

## STRUCTURE AND PROPERTIES OF INORGANIC FILLERS FOR DENTAL COMPOSITES

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The purpose of the present study was to synthesize and evaluate a series of two inorganic fillers based on oxides of elements with high atomic weight, owing to radiopaque effects, used for dental materials. The obtained inorganic fillers were characterized by BET specific surface. The crystalline phases were identified using X-ray diffraction analysis. Interfacial bonding and stability of  $\gamma$ -methacryl-oxypropyl-trimethoxy-silane with glass surface have been studied by means of differential thermal analysis and infrared spectroscopy.

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### 1. Introduction

Modern dental composite materials are a blend of glass or ceramic particles dispersed in a photo-polymerisable synthetic organic resin matrix. The polymer materials are blended together with the finely divided inorganic material such as a barium aluminosilicate glass or other glass compositions having an effective amount of radiopaque oxide that renders the resultant glass radiopaque to X-rays. The quick development of this domain is supported by the challenges of materials science with respect to functionally graded materials [1-5].

Generally the new dental composites consist of a paste created by combining a mixture of cross-linking agents with up to 80 wt % silane-coated glass or ceramic particles (the filler) whose sizes range from 0.04 to 4  $\mu\text{m}$ . Silane is a coupling agent used to promote adhesion on the surface of minerals such as glass or ceramic and also on the surface of organic polymers such as epoxy, polyester or metacrylate resins. In spite of the large number of dental composite materials appeared during the past 15 years, they are all combinations of silane-coated inorganic filler particles. Usually the filler particles are either barium silicate glass, quartz or zirconium silicate, often combined with very small-sized particles of colloidal silica.

The aim of this study is the preparation and characterization of two inorganic fillers and the evidencing of the effect – of the silane agent put on these fillers.

### 2. Experimental

The experimental purpose was to synthesise two types of fillers ( $N_1$ ,  $N_2$ ) with high specific surface area. The samples were prepared by sol-gel method and powder sintering methods. The chemical composition and sintering conditions are presented in Table 1.

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Table 1. Chemical composition (wt%), sintering conditions and specific surface area.

Oxides /fillers	N <sub>1</sub>	N <sub>2</sub>
SiO <sub>2</sub>	-	72.8
ZrO <sub>2</sub>	50	27.2
La <sub>2</sub> O <sub>3</sub>	50	-
Sintering temperature (°C)	900	1200
Specific surface area (m <sup>2</sup> /g)	54.2	75.2

In order to obtain filler materials the sintered samples were provided by silanation with 3-methacryloxypropyl - 1 - trimethoxy - silane (silane A-174). Silanation was carried out in acidulated ethanol-water solution of silane A-174. The ratio of ethanol to water was 9/1. The solution was acidulated at pH 3.5-4 using acetic acid to provide the hydrolysis of methoxy groups of the silane to silanol groups. The amount of silane coupling agent (X) used for the filler treatment was determined using the relationship proposed by Arkles [6]:

$$X=A \times f / \omega$$

where X is the amount of coupling agent in grams needed to obtain minimum uniform coverage, f is the amount of filler (g), A is the surface area of the filler (m<sup>2</sup>/g) and  $\omega$  is the wetting surface of silane (m<sup>2</sup>/g), (for silane A 174 the value of  $\omega$  is 314 m<sup>2</sup>/g). X g silane and 470 g ethanolic solution were stirred and added to the f grams of filler in a mill. The silanised fillers were initially washed with acetone to remove the absorbed free silane and to keep only the chemisorbed one.

An important characteristic of the filler is the surface particles area. The smaller the particle size, the larger is the surface area. BET surface area method was used for specific surface area determination.

X-ray diffraction (XRD) analysis was used to identify the crystalline phases developed in fillers during sintering process. XRD patterns were recorded by means of standard DRON-3M powder diffractometer.

Thermal analysis and infrared spectroscopy were used to check the silanation achievement. Thermal analysis measurements were carried out using a MOM equipment in the temperature range 20-1000 °C, with a rate of 10 °C/min. The IR spectra were registered on a JASCO-610 FTIR spectrometer using the KBr disk technique.

### 3. Results and discussion

The specific surface areas are 52.4 m<sup>2</sup>/g for N<sub>1</sub> respectively 75.2 m<sup>2</sup>/g for N<sub>2</sub> sample (Table 1). These are convenient values, having in view that the surface area of filler particles for a number of commercial composites ranges from 4.4 to 65.6 m<sup>2</sup>/g.

The thermal analysis data (Fig. 1) show that the silanation was accomplished only for N<sub>1</sub> sample as indicated by the exothermal peak corresponding to silane decomposition. DTA runs do not evidence any other thermal events up to 1200 °C.

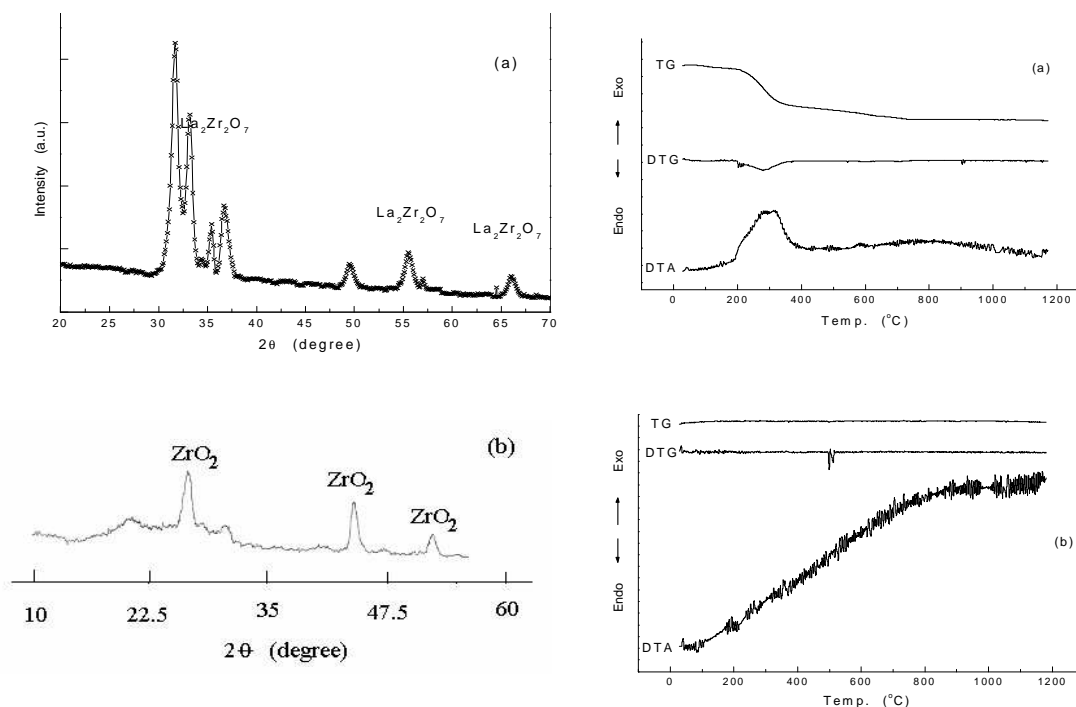


Fig. 1. DRX patterns and DTA curves for (a) N<sub>1</sub> and (b) N<sub>2</sub> samples.

X-ray diffraction patterns (Fig. 1) evidence the development of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and ZrO<sub>2</sub> crystalline phases for N<sub>1</sub> respectively N<sub>2</sub> fillers. In Fig. 1 there are marked the main maximums of diffraction for the La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> particles of N<sub>1</sub> filler powder. This crystalline compound gives diffraction lines situated at 2θ diffraction angle of 33.45° for the 3.11 Å interplanar distance, 55.70° for the 1.91 Å interplanar distance and 66.41° for 1.63 Å interplanar distance. From the diffraction spectrum matching the N<sub>2</sub> powder, treated at temperatures up to 1200 °C, the existence of ZrO<sub>2</sub> crystalline phase was traced at 2θ = 27.3°, 45.2° and 53.6° with corresponding interplanar distances of 3.26, 2.01 and respectively 1.71 Å.

Fig. 2 shows the IR absorption spectra of silanised filler N<sub>1</sub> and unsilanised filler N<sub>2</sub>. The bands recorded in the spectral range 2800 - 3000 cm<sup>-1</sup> are due to asymmetrical and symmetrical stretching vibrations of the CH<sub>3</sub> (2954 and 2888 cm<sup>-1</sup>) and CH<sub>2</sub> (2927 and 2859 cm<sup>-1</sup>) groups from A 174 silanisation agent. The presence of methacrylic group is confirmed by the intense absorption band at 1720 cm<sup>-1</sup> assigned to ν(C=O) bond and the 1636 cm<sup>-1</sup> band assigned to ν(C=C) bond.

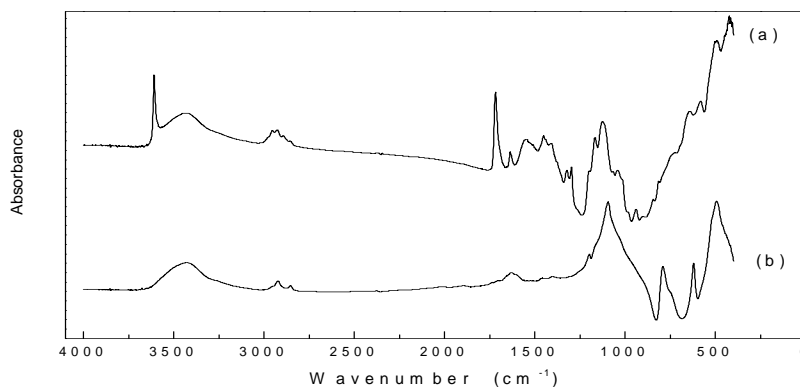


Fig. 2. IR spectra of (a) silanised N<sub>1</sub> and (b) unsilanised N<sub>2</sub> filler.

Important modifications in the 1000-1200  $\text{cm}^{-1}$  range show the formation of Si-O bonds as a result of filler silanisation. The 470  $\text{cm}^{-1}$  band from unsilanised sample is assigned to Si-O-Si bend vibration [7]. In the IR spectrum of  $\text{N}_2$  filler the intense band recorded at 1094  $\text{cm}^{-1}$ , is assigned to Si-O stretching vibrations and its broadening to lower wavenumbers is correlated with the tendency of increasing of nonbridging oxygen atoms. The IR bands at 785 and 618  $\text{cm}^{-1}$  could be assigned to Zr-O stretching vibrations [8], while the intense band at 494  $\text{cm}^{-1}$  is the superposition result of stretching Zr-O and deformation Si-O-S vibrations.

#### 4. Conclusions

The results point out that the not silanised  $\text{N}_2$  samples are not good as fillers.  $\text{N}_1$  samples are silanised, have specific surface area 52.4  $\text{m}^2/\text{g}$ , contain  $\text{La}_2\text{Zr}_2\text{O}_7$  crystalline phase and specific filler properties that recommend them for radiopaque dental composite materials.

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