

The influence of organic-inorganic phase mixtures on degradation behavior of some resin composites used in conservative dentistry

A. CARACOSTEA (OBJELEAN)^{a*}, L. SILAGHI-DUMITRESCU^b, G. FURTOS^b, E. MÎNDRA BADEA^c, M. MOLDOVAN^b

^aUniversity of Medicine and Pharmacy “Iuliu Hatieganu”, Faculty of Dentistry, Department of Dental Materials and Ergonomics, 15 Babes Street, Cluj-Napoca, Romania,

^bBabes Bolyai University, “Raluca Ripan” Chemistry Research Institute, Department of Polymer Composites, 30 Fantanele Street, Cluj-Napoca, Romania

^cUniversity of Medicine and Pharmacy “Iuliu Hatieganu”, Faculty of Dentistry, Department of Department of Preventive Dentistry, 15 Babes Street, Cluj-Napoca, Romania

The ability of advanced dental restorative biomaterials to withstand to masticatory forces and permanent changes in the oral environment implies well balanced properties. The aim of this study is to comparatively assess hydrolysis and mechanical behaviour of three nanohybrid filled resin biocomposites with different polymeric matrix content (Experimental composite, “Raluca Ripan” Chemistry Research Institute, Cluj, Romania; Evetric, Ivoclar Vivadent; Filtek Z550, 3M ESPE) with a traditional Bis-GMA/TEGDMA based nanohybrid restorative composite (Herculite XRV Ultra, Kerr). Standardized shaped specimens specifically prepared according to ISO 4049/2000 were subjected to three-point bending test, compression strength test, diametral tensile strength test and to distilled water and artificial saliva water sorption evaluation, respectively. According to statistical analysis the mechanical performance and water sorption ability of the tested materials highlighted different behaviours dependant on the type and distribution of the filler particles, and on the type of different resin matrix monomers mixtures, respectively.

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1. Introduction

New improvements in nanotechnology have developed new types of dental biocomposites, which have to withstand to different attacks of the oral agents. According to the manufacturers, all of their composite restorative materials may be clinically indicated to all kinds of dental cavities. For a long-term performance of a restorative composite, applied in stress-bearing dental cavities, this could be possible, only if, these materials respond with an increased strength to the masticatory forces and high moisture degree of the oral environment [1-4].

Starting with 2000s, the dental composites evolved from minifilled to nanofilled and nanohybrid restorative materials. The latter ones are a combination of minifillers and nanofillers and thus, are able to incorporate a higher volume of filler particles. It is known that, the higher the filler content, the higher the mechanical properties will be [5-8], especially when pre-polymerized resin fillers (PPRF) are incorporated within the composite materials [6].

Some differences in mechanical strength were detected for different nanohybrid resin-based composites. This could be explained by another important elements which may influence the behaviour of resin composites: the size and distribution of the particles and the type, distribution and amount of resin matrix monomers [4-7]. A smaller size of particles may lead to increased values of tensile and

compressive strength, while a higher filler loading may decrease the polymerization shrinkage, which is related with a high adhesive ability of the resin composite to the hard dental tissues, and thus related to a better diametral tensile strength [2,4].

A well balanced polymerization shrinkage may also be associated with the amount of water uptake by the resin monomer systems. In this case, the composition of the resin matrix is very important and may depend on the type and characteristics of base and dilution monomers [5-7].

Commonly used resin-based dental composites are mainly composed of Bis-GMA (bisphenol A glycidyl dimethacrylate) and TEGDMA (triethylene glycol dimethacrylate) which represent the so-called “traditional resin monomer system”. In time, this system proved to lead to an increased water uptake and polymerization shrinkage, thus new mixtures of resin monomers were developed [7-9]. It was reported that, a mixture of UDMA (urethane-dimethacrylate) and Bis-EMA (bisphenol A polyethethylene glycol diether dimethacrylate) may replace TEGDMA [9-11]. Furthermore, this new combination of the two resin monomers, with higher molecular weight than the well-known dilution monomer, assures a lower polymerization shrinkage and improved properties, but provides an increased viscosity of the resin composite [2,3,5,9,10,11]. To counteract this inconvenient small amounts of TEGDMA or sometimes a mixture with PEGDMA (polyethylene glycol

dimethacrylate) are added to balance the rheological properties of the resin composites [6,11].

Given the fact that, these dental resin composites are placed in the oral cavity, where there is a high degree of moisture combined, also, with high occlusal forces, water uptake may negatively affect the longevity of the restorations, by release of unreacted monomers into oral fluids, detachment of the filler particles and a decrease in time of the mechanical properties [3,6,11-14]. It is also believed that, the water uptake mechanism is a "diffusion-controlled process" which leads to chemical hydrolysis of these restorative dental biomaterials [12-14].

Nowadays, special attention is given on the new nanohybrid type of filler particles combinations and also on the new possibilities of mixtures between different resin monomers to counteract the microleakage and secondary

caries, side effects of polymerization shrinkage and lowered properties of the resin composite restorative materials. Starting from this point, the purpose of our investigation was to comparatively assess the degradation behaviour to water sorption and mechanical performance of an experimental mixture of polymeric matrix-nanohybrid filled composite with two recently appeared nanohybrid resin composites and a traditional nanohybrid restorative resin composite.

2. Materials and methods

Three commercial dental restorative materials and one experimental composite were used for this study. The detailed information regarding the materials are described in the Table 1.

Table 1. Characteristic details of the dental restorative materials used in the study.

Material	Organic matrix*	Inorganic phase*	Particles size (Average)*	Filler distribution wt% (vol%)*	Company
Herculite XRV Ultra (XRVU)	-BisGMA -TEGDMA	-Barium glass filler -Colloidal silica -Prepolymerized filler(PPF)	0.4 µm	79 (59)	Kerr, Orange,US
Evetric (EV)	-BisGMA -BisEMA -UDMA	-Barium glass, -Ytterbium trifluoride, -Mixed oxides, Prepolymers	0.04-3µm	80-81 (55-57)	Ivoclar, Vivadent, Schaan Liechtenstein
Filtek Z550 (Z550)	-BisGMA -BisEMA -UDMA -PEGDMA -TEGDMA	-Zirconia silica -Silica filler	0.005-3µm (clusters 0.6-1.4 µm)	82 (68)	3M ESPE, St Paul,MN, USA
Experimental composite (EC)	-BisGMA -UDMA -TEGDMA	-BaO glass -Quartz - HAP/ ZrO ₂ -Colloidal silica	0.04-3µm	80 (67)	Raluca Ripan Chemistry Research Institute, Cluj-Napoca, Romania
BisGMA: bisphenol A diglycidyl ether dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; BisEMA₆: bisphenol A polyethylene glycol diether dimethacrylate; UDMA: urethane dimethacrylate; PEGDMA: polyethylene glycol dimethacrylate					

* According to the information provided by the manufacturers

The experimental composite was based on chemical compounds synthesized at "Raluca Ripan" Chemistry Research Institute (Babes Bolyai University Cluj-Napoca, Romania) and was prepared as a mono-paste material (A2 shade) (Table 1).

Mechanical properties

The mechanical performance of the studied materials was evaluated with flexural strength (FS), compressive strength (CS) and diametral tensile strength (DTS) tests at 23°C, with a universal testing device (Lloyd Instruments-LR5k Plus) and results recorded with Nexygen Software.

A total of one hundred and twenty specimens (n=10 specimens/each material/test, A2 shade) was used for

mechanical testing according to ISO 4049:2000 and based on ANSI/ADA Specification No.27 [15,16].

The composite materials were applied and compacted layer by layer in standardized Teflon moulds polymerized for 40 seconds from different directions with Optilux 501 halogen light-curing lamp (Kerr, US) with an output light intensity of 800±40 mW/cm². In order to remove any of the air bubbles and to distribute better the material, the moulds were firstly compressed in between two microscope glasses and then, during polymerization to prevent oxygen-inhibited layers both sides of the specimens were covered with Mylar transparent matrices. After curing, the excess material from the specimens and uncured monomers were removed with 400 and 600 grit abrasive paper. Prior the mechanical tests, all the

specimens were measured with a digital caliper (BMI, Digital caliper, Canada) and then stored in distilled water at 37°C for 24 h.

Flexural strength

For this test, rectangular specimens of 25±2mm x 2±0.1mm x 2±0.1 mm were subjected to a 3-point bending test at a cross-head speed of 0.5±0.25mm/min until fracture of the composite material.

The flexural strength, σ_{FS} , was calculated based on the following equation:

$$\sigma_{FS} = 3FL/2bt^2 \text{ (MPa)}$$

where F is the ultimate fracture load of the flexural force (N), L is the distance between the device's supports (20±0.01mm), b is the width of the specimen (mm) and t is the thickness of the tested specimen.

Compressive strength

For the compressive test, cylindrical specimens (4±0.1 mm diameter, 6±0.1 mm height) were subjected to a compression force at a 1±0.3 mm/min cross-head speed until fracture. The compressive strength was calculated using the following relation:

$$\sigma_{CS} = (9.81F)/(0.785d^2) \text{ (MPa)}$$

where F is the ultimate fracture load of the compressive force (N) and d is the diameter of the sample (mm).

Diametral tensile strength

This in vitro mechanical method develops similar forces with the flexural test, but implies the use of cylindrical specimens (6±0.1mm diameter, 3±0.1mm height) subjected to a diametral compressive load on the margins of the samples, which, in the given situation, will induce an opposite and proportional tensile force to the diameter of the sample. Thus, the diametral tensile strength may be considered as an indicator test for the brittleness of a material [2,3,5].

The diametral tensile strength, σ_{DTS} , was measured using the following equation:

$$\sigma_{DTS} = (2F)/(\pi dt) \text{ (MPa)}$$

where, F is the ultimate load at fracture (N), d is the diameter of the specimen (mm) and t is the height of the disc.

Water sorption

The ability of a resin composite material to uptake water may be seen on one hand, as a method to counteract the polymerization shrinkage and on the other hand, the possibility to release in the oral environment uncured

monomers and to shorten the longevity of the restorative material by decreasing its physical and mechanical properties [13,17].

For the present study the following two types of liquids were used to measure the water sorption of the composite materials: distilled water and artificial saliva.

To accomplish the water uptake test disc-shaped samples (15mm diameter and 1mm thickness) (n=10 samples/ each material) were prepared according to ISO 4049/2000/ANSI/ADA Specification No.27 [15,16]. The materials were applied and condensed in standardized Teflon molds, compacted with microscope glasses on both sides and light-cured (halogen light-curing lamp-Optilux 501,Kerr, US) for 40 sec in multiple directions, while were covered with a Mylar transparent matrix to prevent the oxygen inhibited layers. For removal of the excess material and uncured monomer a 400 and 600 grit SiC abrasive papers were used.

All the specimens were dried in a vacuum desiccator at 37°C for 24h. Prior their weight measurement the discs were kept once again in the desiccator at 23°C. The measurements were repeated until a constant weight was obtained. The specimens were divided in two groups and immersed in distilled water and artificial saliva at 37°C for the following reference days: 1, 7, 14 and 30. During the first week the weight was measured daily. The handling of the samples during weight measurement was done each time with care, according to the following protocol: use of tweezers to remove the specimens from the tested medium, use of an absorbent paper for each of them, 15 seconds air-dry and after 1 minute the samples were weighted and then re-immersed in the medium. The protocol cycle was repeated for each of the tested days.

The absorption of water for the above mentioned reference days for both storage media was calculated according to the following formula:

$$W_{sp} = (m_1 - m_2) / V$$

where m_1 is the mass of the sample after distilled water or artificial saliva immersion time (μg), m_2 is the constant mass obtained after the specimen was kept in the desiccator (μg) and V is the volume of the sample (mm^3).

Statistical analysis

The results were analysed with ANOVA and Tukey's post-hoc test for pairwise comparisons at the level of significance of 5%. Possible Pearson's correlations were accomplished to investigate the relation between the average particles size, volume percentage of filler distribution, water uptake (distilled water and artificial saliva) and the analysed mechanical tests. The data were managed using the SPSS 17.0 software for Windows XP (SPSS Inc, Chicago, IL,USA) and XLSTAT 7.5.2. (for Excel, Microsoft Office 2010.)

3. Results

Based on Shapiro-Wilk's and Levene's test all the results showed a normal distribution of variables and homogeneity of variances, respectively, for $p > 0.05$.

Mechanical properties

The statistical data for all the mechanical tests used in the study are described in the Table 2. Analysis of variances (ANOVA) showed significant differences of mechanical degradation among all the studied materials ($p < 0.0001$) (Table 2, Fig. 1, Fig. 2, Fig. 3).

Table 2. Results for Flexural strength, Compressive strength and Diametral tensile strength of the studied materials

Group	σ_{FS} (MPa)	σ_{CS} (MPa)	σ_{DTS} (MPa)
EC	81.47(8.55)a	222.87(11.76)a	38.82(4.08)a
EV	94.49(6.48)be	263.2(12.55)bd	39.9(6.05)a
Z550	122.25(8.24)c	269.53(11.53)cd	51.51(6.05)b
XRVU	91.64(7.19)de	235.38(11.21)a	39.81(6.06)a
F(3,40)	51.866	35.724	11.452
Sig.	.000	.000	.000

Different low case letters from each column indicate statistically significant subsets (Tukey HSD test for $p < 0.05$)

As shown in Table 2 and Fig. 1, the highest statistical significant values of flexural strength were recorded for Z550 among all the resin composites, while the EC had the lowest results ($p < 0.05$). The Tukey HSD multiple comparisons showed no statistical significant different values between EV and XRVU when tested for flexural strength ($p = 0.839$).

Subjected to compressive test, the EC-XRVU and EV-Z550 pairs had registered similar mean values ($p = 0.1$ and $p = 0.63$, respectively). However, the highest statistically significant mean value was obtained for Z550 ($p < 0.05$), followed by EV, XRVU and EC (Table 2, Fig. 2).

No statistical differences were found among EC, EV and XRVU resin composites regarding the diametral tensile strength mean values ($p > 0.05$). The Z550 nanohybrid resin composite was able to withstand to diametral tensile forces and gave the highest statistical mean values compared to the other studied materials ($p < 0.05$) (Table 2, Fig. 3).

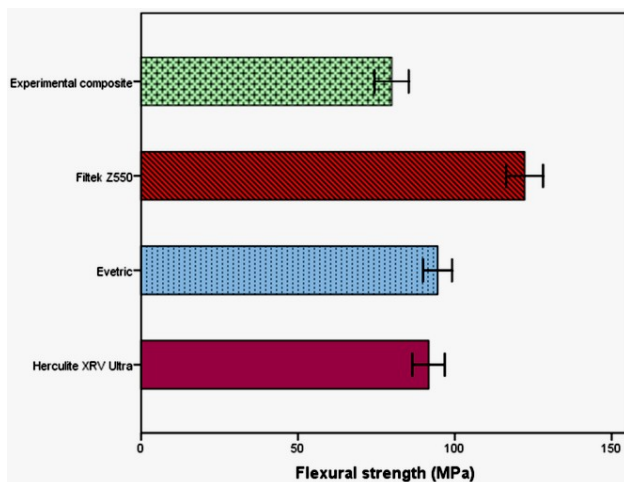


Fig. 1 Bar charts of mean flexural strength values for the tested materials. (Error bars represent 95% CI with $n = 10$).

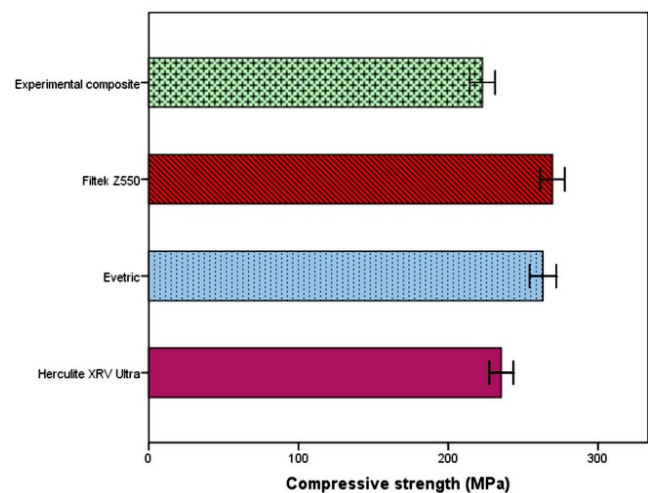


Fig. 2 Bar charts of mean compressive strength values for the tested materials. (Error bars represent 95% CI with $n = 10$).

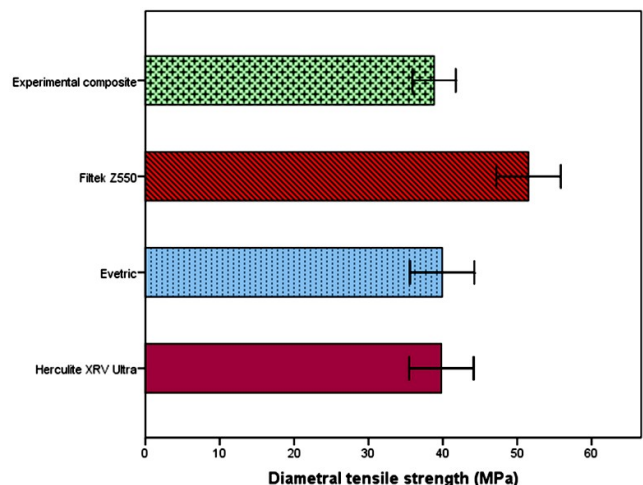


Fig. 3 Bar charts of mean diametral tensile strength values for the tested materials. (Error bars represent 95% CI with $n = 10$).

Water sorption

The One-way ANOVA test by Day results showed statistical significant differences of all of the four

nanohybrid resin based composites regarding immersion in distilled water and artificial saliva for the tested period of time ($p < 0.05$) (Table 3).

Table 3. Results for water sorption of the studied resin composites immersed in distilled water (DW) and artificial saliva (AS) after 1,7,14,30 days ($\mu\text{g}/\text{mm}^3$).

Immersion time	XRVU		EV		Z550		EC	
	DW	AS	DW	AS	DW	AS	DW	AS
1d	28.19 (3.57)a	30.2 (3.58)a	24.19 (3.18)a	26.03 (4.18)a	21.8 (2.75)a	24.03 (4.18)a	29.87 (3.4)a	33.19 (3.34)a
7d	30.59 (5.23)a	30.31 (3.67)a	24.41 (4.19)a	30.19 (3.19)bd	28.21 (4.53)b	29.89 (3.59)be	33.99 (3.89)ac	34.59 (3.6)a
14d	32.75 (3.64)ac	32.71 (4.25)ac	32.57 (3.75)bd	30.09 (3.72)ad	32.89 (3.69)ce	33.49 (3.27)ce	33.83 (3.68)ac	35.2 (3.72)a
30d	35.86 (3.56)bc	35.12 (2.32)bc	28.89 (3.69)cd	32.05 (2.47)cd	36.46 (3.22)de	38.01 (2.14)d	37.85 (3.02)bc	39.71 (2.07)b
<i>F(3,40)</i>	6.426	4.387	11.619	5.415	30.885	30.623	8.609	7.532
<i>Sig.</i>	.001	.01	.000	.004	.000	.000	.000	.000

Different low case letters from each column indicate statistically significant subsets (Tukey HSD test for $p < 0.05$)

Pair-wise multiple comparisons (Tukey HSD, $\alpha=0.05$) revealed a significant higher water sorption in both storage media for XRVU in the day 30 compared with day 1 ($p=0.001$; $p=0.018$) and day 7 ($p=0.031$; $p=0.021$). No statistical differences were found between the other homogenous subsets ($p > 0.05$) (Table 3).

For EV resin composite material, the highest statistical mean value of water sorption in distilled water was found after 14 days and the lowest after 1 day of immersion compared with the day 30 ($p < 0.05$). However, no statistical differences were detected by the Tukey HSD test between the subsets day 1-day 7 and day 14-day 30, respectively ($p > 0.05$). After 1 day of immersion in artificial saliva, the same resin composite had the lowest statistical mean value compared to day 7 and day 30 ($p=0.05$ and $p=0.002$, respectively), as well no statistical differences were found among day 7, 14 and 30, respectively ($p > 0.05$) (Table 3).

After 1 day of immersion in distilled water, Z550 had the lowest significant mean value of water uptake compared to the reference days ($p_{1-7}=0.002$; $p_{1-14} < 0.0001$; $p_{1-30} < 0.0001$), as well after one week of immersion had lowest significant sorption compared with the mean value after 14 days and one month ($p_{7-14} = 0.031$, $p_{7-30} < 0.0001$). No statistical differences were observed between day 14 and day 30 ($p=0.139$). The One-Way Anova comparisons revealed a significant lower mean value for day 1 of water uptake in artificial saliva compared with the evaluated days ($p_{1-7} = 0.002$; $p_{1-14} < 0.0001$; $p_{1-30} < 0.0001$) and a higher significant mean value after one month of immersion compared with day 7 and day 14 ($p_{30-7} < 0.0001$, $p_{30-14} = 0.024$).

After 30 days of distilled water immersion the experimental resin composite (EC) absorbed the highest statistical significant amount of water compared with the first day ($p < 0.0001$). Regarding the other groups of tested days, Tukey HSD post-hoc test showed no statistical differences between their mean values ($p > 0.05$). The

material had a statistical significant higher water uptake in artificial saliva after one month of immersion compared with the tested reference days ($p_{30-1} < 0.0001$; $p_{30-7} = 0.006$; $p_{30-14} = 0.019$). No statistical data were found when the other homogenous subsets of days were compared ($p > 0.05$) (Table 3) after one week and two weeks of artificial saliva immersion ($p=0.098$) (Table 3).

When the reference days of water uptake in distilled water were analysed by Material with One-way analysis of variances, the statistical test showed significant differences between the group of materials for day 1 ($F(3,40)=12.941$, $p < 0.0001$), day 7 ($F(3,40)=8.075$, $p < 0.0001$) and day 30 ($F(3,40)=14.023$, $p < 0.0001$), likewise no statistical differences were found between the studied materials after 14 days of distilled water immersion ($F(3,40)=0.23$, $p=0.875$) (Fig 4).

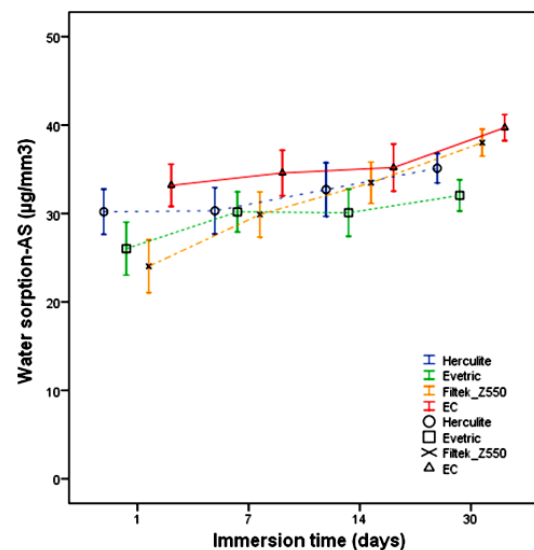


Fig. 4 Mean values of the water sorption of the tested materials immersed in distilled water after 1,7,14 and 30 days ($\mu\text{g}/\text{mm}^3$). (Error bars represent 95% CI with $n=10$).

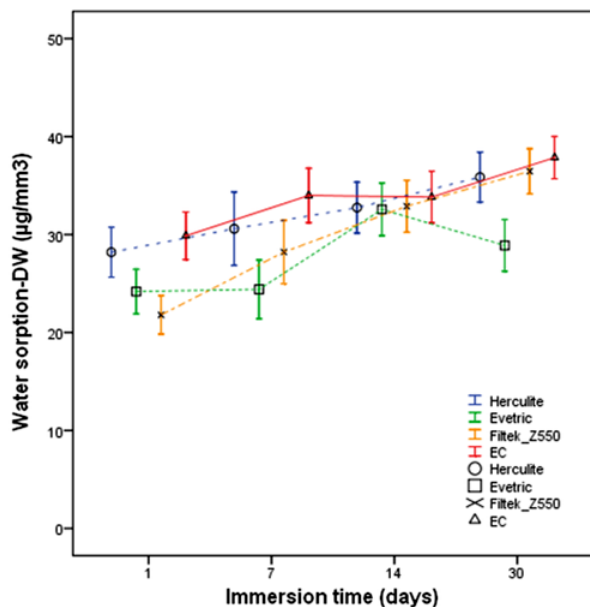


Fig. 5 Mean values of the water sorption of the tested materials immersed in artificial saliva after 1,7,14 and 30 days ($\mu\text{g}/\text{mm}^3$). (Error bars represent 95% CI with $n=10$).

Regarding the water sorption in artificial saliva, ANOVA test by Material showed significant differences among all the group of materials for day 1 ($F(3,40)=11.527$, $p < 0.0001$), day 7 ($F(3,40)=4.04$, $p = 0.014$), day 14 ($F(3,40)=3.204$, $p = 0.035$) and day 30 ($F(3,40)=22.332$, $p < 0.0001$) (Fig. 5).

Based on the graphic from Fig. 4 and on the Tukey HSD post-hoc test results it was observed that in the first day, XRVU had the highest significant water absorption in distilled water compared to EV ($p = 0.042$) and Z550 ($p < 0.0001$) and Z550 had the lowest significant mean value than EC material ($p < 0.0001$). No statistical significant differences were found between the other homogeneous subsets ($p > 0.05$) for the same reference day (Table 3, Fig. 4).

After one week of immersion, EV resin composite exhibited the lowest statistical mean value compared to XRVU ($p=0.02$) and EC material had the highest significant water uptake compared with EV and Z550 ($p < 0.0001$ and $p=0.032$, respectively). The post-hoc test highlighted no statistical significant differences among the other tested materials (Table 3, Fig. 4). Distilled water uptake behaviour after 30 days was significantly lower for EV compared with XRVU, Z550 and EC, respectively ($p < 0.0001$). Likewise, no statistical significant differences were found for the other subsets of tested materials ($p > 0.05$) (Table 3, Fig. 4).

After the first day of artificial saliva immersion, the pairwise multiple comparisons indicated a higher

statistical significant water sorption for XRVU compared with Z550 ($p=0.005$) and between the homogeneous subsets EC-Z550 ($p < 0.0001$) and EC-EV ($p = 0.001$), respectively. No statistical differences were found between the mean values of the other subset groups of materials ($p > 0.05$) (Table 3, Fig. 5).

Immersion for one week in artificial saliva revealed for EC the highest significant water uptake (39.71 ± 2.07 , $p < 0.05$) and similar mean values among the other resin composite materials ($p > 0.05$) (Table 3, Fig. 5).

In the day 14, only the experimental material exhibited a significant higher water sorption compared with EV ($p=0.022$), while the other tested materials had similar mean values ($p > 0.05$) (Table 3, Fig. 5).

After one month of artificial saliva immersion EV resin composite had the lowest mean value of water uptake compared to XRVU ($p=0.021$), Z550 ($p < 0.0001$) and EC ($p < 0.0001$), respectively. For the same period of time, the post hoc test showed for EC the highest values compared with XRVU and EV ($p < 0.0001$) and no statistical differences of water sorption with Z550 ($p = 0.346$) (Table 3, Fig. 5).

At the end of the study, all the materials had a slightly higher water uptake values when immersed in artificial saliva compared with distilled water ($p > 0.05$).

Correlations

a. Correlations between mechanical properties

Pearson's correlation test indicated a statistically significant positive relationship between flexural strength (FS) and diametral tensile strength (DTS) ($r = 0.97$, Sig.(2-tailed) = 0.03) and compressive strength (CS) ($r = 0.83$, Sig.(2-tailed) = 0.172), respectively, and a positive relationship between DTS and CS ($r = 0.7$, Sig.(2-tailed) = 0.3).

b. Correlations between mechanical properties and water sorption

A negative significant correlation was found between compressive strength (CS) and water sorption mean values in both storage media after one day of immersion ($r_{\text{DW}} = -0.988$, Sig.(2-tailed) = 0.01 and $r_{\text{AS}} = -0.978$, Sig.(2-tailed) = 0.02). Likewise, a negative relationship was found between the sorption values and flexural strength (FS) ($r_{\text{DW}} = -0.899$ and $r_{\text{AS}} = -0.919$) and diametral tensile strength ($r_{\text{DW}} = -0.801$ and $r_{\text{AS}} = -0.810$), respectively, with Sig.(2-tailed) > 0.05 (Fig. 6 a,b).

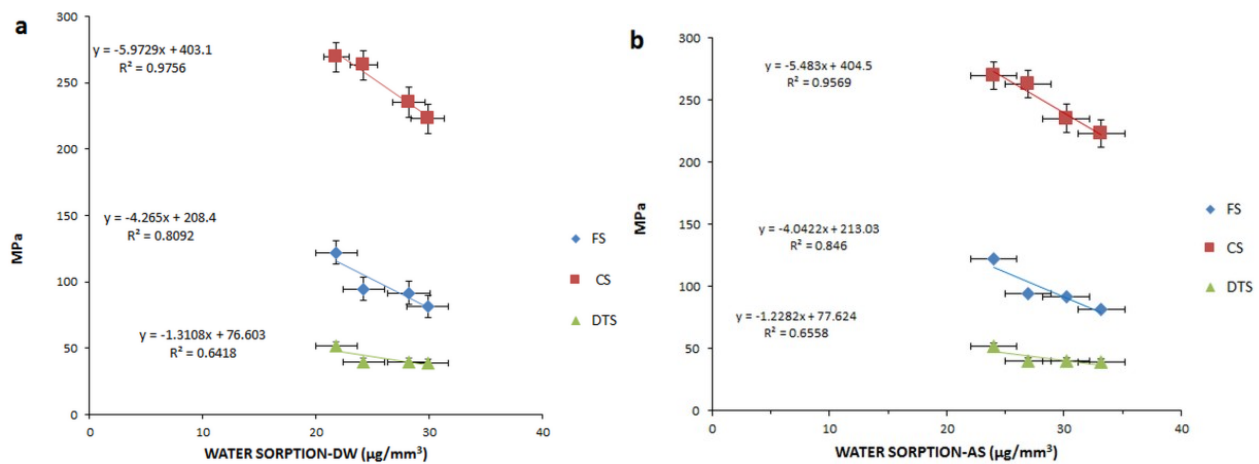


Fig. 6 Correlations between the mean values of the mechanical properties and water sorption of the resin composites immersed at day 1 in a) distilled water (DW) and b) artificial saliva (AS). (Error bars represent standard errors - SE with $n=4$).

c. Correlations between mechanical properties and filler volume fraction and average filler size

There were observed moderate positive correlations between FS, DTS and filler volume fraction ($r_{FS} = 0.34$, $r_{DTS} = 0.56$, Sig.(2-tailed) > 0.05) and a weak relationship with CS ($r_{CS} = 0.124$, Sig.(2-tailed) > 0.05) (Fig. 7).

Pearson's correlation test established a weak negative relationship between the average filler particles and CS ($r_{CS} = -0.22$, Sig.(2-tailed) > 0.05) and a weak positive relationship with FS and DTS ($r_{FS} = 0.005$, $r_{DTS} = 0.26$, Sig.(2-tailed) > 0.05).

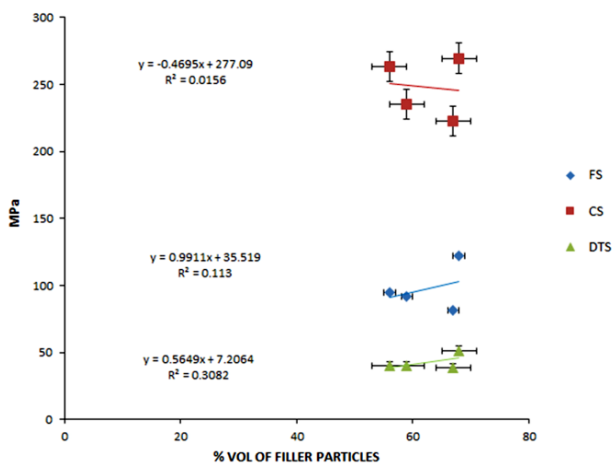


Fig. 7 Correlations between the mean values of the mechanical properties and volume fraction of filler particles of the resin composites. (Error bars represent standard errors - SE with $n=4$).

4. Discussions

Oral cavity is a complex environment, which gathers combined actions of interactive factors and forces. Thus, the opportunity to observe pure interactions or behaviours of the resin-based biocomposites inside the oral cavity is not always possible, especially when new trends of restorative materials are delivered on the dental market.

Nano-technology has greatly evolved in the past years, with release of new resin based composites used for conservative dentistry. Thus, new types of silanized particles (nano-sized fillers and nanomeric clusters) were able to be mixed with resin matrix to result the "nanofilled" resin composite materials [1,2,11,18-22]. It is stated that an increase of filler fraction and a decrease in size of the particles will provide better mechanical and physical properties [1,2,20].

Usually compressive forces occur when wear and abrasion mechanisms act in the oral cavity. Masticatory forces developed during food ingestion, parafunctional forces which lead to bruxism or grinding of the teeth are few of the processes which may influence the mechanical performance of a restorative biomaterial. Thus, the higher the compressive strength values, the higher the resistance to cycling fatigue and wear of the resin-based composite material will be [17]. Likewise, flexural strength combines tensile and compressive forces which usually are met when dental biomaterials have to restore different oral situations. In this case, flexural strength brings information about stiffness of the composite biomaterials and their behaviour in dynamic oral movements.

In his studies, A.R. Curtis et al [6,21], using different storage media and mechanical tests, analysed the degradation behaviour of seven commercial resin based composites: Heliomolar (microfilled), Filtek Z100(microfilled), Filtek Z250(microhybrid), Filtek Supreme XT (Body and Translucent shades) (nanofilled), Grandio (nanohybrid) and Grandio Flow (nanohybrid). The authors showed that the use of "nanomeric clusters" within the composition of nanofilled resin based composites may lead to a reinforcement of the materials and subsequently to an increased degradation strength value compared to the tested microhybrid filled and nanohybrid filled resin composites, respectively. Moreover, it was also reported that a zirconia-silica fillers may exhibit higher mechanical strength compared with a barium glass filler type [20]. In our work only the resin composite Z550, claimed [12] to have zirconia-silica filler particles, had a better mechanical performance among all the tested nanohybrid filled resin based composites. This

behaviour may be explained by the presence of a similar filler distribution with Filtek Supreme XT and the presence of “nanomeric clusters” [11].

For EV was reported a 80-81wt% (55-57vol%) mixture of ytterbium trifluoride prepolymers, mixed oxides, and barium glass filler particles and a combination of Bis-GMA, Bis-EMA and UDMA resin monomers (Table 1). This composition, type and distribution of fillers and resin polymeric matrix is similar with Tetric EvoCeram (nanohybrid resin based composite), provided by the same manufacturer [23]. In our study EV was able to perform better than the traditional XRVU resin composite when subjected to compressive stress, and, likewise, had a similar performance at flexural and diametral tensile tests with the other tested materials. Taking in consideration the filler and resin monomers mixture similarity and the fact that Medline research did not bring any data regarding the mechanical performance of EV, one may only presume that this material can mechanically behave alike with Tetric EvoCeram.

Based on the different filler particles (barium glass, quartz, hydroxyapatite/zirconium oxide, colloidal silica) used within inorganic phase, the experimental resin biocomposite exhibited the lowest values at the three-point flexure test, but it had a similar performance with XRVU and EV, respectively, when subjected to compression and diametral tensile strength. This behaviour may be explained by the use of different fillers mixture properly bonded to resin matrix by a specific coupling agent [5,8,17-19]. Nevertheless, all the mean values of this material after the mechanical tests are in agreement with those recommended by the ISO standards [15,16]. Moreover, our mechanical performance results of XRVU and EC are in agreement with reference [19].

Since, all the materials used in this investigation had a similar volume fraction of filler particles and average filler sizes, respectively, only their type and distribution may influence the mechanical behaviour of the resin based composites. Thus, a positive correlation was found among the assessed mechanical tests for all the resin composites. Furthermore, a statistical relationship was established between the three-point bending test and diametral tensile test, which agrees with the reference [4]. Nevertheless, it is important to mention that, no statistical dependence was found between the mechanical properties, volume fraction of particles and average filler size.

During oral clinical service, a restorative material is forced to withstand not only to different occlusal forces, but also to temperature changes of ingested foods, and further to withstand to a high degree of moisture. Based on the literature findings, regarding water sorption of resin based dental materials [3,6,9,12-14,18,22], the main factors which may strongly influence their behaviour in the oral moist environment are the resin matrix monomers mixture and its hydrophilicity, coupling agent type and filler distribution [7,23,24].

The water sorption behaviour of the tested materials during the reference days, were within a range between $21.8 \mu\text{g}/\text{mm}^3$ (day 1; Z550) to $37.85 \mu\text{g}/\text{mm}^3$ (day 30; EC) for distilled water and between $24.03 \mu\text{g}/\text{mm}^3$ (day 1;

Z550) to $39.71 \mu\text{g}/\text{mm}^3$ (day 30; EC), and are within the maximum values recommended by ISO standards ($40 \mu\text{g}/\text{mm}^3$) [15,16] (Table 3, Fig. 5, Fig. 6).

The residual monomers of Bis-GMA/TEGDMA based resin composites, during water storage were shown to have a higher hydrophilicity compared with UDMA-based composites and with other monomer based materials [3,6,7,9,12,14,25]. In our investigation similar sorption behaviour for both storage media was observed for XRVU and EC at the end of the study. Although the resin matrix used for EC material is a mixture of Bis-GMA (60%), TEGDMA (30%) and UDMA (10%), under the given circumstances, the material is a predominately Bis-GMA/TEGDMA based resin composite and thus, this might be an explanation for its similarity behaviour with XRVU.

The water uptake values of XRVU were found to be higher in our study than those indicated by Sava S. et al [18]. It is important to mention that in our work we have used a halogen light-curing lamp for 40 seconds, while in the in the previously mentioned study, the authors have used a LED device for polymerization of the specimens (40 seconds). Thus, based on the fact that a LED curing unit improves the degree of resin monomers conversion and the physical and mechanical properties [23], it might be possible to explain the differences between our results and those obtained in the reference [18].

At the beginning of the study EV and Z550 resin composite materials started with a significant lower water sorption values in both storage media compared with the other tested materials and after one month, Z550 exhibited a statistical significant higher water sorption in both immersion media among all the materials, while EV had the lowest significant absorption in both storage media. Nevertheless, increased water sorption values were observed after 30 days in both immersion media for all the assessed materials. This could be explain by the possibility of these materials to have a longer saturation period of time than the tested one [6,12,18].

Similar behaviour with Z550 may be observed for different Filtek-related resin composites (Filtek Z350, Filtek Z250, Filtek Supreme XT, etc.), for which were reported [6,10,12,13,24] a high water sorption ability compared with similar restorative dental composites, after several periods of time. These materials have in common the resin matrix monomers mixture and the nanofilled ones have also in common the presence of silica nano-sized fillers, agglomerations of zirconia-silica particles and “nanomeric clusters” of silica [11]. It was thought that the nano-clusters are able to give a certain strength to water degradation by opposing to crack growth [6,21]. It is possible that the presence of a “high specific surface area” [8] provided by the multiple silanised nano-sized particles within agglomerations/non-agglomerations of the filler particles of Z550 and a certain porosity of the nanomeric clusters [6,12,20,21,23,24] to lead to a higher hydrolysis and water sorption, which in time may interfere with the other physical [6,23], optical [10] or mechanical properties [20,21] of the restorative material. Contrary on our findings, Gonulol N. et al [14] has indicated an

intermediary water sorption for Z550, which was statistically lower than Beautifil II (Bis-GMA/TEGDMA based resin composite) and higher than Tetric N-Ceram (Bis-GMA/UDMA/TEGDMA based resin composite). Worth to specify that, in their work, the authors have used a slightly similar water sorption protocol with ours, but they used the ratio percentage of weight gain/loss after 28 days for water sorption to report the results, while in our study the mean values of water degradation were calculated and expressed in $\mu\text{g}/\text{mm}^3$. Thus, both type of results have to be taken in consideration as they were reported, but without using any comparison.

Based on different studies [7,9,23-25], it was shown that the replacement of TEGDMA with Bis-EMA and/or UDMA and the decrease of Bis-GMA percentage within the composition of a resin based composite, may lead to a higher hydrophobicity of the resin matrix. These information are also observed in our study for EV which after 30 days of distilled water and artificial saliva immersion exhibited a statistical lower value of water sorption compared with the other tested resin composites ($p < 0.0001$).

The degradation strength of a restorative resin based composite is not only dependent on separate pure mechanical or water sorption behaviour, but they intricate to the whole phenomenon. Thus, in our investigation was observed a decrease of mechanical performance concurrent with an increase of water sorption in both storage media after the first day of immersion, even if there were not found any statistical differences between the studied oral-like simulated liquids for all the assessed materials (Fig. 6).

5. Conclusions

Within the limitations of this study, the following conclusions may be withdrawn:

- all the materials had a distinct degradation behaviour according to their specific organic-inorganic phase combination;
- the type and distribution of the filler particles have influenced the mechanical performance, while new mixtures of monomers within the polymeric matrix have influenced the water sorption of the tested materials;
- higher filler loading within pre-polymerized nano-aggregates, may lead to a higher water uptake and degradation of the polymeric matrix;
- the mixture of hydrophobic monomers may assure a better strength to water sorption and mechanical reduction.

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