CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 2, No. 1, 2008 Chemistry

Zoubida Seghier[1, 2], Ambroise Diby[1, 3], Vanda Voytekunas[1, 4], Philip Cheang[5] and Marc J.M. Abadie[1, 6]

EFFECT OF FILLER TYPE, CONTENT AND SIZE ON THE UV-CURING DENTAL MATERIALS

[1] *Laboratory of Polymer Science and Advanced Organic Materials — LEMP/MAO, University Montpellier 2, Science and Technology of Languedoc, Place Bataillon, 34095 Montpellier Cedex 05, France, abadie@univ-montp2.fr; marc@ntu.edu.sg*
[2] *University Es-Senia, Oran, Algeria*
[3] *University Cocody of Abidjan, Abidjan, Ivory Cost*
[4] *SIMTech — Singapore Institute of Manufacturing Technology, 71 Nanyang Drive, Singapore 638075*
[5] *School of Chemical & Biomedical Engineering — SCBE, 50 Nanyang Avenue, Nanyang Technological University, NTU, Singapore 639798*
[6] *School of Materials Science & Engineering — MSE, 50 Nanyang Avenue, Nanyang Technological University, NTU, Singapore 639798, marc@ntu.edu.sg*

Received: December 20, 2007

Abstract. A bis-GMA, TEGDMA monomer mixture at weight ratio 2:1 was UV-cured with CQ to form commonly used dental materials. Three types of fillers at different particle size were added at different weight concentrations. Reaction rates *k*, time *vs* rate were studied for all the systems.

Key words: UV-curing, filler, kinetics, bis-GMA, TEGDMA.

1. Introduction

A composite is a combination of at least two chemically different materials (resin and filler) with a distinctive interface separating the components and having properties which could not be achieved by any of the components alone. Filler substances are added to dental composites for various reasons such as improving the strength, reducing the shrinkage and reducing thermal coefficient of expansion, *etc*.

R. Bowen [1] took the first major step toward dental composites used nowadays. He strengthened bis-GMA with ground quartz. The composite was not abrasion resistant or polish able, and the surface was very rough. The problem was solved by the introduction of micro fillers [2, 3]. Filler particles larger than one micron are classified as macro fillers. Conventional macro fillers were usually in the range of approximately 30 microns. An average particle size under 10 microns is found in the present generation of macro filled composites. Filler particles under one micron are generally classified as micro fillers. The only micro fillers commercially available in large quantities are the fumed silicas. A lot of researches [4-6] were done related to fillers on thermal expansion, flexural strength and morphology of dental composites. In this experiment, kinetic aspects of UV-curing of dental materials based on bis-GMA and TEGDMA with different types of fillers were studied in detail.

2. Experimental

2.1. Materials

· 3 types of fillers are used:

1. SDHA (spray dried HA). It has spherical shape and was loosely aggregate together with three ranges of particle: < 25 μm, 45–75 μm, 75–125 μm and density of 3.0 g/ml.

2. RFHA. It has spherical shape and has more dense structure than SDHA with average particle size at 16 мм and density of 3.2 g/ml.

3. ZrO_2. It has irregular shape with particle size less than 1 μm and density of 6.0 g/ml.

The morphology of the three types of fillers is shown in Fig. 1.

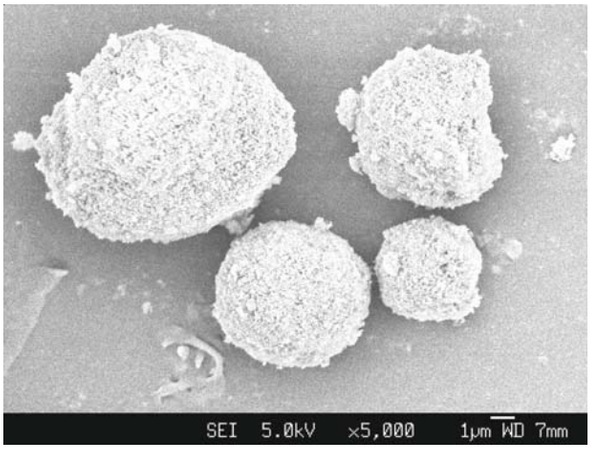
· Dental materials consist of two kinds of monomers initiated by CQ by UV- curing.

1. Bis-GMA: Bisphenol A-diglycidylmethacrylate, which is used as monomer.

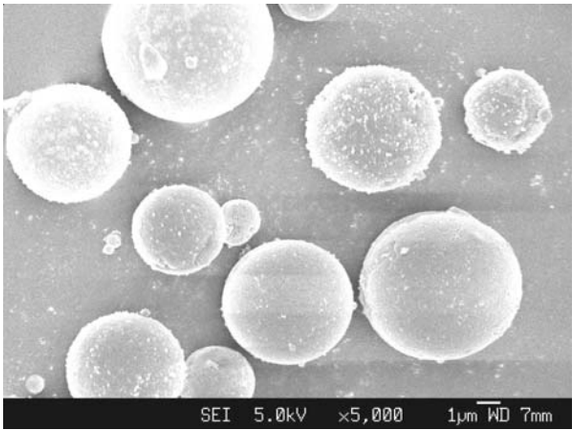
2. TEGDMA: triethyleneglycol dimethacrylate, which is used as monomer.

3. CQ: Camphorquinone, which is used as initiator.

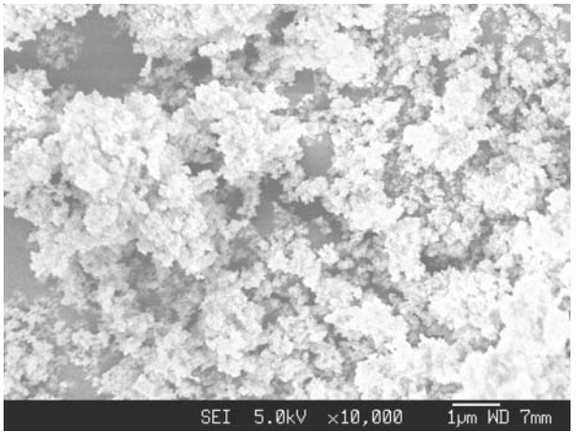
Bis-GMA and TEGDMA were used at 2:1 weight ratio, 3 wt. % CQ was used as initiator for UV-curing.



SDHA



RFHA



ZrO_2

Fig. 1. Morphology of different fillers

2.2. Experimental procedure

Kinetic measurements were performed with the help of the differential photocalorimetry (DPC) technique, which has been described in the previous papers [7-9] and allowed to evaluate the heat flow from a photosensitive formulation that cures when exposed to UV radiation [10] from the lamp at an intensity of $3mW/cm^2$. The stoechiometric mixture amounting to about 2.00 mg monomer mixture and initiator in total was transferred into the DPC pan. Any oxygen allowed to diffuse into the sample will scavenge the initiating radicals, retarding the polymerization. To avoid atmospheric oxygen from diffusing into the sample, a polyethyleneterephthalate (MylarT film) was used as a cover on top of the liquid sample. The DPC pan with the sample was placed into the DPC cell to equilibrate at a preselected temperature followed by isothermal treatment without exposure for 1 min, then exposed to UV radiation for 5 minutes. The exothermic reaction was recorded during the process of photo curing. The kinetic parameters were calculated using an autocatalytic model.

3. Results and Discussion

1. Calculate theoretical enthalpy of pure dental resin with and without fillers.

Since pure dental resin consists of two monomers (bis-GMA and TEGDMA) in one system, we calculate their molar ratio as follows:

Bis-GMA has a molecular weight of 512 and TEGDMA has a molecular weight of 286, the weight ratio of the two monomers is 2:1.

Since the enthalpy is defined on the base of the molar percentage, the 2:1 weight ratio needs to be converted to molar ratio first.

For bis-GMA: $2g/512=3.9063\cdot10^{-3}$ (monomer 1)

For TEGDMA: $1g/286=3.4965\cdot10^{-3}$ (monomer 2)

Molar ratio of monomer 1 is equal to $3.9063\cdot10^{-3}/(3.9063\cdot10^{-3}+3.4965\cdot10^{-3})$, which is 0.528.

Molar ratio of monomer 2 is equal to $3.4965\cdot10^{-3}/(3.9063\cdot10^{-3}+3.4965\cdot10^{-3})$, which is 0.472.

The enthalpy for the mixture of the two monomers is defined as:

$$\Delta H_{mix} = a_1[(n_1\cdot\Delta H_1)/M_1] + a_2[(n_2\cdot\Delta H_2)/M_2]$$

where a_1 and a_2 represent the mole fraction of monomer 1 and 2 respectively; n_1 and n_2 represent the quantity of the double bond in monomer 1 and 2 respectively.

For bis-GMA and TEGDMA, they both have two double bonds in the molecular structure. n_1 and n_2 are both equal to 2.

ΔH_1 and ΔH_2 represent the heat of polymerization (reaction enthalpy) of a single double bond of bis-GMA and TEGDMA respectively. These two monomers both belong to acrylate series, which has a fix ΔH of 13.6 kcal/mol for a single double bond. Applying 1 cal = 4.1868 J, ΔH is 56.94 kJ/mol for acrylate series.

M_1 and M_2 represent the molecular weight of bis-GMA and TEGDMA, which is 512 and 286 respectively.

Thus the ΔH_{mix} of bis-GMA and TEGDMA (2:1 by weight) pure dental material without filler is:

$\Delta H_{mix} = 0.528 \cdot [(2 \cdot 13.6 \cdot 4.1868 \cdot 1000)/512] + 0.472 \cdot [(2 \cdot 13.6 \cdot 4.1868 \cdot 1000)/286] = 305.4$ J/g

When the fillers were added as 10, 20 and 30 wt %, the enthalpy for the filler systems will be 274.8, 244.3 and 213.8 J/g respectively.

Table 1

Experiment results at 303 K

Sample information	Actual enthaphy, J/g	Theory enthaphy, J/g	Induction time, s	m	k, min^{-1}
Pure	128.4	305.4	13.9	0.41	1.028
10%HA25	134.2	274.8	12.5	0.43	1.346
20%HA25	119.5	244.3	11.7	0.46	1.486
30%HA25	106.1	213.8	11.2	0.42	1.517
10%HA47	133.1	274.8	12.0	0.42	1.340
20%HA47	121.1	244.3	11.6	0.42	1.427
30%HA47	96.1	213.8	11.8	0.43	1.430
10%HA71	132.4	274.8	12.3	0.44	1.374
20%HA71	123.7	244.3	11.5	0.44	1.494
30%HA71	109.5	213.8	11.0	0.42	1.563
10%RFHA	136.6	274.8	12.3	0.42	1.313
30%RFHA	120.6	213.8	11.1	0.42	1.464
60%RFHA	64.9	122.2	11.1	0.40	1.480
20% ZrO_2	122.2	244.3	10.7	0.43	1.780
40% ZrO_2	84.8	183.2	10.2	0.43	2.006
60% ZrO_2	60.3	122.2	9.8	0.44	2.335

Note : HA25 means SDHA powder less than 25 μm; HA47 means SDHA powder in the range of 47–75 μm; HA71 means SDHA powder in the range of 75–125 μm. Based on the individual experiment conducted, SDHA has a maximum loading of 30 wt %. RFHA and ZrO_2 both have a maximum loading of 60 wt %.

2. The results of some kinetic parameters for dental materials systems with different types and contents of fillers are listed in Table 1.

The actual enthalpy of the reaction ΔH is the indication of heat generated during the polymerization in an exothermic reaction. The induction time is the time corresponding to 1 % of the monomer conversion. k is the reaction constant which, to some degree, indicates the rate of the reaction. The calculation of the kinetic parameters is based on the hypothesis that the reaction may be described by a differential equation:

$$d\alpha(t,T)/dt = k(T) f(\alpha)$$

where α is the fraction of the converted monomer, $k(T)$ the reaction constant depending on the temperature T and $f(\alpha)$ is a function which represents the hypothetical model of the mechanism of reaction. In the case of the kinetic autocatalytic model the approximated differential equation which is most suitable is:

$$d\alpha(t,T)/dt = k(T) \cdot \alpha^m \cdot (1-\alpha)^n$$

m and n represent the orders of the priming and propagation reaction respectively.

The value of n is fixed at 1.5 and that of m is calculated. From Table 1, it was revealed that all the m calculated fell in the range of 0.4–0.5. This indicated the reaction fitted the autocatalytic model very well.

It has an obvious trend for all the systems that with the increment of the filler, the reaction constant k increases. That meant the reaction became faster when the fillers were added in. It could be explained as the result of fillers' diffusion of the light emitted by the UV lamp. It helps the light to penetrate the dental materials during the curing. This trend could be graphed as in Fig.2 which represents time *vs* the reaction rate.

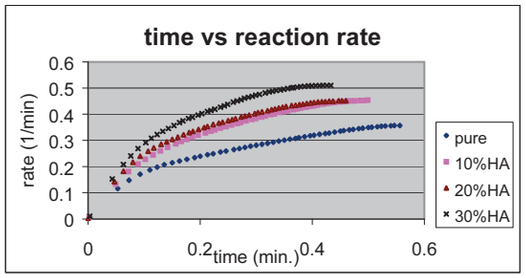


Fig. 2. Reaction rate vs. time of dental material with fillers at different concentration

It was also obvious that with the increment of filler content, the reaction rate *k* increased and in the mean time the induction time of all reactions decreased, as shown in Fig. 3. This meant that with the addition of fillers, the reaction proceeded faster and it took less time to reach 1 % conversion than with the pure dental materials.

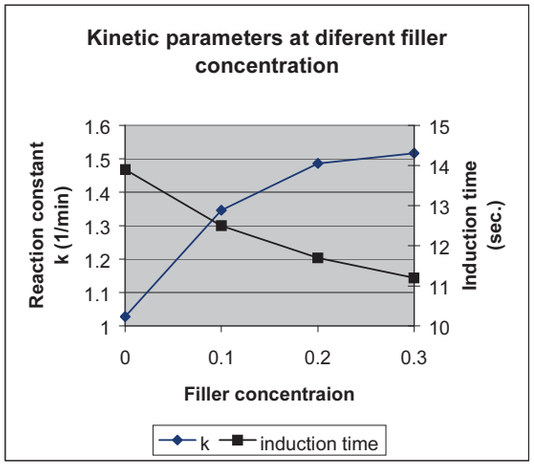


Fig. 3. Effect of filler concentration on the induction time and reaction constant

Note: data were based on pure dental material and that with filler of SDHA (10 %, 20 %, 30 %) less than 25 μm.

As for different types of fillers, it was observed that reaction rate *k* and induction time *t* did not differ essentially for SDHA and RFHA when they were at the same concentration. It was concluded that particle size of filler, especially that of macro filler, did not play an important role in the composites UV-curing kinetics. It was also observed that there was little difference in *k* and *t* when different kind of HA were added in the system. Both SDHA and RFHA had a spherical shape and the same chemical structure. The only difference between these two fillers lied in the micro particles degree of density. RFHA had a much denser matrix than SDHA. However, it did not seem to have any influence on the reaction rate and induction time.

ZrO_2 had a much greater contribution to the increment of the reaction rate comparing to HA powder. Systems with ZrO_2 had higher reaction constant *k* and lower induction time *t* than any other systems with HA powder. This could be due to the fact that ZrO_2 powder diffused UV light better than the HA powder because of its smaller size, irregular shape and different chemical structure. It was found out that when the fillers had the particle size more than 1 μm, *i.e.* macro fillers, this did not have much effect on reaction kinetics such as k when the particle size changed. When the particle size went down to less than 1 μm, *i.e.* micro fillers, the influence on reaction kinetics became very obvious. On the other hand, HA filler presented a spherical shape whereas ZrO_2 filler presented an irregular one. All the above facts (shape, size, and chemical structure) could result in better UV light diffusion to the dental material system during UV-curing.

4. Conclusions

Three types of fillers (SDHA, RFHA and ZrO_2) all accelerated the reaction of bis-GMA and TEGDMA dental material system. The reaction rate increased with the increment of content of fillers in the systems. Fillers with different chemical structure had different reaction acceleration rate. Out of the studied fillers ZrO_2 had the best acceleration effect. Micro fillers had better UV light diffusion rates than macro fillers, which resulted in faster reaction rate.

References

[1] Bowen R.: JADA , 1963, **66,** 57.
[2] Mannerberg F.: Quintess. Internat., 1977, **8** (8)**,** 23.
[3] Michl R.: Quintess. Internat., 1978, **9** (3), 29.
[4] Calais J.: J. Dent. Res., 1988, **67,** 836.
[5] Li Y. and Swartz M.: J. Dent. Res., 1985, **64**, 1396.
[6] Germain H.: J. Dent. Res., 1985, **64,** 155.
[7] Abadie M. and Appelt B.: Dent. Mat., 1989, **1**, 6.
[8] Appelt B. and Abadie M.: Polym. Eng. Sci., 1988, **28** (6), 367.
[9] Abadie M.: Euro. Coating J., 1988, **5,** 350.
[10] Voytekunas V. and Abadie M.: Eur. Chem. Tech. J., 2004, **6,** 67.

ВПЛИВ ТИПУ, КІЛЬКОСТІ І РОЗМІРУ НАПОВНЮВАЧА НА УФ-ЗАТВЕРДЖУВАНІ СТОМАТОЛОГІЧНІ МАТЕРІАЛИ

Анотація. *Мономерну суміш біс-ГМА і ТГМ-3 із ваговим співвідношенням 2:1 затверджували УФ-випромінюванням з камфорохіноном для одержання стоматологічних матеріалів загального використання. Додавались три різних типи наповнювачів, з різними розмірами частин і ваговими концентраціями. Для всіх систем вивчали швидкість реакції та її залежність від тривалості процесу.*

Ключові слова: *УФ-затвердження, наповнювач, кінетика, біс-ГМА, ТГМ-3.*