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Microstructure, mechanical properties and tissue/biomaterial interface behaviour of new dental restorative composites

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Four new dental composites with different inorganic phases were submitted to comparative study regarding their structure, compressive strength, diametral tensile strength, flexural strength and Vickers hardness, as well as composite-hard tissue interface. The composites containing bioceramic show the best integration of silanized filler into the organic matrix. SEM analysis reveals the development between tooth and composite material of a continuous interface consisting in a zone that is different from both bonding resin and dentine. The results of this study prove the effects of filler composition on mechanical properties of the composite resins, and at the same time on the interface between composite and tooth hard tissues.

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1. Introduction

One of the major problems of the researchers and manufactures implied in the field of dental materials is the obtaining of composite resins with an improved adhesion to hard dental tissues [1-4]. This purpose could be achieved both through modifying the inorganic and the organic phase of dental composites. At the same time a good link between them has to be created [5, 6]. Beside adhesion, the mechanical properties of restorative material are crucial in their clinical performance and are strongly related to the composition of filler and organic matrix [7-12]. Modern composite restorations are composed of one or more silane-coated inorganic phases representing filler particles of low dimensions, less than 100 nm, and adhesive resins (reactive monomers and cross-linking agents).

A dental resin reinforced with dispersed hydroxyapatite particles offers several advantages including radiopaque response, wear performance, high polishability and hardness similar to that of natural teeth. In vitro study revealed that the dental composites incorporating silanized hydroxyapatite improve their biocompatibility [5, 7].

Studies evaluating the influence of volume and confinement on marginal adaptation of composite restorations have yielded controversial results [13-20]. In the last decade a lot of research was devoted to development of new filler components [21-24] and adhesives that optimize binding to the reactive moieties on the collagen of the interfacial dentin to relieve tensile/shear stresses [25, 28]. Several *in vitro* studies have tested the performance of adhesives by evaluating the marginal gap formation around restorations placed in extracted teeth [26, 27]. Scanning electron microscopy (SEM) analysis appears to be an efficient and accessible method of examining features such as surface topography, filler size, distribution and interface adhesion [21].

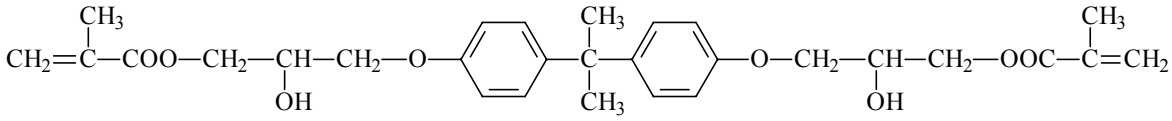
The goal of this research is to study the influence of the fillers (colloidal silica, hydroxyapatite, zirconia-silica sol-gel and new bioceramics) upon the mechanical properties (flexural strength-FS, compressive strength - CS, diametral tensile strength - DTS and Vickers hardness - HV) of four new light-cured dental composites and their attachment to the tooth hard tissues by a "three-step" adhesive system.

2. Materials and methods

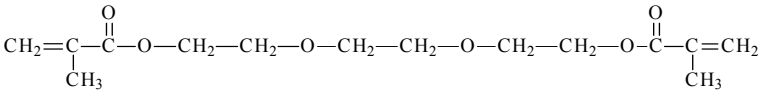
The inorganic phase consists of silanized filler system based on mixture of colloidal silica (SiO_2) (Degussa), hydroxyapatite (HAP) particles, N1 component (SiO_2 : ZrO_2 mixed oxides, weight ratio 2:1, obtained through the sol-gel method) and B2 bioceramic (30-40% SiO_2, 25-35% ZnO, 7-12% Al_2O_3, 8-14% B_2O_3, 3-6% NaF, 3-6% CaF_2 - obtained using the conventional melting method, ground to submicron sized particles and sieved).

The fillers surface was silanized with γ-methacriloyloxypropyl-trymethoxysilane (A174) (Aldrich).

The organic phase - monomers mixture consists of Bis-GMA/TEGDMA in 65/35 ratio with camphorquinone/amine as initiator/activator system. The organic phase was obtained by adding to the prepared Bis-GMA, TEGDMA **(**Aldrich**),** camphorquinone(Aldrich) and amine (N,N dimethylaminomethylmethacrylate) (Aldrich).



Bis-GMA



TEGDMA

The four composites were prepared as monopaste, by dispersing in the organic phase the silanizated bioactive inorganic fillers. The compositions of the light-cured composites noted C*i* (*i* = 1÷4) are given in Table 1.

Table 1. The chemical composition of the investigated dental composites (wt %).

Composite code	Organic phase	Inorganic phase			
		HAP	N 1	B2	SiO_2
C1	22	30	40	-	8
C2	25	20	-	40	15
C3	23	20	20	20	17
C4	30	40	-	-	30

The adhesive used for all the investigated composites consists of a „three-step" adhesive system -

- Acid etch gel : H_3PO_4 (Merck)

- Primer: UEDMA (Aldrich), HEMA (Merck), ethanol (Remed),water.

- Adhesive: UEDMA (Aldrich), Bis-GMA, HEMA (Merck), TEGDMA (Aldrich).

2.1 Characterization of the composites

2.2.1 Mechanical properties

The mechanical tests such as compressive strength (CS), diametral tensile strength (DTS) and flexural strength (FS) were performed at 23^0C with a universal mechanical testing instrument from LLOYD Company. The samples were prepared using teflon molds which did not restrain the displacement of the specimen, so that the formation of cracks and flaws within the material bulk and surface during their preparation was minimized. For the determination of Vickers microhardness a Carl Zeiss Jena instrument equipped with a Nepophot 21 microscope, that permits the measurements of the spot diagonal with a precision of 0.5 %, was used.

Ten specimens were prepared for each mechanical test group with different dimensions according to the standard test (6 mm diameter and 3 mm thickness for DTS and microstructure, 3 mm diameter and 6 mm thickness for CS and 2x2x25 mm for flexural strength and 6.0 mm diameter, 3.0 mm thickness for HV). The composite resins were polymerized with the aid of a 3M XL 2500 lamp for 40 seconds, from several directions. Light-curing was performed by continuous light (600 mW/cm^2). After 24 ± 1 h, the specimens were loaded at a crosshead speed of 0.5 mm/min until fracture. The values of the compressive strength, diametral tensile strength, flexural strength, and Vickers hardness are calculated using the formules:

compressive strength:

$$CS = \frac{9.81F}{0.785d^2} \quad (1)$$

where *F* is the load at fracture and *d* is the diameter cylinder

*diametrical tensile strength***:**

$$DTS = \frac{2F}{\pi dt} \quad (2)$$

where *d* is the diameter and *t* is the thickness of the cylinder.

*flexural strength***:**

$$FS = \frac{3F\ell}{2bd^2} \quad (3)$$

where *l* is the distance between the two supports, *b* is the width and *d* the thickness of the specimens.

Vickers hardness (HV) is calculated with the expression:

$$HV = \frac{2F\sin\frac{136^o}{2}}{d^2} \approx 1.854\frac{F}{d^2} \qquad (4)$$

for F measured in kgf.

The values for mechanical properties were calculated and statistic analyzed by ANOVA tests. For each test the mean value and standard deviation were calculated and compared using the ANOVA test at a significance level of 0.05 %.

-microstructure studies of the dental composites surface and of the interface dentin/enamel/composite were performed using a scanning electron microscope Philips XL 30 ESEM. Micrographs were recorded from specimens obtained using human teeth soaked in artificial saliva for 2 months. Cylindrical cavities (3 mm deep, 2 mm in diameter) were selected from prepared teeth following the classical protocol in oral cavity. The cavity walls were acid etched by applying 37% phosphoric acid to the cavity walls for 15 seconds. After rinsing for the same interval, the excess water was removed with a gentle air spray for 30 s, washed and then dried. The adhesive was applied and light cured for 30 s. Then the cavity was filled with each investigated composite and light cured for 40 s. The composition analysis of the surface of the composites was made by Energy Dispersive X-ray (EDX) method. Specimens with the four investigated composites were prepared in cavities cut in human teeth simulating clinical conditions of light transmission that may occur during restorative procedures.

3. Results

The dental composites prepared under identical light curing conditions, with similar organic monomer matrix composition but with different type and concentration of filler particles show differences both in mechanical strengths and in their behaviour at the interface betwen composite and tooth hard tissues.

3.1 Mechanical properties

The values determined for the flexural strength, compressive strength, diametral tensile strength and Vickers hardness are represented in Fig. 1.

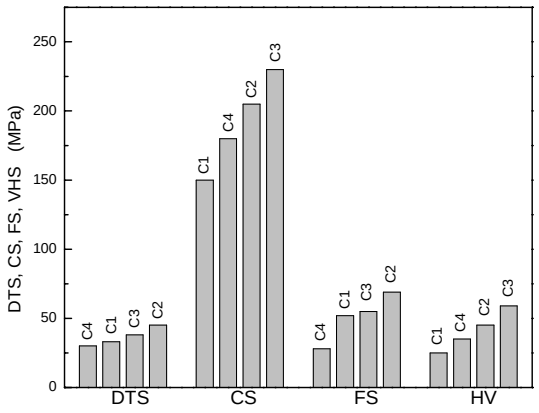


Fig. 1. Diametral tensile strength (DTS), compressive strength (CS), flexural strength (FS) andVickers hardness (HV) of investgated dental composites.

The highest values for all mechanical properties were found for the light-cured C2 and C3 composites that contain HAP, colloidal SiO_2, N1 phase and B2 bioceramic particles as filler. The results reveale high compression strength for all samples. The best performance presented by C3 can not be related to its filler concentration (77 % wt), because all the four composites have quite close filler concentration, between 70 and 78 % wt. It is worth to be mentioned that both for diametral tensile strength and flexural strength the increase is obtained in the same order: C4, C1, C3 and C2. With respect to the compressive strength and Vickers hardness one remarks that the values are increasing in a similar way, but in this case the order is: C1, C4, C2 and C3. These results confirm the relation of tensil and flexural strengths, respectively of compressive strength and hardness of samples, and point out on the oposite behaviour of tensil or flexural strengths versus hardness or compressive strength. The values for all mechanical properties tested, reveale that composites C1 and C4 are less mechanical resistant then C2 and C3 composites, but the results on mechanical strengths for all four composites C1÷C4 are in the limits stipulated by ISO Standards.

3.2 Microstructure

The microstructure of the composites along with the elements entering in their composition, the interface layer between composite and tooth hard tissues, as well as the adhesive penetration on the dentine wall teeth, were analyzed using scanning electron microscopy and energy dispersive X-ray spectroscopy. The results are presented in Fig. 2.

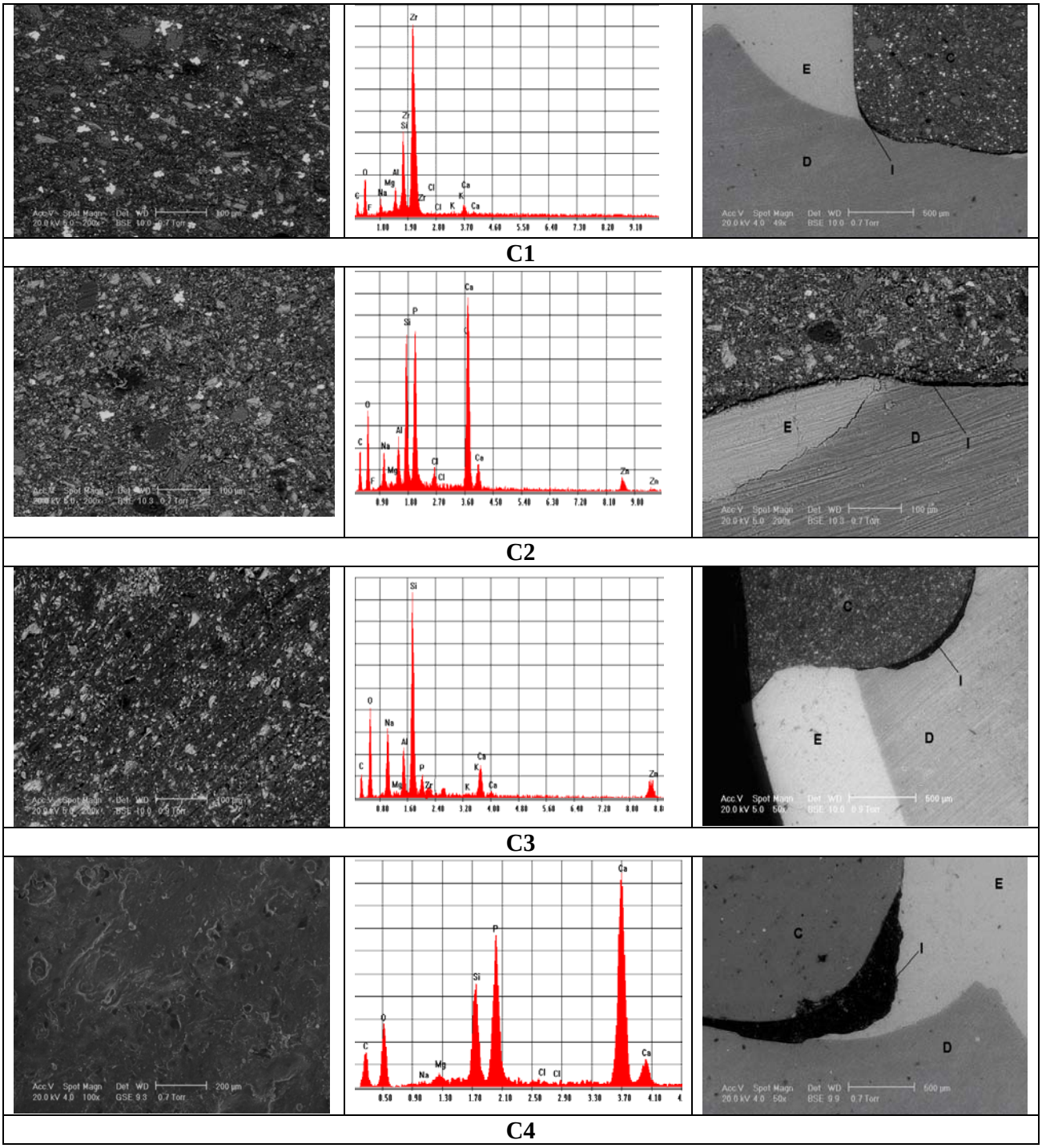


Fig. 2. SEM images of dental composites (left), their EDX spectra (middle) and SEM images of composite / tooth hard tissue interface (right, C-composite, D-dentine, E-enamel, I-interface).

The obtained pictures show a heterogeneous surface of the composites filled with hydroxyapatite and bioceramic particles, where the particle agglomerates - HAP or silica - are clearly noticed. EDX qualitative analyses show the presence of the Si, Zr, Al, Ca, Na, elements for C1 composite, Si, Zn, Al, Ca, P elements for C2 composite and Si, Ca, P for C4 composite. The examination by SEM microscopy shows that the interface between the tooth and the composite material is continuous and proves the occurrence of a zone that is different from composite resin and from dentine too. A great part of the adhesion to the cavity walls took place in

dentine. The micrographs of the teeth restored with C2/adhesive, respective C3/adhesive show continuos layer at the interface dentin - composite.

4. Discussion

Composition characteristics of light-cured composite resins have a greate influence upon their final properties and clinical performance. The filler content, size, type, and distribution, as well as coupling between particles and matrix influence their mechanical properties [4-6]. The results obtained in this study show differences for the mechanical properties of the investigated composites light-cured in the same conditions and with the same organic matrix. Compressive and tensile stresses form the basis of flexural tensions. Hence, the flexural strength might be able to predict more clearly the characteristics of the material from a practical point of view. The greatest value of flexural strength obtained for composite C2, nearly followed by composite C3, could be explained by a good link between polymer and filler particles, as well as by the adequate content and size of hydroxyapatite particles. We suppose that the balance between the size of particles, as well as the appropriately chemical heterogeneity and integration of the filler in the organic matrix, contributed to the good mechanical strength and Vickers hardness values for C3 composite. C3 composite resin has as filler colloidal silica, bioceramic powders and hydroxyapatite submicronic particles in well established ratios. C2 and C3 composites present higher values for mechanical strengths than the composites without bioceramic powders as filler. Even thought mechanical tests have not reached the level of clinical simulation, they represent an important parameter of analyses. Taking into account the influence of the adhesive system on marginal sealing, we conducted this study to verify the hypothesis that interface leakage is influenced by the cavity preparation and by the adhesive used to improve the link between biocomposite material and dentine. Even when no gaps can be observed in this stage, leakage can easily occur between the hybrid interface layer and dentine. All resin-based restorative materials shrink and induce stress at the interface, which may lead to gap formation and interfacial stress.

Several studies have associated the extent of interfacial damage with the efficacy of the adhesive system [14-16]. With one-step adhesives, solvent type seems to influence monomer penetration into the dentin [17, 20]. Some authors assumed that the presence of water in the adhesive composition may be advantageous, because it allows dentin rehydration in case the collagen network is over-dried [18]. Other authors, however, have called attention to the fact that water in excess may cause incomplete solvent evaporation and affect the quality of the adhesive layer [19]. The SEM images (Fig. 2) show the microstructure of the interface between composites and tooth hard tissues and reveal that the stress develops at the level dentine-resin interface. Agglomerate formation of particles has a detrimental effect on the adhesion between filler and polymer, and therefore, on the mechanical properties. It depends on shape and size of cavity, but also on the restoration material. If the forces generated by polymerization shrinkage or by thermo-mechanical strain exceed the bond strength, an observable gap will be formed at the margin of the restoration. Although there is no clear correlation between *in vitro* gap formation and interfacial failures observed *in vivo*, it is reasonable to assume that this marginal gap formation is clinically relevant. The presence of the “three-step” adhesive agent at the dentine-composite interface is found to improve adhesion. Scanning electron microscopic observations of sectioned specimens reveal that applying a coat of bonding agent on the dentinal surface helps in reducing leakage in all four composite systems studied. The bonding mechanism to dentin is effective because the smear layer, intertubular and peritubular dentin are dissolved, collagen fibers expose and, after infiltration of resin monomers, a hybrid layer is formed. In contrast to common belief, clinical effectiveness of adhesive can be predicted. Despite the fact that adhesives are sensitive to mechanical fatigue phenomena, the major factor affecting durability *in vivo* is hydrolysis of interface components, such as collagen and resin, and subsequent elution of the breakdown products. The most validated method for the assessment of this degradation process *in vitro* is the storage of specimens in water. Our samples were stored in artificial saliva and after 2 months the deposition of a thick calcium phosphate layer could be seen. This analysis revealed that, despite the fact that adhesives are sensitive to mechanical fatigue phenomena and their *in vivo* durability is affected by hydrolysis of the interface components, it is possible to realize an effective hybrid layer at the interface of dentin/enamel- composite with high values for mechanical strengths.

5. Conclusions

The results obtained in this study show the differences in the mechanical properties and biointerface of four new composites synthesised under identical light curing conditions, with similar organic monomer matrix but with different type and concentration of filler particles. The composites containing submicrometric bioceramic particles too show the best integration of the filler in the organic matrix and highest mechanical strengths. The addition to filler system of components, which have an increasing effect on tensile and flexural strength, diminishes the compressive strength and the hardness of the specimens. The interface behaviour between composite and tooth hard tissues is also improved by addition of bioglass powder as filler. SEM analysis evidences a good marginal integrity, proving reduced leakage risk. After 8 weeks immersion in artificial saliva, a continuous calcium phosphate layer is formed on the surface, that encourage the expectation for a good *in vivo* behaviour of the investigated dental biomaterials.

Acknowledgements

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