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STUDY ON THERMAL BEHAVIOUR, STRUCTURE AND FILLER MORPHOLOGY OF SOME INDIRECT COMPOSITE RESINS

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Thermal behaviour, microstructure and filler morphology of an experimental indirect composite resin C20 were evaluated in comparison with four trade- mark composite materials for inlays, namely Premise Indirect (PI), Gradia (GD), Ceramage (CG) and Signum Ceramis (SC). The investigations were performed using scanning electron microscopy (SEM), thermogravimetric analysis (TGA) and infrared spectroscopy (FT-IR). TGA shows that C20 presents a higher filler loading (71.3 wt%) then the majority of the trade- mark composites i.e. GD, CG and SC. Premise Indirect contains the highest filler amount (81.2 wt%). FT-IR confirmed that all the composite materials contain an organic matrix based on polymethyl methacrylate network and a SiO_2-based inorganic filler. SEM investigation revealed that the inorganic filler of the experimental material C20 is similar to the one of the Premise Indirect. Both materials are nano-hybrid composites consisting of agglomerates of spherical nano-sized particles and irregular microparticles. The spherical shaped particles allow a higher filler loading, as already indicated by the thermal analysis. The investigations showed that the experimental material has similar characteristics with the majority of the investigated indirect composites.

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Keywords: Indirect composite resin; Thermogravimetric analysis; Infrared spectroscopy; Filler morphology

1. Introduction

Composite resins were introduced in dentistry about 50 years ago and since then they have continuously developed becoming one of the main topics for research in the attempt to improve their properties and expand their clinical application [1-6].

Research on composite resins is focused either on the resin matrix, trying to develop new monomers or on the filler regarding the loading, particle size, silanization and the development of new composition. These studies are important because the mechanical and physical properties of dental composites are influenced by changes in composition and amount of resin matrix, as well as

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concentration, size and distribution of filler particles [7]. Current research on composite resins has led to the development of new materials with reduced filler particle size and increased loading [8].

The traditional composites for restorative dentistry are hybrid or microfilled materials. The hybrid composites contain filler with particles of different sizes, which offer intermediate esthetic properties and excellent mechanical properties. The microfilled materials are formulated with colloidal silica (around 50% in volume), with an average particle size of 0.02 μm. They were developed to improve the aesthetics of composite resins, but their mechanical properties are considered low for restoring regions with high occlusal forces [9,10].

The latest advance in the field is the application of nanotechnology to resin composites, that implies the creation and manipulation of materials and structures in the range of 0.1-100 nanometers by various chemical and physical methods [7,8].

There are two types of nanocomposites available, nanohybrid composites containing milled glass fillers (fine particles) and discrete nanoparticles (40-90 nm), and nanofilled composites, containing nano-sized particles and agglomeration of these particles called “nanoclusters”[9,11]. The nanocomposites combine the good mechanical properties of the hybrids and the superior aesthetics of the microfills [9]. They also present high wear resistance [12], improved optical characteristics and reduced polymerization shrinkage [9,13]. Consequently, manufacturers recommend the use of nanocomposites for both anterior and posterior restorations [7].

There are two categories of composite resins, that are direct and indirect composites. The latter, known also as laboratory processed composites were developed for indirect restorations (inlay) to overcome the deficiencies of direct composites in restoring large cavities, when the direct technique is exceeded because of the polymerization shrinkage of the resin [2,14].The first generation of indirect composites was introduced in the 1980s [2] and since then they continued to develop and improve the clinical performances, leading to the introduction of the second generation of materials with improved structure, composition and polymerization technique. They include materials with microhybrid (diameter of 0.04-1 μ) and nanohybrid filler or nanofilled composite, with increased filler loading, reduced organic matrix and consequently, with improved mechanical, physical and optical properties [2].

This study continues our previous researches with the purpose to develop new indirect and direct composite resins with improved properties [3, 5, 15]. The goal is to present some general characterization i.e. thermal behaviour, microstructure and particle morphology, of an experimental dental material for inlays, in comparison with four commercially available indirect composite materials. The characterization was performed by thermogravimetric analysis, infrared spectroscopy and scanning electron microscopy.

2. Experimental

2.1. Materials

One experimental and four commercially available indirect composite resins were tested in this study. The restorative materials under investigation and their main characteristics, as given by the manufacturers, are summarized in Table 1.

Table 1. Indirect composite resins and their main characteristics, as given by the manufacturer

Material	Manufacturer	Code	Type*	Organic Matrix*	Filler*
Experimental material	ICCRR, Cluj-Napoca, Romania	C20	Nano-hybrid	Bis-GMA UDMA TEGDMA	Hybrid filler (80 wt%): *Barium- based glass (20%) * NP-Silica (30 wt%); * FP-Quartz (30 wt%); * Zn-HAP (20 wt%)
Premise Indirect	Kerr Company Orange, CA, USA	PI	Nano-hybrid	Bis-GMA TEGDMA	Trimodal filler system (84wt%): *PPF-Pre-Polymerised Filler * FP-Barium-based glass, * NP- Silica
Gradia	GC Corporation, Tokyo,Japan	GD	micro-filled (MFR)	UDMA-based resin	Trimodal filler system (75wt%): *PPF-Pre-Polymerised Filler; * FP-Aluminoborosilicate glass * NP-Silica
Ceramage	ShofuInc, Kyoto, Japan	CG	Micro-hybrid	UDMA-based resin	Progressive Fine Structured filler (>73 wt%) * Zirconium Silicate
Signum Ceramis	Heraeus-Kulzer, Hanau,Germany	SC	Nano-hybrid	Resin based on multifunctional methacrylic esters	Glass-ceramic filler (73 wt%) *NP- Silica *FP-Inorganic filler

*Composition according to references [16,17] for Premise Indirect, [18-20] for Gradia, [21, 22] for Ceramage and [23, 24] for Signum Ceramis; Bis-GMA= Bisphenol glycidyl dimethacrylate; UDMA=Urethane dimethacrylate;TEGDMA = Triethylene glycol methacrylate; NP=nanoparticles; Zn-HAP = zinc substituted hidroxyapatite; FP- fine particles;

The experimental composite resin C20 was manufactured at “Raluca Ripan” Institute for Research in Chemistry (ICCRR), Babes Bolyai University, Cluj-Napoca, Romania. The experimental material is derived from another experimental indirect composite Barodent, investigated in other studies [15]. The organic matrix was prepared from the same monomers, that is Bis-GMA (Bisphenol A glycidyl dimethacrylate), UDMA (Urethane dimethacrylate) and TEGDMA (Triethylene glycol methacrylate), using the same light -curing promoters and inhibitors. The inorganic filler was modified by replacing part of the barium-based glass with zinc substituted hidroxyapatite (Zn-HAP), with the purpose to increase the filler loading and enhance the materials mechanical and physical properties. Thus, the new experimental material C20 contains 80 wt% filler amount formed from barium-based glass (fine particles), silica (nanoparticles), quartz (fine particles) and zinc substituted hidroxyapatite (nanostructured). Excepting the Zn-HAP powder (a ceramic material), all the other components were silanized. The experimental composite resin was obtained according to the procedure described in Romanian patents (see RO119112, RO122833 and RO122440).

For each of the investigated materials, bar-shaped specimens (2 mm length, 2 mm width, 2 mm height) were fabricated by placing the composite resin into a silicone mould and covering it with a plastic foil. The specimens were light-cured for 20 seconds from one side using a light activation unit (Demi LED Curing Unit, Kerr Corporation, Orange, CA, USA). Then they were removed from the mould and subjected to a post-curing protocol, according to the manufacturer’s instructions as follows: the experimental C20 and Premise Indirect materials were additionally polymerized using a heat and pressure curing protocol**,** while Gradia, Ceramage and Signum Ceramis were additionally light-cured in special curing units.

2.2.Characterization of the dental materials

Thermogravimetric analysis. The thermal behaviour of the indirect composite resins was investigated by thermogravimetric analysis (TGA), using a Mettler Toledo TGA/ SDTA851 instrument. For this purpose, the bar-shaped specimens were minced into small fragments and samples of 30-35 mg were heated, in alumina crucibles, from room temperature to 1000 °C, at a rate of 20 °C/min. The heating was performed in nitrogen atmosphere (35 mL/min), with air purging (35 mL/min) at 650 °C. Thermogravimetric (TG) and differential termogravimetric (DTG) analysis were used to monitor the mass changes with temperature.

Scanning electron microscopy: The morphology of the filler particles was determined using scanning electron microscopy (SEM) with a Quanta 3D (FEI Eindhoven, NL) Microscope, at 30 kV. SEM investigation was performed on both fractured and calcined composite materials. For this, bar-shaped specimens were prepared from each of the tested materials and fractured in small pieces. Some of them were calcined in air, at 750°C, in order to remove the organic matrix. The fractured and calcined pieces of the composites were sputter-coated with gold, using an Automatic Sputter Coater-(AGAR Scientific).

Infrared spectroscopy. Fourier transform infrared spectroscopy (FT-IR) was conducted using solid phase analysis, in the mid-infrared spectral range. A Nicolet 6700 FT-IR Spectrometer (ThermoScientific, USA) running the OMNIC^{TM} software was used to collect the infrared spectra, which utilized the selected range of 400 to 4000 cm-1, with a spectral resolution of 0.125 cm^{-1}. In the study, potassium bromide (KBr) pellet technique has been used in the identification procedures. The quantity of about 0.1 mg dry tested compound was mixed with potassium bromide of about 30 mg and ground mechanically in the agate mortar. The mixture was exposed to the pressure of approximately 1.75 tons in a press to produce a thin disk of ~7 mm.

3. Results and discussion

The present study is dedicated to the general characterization i.e. thermal behaviour, (micro)structure and particle morphology, of one experimental composite resin for indirect restorations (inlays), in comparison with four already known similar materials (Table 1).

3.1. Thermal behaviour of the dental materials

In order to determine the amount of filler particles and the thermal behaviour of the organic matrix, the composite materials were investigated by thermal analysis. Thermogravimetric analysis was utilized to accurately measure the variation of the specimen mass as temperature was increased, to monitor the thermal degradation of the resin and to evaluate the quantity of residuum left after organics removal. TGA investigations allow to identify all the temperature-dependent mass changes of the organic matrix and inorganic filler during the sample heating (TG curves) and to locate the points of maximum degradation rate (peaks on DTG curves). In order to simultaneously evaluate the thermal behaviour of the resin and the amount of inorganic residuum, the measurements were carried out in nitrogen up to 650°C and in air above this temperature. The air purging removes the carbonaceous depot left after the thermal degradation of the organic matrix.

The five indirect restorative materials differ by the thermal behaviour of the organic matrix as well as by the amount of the inorganic residue i.e. the quantity of the material remnant after all organic component had been volatilized, due to the air purging stage. The thermogravimetric curves of the materials i.e experimental product (C20), Gradia (GD), Premise Indirect (PI), Ceramage (CG) and SignumCeramis (SC) are depicted in Fig.1.

The weight loss profile of the five indirect restorative materials is mainly determined by the thermal degradation of the organic matrix. From room temperature to 650°C, in nitrogen atmosphere, the resin decomposes in one or two major weight-loss steps to leave a carbonaceous residuum, a mixture of inorganic filler and charcoal. A very small decomposition step could be noticed below about 250°C, especially for C20 and CG composite. At about 650°C, a small mass-loss step can be noticed, corresponding to the removal of charcoal by burning. Above 700 °C, after the burning stage in air, all the materials are thermally stable thus illustrating that the organics and charcoal were completely removed and that the inorganic filler does not suffer any mass change at high temperature. Consequently, the amount of inorganic filler from the composites can be estimated by the amount of TGA residuum left after air-purging. The total weight-loss of the materials varies between 18.8% for SC and 34.2% for CG sample, thus illustrating a different amount of organic matrix.

It is well known that, the inorganic fraction from a dental composite material can be estimated by the ratio between the final weight of the sample and its nominal value, when the TGA investigation is performed in normal atmosphere, with an air-cooling stage in the end. Our TGA technique is equivalent to the one described in the literature [7, 25,26].

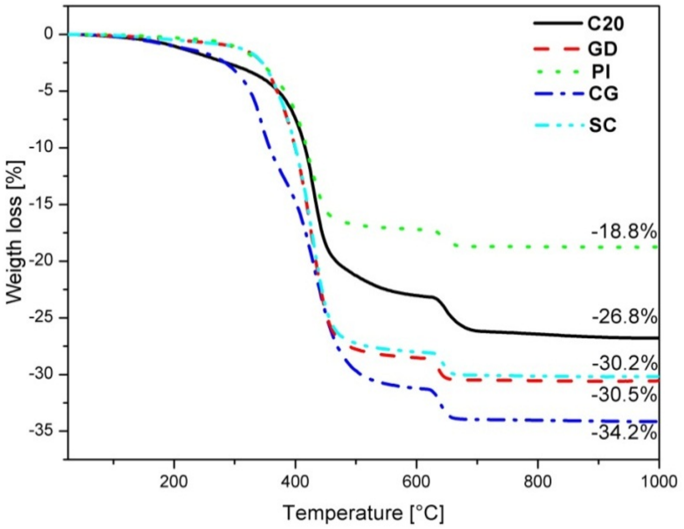

Fig.1. Thermogravimetric curves of the experimental (C20) and commercial products, Gradia (GD), Premise Indirect (PI), Ceramage (CG) and Signum Ceramis (SC), determined in nitrogen, with air-purging at 650 °C

The temperature intervals, weight-loss values, temperatures with the maximum degradation rate as well as the significance of the weight-loss processes are shown in table 2. The percent amount of TGA residuum, which indicates the weight proportion of the inorganic filler is also given.

The initial very small weight-loss step of 0.5-1.9% is associated with the removal (up to 250°C) of monomers, solvents and water from both the matrix and inorganic filler. The last small weight-loss step of 1.6-3.7 % is associated with the ignition in air of the carbonaceous residuum from the decomposition of resin in nitrogen. This process is not related with the composite itself, but with the TGA technique. Instead, the major mass-loss steps are associated with the thermal degradation of the resin, in inert atmosphere.

Table 2.Thermogravimetric data of the indirect composite materials tested.

Code	Temperature (°C)	Weight loss			Process	Residuum mass (%)
		Amount (%)		Peak (°C)		
C20	25-250	1.9	26.8	228	Removal of monomers, solvents, water	73.2
	250-600	21.2		428*	Degradation of organics	
	600-1000	3.7		654	Charcoal burning	
GD	25-250	0.7	30.5	208	Removal of monomers, solvents, water	69.5
	250-580	27.7		425*	Degradation of organics	
	580-1000	2.1		637	Charcoal burning	
PI	25-250	0.5	18.8	192	Removal of monomers, solvents, water	81.2
	250-580	16.7		421*	Degradation of organics	
	580-1000	1.6		646	Charcoal burning	
CG	25-220	1.2	34.2	184	Removal of monomers, solvents, water	65.8
	220-380	11.2		349	Degradation of organics	
	380-580	18.7		433	Degradation of organics	
	600-1000	3.1		641	Charcoal burning	
SC	25-250	0.7	30.2	195	Removal of monomers, solvents, water	69.8
	250-600	27.2		425*	Degradation of organics	
	600-1000	2.3		645	Charcoal burning	

* small shoulder at about 350°C

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Thermogravimetric analysis of dental composite gives good information about the structure and the amount of the organic matrix. Studies referring to the thermal degradation mechanism of neat and composite dental resins based on Bis-GMA, Bis-EMA, UDMA and TEGDMA pointed out that differences in the chemical structure of the resins considerably influence their degradation behaviour [9,27]. It was revealed that the neat dental resins Bis-GMA and Bis-EMA show one-step degradation mechanism with a maximum rate corresponding to 415 and 424 °C respectively, whereas the neat resins TEGDMA and UDMA show two degradation steps with maximum rate at 306 and 403 ° for TEGDMA and 357 and 444°C for UDMA.

Based on the above mentioned TGA data, the dominant component of the composite dental materials could be evaluated. It was revealed that, C20, GD, PI and SC composite resins exhibit mainly one-step degradation mechanism illustrated by one DTG peak at 428 (21.2 wt%), 425 (27.7 wt%), 421(16.7 wt%) and 425 °C (27.2 wt%) respectively. The DTG peak is asymmetric and contains a small shoulder at about 350°C in every case. These results confirm that C20, GD, PI and SC composites contain both aromatic and aliphatic dimethacrylate resins, and suggest that the aromatic content (Bis-GMA or/and Bis-EMA) is higher that of the aliphatic (TEGDMA or/and UDMA). They also confirm that PI composite contains less organic matrix than the others. On the contrary, Ceramage (CG) material shows two strong peaks at 349 (11.2 wt%) and 433°C (18.7 wt%), which suggest that this composite is based on aliphatic (UDMA and/or TEGDMA) resins.

TGA investigation showed that the experimental composite presents a higher filler amount (71.3 wt%) in comparison with the majority of the investigated materials, i.e. CG (65.8 wt%), Gradia (65.8 wt%) and Signum Ceramis (69.8 wt%) composites. It was also confirmed that PI composite has the highest percentage of inorganic fillers (81.2 wt%), thus suggesting a higher amount of nanofiller [28].

Mention has to be made that in all cases, differences were found between our data and those given by the manufacturers. There are some possible explanations i.e.: variable thickness and amount of silane used for filler treatment, presence of the "organic filler" (pre-polymerised resin) considered as part of the content, water evaporation and decomposition of some inorganic component from the filler [25].

3.2. Infrared absorption spectroscopy

FTIR studies on the dental materials were conducted using solid phase infrared spectroscopy, in the mid-infrared spectral range. The normalized spectra of the composite materials are depicted in Fig. 2.

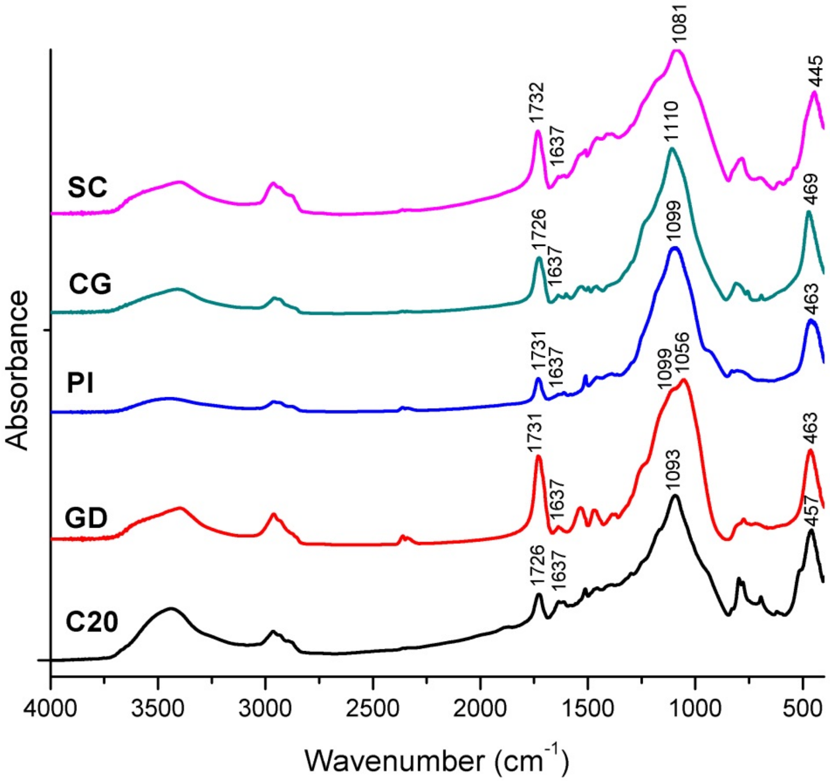

Fig.2. FT-IR spectra of the investigated indirect composite resins: experimental (C20), Gradia (GD), Premise Indirect (PI), Ceramage (CG) and Signum Ceramis (SC)

The FTIR spectra are very similar on the entire 400-4000 cm^{-1} region, showing spectral features related to the chemical structure of polymethyl methacrylate-based matrix filled with inorganic particles. All spectra exhibit a relative strong symmetric absorption band situated between 1726 and 1732 cm^{-1} corresponding to the ester group (COOCH3) that is ascribed to the organic matrix i.e. Bis-GMA, UDMA or TEGDMA [29]. The position and the intensity of this sharp well-defined peak assigned to the carbonyl C=O stretching is in direct relation with the composition and polymerization degree of the dental material. The presence of polyethylene (-

CH_2-) group is also confirmed by the bands situated between 2891-2963 cm^{-1} in C20 and 2873-2958 cm^{-1} in CG sample.

According to FTIR investigation, all the dental materials under test possess residual acrylate monomers, as illustrated by the band at 1637 cm^{-1} visible in all spectra. It is well known that, the degree of photopolymerization of dimethacrylate monomers such as Bis-GMA, UDMA or TEGDMA, which is expressed by the amount of double vinyl bonds remaining in the sample exposed to irradiation, is shown by the intensity of the peak at 1637 cm^{-1} referring to the C=C stretching[30]. The relative absorption intensity of this band suggests that the polymerization degree is rather low for the experimental dental material C20, while it is high for PI composite. The highest material conversion achieved for Premise Indirect composite is the consequence of the trimodal curing (light, heat and pressure) [31].

FTIR spectra confirm that all the dental composite contain SiO_2-dominated inorganic fillers. The most intense absorption band from all spectra is due to vibrations in SiO_4 tetrahedron of the silicon dioxide network from quartz, silica or glass that are present in all fillers (table 1). In fact, SiO_4 tetrahedra form Si-O-Si chains whose vibrations generate specific absorption peaks situated between 1081 cm^{-1} (SC composite) and 1110 cm^{-1} (CG composite), assigned to Si-O-Si asymmetric stretching, and between 445 cm^{-1} (SC composite) and 469 cm^{-1}(CG composite) assigned to Si-O-Si bending. The asymmetric shape of the first band is a real marker for the presence of silica in sample [32]. The less intense broad band appearing at about 3440 cm^{-1} is assigned to silanol Si-OH stretching.

Mention has to be made that the inorganic filler of the experimental material C20 contains 20% zinc substituted hidroxyapatite and 80% silicon dioxide-based compounds i.e. colloidal silica, quartz and barium –based glass. Due to the strong FTIR fingerprint of silicon dioxide, the characteristic bands assigned to phosphate group at 1046 and 1120 cm^{-1} (PO_4 stretching) and 603 and 547 cm^{-1}(PO_4 bending) were difficult to observe.

Thus, the FTIR analysis confirmed that all the composite materials contain an organic matrix based on polymethyl methacrylate network and a SiO_2-based inorganic filler.

3.3. Scanning electron microscopy

The morphology and dimension of filler particles were determined by scanning electron microscopy, using different magnifications and procedures for sample preparation.

For the beginning, the bar-shaped specimens from each material were broken and SEM observation was performed on the fracture surfaces, a technique frequently used for composite evaluation [33]. The SEM images for some of the indirect composite i.e. experimental material (C20), Gradia (GD) and Premise Indirect (PI), are presented in Fig. 3. The micrographs taken on fracture do not allow to evaluate precisely the morphology or dimension of the filler particles, due to the organic matrix. For instance, the individual particles of the inorganic material are difficult to observe, especially in C20 and PI samples.

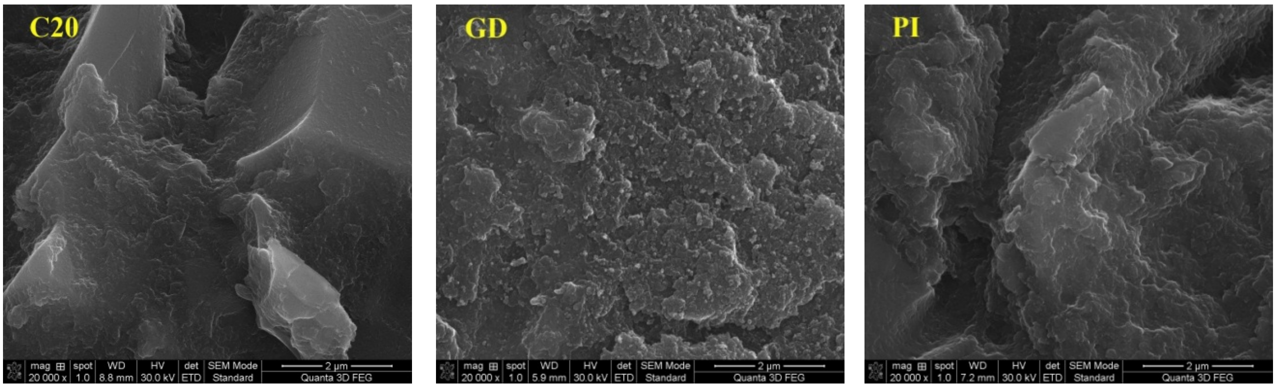

Fig. 3. SEM micrographs of some of the fractured specimens, at 20000X magnification: experimental (C20), Gradia (GD) and Premise Indirect (PI)

In order to reveal the true particle size and morphology of the inorganic filler, all composite resins were "burned off" [34]. Representative SEM images of each material at 20,000x and 80,000x (inset) are presented in Fig. 4.

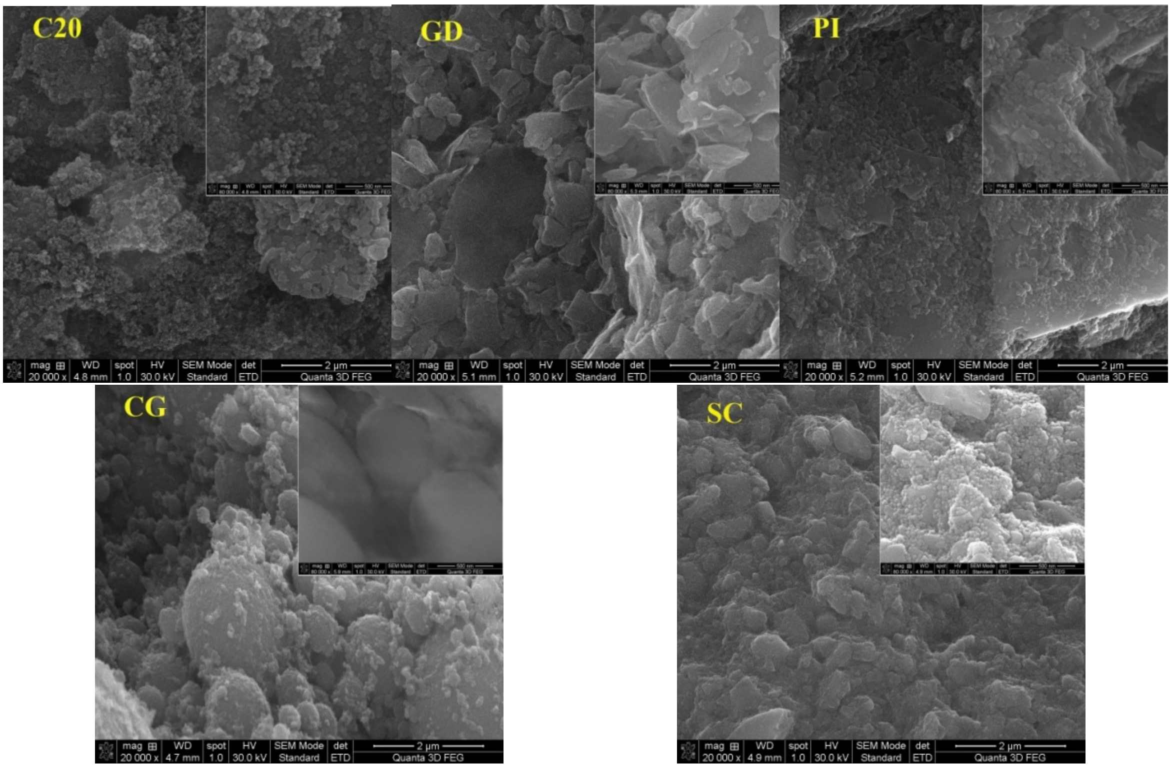

Fig. 4. SEM images of the fillers for the investigated materials at 20000x and 80000x magnification (inset pictures):experimental (C20), Gradia (GD), Premise Indirect (PI), Ceramage (CG) and SignumCeramis (SC)

Filler morphology ranged from spherical (CG), to mixed, spherical and irregular (C20, SC, PI), to jagged irregular (GD) particles. As expected, the dimension of filler particles also varied among the composites.

The experimental composite C20 is a mixture of agglomerates of spherical nano-sized particles of 40-100 nm and irregular microparticles of 1 to 4 µm. Gradia composite (GD) contains jagged irregular shaped particles with an average size under 2 µm. Premise Indirect material (PI) presents nano-particles (20-40 nm) dispersed between rather large irregular particles ranging from 0.5 to 4µm. Ceramage composite (CG) contains only spherical nanoparticles (20-40 nm) and nanoclusters (that is, aglomerates of nanoparticles) of 0.5-2 µm. Distribution of filler particles in SignumCeramis (SC) is rather uniform. The composite contains spherical particles ranging from 40 to 80 nm distributed among irregular grains with an average dimension of 0.5-1 µm. The majority of the investigated materials contain spherical particles, which were introduced with the purpose to improve the filler packing, to allow an increased filler load and to enhance the fracture strength of the materials [25].Currently, there is no consensus on the positive effect of a certain particle size and shape (spherical or irregular) on the mechanical properties [26].

4. Conclusions

Thermal behaviour, microstructure and filler morphology of an experimental indirect composite resin C20 were evaluated in comparison with four commercially composite materials for inlays, namely Premise Indirect (PI), Gradia (GD), Ceramage (CG) and Signum Ceramis (SC).

The thermogravimetric analysis shows that C20 presents a higher filler loading (71.3 wt%) then the majority of the commercially composites i.e. GD, CG and SC. Premise Indirect contains the highest filler amount (81.2 wt%). The thermal analysis also suggest that the organic matrix of Ceramage composite is based on UDMA, while the resin from the other composites consist mainly Bis-GMA. Infrared spectroscopy confirmed that all the composite materials contain an organic matrix based on polymethyl methacrylate network and a SiO_2-based inorganic filler. Excepting PI sample, the experimental and the control composites contain residual acrylate monomers The scanning electron microscopy revealed that the inorganic filler of the experimental material C20 is similar to that one of the Premise Indirect. Both materials are nano-hybrid composites consisting of agglomerates of spherical nano-sized particles and irregular microparticles. The spherical shaped particles allow a higher filler loading, as already indicated by the thermal analysis.

The investigations showed that the experimental material has similar characteristics with the majority of the investigated indirect composites.

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