

PHOTOINITIATED FUNCTIONALIZATION OF MINERALS FILLERS FOR DENTAL COMPOSITES

Samir BAYOU,^a Mohammed MOUZALI,^{a,*} Laurence LECAMP^b and Philippe LEBAUDY^b

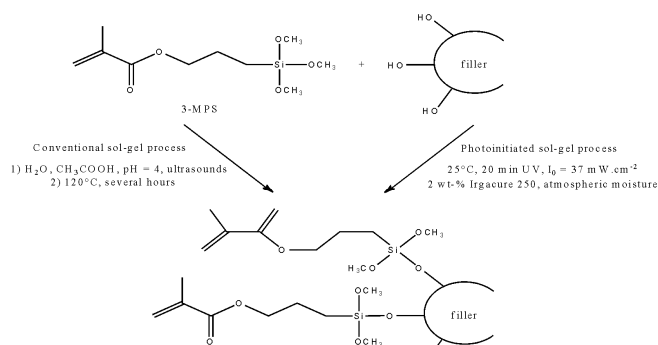
^aLEPCMAE, Faculté de Chimie USTHB BP32 El-Alia Alger, Algérie

^bNormandie Université, INSA de Rouen, CNRS UMR 6270, FR 3038, Avenue de l'Université,
BP 08, 76801 Saint Etienne du Rouvray, France

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Organosilanes bearing alkoxy silane are widely used in sol-gel process. In this process, the hydrolysis reaction is usually carried out in aqueous or hydroalcoholic solutions and the condensation reaction requires high temperatures. The hydrolysis of the alkoxy silanes in the presence of water is fast and can be considered as complete. The obtained silanols can then condensate into oligomers by a much slower reaction that depends on temperature. Our objective is to devise a simple synthesis way for grafting such coupling agent onto the mineral fillers surface without using solvent and heating. Mineral fillers are used as reinforcement in dental composites based on Bis-GMA/TEGDMA.

The way developed in this work involves a photoinitiated sol-gel process. It consists in using a photoacid generator to activate the hydrolysis and condensation reactions under atmospheric humidity. Mineral oxides usually used in dental materials were chosen as inorganic filler: the zirconia (ZrO_2) which is a radiopacifiant agent and the alumina (Al_2O_3) which allows improving the mechanical properties of the composite. A kinetic study of the self-condensation of the 3-MPS used as coupling agent in the presence of Irgacure 250[®] as photoacid generator was carried out and the operating conditions (irradiation intensity and time) of the functionalization reaction were optimized. Grafted fillers were characterized by FTIR spectroscopy and thermogravimetric analysis. FTIR and TGA analyses of the particles after treatment allow confirming the grafting. Compared to the conventional way, the photoinitiated process proves to be faster, easier, less expensive in energy, and much more efficient in terms of 3-MPS grafted quantity.



INTRODUCTION

Commercial restorative composites currently contain a mixture of various crosslinking dimethacrylates and mineral fillers and many investigations are conducted about the reduction of polymerization shrinkage, the improvement of biocompatibility, wear resistance and processing properties. Using optimized filler particles can contribute to the development of such materials.

The dental composite consists of a resin matrix and a reinforcement. The resin matrix consists of a polymer network based on Bis-GMA / TEGDMA. These dimethacrylate monomers polymerize in presence of radical initiator.

In dental materials, the use of mineral fillers has several effects. The first one is the increase of the formulation viscosity which allows an easier implementation and application of the paste. The second one is the reduction of the volume

* Corresponding author: mmouzeli@gmail.com

shrinkage during the resins polymerization.¹⁻⁶ In both cases, the concentration, the morphology and overall the size of the filler particles have a great importance. Indeed, the smaller the particles, the higher the contact area and therefore the mixture viscosity, on the one hand,^{7,8} and the weaker the intergranular phase and thus the lower the volume shrinkage⁹⁻¹² on the other hand. The increase of the fillers percentage also has the effect of improving the mechanical properties (especially if the rate of fillers is higher than 60 % in volume) and of decreasing the thermal expansion coefficient. It should be noted that most of these aforementioned improvements are only possible if strong and durable bonds are established between the fillers and the organic matrix. In this aim, mineral fillers usually undergo a surface treatment called sizing (or silanization) using a bi-functional coupling agent. The major obstacle to the use of nanocharges prepared *ex situ* is the difficulty of compatibilizing these nanocharges in the organic matrix by the used conventionally route for microcharges: silanization. The use of organomineral hybrid materials obtained by the sol-gel process can solve this problem.

The sol-gel process is nowadays a common way to functionalize fillers. As a general rule, this process implements hybrid precursors of formula $M(OR)_z$ where OR is an alkoxyde group and M is a metal such as Si, Sn, Ti, Zr ... The sol-gel process is usually carried out on aqueous media and in the presence of a catalyst (acid or basic). Condensed species are then created, leading to a viscous sol (aggregation of crosslinked inorganic oligomers

forming a colloidal solution) and thereafter to a gel (solid network). In 1978, Fox and al first described a photoinitiated sol-gel process.¹³ They showed that the Brönsted superacids generated during the photolysis of some cationic photoinitiators can activate hydrolysis and condensation reactions of a silicate compound (Scheme 1).

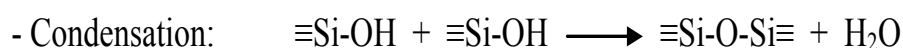
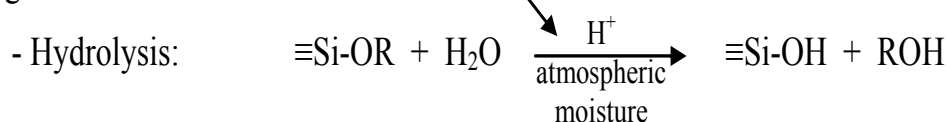
More recently, this photoinitiated process knows a revival of interest¹⁴ because of some advantages: (i) fast reaction rate compared to the conventional sol-gel method; (ii) no requirement of water addition. This synthesis method has been applied in varied domains according to the used hybrid precursor.

In dental composites, 3-methacryloxypropyltrimethoxysilane and octyltrimethoxyacryloxy-propyltrimethoxysilane are usually used as hybrid precursor. Indeed, both these molecules exhibit a good compatibility towards organic and mineral media thanks to, on the one hand, the $-Si-OCH_3$ groups which can be easily hydrolyzed and connected with the free OH functions present on the fillers surface, and on the other hand, the methacrylate function which can react with the methacrylic double bonds of the matrix in a later polymerization step.¹⁵⁻¹⁷ The hydrolysis and polycondensation of these precursors lead to an inorganic network that possesses a strong potential for reducing the polymerization shrinkage stress of the overall composite.^{18,19} However, to the best of knowledge, no investigation has been carried to functionalize mineral fillers by a photoinitiated sol-gel process.

a) Photolysis of onium salt:



b) Sol-gel reactions:



Scheme 1 – Schematic representation of the sol-gel polymerization catalyzed by super acid generated from photolysis of onium salt.

Hence, this work aims to study the photochemical functionalization of zirconia and alumina nanoparticles commonly blended in dental composites based on Bis-GMA/TEGDMA (75/25). The hydrolysis and condensation reactions are conducted with 3-MPS as coupling agent. The efficiency of photoinitiated and conventional sol-gel processes are especially compared.

EXPERIMENTAL

1. Materials

Two mineral oxides were used as inorganic fillers: the zirconia (ZrO_2 , Aldrich) and the alumina (Al_2O_3 , Evonik). The physicochemical characteristics of these powders are shown in Table 1.

3-methacryloyloxypropyltrimethoxysilane (3-MPS, 98%, Aldrich) and Irgacure 250® (BASF) were used as coupling agent and photoacid generator, respectively (Scheme 2).

2. Functionalization of the fillers

2.1. Conventional sol-gel process

The protocol followed in this work was inspired by Peditto's work dealing with the compatibilization of nanosilice fillers and an epoxy matrix using epoxy cyclohexylethyltrimethoxysilane as coupling agent.²⁰

0.2 mL of hybrid precursor 3-MPS was solubilized in 100 mL of distilled water. The pH of the solution was adjusted to 4 by the addition of glacial acetic acid. After 15 min under ultrasounds, 1 g of ZrO_2 was added. The whole solution was placed again under ultrasounds for 2 hours. The reaction of condensation was then carried out in an oven at 120°C for 4 hours.

The functionalization of the Al_2O_3 filler was carried out according to the same protocol by using 1 mL of 3-MPS and 2 g of Al_2O_3 . The condensation reaction was carried out for 7 hours.

The functionalized fillers were washed 3 times with distilled water, then 3 times with chloroform, filtered and dried at 120°C for 2 hours.

2.2. Photoinitiated sol-gel process

Formulations comprising 70 wt-% of ZrO_2 and 30 wt-% of 3-MPS or 40 wt-% of Al_2O_3 and 60 wt-% of 3-MPS were prepared. The filler quantities chosen here correspond to the maximum amounts which can be dispersed in the 3-MPS and 2 wt-% of Irgacure 250® was then added. The whole was mixed under magnetic stirring at room temperature for 20 minutes.

These formulations were then displayed on a glass plate by means of a calibrated bar allowing a deposit of 80 μm thick layer. The reaction of grafting was then carried out under atmospheric humidity and an UV radiation coming from a xenon-mercury lamp (LC8, Hamamatsu, Japan). The radiation was polychromatic and its intensity was measured at 254 nm with a radiometer (Intraspec II Oriol VLX-3W).

The functionalized particles were washed 3 times with chloroform and dried under vacuum before being crushed.

3. Analytical techniques

3.1. FTIR spectroscopy

The apparatus used is a spectrometer 2000 FT-IR Perkin Elmer equipped with an ATR cell (MKII Golden Gate of Specac). The mixture (3-MPS/Irgacure 250) was spread on the ATR crystal before to be UV-cured at room temperature under atmospheric moisture. The irradiation was made through the same xenon-mercury lamp as previously mentioned.

The decrease of the absorption band characteristic of the reactive function ($Si-OCH_3$) was followed at 2840 cm^{-1} . The condensation yield was then calculated as follows:

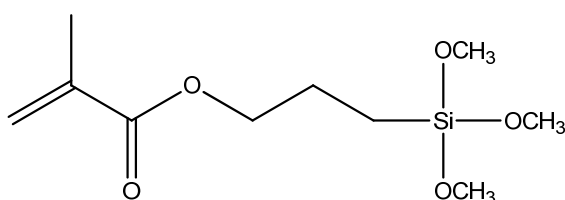
$$Yield(\%) = \frac{A_0 - A_t}{A_0} \times 100$$

where A_0 and A_t are the absorbance of the characteristic absorption band at initial and t times, respectively.

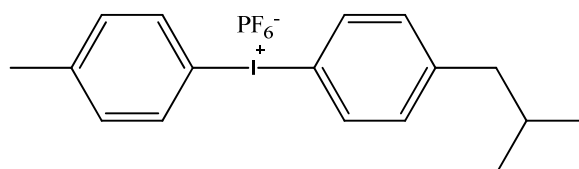
Table 1

Physicochemical characteristics of the used fillers

Fillers	Density	Diameter (nm)	Specific surface (m^2/g)
Al_2O_3	3.9	10	100
ZrO_2	5.8	< 100	50



3-MPS



Irgacure 250®

Scheme 2 – Chemical formula of the photoinitiated sol-gel process reactants.

3.2. TGA analysis

Thermogravimetric analysis was performed on a TA Instruments apparatus (TGA Q500). Samples were submitted to an isotherm at 100°C during 1 hour and then to a heating rate of 10°C.min⁻¹ up to 800°C. The overall analysis was carried out under nitrogen atmosphere.

RESULTS AND DISCUSSION

1. Optimization of the condensation reaction

The photoinitiated self-condensation of the 3-MPS in the presence of Irgacure 250 ® was first studied in order to optimize the operating conditions. In this aim, the disappearance kinetics of the methoxysilane band at 2840 cm⁻¹ was followed by infrared spectroscopy at room temperature for various irradiation intensities (Figure 1).

As expected, for incident light intensities lower than 37 mW.cm⁻², hydrolysis rate and yield increase with the irradiation intensity because of the increase of superacid amount generated by photolysis. According to Scheme 1, the reaction requires a sufficient amount of atmospheric humidity to be initiated. For high luminous intensity values, the heat given off by the UV lamp is greater, causing a reduction in atmospheric

humidity in the reaction medium, thereby reducing the conversion of the Si-O-Me functions. The light intensity emitted must be of sufficient value to initiate the reaction but with less heat generation from the lamp so as not to alter the atmospheric humidity. Figure 1 illustrates this variation well, showing that an intermediate intensity of 37mW/cm² gives the highest conversion. This produced heat decreases the atmospheric moisture in the reaction medium. Such a result means that the moisture is necessary to the run of the reaction. It should be also noticed that no methacrylic double bond conversion has been observed during this process (data not shown). In the following study, the photoinitiated grafting reaction was carried out at room temperature with a light intensity of 37 mW.cm⁻² at 254 nm. An irradiation time of 20 min was set.

2. Functionalization of mineral particles

The functionalization of ZrO₂ and Al₂O₃ particles was carried out according to both processes (conventional and photoinitiated) described in the experimental part and illustrated in Scheme 3.

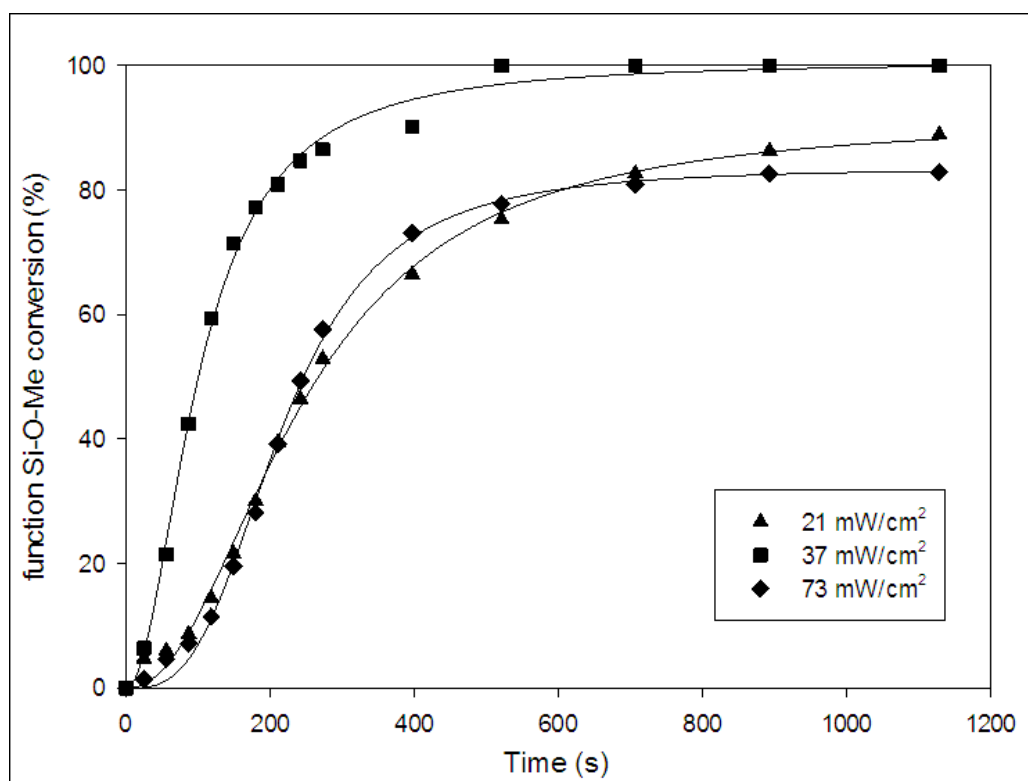
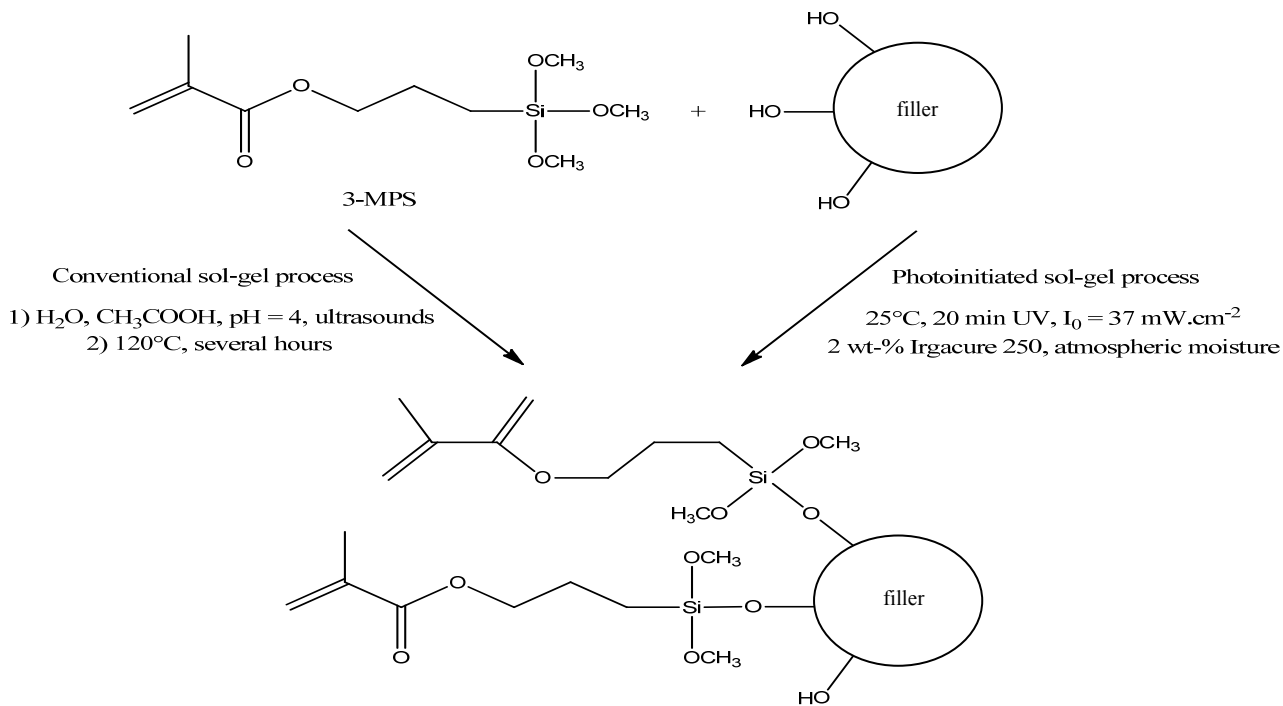


Fig. 1 – Influence of the irradiation intensity on the conversion kinetics of Si-O-Me functions.



Scheme 3 – Schematic representation of both conventional and photoinitiated 3-MPS grafting processes on fillers bearing hydroxyl groups.

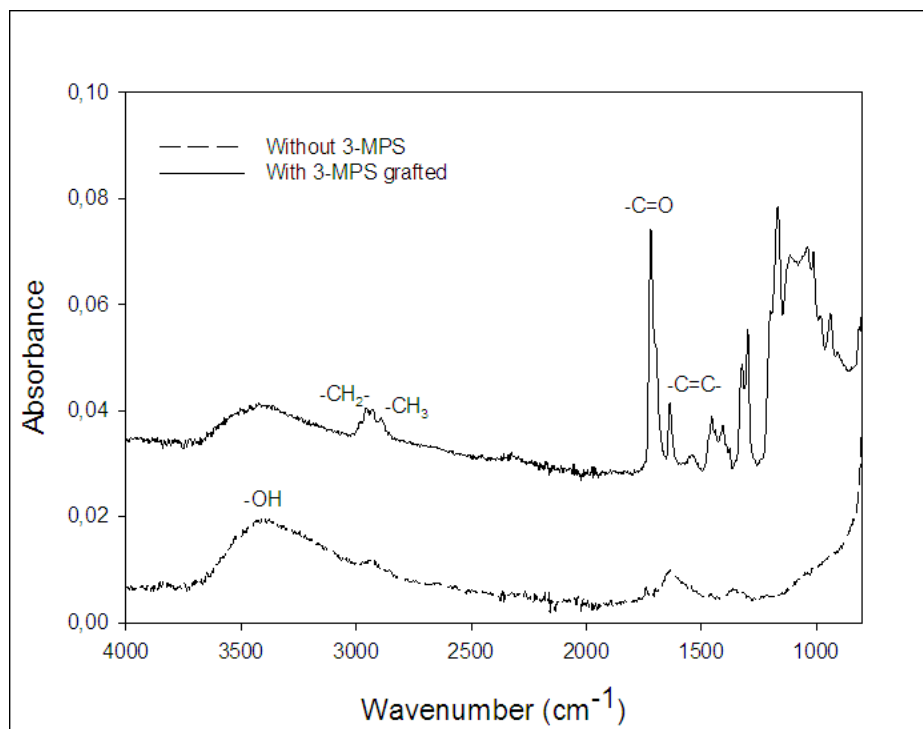


Fig. 2 – FTIR spectra of zirconia before and after functionalization.

During the exposure to UV radiation in the presence of atmospheric moisture, Irgacure 250 ® generates protons which initiate the methoxysilane functions hydrolysis, allowing the condensation of 3-MPS on the hydroxyl functions of mineral fillers. Compared to the conventional process, the photo-

chemical one presents the advantages of making the reaction without solvent and at room temperature, in one step and with a highest reaction rate.

Zirconia FTIR spectra before and after functionalization are presented for example in Figure 2.

Whatever the grafting method used, the IR spectra of the 3-MPS-grafted fillers show the disappearance of the band at 2840 cm^{-1} (CH_3 -symmetrical elongation) characteristic of the Si-O-Me functions, proving that the hydrolysis reaction took place, in favor of the appearance of two new absorption bands at 1637 and 1714 cm^{-1} which characterize the $\text{C}=\text{C}$ bond of the methacrylate group and the $\text{C}=\text{O}$ bond of the carbonyl group existing in the 3-MPS, respectively.

The presence of organic matter on the surface of the fillers was confirmed by thermogravimetric analysis. Table 2 collects the weight loss of the different fillers before and after 3-MPS grafting according to both conventional and photoinitiated processes.

The thermal behavior of the coupling agent was also characterized before and after UV exposure once self-condensed. We notice, for both grafting processes, a weight loss which is added to the one observed with the nonfunctionalized fillers. This loss corresponds to the degradation of the coupling agent transplanted to the surface of the fillers. The absence of weight loss towards 150°C (boiling point of 3-MPS) confirms the absence of non-grafted molecules of 3-MPS.

The grafting quantity of 3-MPS can be evaluated from the following formula²¹:

$$Q(\mu\text{mD}/\text{m}^2) = \frac{m_i - m_f}{S_{\text{spec}} \times M \times m_i} \times 10^6$$

where $(m_i - m_f) / m_i$ corresponds to the weight loss percentage of organic matter between 100°C and 800°C , M (g/mol) is the molar mass of the grafted fragment (in our case, $M = 203\text{ g/mol}$) and S_{spec} ($\text{m}^2\cdot\text{g}^{-1}$) is the specific surface of the mineral particles.

The results of Table 3 show that the functionalization of fillers by photochemical way is much more efficient than by conventional way.

3. Influence of the functionalization of fillers

The photopolymerization of the formulations containing, Bis-GMA/TEGDMA monomers,

photoinitiator and functionalized fillers was studied with the same operating conditions as previously (Figure 3). We notice for both systems, there is no notable modification of the Bis-GMA / TEGDMA conversion in the presence of the functionalized filler.

4. Comparison with commercial composites

The study of the commercial composites in the same conditions of irradiation shows kinetics of the reaction equivalent to those obtained on our formulations (Figure 4).

5. Mechanical properties

The mechanical properties of experimental composites based on Bis-GMA/TEGDMA were determined by measurement of the hardness Persoz (SP0500, Labomat, France). The analyzed samples were prepared on a glass plate in a mold of 8 mm in diameter and 1 mm in thickness and polymerized in the same conditions of irradiation as previously. We noticed, in the case of the incorporation of functionalized fillers, a decrease of the hardness as the fillers content increases. This can be attributed to, the incompatibility of the filler and the organic phase which gives rise to a non uniform dispersion of the mineral particles in the Bis-GMA/TEGDMA matrix.

Furthermore, the functionalized fillers through conventional sol-gel process lead to an increase of the hardness at a constant rate of filler, revealing best dispersion and compatibilization of the filler in the resin.

The results of hardness, in the case of the of photoinitiated process, are the weakest although the grafted 3-MPS is more important than in the conventional process (Figure 5). There is more important side condensation reaction of the 3-MPS molecules under UV irradiation, leading to lower the grafting particles. The filler phase is less compatible with the organic matrix; the weak dispersion of particles inside the composite lowers the hardness.

Table 2

Thermogravimetric analysis of fillers before and after functionalization

Filler	T ($^\circ\text{C}$)	Weight loss (%) between 100°C and T		
		Before grafting	After conventional grafting	After photoinitiated grafting
Al_2O_3	150°C	0.6	0.6	0.6
	800°C	3.5	15.6	36.3
ZrO_2	150°C	0.0	0.2	0.2
	800°C	0.4	3.5	16.2

Table 3

Grafting results of 3-MPS depending on the sol-gel process used

Filler	Al ₂ O ₃		ZrO ₂	
	Conventional	Photoinitiated	Conventional	Photoinitiated
Weight loss (%)	12.1	32.8	3.1	15.8
Grafting yield (%)	36.3	82.1	18.0	52.5
Grafted quantity Q ($\mu\text{mol.m}^{-2}$)	6.0	16.2	3.1	15.6

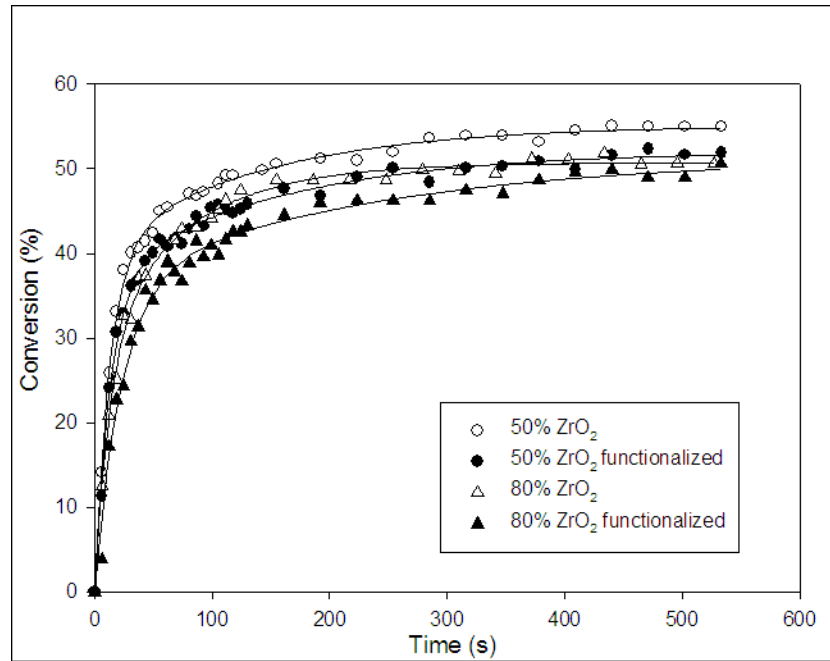
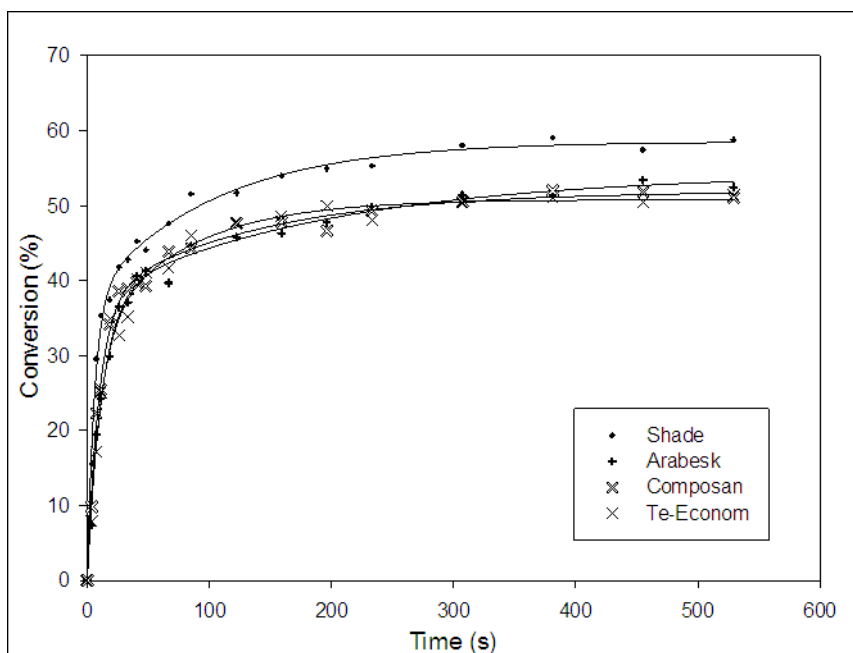
Fig. 3 – Conversion vs. time of Bis-GMA/TEGDMA with various ZrO₂ contents during the irradiation.

Fig. 4 – Conversion vs. time of the commercial composites.

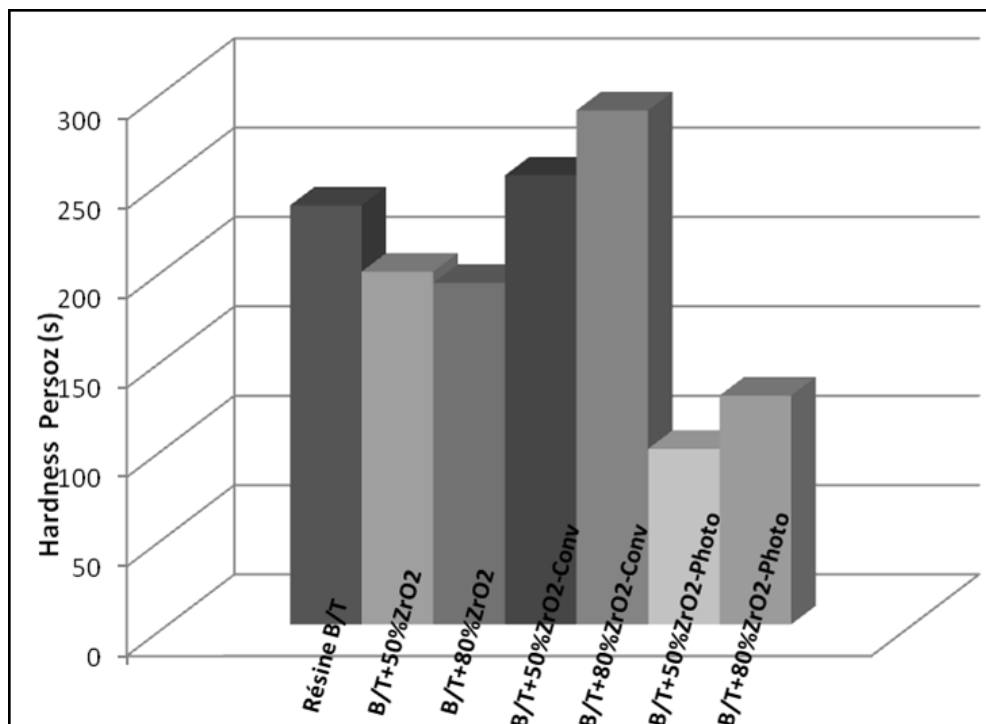


Fig. 5 – Hardness Persoz of composites with Bis-GMA / TEGDMA containing different contents of functionalized ZrO₂.

CONCLUSIONS

The grafting of the trialkoxysilane 3-MPS, on alumina and zirconia nanoparticles surface was implemented according to two sol-gel processes: a conventional way carried out in aqueous solution under heating and a photochemical way without solvent and heating. The FTIR and TGA analyses of the obtained products confirm the establishment of covalent bonds between the 3-MPS and the fillers and that higher quantity of 3-MPS can be grafted by condensation on the fillers surface by using the photochemical way compared to the conventional way.

Thus, the sol-gel photoinitiated process is a technique well adapted for the functionalization of the fillers for dental composites. However, a judicious choice and a mastery of the various parameters used during the synthesis by this way, as the conditions of hydrolysis and condensation must be taken into account.

The measures of hardness of composites containing these functionalized fillers show that the grafting by photochemical way is inhomogeneous. The study of the photocuring of these formulations shows that the modification of the fillers surface influences the polymerization reaction kinetics. However, it modifies in a notable way the mechanical properties of the composite.

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