

POLYMERIC COMPOSITES FOR DENTISTRY. II. PHYSICAL INVESTIGATIONS ON NEW DENTAL COMPOSITES

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New composite materials, consisting in a polymer matrix filled with an inorganic glass, have been synthesized and characterized with the aim of dental usage. The research involved the synthesis and investigation of new glass filler having the composition in the CaO-Al₂O₃-SiO₂ system that was used as such, or treated with silane. This study was continued with the generation of the polymer matrix based on 2,2 propyl bis-phenyl glycidyl dimethacrylate (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA) monomers. Composites containing Bis-GMA and TEGDMA at the ratio (wt/wt) of 75/25, filled with 80% wt filler, treated or not treated with silane have been prepared. The synthesis was followed by investigation of several properties of the silanized composite in comparison with the non-silanized one, namely viscoelastic behavior and mechanical properties - elasticity and flexural strength.

INTRODUCTION

Hard dental tissues (enamel and dentine) are natural composite materials and consist in collagen biopolymers and hydroxyapatite microcrystals. In a quest to mimic the natural tooth composition, numerous studies involved the synthesis and characterization of various synthetic dental composites having as a continuous phase a polymeric matrix and as disperse phase different fillers, in various amounts. To bond the filler particles to resin matrix, the filler was generally coated with a silane coupling agent.

In previous papers we have reported the synthesis of a new glass to be used as filler^{1,2} in dental composites, and the synthesis of new composites based on a polymeric matrix filled with different amounts of filler, as well as their main features. To obtain further characterization, we have carried out investigations employing the newly synthesized glass in the CaO-Al₂O₃-SiO₂ system, with the inorganic phase content in the range of 80% (wt). The filler was treated with a

silane γ -methacryloxypropyltrimethoxysilane (MPTS). The monomers used were 2,2 propyl bis-phenyl glycidyl dimethacrylate (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA).

MATERIALS

Synthesis

This study involved a new glass filler that was previously reported and characterized.^{1,2} The polymer matrix was synthesized by employing a weight ratio of Bis-GMA to TEGDMA 75/25 (wt%) and camphoroquinone (CQ) and N,N-dimethylaminoethyl methacrylate (DMAEMA) have been used as photoinitiators. The synthesis method was described elsewhere.¹ The newly synthesized glass filler, with a particle size of <10 μ m, was kept as such, or further treated with MPTS and was subsequently incorporated into the matrix using load concentration of 80% (wt). The syntheses of the composites were performed into

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special moulds. Each paste (named D and S, as reported in Table 1) was placed into a polyethylene mould (25 mm diameter, 1.5 mm thickness). Both

top and bottom surfaces were irradiated for 180 s. The composites were further characterized from the mechanical point of view.

Table 1

Compositions of experimental composites (wt%)

Material code	Bis-GMA	TEGDMA	CQ	DMAEMA	Glass
D	14.81	4.93	0.19	0.06	80
S	14.81	4.93	0.19	0.06	80 (treated with silane)

Silanization Method

The silane was diluted with ethanol, so that the final concentration of the silane in solution was 10% (wt), by a known method³ intended to form a polysiloxane layer on the surface of the glass powder. The same experimental procedure was applied for the glass obtained in bar-shape (length-10 mm, height-5 mm, width-5 mm) for comparison purposes. However, the amount of glass powder in the silane treated composite might be in lesser amount than in the resin containing glass without silane treatment, since silane treatment coats the glass with a polysiloxane layer.⁴

EXPERIMENTAL

Effectiveness of silanization on glass was assessed by employing contact angle measurements and Differential Thermal Analysis (DTA).

The contact angle measurements employed a Kruss G1 Drop Shape Analysis and the measurements were performed in air, at room temperature by sessile drop technique. Advancing and receding angles were obtained by increasing or decreasing the drop volume until the three-phase boundary moved over the surface. The investigations involved the glass, poured in a bar-shape (length-10 mm, height-5 mm, width-5 mm) with or without silane treatment. The investigation continued with the confirmation of the silanization effect on composites. 10 specimen disks, obtained as previously reported, were considered for this determination and on every sample 10 measurements were performed, placing the liquid drops in different parts of the sample surface.

DTA was carried out by using a Perkin Elmer 7-DTA and involved the following conditions: heating rate of 10°C/min, over the interval 25 – 1500°C, in argon flow (20 ml/min). The samples for DTA were fine glass powders with particle sizes <10 µm, treated with silane.

Measurement of the viscoelastic properties was performed by Dynamic Mechanical Thermal Analysis (DMTA) using a Dynamic Mechanical Thermal Analyzer MK III, Rheometric at 1 Hz and a heating rate of 5 °C/min. The measurements were carried out over a temperature range 30-250 °C (type of deformation: single canty-lever bending, peak to peak applied deformation: 16µm). This investigation was applied to bar-shaped specimens obtained in HDPE

moulds and cut to required dimensions appropriate for this test (length-20 mm, height-2.5 mm, width-15 mm).

Mechanical testing involved the investigation of the elasticity and flexural strength and was performed on 10 rectangular-shaped specimens that were moulded and irradiated for 180 s on both sides by the method reported in the case of the disks and cut to the desired shape on a lathe (length-50 mm, height-5 mm, width-5 mm).

The elastic modulus was obtained non-destructively from the fundamental period of the vibrating specimens as reported in literature,⁵ by employing a signal analyzer (Grindo Sonic - J.W. Lemmens). As the Poisson's ratio (μ) depends on the material itself, but varies between 0.25 and 0.35 for dental composites, a constant value of 0.30 was chosen since it was found that a change of μ by 0.05 resulted in changes of Young's modulus considerably less than the standard deviation.⁶

A universal testing machine (Sintech 10D, MTS; USA) equipped with a 5KN load cell, at a crosshead at 0,1mm/min was used for the flexural test. The flexural strength (FS) was obtained by measuring the load at fracture and it was computed using the formula:

$$FS = \frac{3 \times F_m \times l}{2 \times b \times h^2} \text{ (MPa)}$$

where F_m is the peak load in N, l is the distance between the two supports in mm, b is the width of the specimen in mm and h is the height of the specimen in mm.

RESULTS

The role of silane as a coupling agent between the glass filler and the matrix is explained by the nature of the MPTS, which is a bifunctional molecule,⁷ having an organic functional radical that can co-polymerize with the resin part of the composite, and three alkoxy groups ready to react with surface hydroxyl groups of the glass.

To verify the presence of the silane in the composite, the wetting of the materials was examined for distilled water. The advancing and receding angles were measured and Figure 1 reports the aqueous wetting data.

The DTA analysis revealed for the silanized glass a decomposition registered below 500°C, attributable to the decomposition of the organic

silane itself (see Figure 2). The peaks registered at higher temperatures are belonging to the inorganic glass, ² namely: the inflexion point recorded at 789°C corresponds to the glass transition range,

whereas the exothermal peak at 946° may be attributed to the precipitation of crystalline phases. The value of 1427°C represents the liquidus temperature.

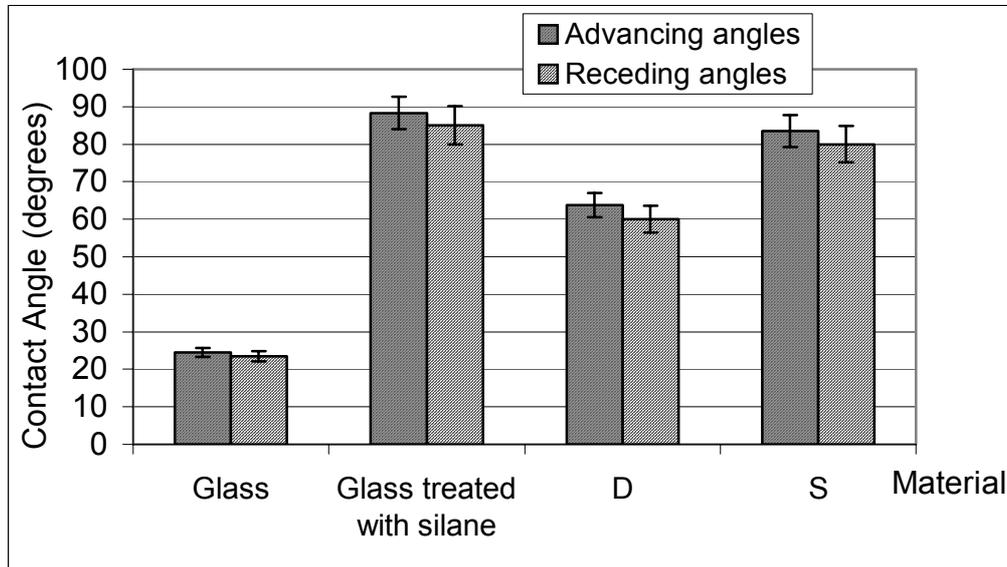


Fig. 1 – Advancing and receding contact angles in water on selected materials. The bar within the box represents the standard deviation of the data set.

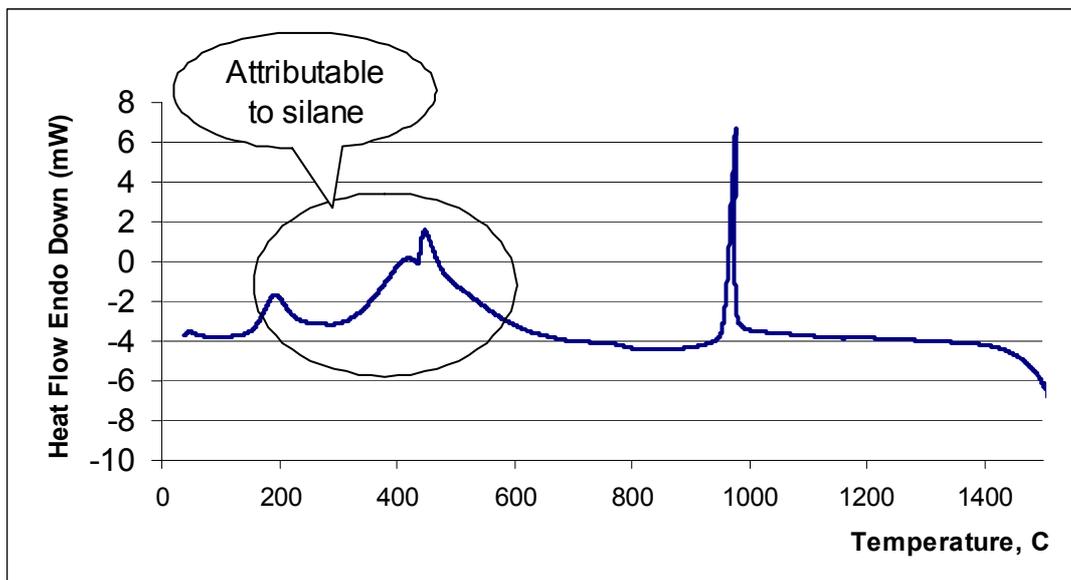


Fig. 2 – DTA analysis of silanized glass.

In order to evaluate the main features of the changes in mechanical properties of the cured composites, that are induced by the state transitions as temperature is varying, DMTA measurements of storage modulus (E'), and loss factor ($\tan \delta$) were performed. Glass transition temperatures, T_g , were measured as the maximum of the $\tan \delta$ curve in the DMTA thermograms. The data in the Figure 3

show T_g of the cured composites ($T_{gD} = 177^\circ\text{C}$, $T_{gS} = 186^\circ\text{C}$).

The values of the E and FS in the case of D and S composites were $E_S = 20.6$ GPa and $E_D = 14.84$ GPa and $FS_S = 55.4$ MPa and $FS_D = 53.7$ MPa, respectively.

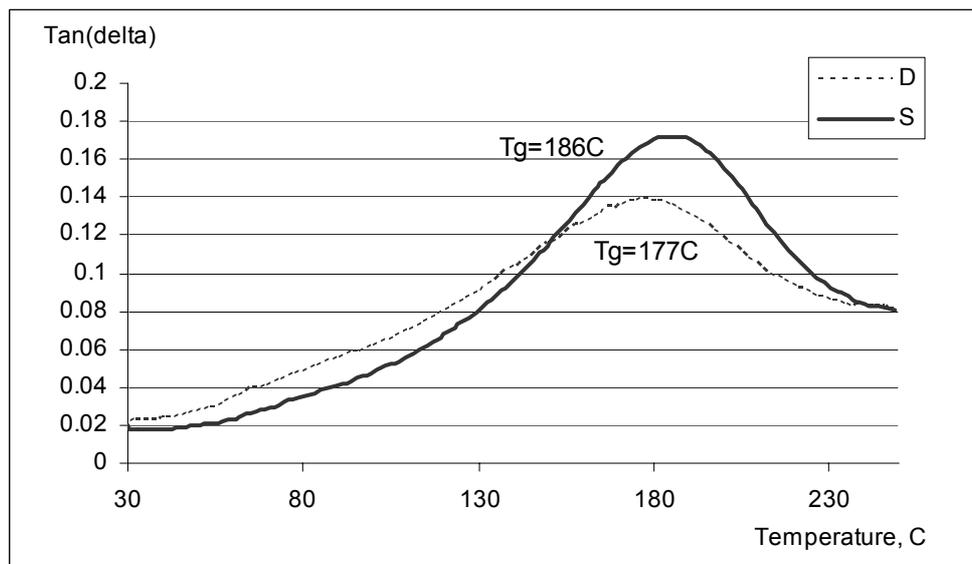


Fig. 3 – T_g - composition dependency on selected materials.

DISCUSSION

Following the previously described methods,^{1,2} the glass filler was subjected to a silanization treatment and investigation of the thus synthesized composite (code S), in comparison with the non-treated one (code D).

Silane has a role of a coupling agent between the glass filler and the matrix and this is explained by the nature of the MPTS, which is a bifunctional molecule,⁷ having an organic functional radical – methacryloxypropyl – that can co-polymerize with the resin part of the composite, and three alkoxy groups ready to hydrolyze in the water-alcohol solution and then to react with surface hydroxyl groups on the glass.⁸ The result of this treatment, might be the formation of covalent bonding and, hence, the improvement of the adhesion between the inorganic filler and organic polymer matrix.^{9,10}

During the synthesis of the silanized composite, the silanization process is a critical step, this being the reason for the special attention devoted to the study of its efficacy. Contact angle value of a liquid spread on a substrate has been used as an indicator of total surface energy and wettability of the substrate.¹¹ To verify the presence of the silane in the composite, the wetting of the materials was examined for distilled water and the advancing and receding angles were measured. As the MPTS provides a hydrophobic treatment, it can be noticed that the contact angles values increase with the presence of silane. As can be noticed the difference between the advancing angles and receding one is quite small (varying between 1 and 4°), this

proving, according to literature,^{12, 13} a small surface roughness of our materials.

All the obtained T_g are well above the temperatures met in the mouth, thus being fitted for potential dental utilization. In the case of the S composite, the value of T_g is shifted to higher temperatures, as the compatibility between the matrix and the filler is better, and so the chain mobility decreases.

The elasticity and flexural strength investigations for the composites obtained with, or without the silanization treatment suggest that the best material is that obtained with a silanization treatment performed on filler. However, dispersion of a large fraction of glass filler into the highly viscous resin matrix represents a rather difficult technical problem, especially when it is performed by hand spatulation. Thus, the differences in values for FS might be influenced by homogeneity of the samples, as the glass filler phase was manually incorporated. Nevertheless, the composite with 80% wt glass, treated with silane, showed good values in comparison with other commercially available composites, as reported by literature.^{14, 15}

CONCLUSIONS

The present study aimed the synthesis and physical investigations of new composites with innovative glass filler to be used in dentistry. The newly synthesized glass based on the CaO-Al₂O₃-SiO₂ system, used as filler, was a white powder, with particle sizes carefully selected. The study

continued with the silanization of the glass filler and its incorporation into the composites using a load of 80% filler (wt), based on previous tests. The effectiveness of silanization was attained by means of contact angle measurements and DTA, proving to be successful. Other useful properties have been evaluated: viscoelastic properties by employing DMTA revealed that all the obtained Tg were well above the temperatures met in the mouth, thus being fitted for potential dental utilization; mechanical point of view was considered and the Young modulus and flexural strength were also acquired and their values indicated a material fitted for further dental utilization.

It seems that the composite materials, developed with silanization performed on the glass filler prior to the composite synthesis, have better properties, proving to be potentially useful in dental composites area.

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