

## DEVELOPMENT OF FLUOROCARBON/SILICA COMPOSITES VIA SOL-GEL PROCESS

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### ABSTRACT

Fluorocarbon/silica composites have interesting physical-chemical properties, combining the great resistance to chemical products, the electric insulation, and the thermal stability of fluorine polymers with the optical, magnetic, and dielectric properties of silica. Due to the unique mechanical, thermal, and dielectric properties of fluorocarbon and silica composites, there is interest in their application in the development of fuel cells, the production of integrated circuit boards (ICB), and packages for the transportation of integrated circuits. The sol-gel process is a chemical route to prepare ceramic materials with specific properties that are hard or impossible to obtain by conventional methods. Fluorocarbon/silica composites were obtained by the sol-gel method from tetramethoxysilane – TMOS and fluorinated hydrocarbons with low molecular weight and main chains with 10 - 20 carbon atoms previously obtained from PTFE scraps irradiated with a <sup>60</sup>Co  $\gamma$  source in oxygen atmosphere with a dose of 1 MGy. Syntheses were performed in 125-mL reaction flasks in basic medium at 35 °C and in acid medium at 60 °C with N-N dimethylformamide as a chemical additive for drying control. After synthesis, the material was thermally treated in an oven with electronic temperature control. The monoliths obtained were characterized by Fourier transform infrared spectroscopy (FTIR), electron microprobe and by a standard nitrogen adsorption-desorption technique.

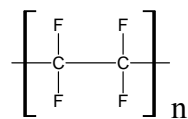
### 1. INTRODUCTION

Fluorocarbon/silica composites have interesting physical-chemical properties, combining the great resistance to chemical products, and the high electric insulation and thermal stability of polymers with the optical, magnetic, and dielectric properties of silica. Due to the unique mechanical, thermal, and dielectric properties of fluorocarbon and silica composites, there is an interest in their application in the development of fuel cells, integrated circuit boards (ICB), and packages for the transportation of integrated circuits [1,2].

The sol-gel process is a chemical route for the preparation of ceramic materials with specific properties difficult or even impossible to obtain by traditional processes, combining the control of composition and structure at molecular level under relatively mild conditions. The synthesis of SiO<sub>2</sub> from liquid silicon metal-organic precursors is probably the most investigated sol-gel process. Typically, it involves hydrolysis and condensation of a metal-organic precursor, such as tetramethoxysilane in an appropriate solvent, such as methanol,

either with or without a catalyst. As the reaction proceeds and the viscosity increases, a gel is formed. It is typically made of  $\equiv\text{Si-O-Si}\equiv$  bonds, which form a network within which the reaction products are trapped. When such products are removed via evaporation, a nanoporous structure results. The reaction conditions, the type and concentration of the precursors, water concentration, pH, temperature, solvent, pressure, and other parameters affect the properties of the gels. The adjustment of these parameters allows the production of a large variety of materials with varying nature, from glasses to ceramic materials and composites in different forms: fibers, thin films, monoliths, powders, and grains [3,4].

Fluoropolymers are characterized by their resistance to chemical attacks and high thermal stability, having a broad range of applications in modern technology, from the manufacture of O-rings for the production of computer chips to communication satellite reflective coatings. Polytetrafluoroethylene – PTFE is a highly ordered linear non-branched chain crystalline fluoropolymer with structure:



Although PTFE is highly stable and hardly degradable, when exposed to ionizing radiation, such as  $\gamma$  radiation or an electron beam, it undergoes physical and chemical property changes [5]. The degradation of PTFE is characterized by competitive and consecutive reaction. Nevertheless, there is no consensus on the exact mechanism of this process [6]. The irradiation atmosphere, dose, and temperature are some of the factors that affect the product obtained. The predominant effect of ionizing radiation on PTFE is the degradation caused by the break of polymeric chains, generating low molecular weight products. This process is initiated by the rupture of the C-C and C-F bonds, forming primary and secondary radicals [5].

The degradation of PTFE by high-energy irradiation with a high dose in presence of oxygen or air gives perfluorinated carboxylic acids, among other compounds. Part of the PTFE is converted into carbonyl difluoride. PTFE hydrophobicity and organophobicity are sensibly reduced by these functional groups, allowing its homogenization by other means, such as aqueous and organic dispersion with polymers, paints, lubricating resins. The functionalized products have been used to incorporate other materials in the production of composites that combine the properties of PTFE with those of conventional materials [6, 7].

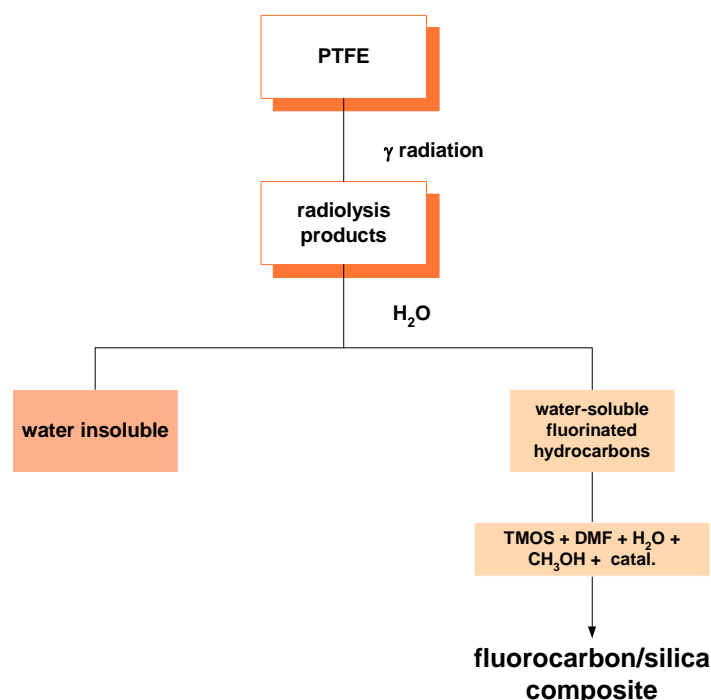
Polytetrafluoroethylene - PTFE - scraps were irradiated with  $\gamma$ -ray from a  $^{60}\text{Co}$  source with approximately 55000 Ci activity at room temperature under wet oxygen atmosphere [8]. Fluorocarbon/silica composites were obtained by the sol-gel method from tetramethoxysilane – TMOS - and water-soluble fluorinated hydrocarbons obtained from irradiated PTFE scraps. After synthesis, the materials were thermally treated in an oven with electronic temperature control.

The monoliths obtained were characterized by Fourier transform infrared spectroscopy (FTIR) and electron microprobe. The specific (BET) surface area [9], total pore volume, and mean pore radius [10, 11] of the dry gels were determined.

## 2. EXPERIMENTAL

Fluorocarbon/silica composites were synthesized by the sol-gel method from water-soluble fluorinated hydrocarbons - with molar masses between  $700 \text{ g.mol}^{-1}$  and  $1500 \text{ g.mol}^{-1}$  and main chains between 10 and 20 carbon atoms -, obtained by the radiolysis of PTFE [8] and using tetramethoxysilane -TMOS - ( $>99\%$  Aldrich, m.w.  $152.22$  and  $\rho = 1.032 \text{ g.ml}^{-1}$ ) as a precursor, and methanol ( $\text{CH}_3\text{OH}$  m.w.  $32.04 \text{ g}$ ,  $\rho = 0.79 \text{ g.ml}^{-1}$ , QM). The reactions were performed in acidic ( $\text{HNO}_3$  p.a., ISO,  $65\%$ , Merck) and basic ( $\text{NH}_4\text{OH}$ ,  $25\%$ , p.a.,  $\rho = 0.91 \text{ g.ml}^{-1}$ , Merck) media. N-N-dimethylformamide - DMF (spectroscopy grade, m.w.  $73.10 \text{ g}$  and  $\rho = 0.95 \text{ g.ml}^{-1}$  from J.T. Baker) was used as drying control chemical additive - DCCA.

Fig. 1 is a flow chart for the syntheses of fluorocarbon/silica composites by sol-gel processing.



**Figure 1. Syntheses of fluorocarbon/silica composites by sol-gel processing.**

The composites were synthesized in borosilicate glass reaction flasks connected to condensers at  $35 \text{ }^\circ\text{C}$  (solutions type I and II) or  $60 \text{ }^\circ\text{C}$  (solutions type III) on an electric hot plate under constant stirring until the homogenization of the mixtures.

For solutions type I and II, the molar ratios of TMOS, DMF,  $\text{CH}_3\text{OH}$ , and  $\text{NH}_4\text{OH}$  were kept constant, while the concentrations of  $\text{H}_2\text{O}$  and the water-soluble fluorinated hydrocarbons, the PTFE radiolysis products, were varied. For solutions type III, the molar ratios of TMOS, DMF,  $\text{CH}_3\text{OH}$ , and  $\text{HNO}_3$  were kept constant, while varying the concentrations of  $\text{H}_2\text{O}$  and

the water-soluble fluorinated hydrocarbons, the PTFE radiolysis products, as shown in Table 1.

**Table 1. Reagents concentrations**

| Solutions<br># | Reagents<br>(molar ratios, except for CF) |     |                    |                   |                      |                  |     |
|----------------|---|-----|--------------------|-------------------|----------------------|------------------|-----|
|                | TMOS                                      | DMF | CH <sub>3</sub> OH | H <sub>2</sub> O‡ | NH <sub>4</sub> OH   | HNO <sub>3</sub> | CF* |
| <b>I</b>       | 1   | 1.4 | 2.7                | 2                 | 3.7x10 <sup>-4</sup> | -                | v▪  |
| <b>II</b>      | 1   | 1.4 | 2.7                | 10                | 3.7x10 <sup>-4</sup> | -                | v▪  |
| <b>III</b>     | 1   | 2   | 1.84               | 10                | -                    | 0.05             | v▪  |

CF\* = water-soluble fluorinated hydrocarbons, PTFE radiolysis products.

‡ = variable (depends on CF amount).

v▪ = from 0 mg to 0.2 mg

The samples were dried in an oven with electronic temperature control. Fig. 2 shows a typical monolith, type I obtained after thermal treatment.



**Figure 2. Fluorocarbon/silica composite, type I after drying at 150 °C.**

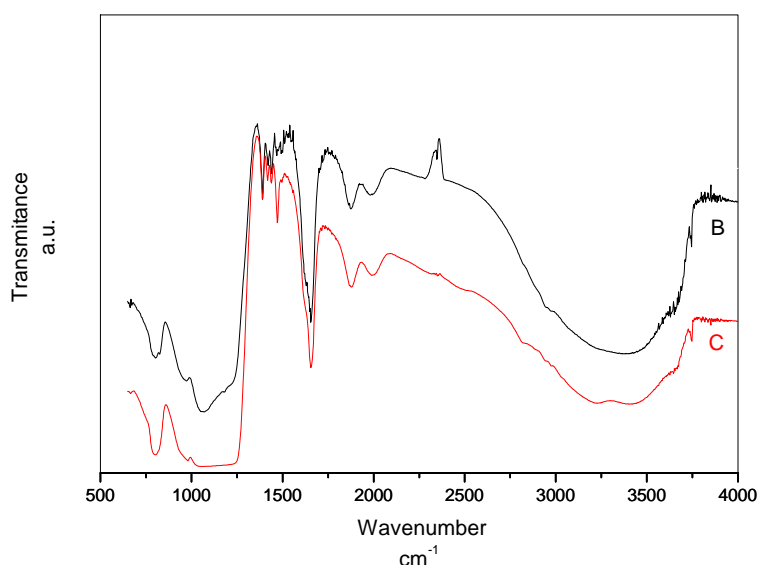
The composites synthesized with higher concentrations of water-soluble fluorinated hydrocarbons obtained by the radiolysis of PTFE were opaque whitish.

### 3. ANALYSIS AND CHARACTERIZATION

#### 3.1. Infrared Spectroscopy

Infrared spectra in the wavenumber range from  $650\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$  were collected in the reflection mode with a Centaurus microscope (magnification 10X, observed region  $150\text{ }\mu\text{m} \times 150\text{ }\mu\text{m}$ ) attached to a FTIR Nicolet - Nexus 470 - spectrometer. The spectral resolution was better than  $4\text{ cm}^{-1}$  and the spectra were averaged over 64 scans. The spectrometer configuration was: ever-glow source, Ge-coated KBr beamsplitter and HgCdTe detector under nitrogen purge. The reference spectra were taken in the standard mirror mode in regions with no organic trace.

In Fig. 3, the spectrum of compound **C**, the composite (type III) with the highest fluorocarbon amount added showed characteristic absorptions due to organic fluorine compounds. A very intense band in the region from  $\sim 1090\text{ cm}^{-1}$  to  $\sim 1260\text{ cm}^{-1}$  can be observed due to the strong C-F coupling and C-C stretching vibration of the polyfluorinated compounds. Functional groups such as  $-\text{CH}_2\text{F}$  give bands in regions  $\sim 3100\text{ cm}^{-1}$  and  $\sim 2900\text{ cm}^{-1}$  [12]. Sample **C** presented a peak around  $1470\text{ cm}^{-1}$ , a low molecular weight perfluorohydrocarbon, FISCHER et al. 1998 [13]. Sample **B** (type III), which also contained water-soluble fluorocompounds ( $\sim 0.1\text{ mg}$ ), presented a small peak in the same region.



**Figure 3. Typical infrared spectra of the obtained composites.**

#### 3.2. Nitrogen Adsorption

Specific surface area and pore size distribution were determined by  $\text{N}_2$  adsorption using the BET and BJH methods [9-11], respectively, in Autosorb Quantachrome Nova 1200. The total pore volume was determined at  $P/P_0 > 0.99$ . The samples were outgassed for 2:00 h at  $120\text{ }^\circ\text{C}$

before analysis. All data analysis were performed using the NovaWin V.10 © 1997-2007 Quantachrome Instruments software.

Table 2 shows the pore structure parameters for type III samples containing different fluorocarbon ratios. A significant difference was observed in the surface area and pore diameter values for these materials, which may be an indication of the presence of fluorocarbons in the silica pore structure. Comparing samples A (type III, without fluorocarbon addition), B and C, we observe that the surface area and the average pore diameter were reduced according to the fluorocarbon increasing.

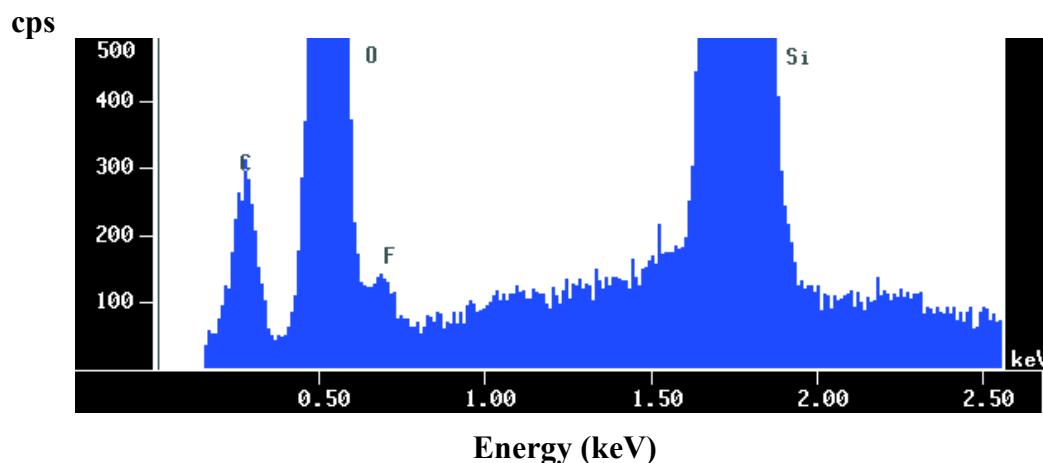
**Table 2. Specific surface area, specific pore volume and average pore diameter**

| Sample | Specific surface area<br>$\text{m}^2 \cdot \text{g}^{-1}$ | Average pore<br>diameter<br>nm | Pore volume<br>$\text{cm}^3 \cdot \text{g}^{-1}$ |
|--------|---|--------------------------------|--|
| A      | 608   | 6.2                            | 1.09   |
| B      | 408   | 8.5                            | 1.16   |
| C      | 255   | 12.3                           | 1.05   |

### 3.3. Electron Microprobe

The analyses were performed in a JEOL JXA apparatus, model 8900RL of the microanalysis laboratory of the UFMG/CDTN consortium operating with electron beam acceleration voltage of 25 kV, current of  $1.2 \times 10^{-10}$  A, and approximate area of  $100 \mu\text{m} \times 100 \mu\text{m}$ .

The electron microprobe was used to determine the elements with atomic numbers higher than 11 that might be present on the surface of the materials. Carbon, silicon, and oxygen were observed, and in the samples containing fluorocarbons, fluoride was also observed. Fig. 4 shows a typical spectrum of a composite containing water-soluble fluorinated hydrocarbons obtained by the radiolysis of PTFE.



**Figure 4. Typical spectrum of fluorocarbon/silica composite obtained with the electron microprobe.**

#### 4. CONCLUSIONS

A significant recycling of scrap PTFE uses the irradiation process to reduce the molecular weight to a range in which it can be comminuted to a micropowder that are compounded into inks, plastics, coatings, lubricants and elastomers. In this work, water-soluble fluorinated hydrocarbons obtained from irradiated PTFE scraps were used to synthesize fluorocarbon/silica composites via sol-gel process, obtaining a composite with high homogeneity. The monoliths obtained were characterized by Fourier transform infrared spectroscopy (FTIR) and electron microprobe. The specific (BET) surface area, total pore volume, and mean pore diameter of dry gels were determined. The addition of fluorocarbon compounds results in a decrease of the specific surface area and the mean pore diameter of the monoliths.

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