed in hot resin; b) Solvent-blended solution mode, where silica particles are dispersed in epoxy resin/acetone mixture in order to prevent the agglomeration of the inorganic phase. The silica particles had the specific surface area calculated from BET (Brunauer-Emmett-Teller) equation, while the BJH (Barrett-Joyner-Halenda) equation was used to determine pore volume and average diameter. Silica particles presented high surface area and pores arranged in hexagonal nanoscale diameter. The TEM images for irradiated silica particles have confirmed the hexagonal pore ordering in SBA-15 even using low gamma absorbed doses. The infrared absorption spectra (FTIR) confirmed that the added organic solvent has been effectively removed. Images of optical microscope revealed dispersion of the components by solvent-blended solution mode allows a better components interaction.

1. INTRODUCTION

The structural arrangement obtained by epoxy resin with nanostructured mesoporous silica particles improve properties to this composites compared to original polymeric material, where the advantage is application of small amounts of filler in the polymeric matrix [1,2].

The cured epoxy matrix is obtained by reacting highly reactive epoxy groups with a compatible curing agent. During the reaction, crosslinking is formed and a thermorigid structure is achieved after complete curing under room conditions or even at elevated

temperatures. The epoxy matrix post-cure is a rigid but fragile material. Although its improvements in mechanical and thermal properties, the addition of inorganic reinforcements in its structure inhibits its high brittleness, increasing the material resistance and preventing crack propagation in the final structure [3].

SBA-15 mesoporous silica has a hexagonal pore structure in nanometer scale, high surface area (500-1000 m²/g) and other intrinsic characteristics such as thermal, mechanical and hydrothermal stability [4,5]. In this structure, pores in meso dimensions and microporous can be observed. Around each mesopore, there is a microporous network called “crown” that interconnects one pore to the other. The orderly porous configuration in this material is linked to the use of structure directing agents (surfactants). The concentration of employed surfactant promotes an increase in medium stability, favoring the formation of micelles. At first, the micelles become spherical and elongate after the addition of the silica precursor initiating the hexagonal architecture characteristic of the SBA-15 and, in continuity of the process, the structured walls are being designed [5].

Usually the synthesis of SBA-15 is achieved from an organic triblock copolymer with an acidic silica source followed by a hydrothermal treatment in an oven and calcination to remove the surfactant [4,5].

Although the mesoporous nanostructured particles concentration in epoxy resin is small, it should be noted that the properties of the composite are directly linked to the effective dispersion and interface adhesion of components [2].

Nanoscale reinforcements have a great tendency to agglomerate, so the evaluation of the degree of nanostructure dispersion in the polymer is necessary. The particles dispersion may be performed in two ways: a) Melt blending and b) solvent-blended solution [1]. In melt blending mode, the polymer is heated above its melting point or glass transition point (T_g) and then the inorganic fraction is added to the medium. In solvent-blended solution mode, the polymer is mixed in an organic solvent and particles are added. In this last mode, the dispersion becomes more effective compared to melt blending, however it is limited to the use of an appropriate solvent that can be removed from the medium without interfering with the final properties of the materials [2].

The use of ionizing radiation to replace the hydrothermal step is an alternative in the preparation of SBA-15. In this work the surfactant and the silica precursor dissolved in acid solution are exposed to radiation in a Gammacell (dose rate: 0.592 kGy/h), with absorbed doses at 0.5 kGy, 10 kGy and 25 kGy, before calcination step.

2. MATERIALS AND METHODS

In this work, the materials and methods involved silica particles synthesis and its dispersion to obtain the epoxy composites and these both materials characterization as following:

2.1 Silica Particles Synthesis Methodology

2.1.1. SBA-15 particles

Mesoporous silica was synthesized from the dispersion of Pluronic 123 (PE20PPO70PE20 → (ethylene poly-oxide) 20 - (propylene poly-oxide) 70 - (ethylene poly-oxide) 20 -); 1.6 mol/L HCl acid solution for 1h at room temperature until complete dissolution of the surfactant. The silica precursor (Tetraethylortosilicate - Sigma Aldrich) was added while maintaining constant stirring for 5 min.

Classical chemical reaction method (hydrothermal method): the mixture was carried on an oven at 100 °C during 48 h.

Irradiation Process: The mixture was transferred to a glass container and placed inside the Gammacell irradiator (⁶⁰Co - Model 220 series 142). Absorbed doses at 0.5, 10 and 25 kGy were applied.

The next step is common for both methods: the obtained material was washed and filtered thoroughly in distilled water and dried at room temperature. The final product was obtained after calcination of the samples at 540 °C for 5 h in N₂ and 3 h in atmosphere air.

2.1.2. Composites

The composites were prepared by dispersing the SBA-15 particles, from irradiation process at 25 kGy in concentration values of 1 % and 2 %, in epoxy resin following these methodologies:

a) Melt blending mode: 100 wp of epoxy resin Araldite® GY260 Bisphenol A by melting the organic phase at 100 °C of a hot plate under magnetic stirring;

b) Solvent-blended solution mode: 100 wp of epoxy resin Araldite® GY260 Bisphenol A [7] mixed to acetone a.g. under magnetic stirring. After solvent evaporation the mixture was dried in oven at 80 °C.

After dispersion in both methods, is added 85 wp of carboxylic acid derived anhydride-based HY2918 hardener and 0.5 % of the accelerator DY062 [7], under stirring. The composites were cured in oven for 8 hours at the following temperature program: T_{room} to 80 °C (4 h) and 80 °C to 120 °C (4 h) [7].

2.2 Characterization

2.2.1 Silica particles

The SBA-15 particles morphology were examined by Transmission Electron Microscopy (TEM), in a JEOL-JEM-2100 microscope.

Nitrogen adsorption was measured at -196 °C using a Micromeritics ASAP 2010 volumetric adsorption analyzer. Specific surface area was calculated based on the BET (Brunauer-

Emmett-Teller) equation, while the BJH (Barrett-Joyner-Halenda) equation was used to determine the pore volume and its mean diameter.

2.2.2 Silica-epoxy Composites

FTIR spectra analysis were performed to verify solvent removal in the mixture of silica particles dispersed in epoxy resin, by Fourier Transform Infrared analyser - Nicolet 4700 FT-IR Spectrometer using the medium infrared frequency region from 4000 to 400 cm^{-1} , with resolution of 4 cm^{-1} and 40 scans to compare the epoxy resin spectra before and after solvent addition.

The silica particles dispersion in cured epoxy composites was evaluated by Zeiss optical microscope Imager M2m model with 200x resolution, DIC filter and polarized light.

3. RESULTS AND DISCUSSION

3.1 Silica particles

The obtained silica particles by hydrothermal (classical) method presented surface area values in the range of 500-1000 m^2/g , which is the range values of commercial SBA-15 particles. The pore volume (V_{pore}) of 0.87 cm^3/g and pore mean diameter ($\varnothing_{\text{pore}}$) of 52 Å, that converge to these parameters presented to the commercial particles.

Irradiation method applied at 0.5 kGy to 25 kGy allowed particles with low diameter pore about 33 Å and pore volume about 0.3 cm^3/g , as presented in Table 1. Irradiation process produces silica mesoporous particles even in low absorbed doses.

In this work, the silica mesoporous SBA-15 obtained by irradiation process at 25 kGy was elected for dispersion in epoxy resin to produce the composites because of its pore volume value, that is a bit higher.

Table 1: BET/BJH results for SBA-15 particles

Sample particle (SiO ₂)	S (m ² /g)	V pore (cm ³ /g)	Ø pore (Å°)
Hydrothermal (classic method)	610	0.87	52
0.5 kGy	535	0.34	33
10 kGy	428	0.28	33
25 kGY	509	0.37	34

The micrographies of particles morphology by TEM is shown in Fig. 1. The images show an hexagonal pore network and channels homogeneity in SBA-15 particles obtained by classical and irradiation processes. The synthesis was uniformly conducted throughout performed processes.

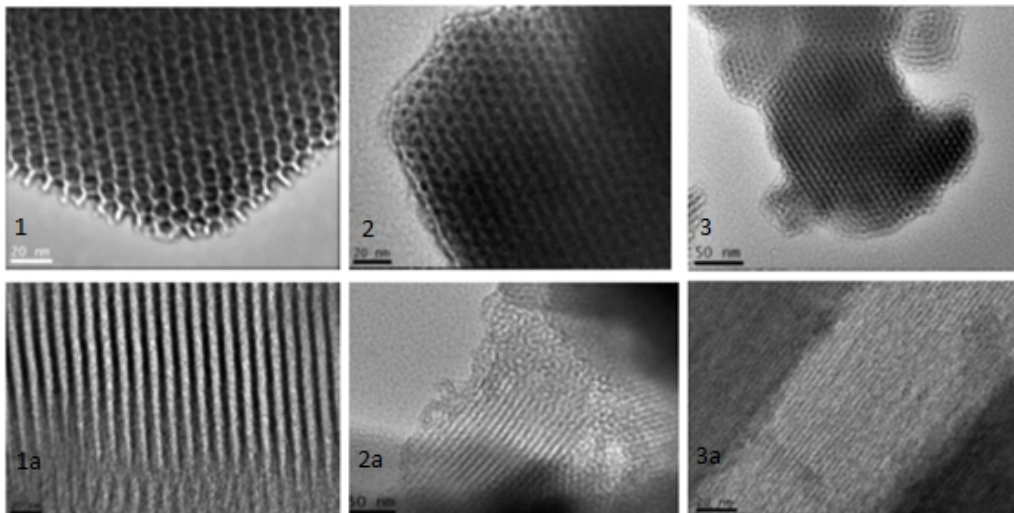


Figure 1: TEM images of: 1)/1a) hydrothermal SBA-15; 2)/2a) SBA-15 at 0.5kGy and 3)/3a) SBA-15 at 10kGy.

3.2 Particles dispersion and silica/epoxy composites

The infrared spectra of silica particles synthesized by irradiation process at 25 kGy dispersed in epoxy resin and the standard epoxy resin, without silica particles, are shown in Fig. 2. These results show no interference of epoxy resin/acetone mixture compared to epoxy resin standard.

The carbonyl group (-C=O) of acetone has an intense absorption band in 1870 cm^{-1} to 1540 cm^{-1} [6]. This region is absent in both spectra. It suggests that after particles dispersion, the solvent evaporation is effective in worked setted conditions.

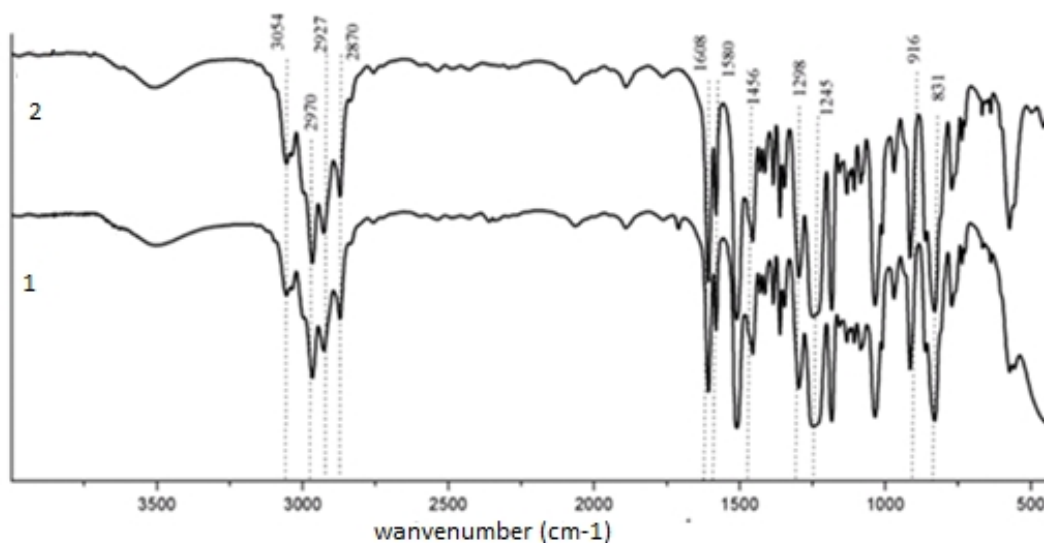


Figure 2: FTIR Spectra: 1) standard epoxy resin and 2) SBA-15 in epoxy resin/acetone mixture.

The optical micrographies of silica/epoxy composites are shown in Fig. 3. These images show a smooth surface in cured epoxy standard sample, but the surface presents a big roughness region in silica/epoxy composite obtained by particles dispersion in melted resin method and the roughness region is lower in silica/epoxy composite obtained by particles dispersion in resin diluted in organic solvent method. These results suggests resin/acetone mixture allows high silica particles dispersion compared to the melted resin method. This last method seems to form big silica particles aggregates.

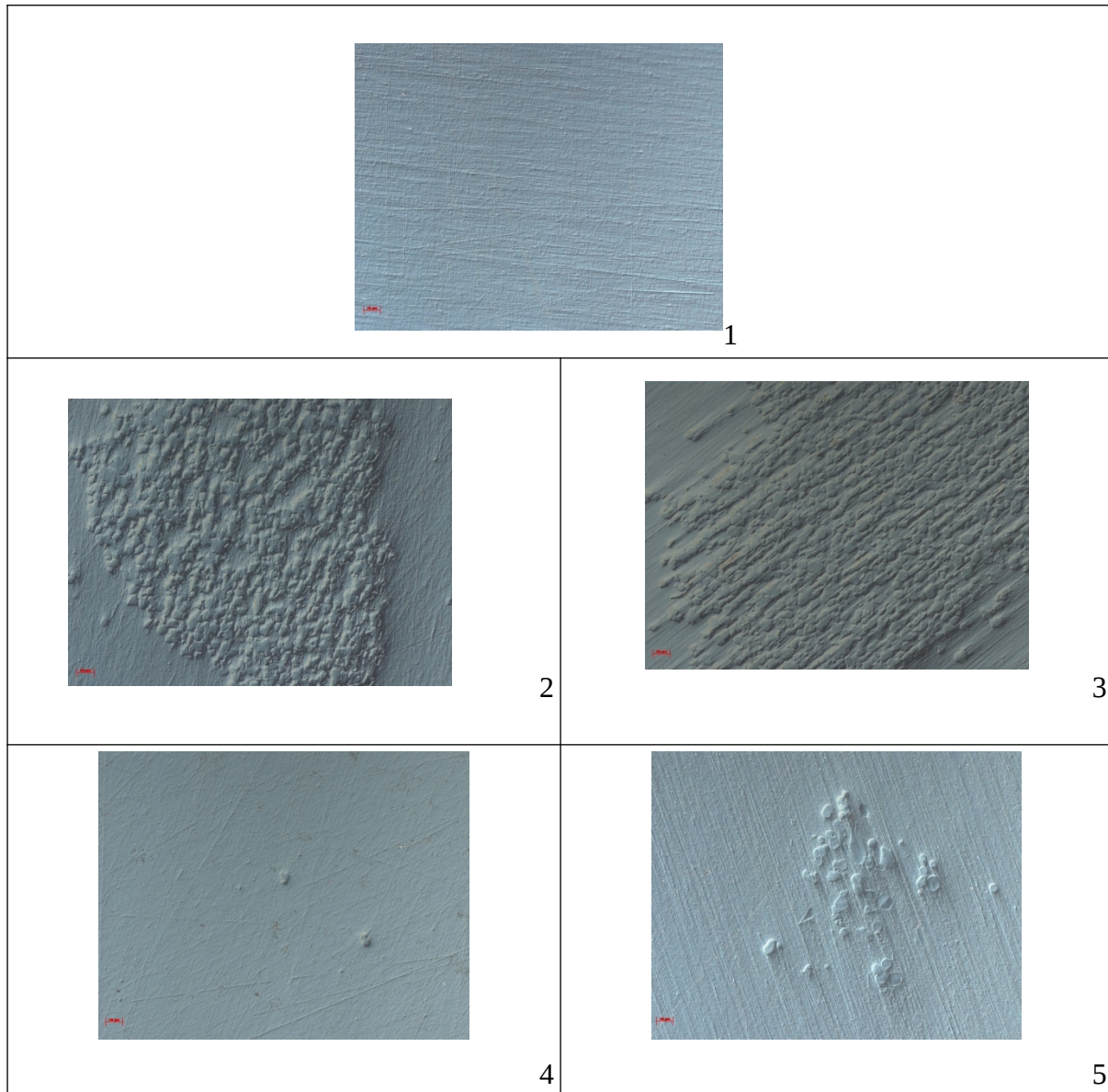


Figure 3: Optical images of: 1) standard epoxy resin; particles dispersion in melt-blending mode 2) 1 % and 3) 2 % silica/epoxy composites; particles dispersion in solvent-blended solution mode 4) 1 % and 5) 2 % silica/epoxy composites.

4. CONCLUSIONS

The TEM images obtained for irradiated silica particles, have confirmed the hexagonal nanostructure pore ordering in SBA-15, even using low gamma absorbed doses. Irradiation process allow particles surface area in conformity of commercial standard SBA-15, although its low pore diameter and volume.

The silica particles are better dispersed when resin/acetone mixture method is used if compared to resin melting method.

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REFERENCES

1. S. Salimian, A. Zadhoush, A. Mohammadi, “A Review on New Mesostructured Composite Materials: Part I. Synthesis of Polymer-Mesoporous Silica Nanocomposite”, *Journal Reinforced Plastic & Composites*, **37 (7)**, pp. 441-459 (2018).
2. L. Wei, N. Hu, Y. Zhang, “Synthesis of Polymer – Mesoporous Silica Nanocomposites”, *Materials*, **3**, pp. 4066-4079 (2010).
3. G. Marinucci, “Materiais Compósitos e Poliméricos: Fundamentos e Tecnologia”, Artliber, São Paulo, Brazil (2011).
4. J. R. Matos, L. P. Mercuri, M. Kruk, M. Jaroniec, “Toward the synthesis of Extra Large-Pore MCM-41 Analogues”, *Chem. Mater*, **13**, pp. 1726-1731 (2001).
5. M. E. Johansson, “Controlling the Pore Size and Morphology of Mesoporous Silica” Sweden-Linköping University, Linköping, Sweden (2010).
6. R. M. Silverstein, G. C. Bassler, T. C. Morrill, “Identificação Espectrométrica de Compostos Orgânicos”, Ed. Guanabara, Rio de Janeiro, Brazil (1987).
7. “Sistemas epoxi para Composites; Filament winding – Maxepoxi”, https://www.maxepoxi.com.br/pdf/composites_a_calor_2015.pdf (2015).