SALIVA STUDY FOR A NOVEL DENTAL COMPOSITE WITH POLYMERIC MATRIX

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Novel composite materials based on polymer matrix with inorganic filler were characterized to evaluate their potential application in dentistry. Previously reported filler and composites were investigated in correlation with their behavior in artificial saliva. The saliva study involved pH and microhardness determinations, ions release and saliva sorption during soaking in saliva for 30 days. The conclusion assessed was that the investigated composite materials showed a good behavior, comparable with commercially employed dental composites.

INTRODUCTION

For decades, the dental profession has searched for aesthetic materials to replace the traditional amalgam restorative, providing that the new biomaterials would exhibit properties comparable to amalgam.[1] The dental composites seemed to offer an appropriate combination of properties to replace the amalgam, but they lack its ability to produce a better seal with time and are more easily affected by saliva exposure.[2] That was the reason for this study and it involved the investigation of the effects of artificial saliva on newly synthesized dental composites.

Dental restorative composites are heterogeneous materials having a polymeric matrix (continuous phase) in which fillers of various types, sizes, shapes and morphologies are embedded (disperse phase).[3] An interfacial phase bonds the continuous and disperse phases into a unitary material. The polymeric matrix of a dental composite is typically formed by free radical polymerization of a resin that is usually of the methacrylate class.[4] Polymerization is started by the formation of initiating radicals by photochemical reactions.

The monomers used in this study were 2,2 propyl bis-phenyl glycidyl dimethacrylate (Bis-GMA) and triethylenene glycol dimethacrylate (TEGDMA). Both monomers have a common feature, namely they contain two double bonds in their molecules. Consequently, such structures are able to form networks, from the very beginning of the photopolymerization process.[5] As TEGDMA contains a hydrophilic sequence (oligo-ethylene glycol), this monomer was used in small amounts, rather as a diluent for Bis-GMA (which is characterized by a high viscosity at room temperature-1200 Pa s). The filler employed was a glass in the $CaO-Al_2O_3-SiO_2$ system, with the inorganic phase content of 80% (wt).

MATERIALS

The monomer system employed was Bis-GMA and TEGDMA at a ratio of 75/25 (wt%), purchased by Aldrich Chem. Co, used as received without further purification (see Fig. 1). In order to perform the UV-curing process, camphoroquinone (CQ) and N,N-dimethylaminoethyl methacrylate (DMAEMA) (Aldrich

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Chem. Co) used as photoinitiators, were added to each mixture, at a ratio CQ/DMAEMA 3/1 (wt).[6] The synthesized glass filler, having the composition (by mole) 50% SiO_2, 25% Al_2O_3, 20% CaO, 4% CaF_2, and 1% ZnO, reported elsewhere,[7] with a particle size of <10 μm, was subsequently incorporated into the polymeric matrix using load concentrations of 80% (wt). The filler was kept as such or treated with a silane 3-(Trimethoxysilyl)propyl methacrylate (MPTS), by a known method [8] (see Table 1).

The synthesis of the composites was performed into HDPE moulds (25 mm diameter, 1.5 mm thickness), employing a 500 W medium pressure Hg lamp (Helios Italquartz), at room temperature, under nitrogen atmosphere.[9] Both top and bottom surfaces were irradiated for 180 s, in steps of 30 s. The light intensity at the sample surface was 50 mW/cm^{2}. The polymerization reaction was completed by heating off the rigid composites at 60°C. They were allowed to post-polymerize for 24 h. The rigid disk products were used for further investigations.
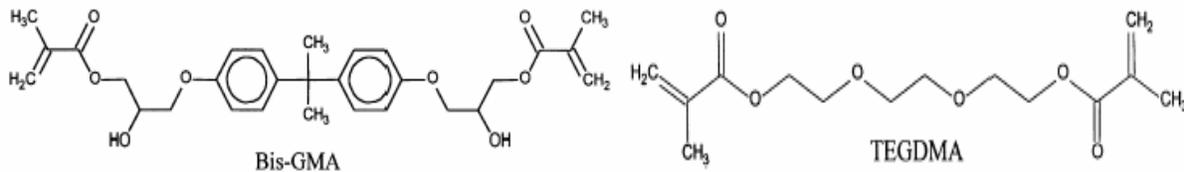

Fig. 1 – Bis-GMA and TEGDMA structures.

Table 1

Compositions of experimental composites (wt%)

Material code	Bis-GMA	TEGDMA	CQ	DMAEMA	Glass filler
A	74.02	24.67	0.98	0.32	-
D	14.81	4.93	0.19	0.06	80
S	14.81	4.93	0.19	0.06	80 (treated with silane) *

* the amount of powder in the silane-treated resin might be in lesser amount than in the resin containing glass without silane treatment, since silane treatment coats the glass with a polysiloxane layer, thus the absolute amount of glass might be smaller.[10]

EXPERIMENTAL

An extensive study of the behavior of the A, D and S materials in artificial saliva (composition of artificial saliva is reported in Table 2) was performed and the following properties were evaluated: pH variation, microhardness (Vickers), saliva sorption, and cations release. The saliva study employed 10 specimen disks of each A, D and S samples that were kept in an incubator (Incubator Bicasa, ALPHA) at 37°C, in containers containing artificial saliva, for periods ranging from 1 h to 720 h (30 days).

Table 2

Composition of the artificial saliva at a pH=5.00[11-12]

NaCl (g)	KCl (g)	$CaCl_2$ $2H_2O$ (g)	NaH_2PO_4 $2H_2O$ (g)	Urea (g)	Distilled Water(mL)
0.4	0.4	0.795	0.78	1	1000

The *pH investigations* employed a pHmeter Hanna Instruments (Hanna pH Tester Checker SIGMA). The immersion liquids were controlled at intervals ranging from 1 h to 720 h, after proper agitation of solutions.

In order to investigate the *cations release* in saliva, specimens of A, D and S samples were immersed into saliva for 30 days, at 37°C. After the incubation, the immersion solution was removed and tested by atomic absorption spectrophotometry (1100B-acetylene and 5000PC-graphite; Perkin-Elmer, Wellesley, Mass). The solution was analyzed for calcium, aluminium, zinc and silicium ions. Each sample was analyzed for all 4 ions, measured as μg/L (ppm), averaged across 5 replicates.

The *microhardness measurements* were measured on 10 specimen disks before and after soaking in saliva, for periods ranging from 1 to 720 h, at ten different randomly selected sites on each specimen. The equipment employed was a Vickers microhardness equipment-Leitz Wetzlar (Germany). Vickers microhardness number (VHN) was determined from the following equation:

$$VHN = 1.854 \times \frac{F}{d^2}$$

where F is the load (kgf) and d the length of the diagonal indentation (mm) (arithmetic mean of 10 measurements). As VHN value should normally be expressed as a number only,[13] we have reported it without the units.

The measurements were performed on samples kept in no refreshed saliva, as the VHN of conventional composite dental materials that were also stored in saliva that was refreshed daily showed values comparable to those where the saliva was changed more rarely.[13]

For *saliva sorption* determination 10 specimen disks of each A, D and S samples were prepared and placed in a desiccator containing dried silica gel. After 24 h, they were removed, stored in an oven at 25°C for 1 day and weighed with a precision of 0.001 mg. The disks were immersed in saliva at 37°C for 1, 10, 20 and 30 days, then removed, dried for 2 minutes in air and weighed (m_2). After this weighing, the specimens were reconditioned to a constant mass (m_3). The values of saliva sorption (SS) were calculated for each disk using the following formula:[15]

$$SS = \frac{m_2 - m_3}{V}, \mu g/cm^3$$

where V is the sample volume.

RESULTS AND DISCUSSION

This laboratory study employed an UV light source that approximated the spectral distribution of commercial dental curing sources ($\lambda = 420\text{-}500$ nm) [16] and the light intensity on the samples surfaces, while allowing large areas to be cured, appropriate for the intended investigations. To complete the curing of composites, a subsequent mild heating [17] and 24 h postpolymerization period [18,19] were employed.

The pH determinations (see Fig. 2) revealed an increase of one unit towards the base character in the case of composites D and S. This is a good tendency as the tooth structures are affected by acidic medium, an increase in the pH value being explained by ions released into saliva by the glass filler. The polymeric matrix seemed not affected by soaking in saliva. To check this tendency, the pH determination was correlated with the ions release that revealed the presence of Ca cations in the immersion fluid. The results of the atomic absorption analysis of the solutions are presented in Table 3, and illustrate an increase only in the case of Ca^{2+} concentrations of 1 ppm, for both composites (D and S).

During exposure to saliva, cations from the composites may be liberated from the glass filler *via* an acid-base reaction with saliva acidic part. The composites contain no water in their composition thus any contribution of the acid-base reaction to overall setting must occur after exposure of the material to saliva. Were this to be the case, the conventional prediction would be that this exposure to saliva should lead to an improvement in mechanical properties (and this appears to be the principle of our materials as presented in Fig. 3), despite the possible counter-effects of dissolved water that acts as a plasticizer from the point of view of the resin.[20]
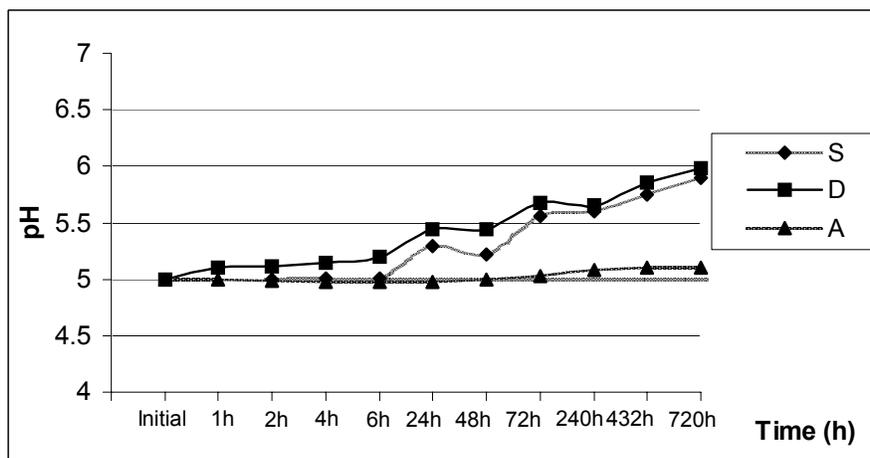

Fig. 2 – pH variation over time for soaking in saliva of selected materials.

Ion	Quantity in final solution, ppm			Quantity in saliva, ppm
Sample	S	D	A	
Ca^{2+}	15.80 (1)	15.80 (1)	14.80 (-)	14.80
Al^{3+}	Not detectable*	Not detectable*	Not detectable*	Not detectable
Si^{4+}	Not detectable*	Not detectable*	Not detectable*	Not detectable
Zn^{2+}	Not detectable*	Not detectable*	Not detectable*	Not detectable

* the analysis was performed with both Atomic Absorption Spectrophotometers (acetylene flame and graphite furnace, the latter being more sensitive).

During the soaking in aqueous solution of saliva, unreacted monomers might leach out and thus, by the removal of the monomer molecules that have a plasticizer effect, the micro-hardness values would increase. However, by monitoring the A sample behavior, we can affirm that the last phenomenon seemed not to have an effect on the composites, thus the hardening being mainly attributable to the acid-base reaction.
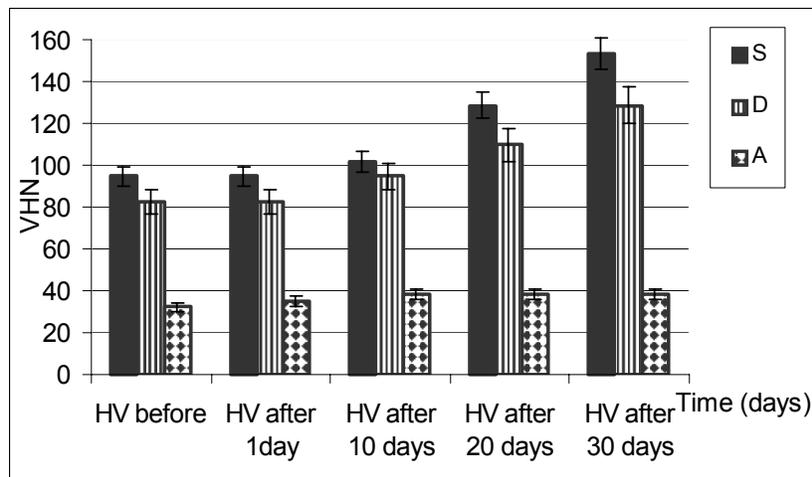

Fig. 3 – Microhardness variation in saliva over time for selected materials.

The specimens stored in artificial saliva showed an increase in the final weight after final desiccation (see Fig. 4). According to ISO 9000s standard for dental restorative resins, the water up-take should be lower than 50 μg/mm³,[21] thus our composites being suited for dental usage. Having this indication for water, we can assert that saliva values are better as, in theory, polymers immersed in distilled water should absorb more water than those stored in artificial saliva, due to the effect of the osmotic pressure. Most of the specimens tested reached over 80% of their final volumetric expansions and changed in weight within the first 20 days. Afterwards they followed a slower and gradual increase in the volume and weight, suggesting an asymptotic tendency. One positive effect of water absorption for composites is that it provides a mechanism for the potential compensation of polymerization shrinkage although measurements of marginal adaptation have revealed that hygroscopic expansion does not always cause complete closure of contraction gaps around composite materials.[22]

Water sorption for composites incorporating treated or nontreated glass filler were in the same range, though lower values were found for those formulated with silanized filler. The results for surface microhardness and saliva sorption showed similar tendencies for S and D composites, with no significant differences in values at 1 day or 10 days.

Nevertheless, the results for saliva sorption cannot be easily translated to *in vivo* behavior. When a material is constrained within a cavity, the extent of water up-take and swelling may be limited by the restraining forces imposed by the cavity walls.[2]
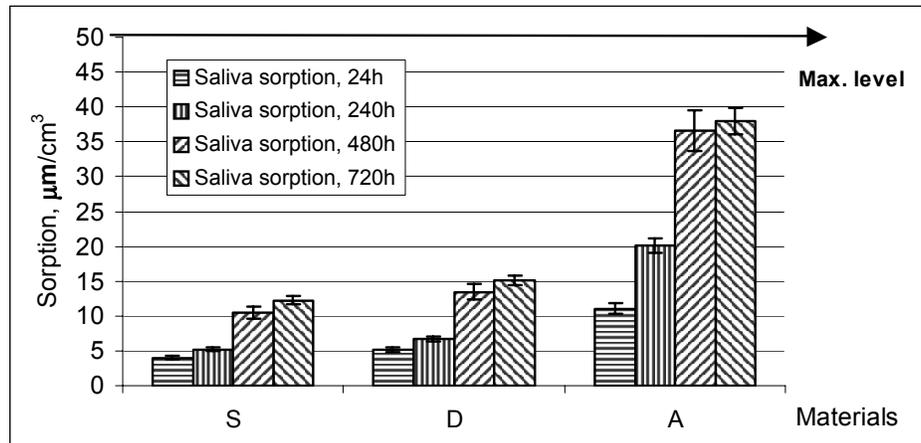
Fig. 4 – Saliva sorption variation in time for selected materials.

CONCLUSIONS

The present study focused on the characterization of novel composite materials with innovative filler to be used in dentistry. An extensive study of the behavior of the synthesized materials in artificial saliva was performed and the following properties were evaluated: pH variation, cations release, microhardness (Vickers) and saliva sorption.

Based on our findings, composites S and D synthesized with and without silane respectively, were comparable as saliva behavior concerns and the expected large differences between them were not found, this being in agreement with several studies involving micro- and nano-fillers.[23-24] Composite S, synthesized with silane, proved to be the best material and possessed good properties as compared with other materials reported by the literature[25], proving to be potentially useful in dental composites area, in both direct and indirect applications.

Nevertheless, clinical degradation of the investigated materials is likely to be more complicated, as the biological environment causes specific chemical and mechanical degradation processes. This is the reason why further research involving biological testing is necessary as a must condition for the closure remarks on this composite.

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