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STRUCTURAL ANALYSIS ON PHOTOPOLYMERIZED COMMERCIAL DENTAL COMPOSITES

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În acest studiu sunt prezentate principalele caracteristici ale unor compozite dentare disponibile comercial, obtinute prin tehnici avansate (SEM, EDAX, XRD, TGA, DTG).

Selecția materialelor a fost făcută funcție de compoziția rășinii (doi, trei sau patru monomeri), dimensiunea particulelor şi morfologia acestora. Au fost analizate 3 tipuri de compozite fotopolimerizabile: Venus (Heraeus Kulzer, Germany), Tetric Ceram (Ivoclar Vivadent, Liechtenstein), Filtek Supreme (3M ESPE, USA). Scopul studiului a fost compararea morfologiei acestora precum si al compoziției chimice şi mineralogice. Rezultatele obtinute ar putea constitui o bază de plecare pentru realizarea unor compozite superioare.

In this paper are reported the main characteristics of some commercially available dental composites, resulted from advanced techniques (SEM, EDAX, XRD, TGA, DTG).

The selection of materials for this investigation was based on the resin composition (two, three or four monomers), filler size and morphology. Three visible-light-cured composites were used: Venus (Heraeus Kulzer, Germany), Tetric Ceram (Ivoclar Vivadent, Liechtenstein), Filtek Supreme (3M ESPE, USA). The aim of this study was to compare their morphology and chemical-mineralogical compositions. The obtained results could be an excellent starting point in designing superior composites.

Keywords: dental composites, dimethacrylate, filler, organosilane

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1. Introduction

The majority of dental resin composites are hybrid materials consisting of polymer groups that are reinforced by an inorganic phase of glass fillers which may have different compositions, particle sizes and filler percentages. In simplified terms, dental resin composites are derived from three chemically different materials:

- Organic matrix or organic phase;
- Filler or disperse phase
- Organosilane or coupling agent to bond the filler particles to the organic matrix

Filler particles vary considerably in respect of their chemical composition (SiO_2, ZrO_2, zirconium silicate, barium zirconate, barium aluminum fluoride glass, YbF_3), morphology and dimensions. [1, 2, 3]

The most common coupling agents are organic silicon compounds called silanes. The silane accomplishes coupling as follows: the methoxy groups on the silane hydrolyse to -OH groups (eliminating CH_3OH), which react with the adsorbed moisture (-OH groups) on the filler, to form covalent Si-O-Si bonds (eliminating H_2O) on the glass surfaces. During the setting reaction of the organic resin matrix the methacryloyl groups of the silane react with the resin and hence form bonds between the filler and resin (Fig. 1) [4, 5, 6, 7]:

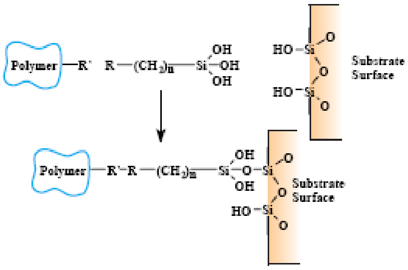

Fig. 1. Simplified reaction of organosilane with silica surfaces and polymer matrix

In the applied commercial resin-based composite restoratives, mixtures of cross-linking dimethacrylates are used as organic resins because dimethacrylates give rise to the formation of a polymer network. The most popular cross-linking dental dimethacrylate is ***bisphenol – A glycerolate dimethacrylate (Bis-GMA)***. This resin had some important advantages, including reduced shrinkage during polymerization and the ability to form cross-links (which are stronger than linear polymers) during polymerization [8, 9].

However, the higher viscosity of BIS-GMA made it more difficult to incorporate more filler and to mix the cured composite. To solve this problem, different monomers with lower viscosities were added: ***ethoxylated bisphenol A***

dimethacrylate (Bis-EMA), urethane dimethacrylate (UDMA), triethylene glycol dimethacrylate (TEGDMA) (Fig. 2). [10, 11]

The organic phase contains the photo-initiating system: camphorquinone which undergoes a redox reaction with the reducing agent (a tertiary amine) to produce radicals for free radical polymerization of the dental composites.

During the crosslinking reaction a 3D network composed of randomly dispersed filler particles is formed (Fig. 3).

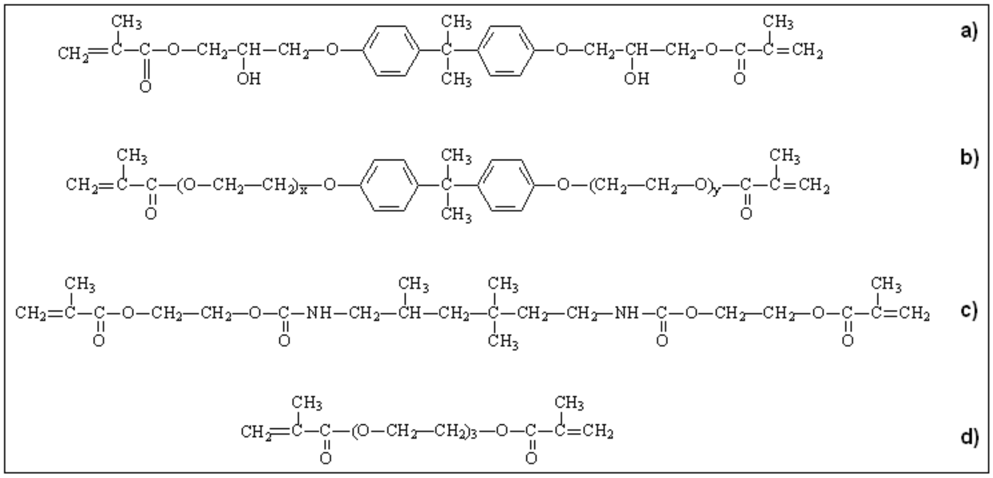

Fig. 2. Chemical structures of the monomers used to formulate the resins: a) Bisphenol – A glycerolate dimethacrylate (Bis-GMA); b) Ethoxylated bisphenol A dimethacrylate (Bis-EMA); c) Urethane dimethacrylate (UDMA); d) Triethylene glycol dimethacrylate (TEGDMA)

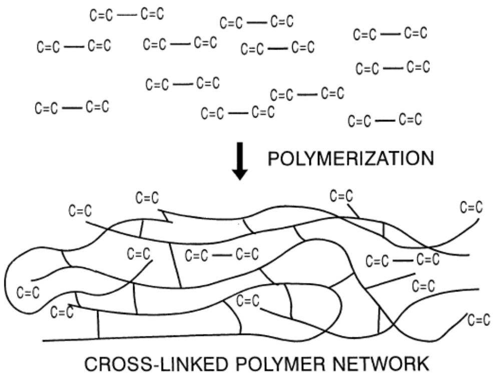

Fig. 3. The crosslinking reaction

2. Materials and methods

2.1. Selection of materials

Three commercially available resin composites were used in this study. The selection of materials for this investigation was based on the resin composition (two, three or four monomers), filler size and morphology (Table 1). Venus (hybrid resin composite), Tetric Ceram (micro-filled/hybrid resin composite) and Filtek Supreme (nano-particle resin composite) were selected for the experimental groups.

Table 1

The materials investigated and their composition

Composites	Resin	Filler	Wt %	Vol %	Size
Venus *(Heraeus Kulzer)*	BisGMA, TEGDMA	Barium aluminum fluoride glass Silicon dioxide Calcium (traces)	78	61	0.7-2 µm 0.01-0.04 µm
Tetric Ceram *(Ivoclar Vivadent)*	BisGMA, TEGDMA, UDMA	Barium aluminum fluoride glass Silicon dioxide YbF_3	78	68	0.7 µm
Filtek Supreme nanofilled *(3M ESPE)*	BisGMA, BisEMA, UDMA, TEGDMA	Zirconia/silica Silica	78.5	59.5	0.6-1.4 µm cluster 5-20 nm particle 20 nm silica

2.2 Samples preparation

The samples were prepared using PTFE (polytetrafluoroethylene) moulds which allowed the production of cured specimens (thickness = 2mm). After inserting the materials into the moulds, a transparent polyester strip was placed on top of them in order to avoid the oxygen-inhibited superficial layer with lower hardness. Visible light was radiated to top surfaces, using an commercial Led Emitting Diode (LED) device for 60s. This curing unit has a light intensity of approximately 700 mW/cm^2 and emits light in the wavelength range of 430-480 nm. After polymerization, the composite was carefully removed from the mould.

Fig. 4. LED device and the restorative material protrude from the syringe

2.3 Samples characterization

The morphology of composites was examined by scanning electron microscopy (SEM) with an HITACHI S2600N equipment. Prior to SEM examination, the specimens were sputter-coated with silver in order to avoid charge accumulation. The SEM images have been accomplished at electron acceleration voltage of 25 kV, up to 5 μm resolution with a magnification between 1000x...10.000x. For all the samples a selection of the most eloquent micrographs was carried out (5000x and 10 000x magnification, 5 and 10 μm resolution).

After SEM images catching the samples were qualitatively analysed throught EDAX (energy dispersive X-ray analysis). Due to Ag coating of the samples, all EDAX spectra show the Ag peak.

To identify the mineralogical composition of the different crystalline phases, X-ray diffraction (XRD) analyses were done (XRD-6000 SHIMATZU diffractometer, scanning domain 2θ = 5 - 65°)

Thermal decomposition profiles of the composites were recorded using a TA Q500 equipment. 10 milligrams of each specimen was heated from 30° up to 600°C, at the rate of 20°C/min, in N_2 atmosphere (gas flow 40ml/min). After each measurement, the machine was cooled to below 30°C.

3. Results and Discussion

SEM micrographs and EDAX spectra of the studied composites are presented in Figs. 5-7.

For Venus composite, the SEM images show a uniform mophology with small (0.01-0.04 μm) and large (0.5-2 μm) particles trapped in the continuous matrix. From the EDAX spectrum can be observed that, in addition to the usual elements founds in dental composites (barium, silicon, aluminium), it also contains calcium, which improve the biocompatibility with the dental tissues (Fig. 5).

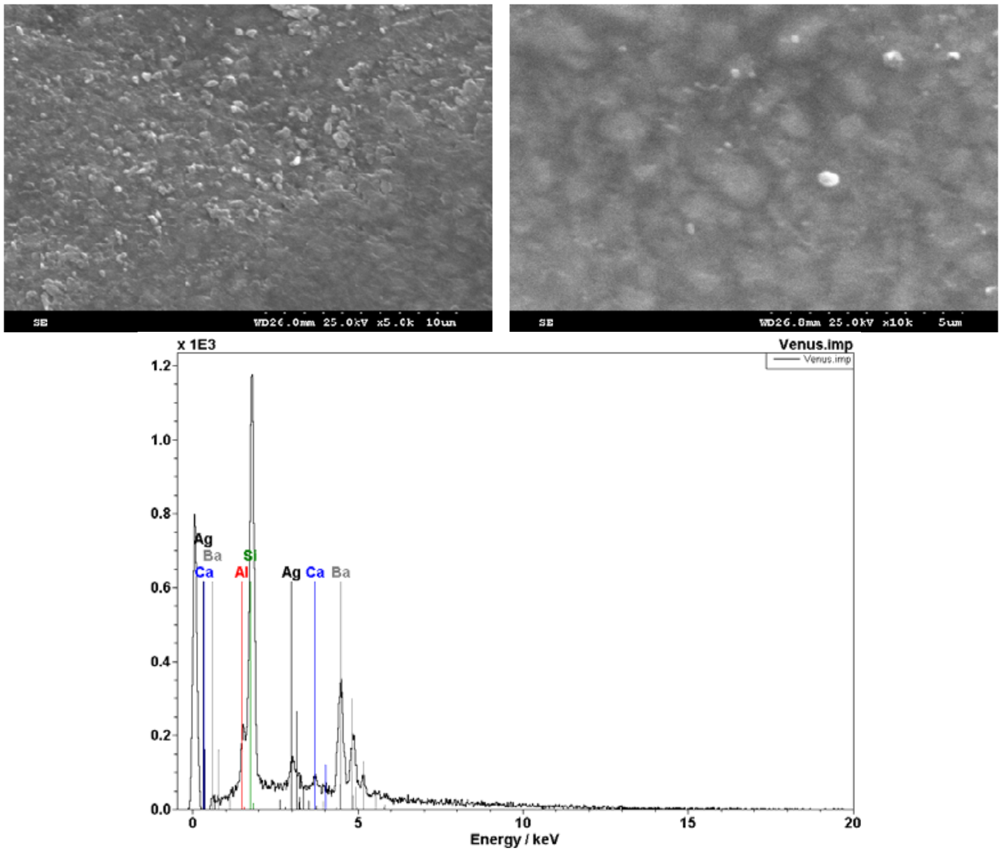

Fig. 5. SEM micrographs and EDAX spectrum for Venus composite

For Tetric Ceram composite, the SEM images reveal a remarkable structural homogeneity due to small size of the particles. The EDAX spectrum shows the same elements as in Venus composite, but we can find additionally ytterbium (Fig. 6). Also, it can be observed the high percentage of filler loading, every particle being surrounded by a continuous organic film. This thing is important in order to improve the mechanical properties and to obtain a high stability in the oral medium.

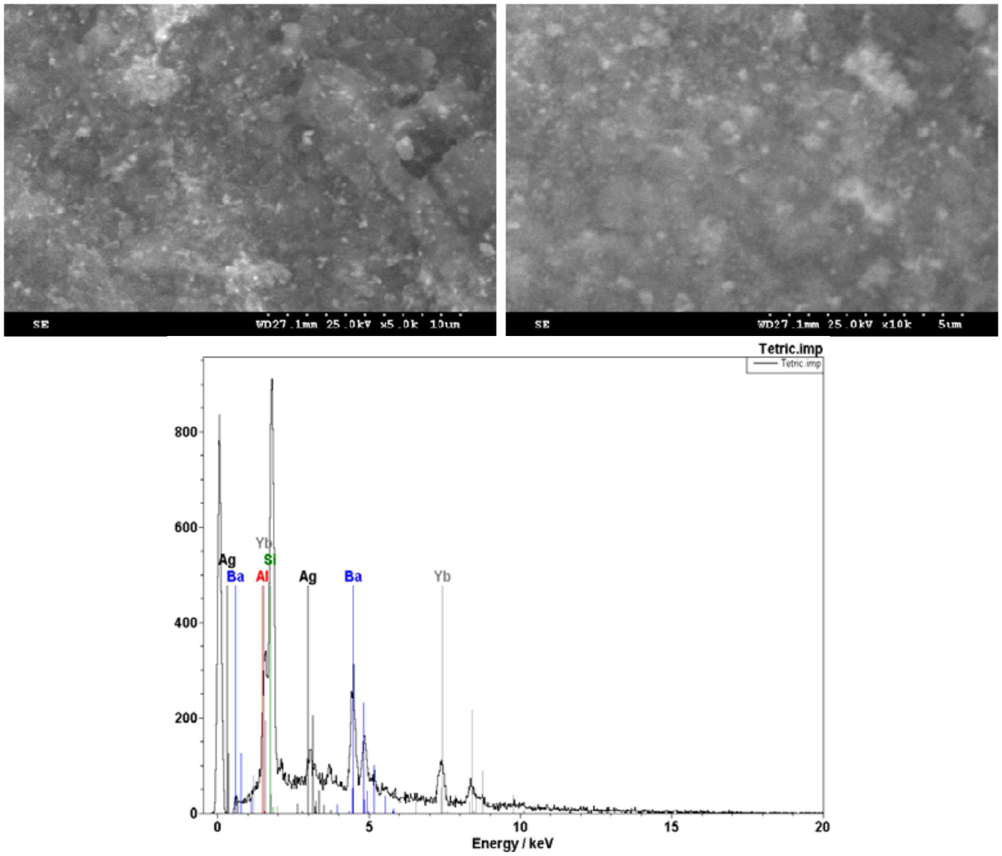

Fig. 6. SEM micrographs and EDAX spectrum for Tetric Ceram composite

The Filtek Supreme is a nanocomposites based on a combination of nanoparticles (individual nanoparticles of monodispersed silica, 5-20 nm) and nanoclusters.

From the corresponding SEM micrographs (Fig. 7) it can be observed two types of nanoclusters. One type of nanocluster consists of agglomerates of primary zirconia/silica nanoparticles. The size of particles from the nanoclusters varies among 2 – 20 nm, while the spherical conglomerates are between 0.6-1.4 µm. The second type of nanoclusters, made of silica particles (75 nm), have the same diameter with the first one (0.6 µm).

The EDAX spectrum prove a different filler composition in comparison with Venus and Tetric Ceram composites: silicon is found, but barium and aluminium oxides are substituted by zirconia.

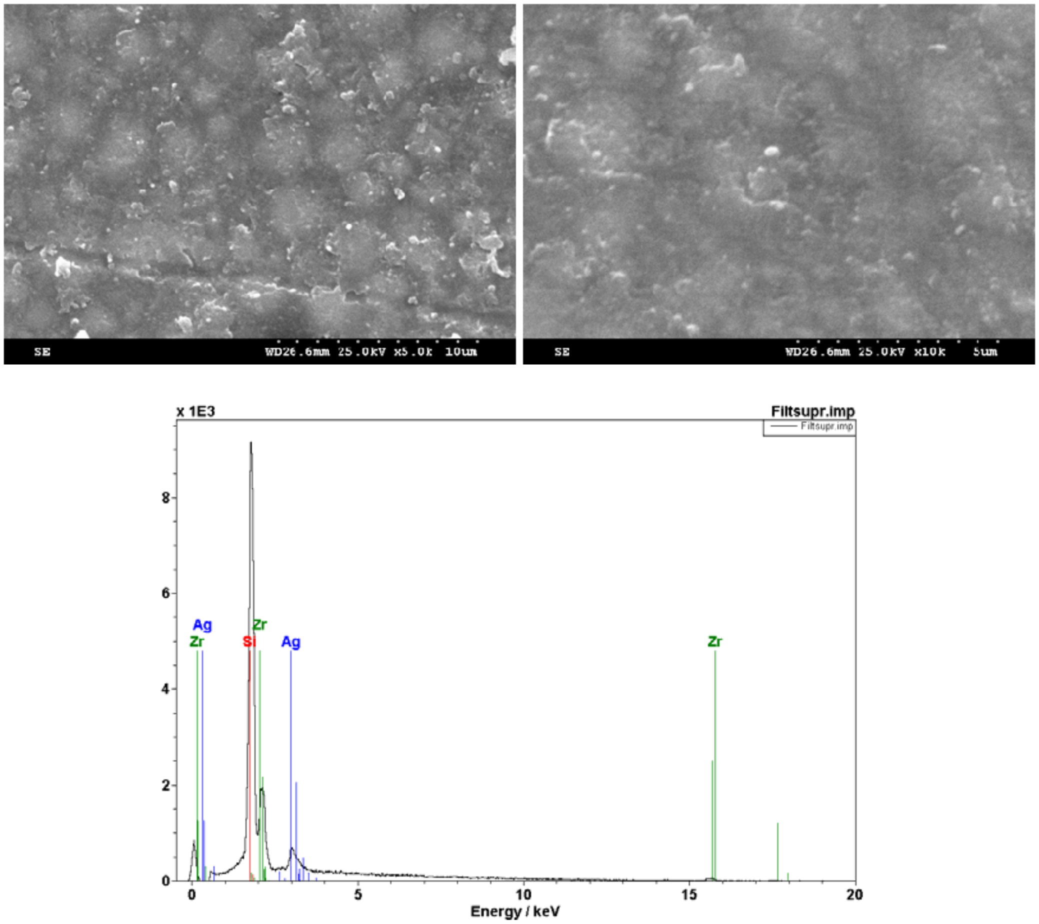

Fig. 7. SEM micrographs and EDAX spectrum for Filtek composite

The XRD patterns of the composites (Fig. 8-10) show a good correlation with EDAX spectra and with SEM images.

The XRD pattern for Venus composite (Fig. 8) sugests a predominantly amorphous character through presence of the halo in the small angles range (2θ = 15 - 35°); also, could be observed roentgen ray interferences with a reduced intensity, which sugests an incipient occurrence of some mineralogical phases, like:

- silica (SiO_2 – 4.48 Å, 4.25 Å, 4.03 Å and 3.94 Å) and barium ortosilica ($2BaO\cdot SiO_2$ – 3.79 Å, 3.69 Å, 3.52 Å, 3.02 Å, 2.92 Å şi 2.87 Å);
- fluorinated compounds: BaF_2 (3.57 Å, 3.10 Å, 2.20 Å and 1.87 Å) and CaF_2 (3.14 Å, 1.92 Å and 1.63 Å). The fluorinated compounds observed in spectra, have the role to improve the biocompatibility and give a decay profilaxis effect to the material.

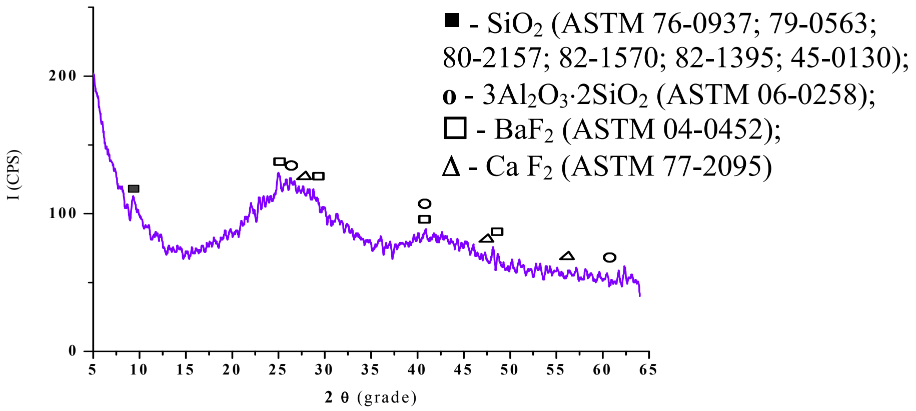

Fig. 8. XRD pattern for Venus composite

In Fig. 9 is presented the XRD pattern for Tetric Ceram composite. The sample contains a mineral powder rich in fluorine (YbF_3 – 3.61 Å, 3.39 Å, 3.18 Å, 2.82 Å, 2.47 Å, 2.03 Å, 1.99 Å, 1.91 Å, 1.87 Å, and BaF_2 – 3.6 Å, 3.10 Å, 1.87 Å, 1.55 Å). Yterbium confers an optimum radiopacity, and in association in YbF_3 presents decay profilaxis properties.

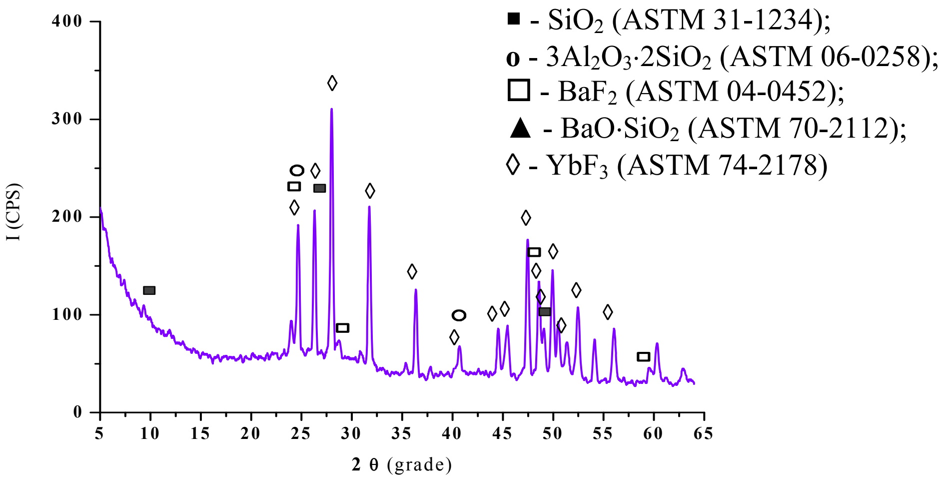

Fig. 9. XRD pattern for Tetric Ceram composite

In Fig. 10 is presented the XRD pattern for Filtek Supreme composite. This specimen contains cubic ZrO_2 (2.96 Å, 2.56 Å, 1.81 Å, 1.54 Å), tetragonal ZrO_2 (2.92 Å, 2.57 Å, 1.83 Å, 1.80 Å, 1.55 Å) and SiO_2 (3.99 Å, 2.55 Å, 2.02 Å). The XRD pattern configuration in correlation with SEM images reveal that in

Filtek Supreme composite the mineral powder presents a lower structural degree; this could explain the nanoclusters formation.

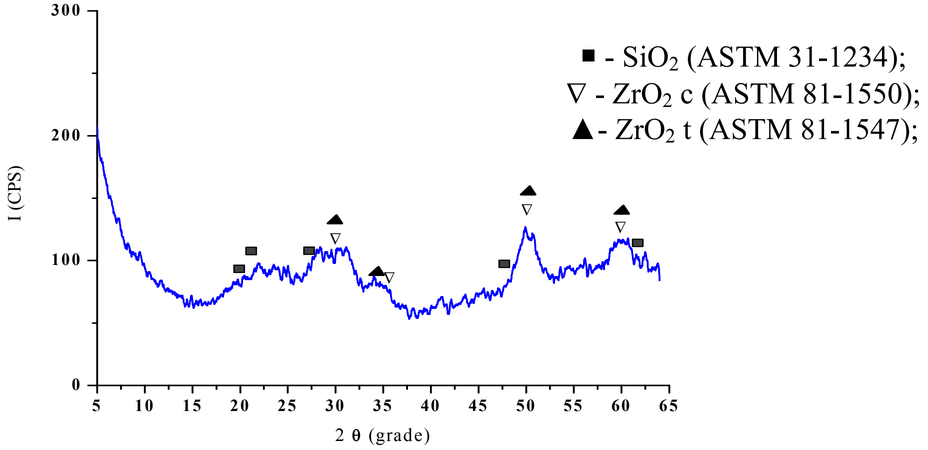

Fig. 10 XRD pattern for Filtek Supreme composite

In Figs. 11 are presented DTG curves of dental composites. The samples were heated from room temperature (23°) up to 600°.

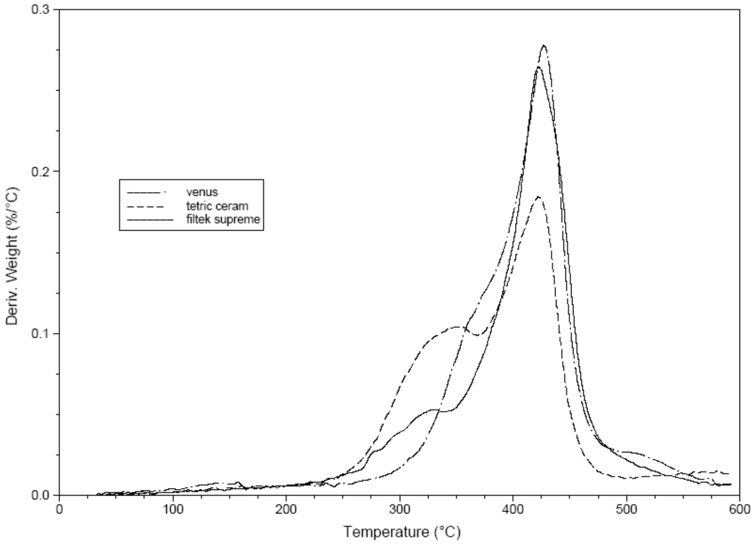

Fig. 11. DTG curves for the studied dental composites

The weight loss (Table 2) from the TG curve is attributed to organic resins because the innorganic filler, mainly made from silica, is stable at high temperatures.

Table 2

Thermal degradation behaviour for the dental composites

Composite	Weight loss (%)	T_{in} (^oC)	$T_{max.}$ (^oC)
VENUS	24.54	305.6	426.76
TETRIC CERAM	22.01	254.21	352; 422.98
FILTEK SUPREME	23.38	240	422.22

It can be observed that the studied composites are stable under 250^{o}C. After 250°C the degradation process starts. Tetric Ceram has the lowest weight loss (22 %) because of the high percentage of filler particles (68 %v).

The thermal behaviour of dental composites was found to be complex and strongly dependent on the:

- different monomers proportions in the resin composition;
- ratio between monomers/fillers;
- thermal stability of the coupling agent

6. Conclusions

The adding of inorganic filler is required in order to increase the material resistance, that allow to be used in posterior restorations, with high masticatory forces.

The composite resin properties and in vivo performances are strongly influenced by the type of matrix polymer, percentage of filler particles, filler particle size, morphology and chemical composition (SiO_2, ZrO_2, zirconium silicate, barium zirconate, barium aluminum fluoride glass, YbF_3).

R E F E R E N C E S

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