

Physico-chemical and Mechanical Characterization of Some Experimental Dental Nanocomposites

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A series of six new experimental light-curing dental composites based on two Bis-GMA-type oligomers, quartz and nano-fluorohydroxyapatite (nano-FHAP), in different ratios, were prepared. The paper refers to the characterization of organic and inorganic phases from the uncured composite pastes and determination of the properties of the light-cured composite materials. Differential scanning calorimetry was used to measure the heat of polymerization of the monomer mixtures. Investigation of nano-FHAP was made by transmission electron microscopy TEMBF, HRTEM and X-ray diffraction. The mechanical strengths, water sorption and solubility were determined. We came to the conclusion that for the same monomer mixture, the water sorption and solubility values increased with the content of nano-FHAP in the composite material, but there remained in the limits of ISO 4049/2000 for the compositions comprising up to 50% nano-FHAP in the filler. The highest mechanical strengths were obtained in the case of composites containing 75% quartz in the filler.

Keywords: dental nanocomposites, extent of polymerization, mechanical properties, water sorption, solubility

Today, resin composite materials are frequently used for direct restoration of anterior teeth, as pit and fissure sealants for the prophylaxis of caries with children, and in prosthetic dentistry for the preparation of composite veneers, inlays and onlays by the photo-barro-thermal polymerization [1-3].

In spite of the improvements brought to the dental composite materials, which have expanded indications for their use, present-day resin composites still have shortcomings limiting their application and sometimes causes clinical problems. Loss of anatomic form in time due to an inadequate resistance to wear, chromatic instability, water sorption, marginal leakage due to polymerization shrinkage, and the appearance of the secondary decays because of the accumulation of the bacterial plaque (*Streptococcus mutans*) are often cited as being the main problems of resin composites [4, 5].

The reduction of the secondary decays formation can be obtained by the incorporation of an anticariogenic agent into the organic or inorganic phase of the composite [6, 7]. Fluoride is well-documented as an anticariogenic agent [8-10]. Nano-fluoroapatite and nano-fluoridated hydroxyapatite have excellent biocompatible remineralization properties and it seems that they could be used as a fluoride-releasing reservoir for constant fluoride release [11].

Joining the research activities in the field, our studies have as the major objective to develop new resin composites with improved properties and performances. The aims of the present work were to elaborate a series of six new dental light-curing composites based on two Bis-GMA-type oligomers and nano-fluoro-hydroxyapatite synthesized in our laboratory, to characterize the components of the uncured composites and to determine the properties of the light-cured composite materials.

Experimental part

Obtaining and characterization of the organic phase

A series of monomer mixtures were prepared using two Bis-GMA type oligomers, synthesized in our laboratory, as base monomers and triethyleneglicol dimethacrylate (TEGDMA) as a dilution monomer. New oligomers Bis-GMA336 and Bis-GMA356 were synthesized starting from commercial epoxy resins DER 336 DER 356, respectively (Dow Company), by reaction of epoxy resins with methacrylic acid [12]. Monomer mixture containing commercial Bis-GMA (Aldrich) and TEGDMA was used as a reference. The ratio between Bis-GMA type monomer and TEGDMA was 65/35. In the composition of the monomer mixtures, besides the methacrylic monomers, a photosensitizer, camphorquinone (CQ), in an amount of 0.5%, and an accelerator dimethylaminoethyl methacrylate (DMAEM), in an amount of 1%, were added. Butylated hydroxy toluene (BHT) was added in a quantity of 650 ppm related to the monomer mixtures.

The copolymers were obtained from the corresponding monomer mixtures by exposing to a visible radiation in the wavelength range of 400-500 nm. The radiation was generated by an Optilux dental lamp.

Differential scanning calorimetry was used to measure the heat of polymerization of the monomer mixtures. The extent of polymerization was determined by measuring the area of polymerization exotherm (H_p).

The extent of polymerization was calculated according to the formula (1):

$$c\% = \frac{\Delta H_{mit} - \Delta H_t}{\Delta H_{mit}} \cdot 100 \quad (1)$$

where $c\%$ represents the extent of polymerization after t irradiation time of the sample

ΔH_{init} - heat of polymerization of the initial system

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Table 1
COMPOSITION OF THE EXPERIMENTAL LIGHT-CURING COMPOSITES

Component/ composite	Bis-GMA0, g	Bis-GMA336, g	Bis-GMA356, g	TEGDMA, g	FHAP, g	Quartz, g
C1.	18.57			10	31.715	31.715
C2.		18.57		10	31.715	31.715
C3.			18.57	10	31.715	31.715
C4.	18.57			10	17.857	53.573
C5.		18.57		10	17.857	53.573
C6.			18.57	10	17.857	53.573
C7.	18.57			10	53.573	17.857
C8.		18.57		10	53.573	17.857
C9.			18.57	10	53.573	17.857

ΔH_t - heat of polymerization of the system after t seconds of irradiation

Obtaining and characterization of the inorganic phase

The inorganic filler used in the experimental composites was a mixture made of synthesized fluoridated hydroxiapatite (nanofiller) and quartz (macrofiller).

The fluorohydroxyapatite (FHAP) was prepared using thermally untreated hydroxyapatite synthesized in our laboratory and CaF_2 as starting materials. Reaction was performed at 50°C and $\text{pH}=8-9$. After five days the mixture was vacuum filtered, then washed with distilled water to $\text{pH} 7.4$. After drying, the powder was heat treated at 800°C for 2 h.

The surface area of the quartz particles was $6.25 \text{ m}^2/\text{g}$, with the particle sizes between $10-40 \mu\text{m}$.

Silanation of quartz was carried out with 3-methacryloxypropyl-1-trimethoxy-silane (silane A-174).

The TEM investigation of FHAP was done as follows. A drop of alcoholic suspension of FHAP was placed on a carbon film coated copper grid and investigated by transmission electron microscopy, selected area electron diffraction (SAED) and energy dispersive X-ray spectrometry (EDSX) by using a high resolution transmission electron microscope (HRTEM) TECNAI F30 G²STWIN with EDAX spectrometer.

The X-ray diffraction investigation of FHAP was performed using a Panalytical X Pert Pro MPD X-ray diffractometer. A monochrome CuK_α radiation filtered with Ni filter was used. The X-ray patterns were registered and processed by the diffractometer soft.

Obtaining of the experimental light-curing composites

The experimental light-curing composites were prepared as monopastes from the monomer mixtures and the hybrid filler. The ratio between monomer mixture and hybrid filler was 1/2.5.

The compositions of experimental light-curing composites were presented in table 1.

The cured composites were obtained from the corresponding composite pastes by exposing to a visible radiation in the wavelength range of $400-500 \text{ nm}$. The radiation was generated by a dental lamp.

Determination of mechanical properties

The determination of compression strengths and flexural strengths was done as was described in a previous paper [12].

Determination of water sorption

Disk specimens of composites $15 \pm 1 \text{ mm}$ diameter, $1 \pm 0.1 \text{ mm}$ thickness were prepared in a mold by exposing each side to a visible radiation in the range of $400-500 \text{ nm}$ for 40 s using a dental lamp. Water sorptions were

determined according to ISO 4049/2000 at 1, 2, 3, 4 and 7 days of storage in water.

The values for water sorption (W_{sp}), for each of the specimens were calculated using the formula:

$$W_{sp} = \frac{M_2 - M_3}{V} \quad (2)$$

M_2 - the mass of the specimen after immersion in water [μg],

M_3 - the mass of the reconditioned specimen [μg],

V - volume of the specimen [mm^3]

Determination of solubility

Disk specimens of composites $15 \pm 1 \text{ mm}$ diameter, $1 \pm 0.1 \text{ mm}$ thickness were prepared in a mold by exposing each side to a visible radiation in the range of $400-500 \text{ nm}$ for 40 s using a dental lamp.

Solubility values were determined according to ISO 4049/2000 [21] at 1, 2, 3, 4, and 7 days of storage in water. The values for solubility in water (W_{st}), for each of the specimens were calculated using the formula:

$$W_{st} = \frac{M_1 - M_3}{V} \quad (3)$$

M_1 - is the conditioned mass, prior to immersion in water [μg],

M_3 - is the mass of the reconditioned specimen [μg],

V - volume of the specimen [mm^3]

The structures of composites before and after immersion in water were examined using a Inspect S (FEI) scanning electron microscope.

Results and discussions

Determination of extent of polymerization of the monomer mixtures

A crosslinked three-dimensional network is formed by the polymerization of the monomer mixtures existing in the dental diacrylic resins. During the polymerization of dimethacrylate monomers, the gel effect occurs, leading to the closing of macroradicals and unreacted monomers in the crosslinked network. The commercial diacrylic resins, investigated in the literature have between 25 and 50% unreacted methacrylate groups (Asmussen, 1982; Ferracane, 1994).

The extent of polymerization of monomer mixtures containing Bis-GMA type monomers (commercial Bis-GMA₀ (Aldrich), Bis-GMA₃₃₆ and Bis-GMA₃₅₆) and TEGDMA, as a function of time of exposure to visible light (10 -180 s) were investigated by DSC. As an example, below are shown the results obtained for the Bis-GMA₃₅₆/TEGDMA monomer mixture.

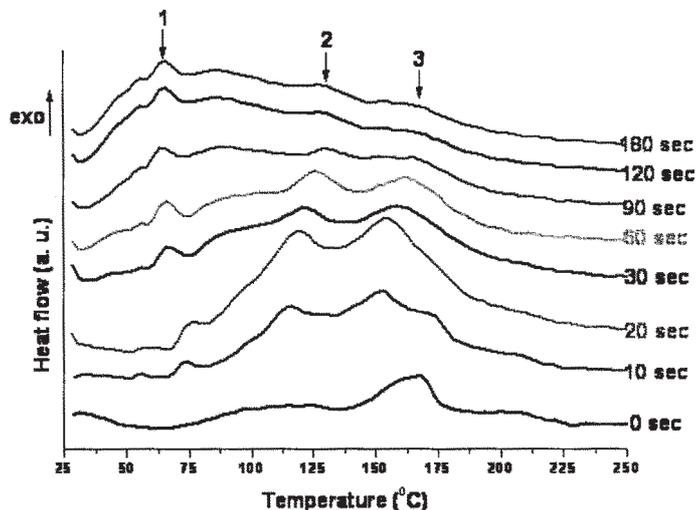


Fig.1. DSC curves recorded for the monomer mixture containing 65% BisGMA₃₅₆/35% TEGDMA

Time of exposure	ΔH , J/g	Extent of polymerization, %	T ₁ , °C	T ₂ , °C	T ₃ , °C
0 sec	15.85	0	-	-	167.7
10 sec	13.66	13.81	73.4	115.5	153.5
30 sec	11.83	25.36	67	122.1	161.3
60 sec	9.082	42.7	66	125.8	163.4
90 sec	4.985	68.54	64.3	128.0	163.4
120 sec	4.582	71.09	64.3	131.6	166.4
180 sec	3.042	80.8	65.2	127.7	169.4

Table 2
EXTENT OF
POLYMERIZATION OF
MONOMER MIXTURE
CONTAINING 65%
BISGMA₃₅₆/35% TEGDMA

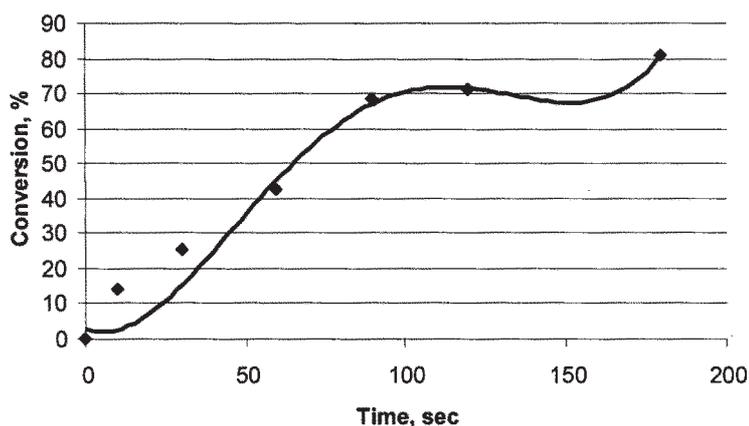


Fig. 2. Conversion-time curve for the monomer mixture containing 65% BisGMA₃₅₆/35% TEGDMA

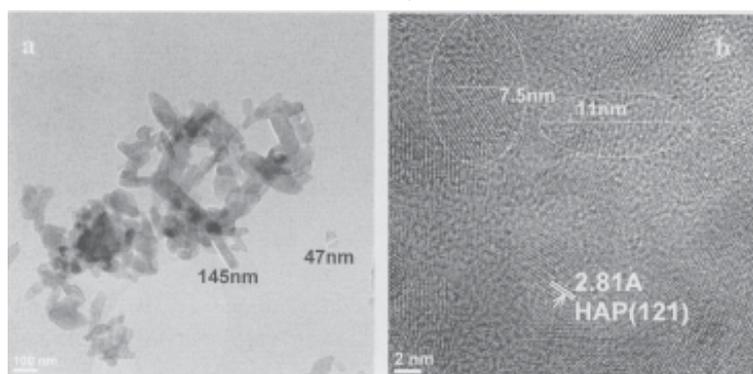


Fig.3. Transmission electron microscopy image in bright field (TEMBF) of synthesized FHAP (a). High resolution transmission electron microscopy (HRTEM) image of FHAP (b)

From figure 1 there can be seen several exothermic peaks of polymerization reaction initiated by CQ-amine system, the data resulting from analysis of these curves being summarized in the figure 2 and table 2.

From the figure 2, one can observe that the conversion of monomer mixture containing 65% BisGMA₃₅₆ and 35% TEGDMA increases with time of exposure to visible light, reaching the value of about 70% after 90 s of exposure, remains at this value until 160 s of exposure, and then increases sharply to 80% for 180 s of exposure.

Investigation of FHAP by transmission electron microscopy TEMBF and HRTEM

The investigation of FHAP by transmission electron microscopy and X-ray diffraction reveals the existence of a majority crystalline phase with a hexagonal crystalline network.

Transmission electron microscopy in bright field (TEMBF) image (fig. 3a) and high resolution transmission electron microscopy (HRTEM) image (fig.3b) show that the particles of the majority phase have nanometric sizes

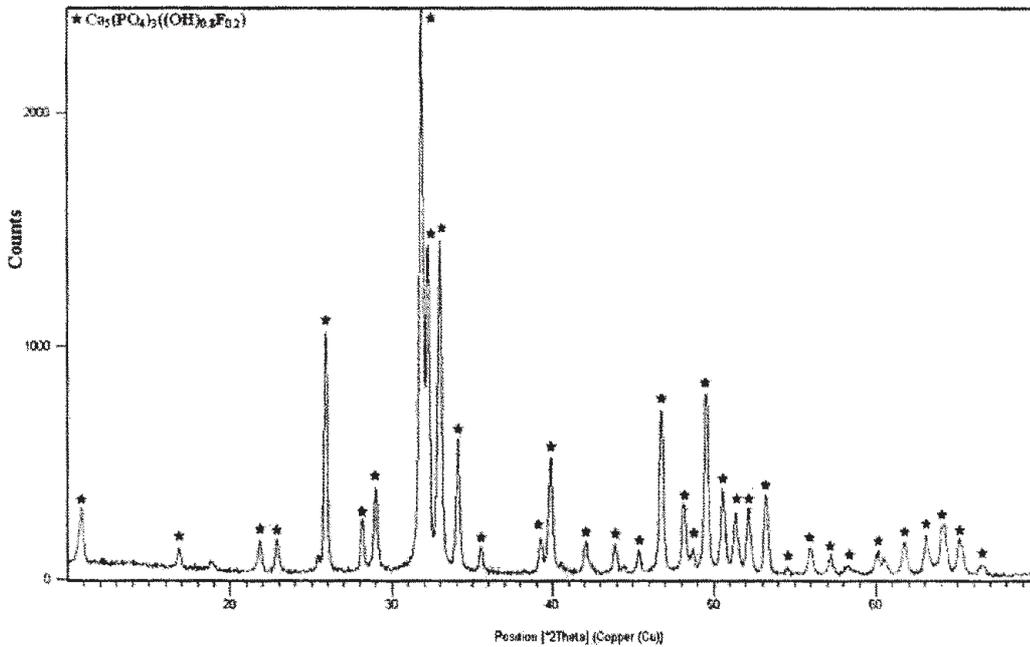


Fig.4. X-ray diffraction pattern for FHAP

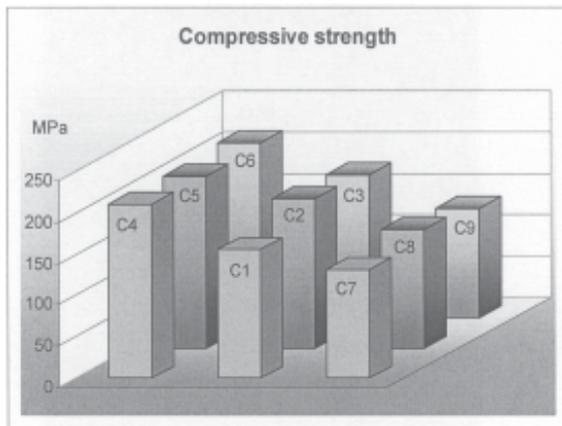


Fig.5. Compressive strength of experimental composites

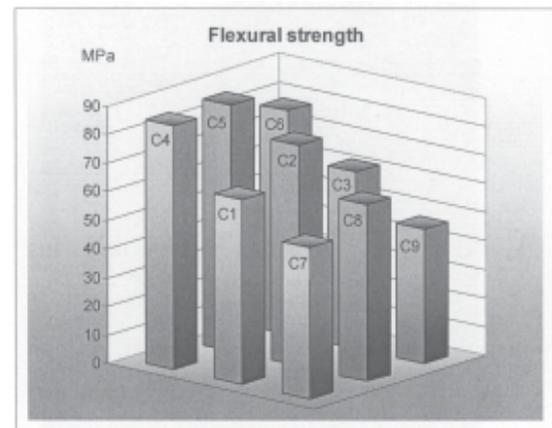


Fig.6. Flexural strength for composites experimental restoration

that are grown in the form of rods with lengths between 15 and 160 nm and thickness around 10 nm.

The investigation of FHAP by transmission electron microscopy and X-ray diffraction reveals the existence of a majority crystalline phase $\text{Ca}_5(\text{PO}_4)_3(\text{OH})_{0.8}\text{F}_{0.2}$ - with a hexagonal crystalline network.

Determination of mechanical properties

High mechanical properties are particularly important in the process of mastication, where the greatest loads are experienced by the tooth structures. Compressive strength (CS) and flexural strength (FS) are important parameters for the comparison of dental restorative composites.

Determination of compressive strengths

Compressive strengths of the experimental composites as a function of composition are shown in figure 5.

Compression strength values obtained for composites based on Bis-GMA₀ monomer were in the range of 132.4 and 211.54 MPa, the CS values for Bis-GMA₃₃₆-based composites ranged from 143.99 to 217.87 MPa and CS values for composites that contained Bis-GMA₃₃₆ oligomers ranged between 132.5 and 212.5 MPa. The highest values for CS were obtained for Bis-GMA₃₃₆-based composites.

For the same powder/liquid ratio $P/L = 2.5/1$ in the series of composites containing the same mixture of monomers, compressive strength increases with

increasing of quartz content in the filler, respectively with the decreasing of fluorapatite content. Composites filled with 75% quartz / 25% FHAP showed the greatest resistance to compression in the following order: oligomer Bis-GMA₃₃₆-based composite (217.87 MPa) > oligomer Bis-GMA₃₃₆-based composite (212.87 MPa) > oligomer Bis-GMA₀-containing composite (211.54 MPa).

Determination of flexural strengths

Flexural strengths of the experimental composites as a function of composition are presented in figure 6.

Flexural strengths obtained for composites based on Bis-GMA₀ oligomer were in the range from 52.6 to 84.97 MPa, strength values recorded for composites based on Bis-GMA₃₃₆ oligomers ranged from 61.46 to 86 MPa, and FS values for composites containing-Bis GMA₃₃₆ oligomers ranged from 46.81 to 87.77 MPa.

For the same powder/liquid ratio and for the same mixture of monomers, flexural strengths increase with increasing of quartz content in the filler. Comparing the experimental composite materials in terms of type Bis-GMA oligomers used, the highest levels of resistance to flexural was shown by the composites derived from Bis-GMA₃₃₆ oligomers, followed by composites based on Bis-GMA₀ and then by composites containing Bis-GMA₃₃₆ oligomers. The results show that for composites based on Bis-GMA type oligomers, mechanical strengths are mainly

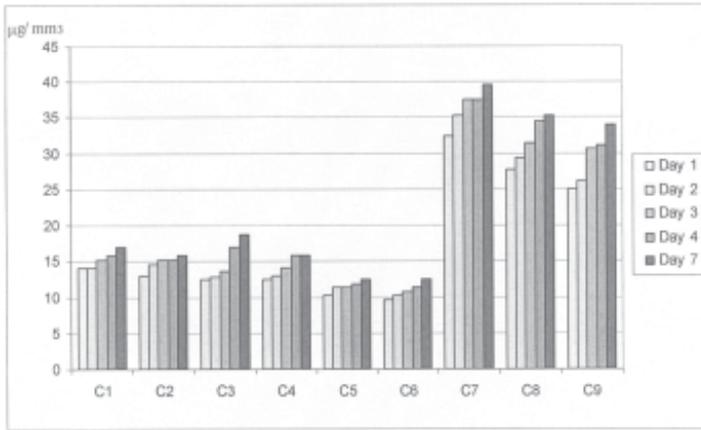


Fig.7. Water sorption of experimental composites depending on storage time

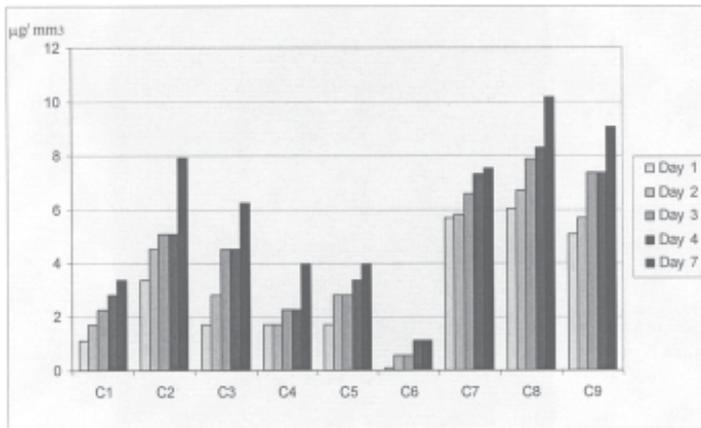


Fig.8. Solubility in water of experimental composites depending on storage time

influenced by the nature of the inorganic phase and secondly by the structure of Bis-GMA oligomer in the mixture.

Determination of water sorption and solubility Determination of water sorption

Dental composites are generally regarded as insoluble structures with high chemical stability. However, these materials can absorb water and chemicals present in the saliva. Also, they may release certain compounds in the oral environment. These phenomena of sorption and solubility lead to a series of physical and chemical processes that can produce negative effects on the structure and properties of composite materials.

The phenomenon of water sorption is influenced mainly by polymer network structure, the nature and quality of inorganic filler and by polymer / inorganic filler interface. Most water diffuses into the intermolecular spaces within polymer matrix, or along the interface of filler / polymer. Small water molecules, connected by hydrogen bonds, can interact with polar groups of the polymer, water sorption being influenced by the position of these groups in three-dimensional polymer network.

Water sorption values of the experimental composites as a function of storage time are shown in figure 7.

From figure 7 it can be seen that water sorption values for all composites increase with the storage time. For the same monomer mixture, the water sorption values increased with the content of FHAP in the composite material, the highest values being recorded for the experimental composites which contained 75% FHAP (C7, C8 and C9). These results suggest that water molecules can easily penetrate in the composites besides the nano-FHAP.

For the same filler, the lowest values were recorded for the composites based on Bis-GMA356 monomer (C6 and C9 composites), and the highest values were obtained in

the case of Bis-GMA0-based composites (C4 and C7 composites). These results suggest that in the composites, Bis-GMA356 leads to the obtaining of polymer networks with a greater degree of crosslinking, fact that makes the penetration on water molecules more difficult in the three-dimensional network.

All the experimental composites presented water sorption values within the limits imposed by the current international standard ISO 4049 ($W_{pl}=40 \text{ mm}^3$). It can be noticed that very low values were obtained in the case of C6 experimental composite based on Bis-GMA356 and FHAP/quartz ratio of 1/3.

Determination of solubility in water

Solubility in water of the experimental composites as a function of storage time is shown in figure 8.

From figure 8 one can observe that solubility in water for all composites increased with storage time, reaching the highest value after 7 days.

For the same monomer mixture, the solubility values increased with the content of FHAP in the composite material, the lowest values being recorded for the experimental composites which contained 25% FHAP. This behaviour can be explained by the fact that FHAP having nanometric dimensions, can be easily extracted from the composite by the water.

For the same filler, the lowest values were recorded for the composites based on Bis-GMA356 monomer (C3 and C6 composites), and the highest values were obtained in the case of Bis-GMA336-based composites. These results suggest that Bis-GMA356 leads to the obtaining of polymer networks with a greater degree of crosslinking, fact that makes the extraction of small molecules from the composites more difficult.

All the experimental composites presented solubility values within the limits imposed by the current international standard ISO 4049 ($W_{sl}=7.5 \mu\text{m}^3$), except C2, C8 and C9

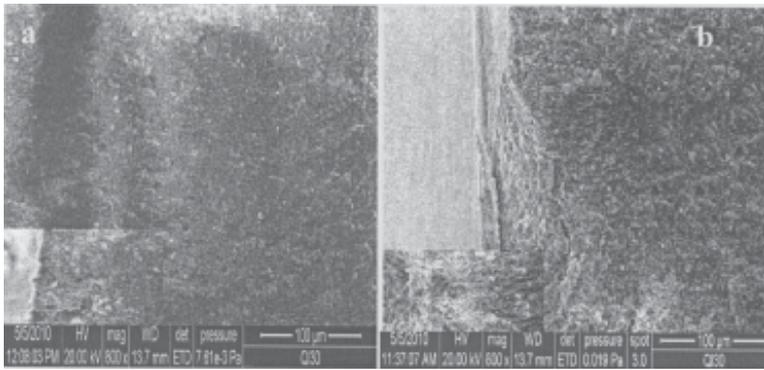


Fig. 9. SEM photographs (x800 / x3000) illustrating the fractured surface of composite C₃ before immersion (a) and after 7 days storage in artificial saliva (b)

composites. It can be noticed that very low values were obtained in the case of C6 experimental composite based on Bis-GMA356 and FHAP/quartz ratio of 1/3.

SEM photographs illustrating fractured surfaces of C3 composites before (a) and after 7 days storage in water (b) are shown in figure 9.

SEM photomicrographs of C3 composite in the fractured surfaces, prior to immersion in water (a), show a homogeneous structure with fine striations due to fracture. After storage in water, C3 composite shown an uneven surface without gaps or fissures.

Conclusions

A series of six experimental dental light-curing composites based on Bis-GMA336 and Bis-GMA356 monomers and a hybrid filler consisted of quartz and fluorhydroxyapatite, in different ratios, were prepared.

Differential scanning calorimetry was used to determine the extent of polymerization of the resins. The obtained results pointed out that the conversion increases with the time of exposure to the visible light, reaching the value of 80% after an exposure time of 180 s.

The mechanical properties, compressive strengths and flexural strengths of the experimental cured composites were determined. For the same powder/liquid ratio P/L = 2.5 / 1 in the series of composites containing the same mixture of monomers, compressive strength and flexural strengths increase with increasing of quartz content in the filler, respectively with the decreasing of fluorapatite content. The highest value for CS (217.87 MPa) was recorded for the composite that contained Bis-GMA336 and the hybrid filler consisted of 75% quartz / 25% FHAP. The highest values for FS (87.77 MPa) was obtained in the case of the composite based on Bis-GMA356 monomer and the hybrid filler consisted of 75% quartz / 25% FHAP.

The water sorption and solubility values were lowest in the case of composites containing the hybrid filler comprising 75% quartz and 25% FHAP. For the same filler, Bis-GMA356 led to the obtaining of composite materials with the lowest water sorption and solubility.

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