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LIGHT CURABLE DENTAL COMPOSITES − KINETICS BY PLASMA AND HALOGEN LAMPS

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Abstract. A series of commercial dental composites curable by visible light have been investigated and compared in terms of their photoreactivity thanks to the photocalorimetry technique by using two different types of lamps, a conventional lamp (halogen lamp) from ESPE and a plasma lamp, Apollo 98[E] manufactured by DMDS. In terms of kinetics, dental composites cure in just a few seconds with plasma lamp compared to 20-40 s with halogen lamp allowing dentists to save time. Recent investigations on new composite systems having low contraction show that they are less photoreactive compared to former systems.

Keywords: dental polymers, composites, visible light curing of polymers, photocalorimetry, kinetics, activation energy.

1. Introduction

Over the last thirty years there has been a constant development in the use of photochemistry [1-3] (UV and visible, and more recently E-Beam) in various sectors of application, mainly in the coating industry, graphic arts, micro- and nanoelectronics, dental composites and composites themselves. This development is mainly due to the fact that this technology, based on the use of energy of photons (or electrons for E-Beam) is to be simple, quick in processing and allows the formation of a three dimensional network system in less than few seconds.

This technology has been applied in odontology, specifically in treatment of teeth and their restoration. Nowadays amalgam is not anymore used for safety reasons and has been replaced by dental composites. However the optimization of photosensitive formulation is often concerned with an empirical approach based essentially on experience and closely guarded know-how of the formulator than on a rational and scientific process.

In dentistry only lights emitting in the visible range are accepted whereas UV A, UV B and especially UV C of short wavelengths which could strongly affect human living tissues due to the high energy emitted by these types of wavelengths are forbidden. Generally the blue light – in the range of 450–480 nm and corresponding to energy of 264.6 kJ/mol to 247.9 kJ/mol is considered to be safe for the patient.

In this paper we will describe a new technique which has been developed to study and optimize any photosensitive formulation – differential photocalorimetry DPC - and which was modified and adapted to permit the use of halogen or plasma lamps used by dentists.

We will also consider and compare the photoreactivity of different photosensitive dental composites by using traditional lamp, *i.e.* halogen system to a plasma lamp emitting in the same region of the spectrum – blue light; kinetic parameters such as enthalpy, degree of conversion, rate constant, Arrhenius parameters, will be considered.

2. Experimental

2.1. Light Sensitive Formulation

Photocurable dental composites are mainly composed of inorganic fillers (about 80 % or more), a photoinitiator (generating free radicals upon exposure to light), organic resins (epoxies or urethane modified acrylates) and additives. Under exposure to light and although the mixture is already pasty, the system hardens giving an insoluble and infusible three dimensional network. Mechanical properties of such a composite strongly depend on the crosslinking reactions (minimizing residual functions entangled into the matrix) [4, 5].

2.1.1. Phtoinitiator system

Photointiators are chemical substances which, upon exposure to light, decompose to give active species, generally free radicals used in odontology, although there is a tendency and interest to use cationic species, *i.e.* Bronsted acid H+ in the future due to the fact that in contrast to radical polymerization, cationic polymerization is not inhibited by the presence of oxygen. Nethertheless radiation curing in restorative odontology is dominated by photointitated radical polymerization process.

The photoinitiator used should absorb in a visible light, blue light and the more common one – the camphorquinone CA (Fig. 1). Its decomposition works according to a bimolecular process in the presence of a large variety of H donors or electron donors such as amines, principally DMPT N,N-dimethyl-*p*-toluidine, DEPT N,N-diethanol-*p*-toluidine or others(Fig. 2). The mechanism of production of radicals from camphorquinone is done by hydrogen abstraction through a singlet and triplet state of the chromophor group of CA, formation of triplet-exciplex with hydrogen donor which then, decomposes by electron transfer and H-transfer by

producing amine radicals. These radicals are considered as the initiating radicals while the ketyl-type radicals were demonstrated to undergo radical coupling with the growing macromolecular chains or coupling each other to form a pinacol (Fig. 3).
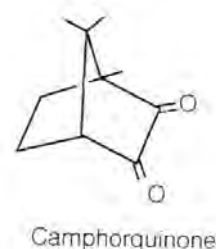

Fig. 1. Chemical structure of camphorquinone

2.1.2. Monomers and oligomers

The special requirements of monomers used in restoratives are quite specific and severe. They should be biocompatible, have good physical properties, chemical stability in the oral environment, color stability, high reactivity at low temperature, good shelf life, taste and odor free as far as possible. These criteria are presently met only by the methacrylate functions and within this group by the high molecular weight resins.

Multifunctional methacrylates, preferably bi-functional monomers, are therefore used in practically all dental composites. The general formula of these bifunctional monomers could be represented by:

$$MA – R – MA$$

where **MA** represents the active methacrylic acid ester function and **R** any of innumerable organic compounds. They are usually aromatic rings (Bowen resins), urethane prepolymers (Fujikawa resins), aliphatic chains, polyethers or recent combination of aromatic structures and polyethers (Fig. 4).
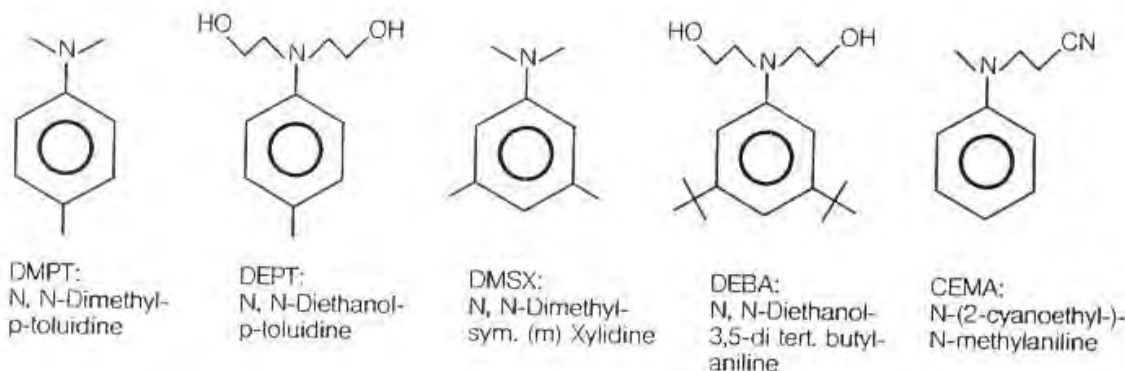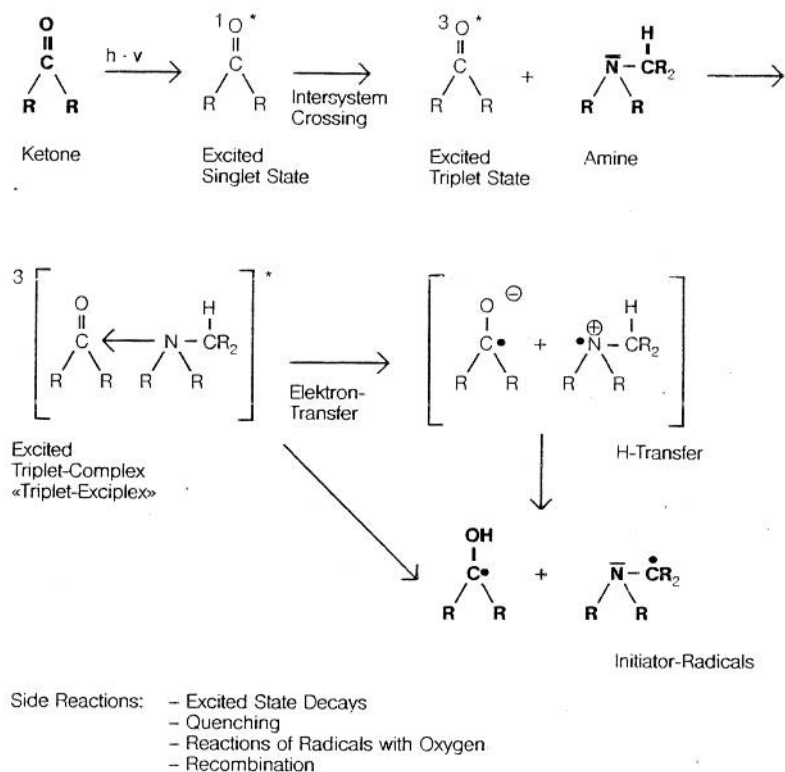

Fig. 2. Different amines used as accelerator (H donor)

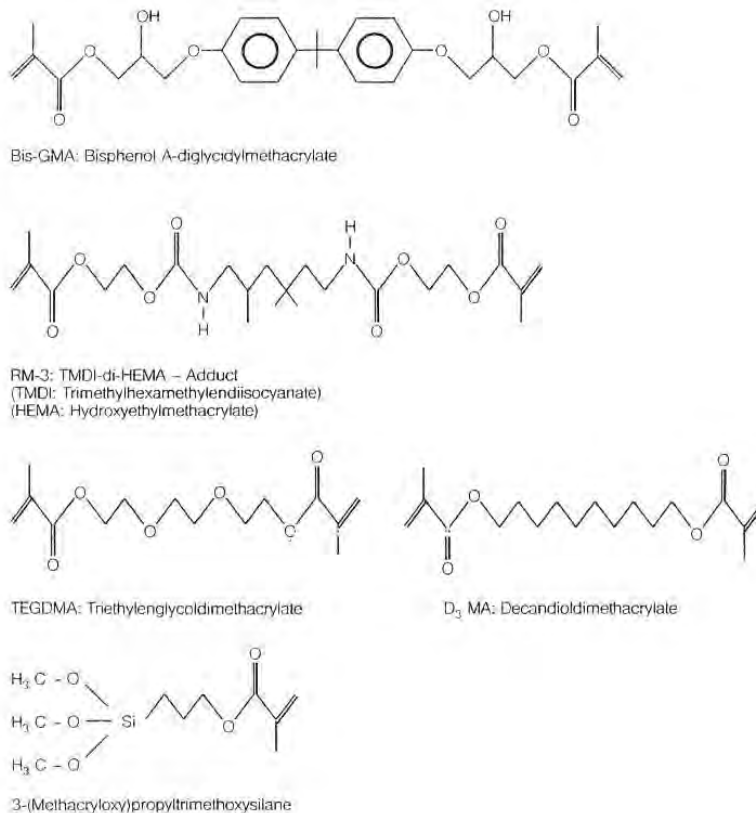**Fig. 3.** Mechanism of formation of radicals with camphorquinone/amine system when exposed to visible light

Fig. 4. Chemical structure of some monomers/oligomers used in odontological formulation

2.1.3. Fillers

Filler substances are added to dental composites for strength, handling properties, shrinkage reduction, radio capacity and to reduce thermal coefficient of expansion [6]. Most of the fillers used are:
- glass and glass ceramic;
- some silicates;
- silicone dioxide.

The interest of silicone dioxide is that it is fairly easy to create a bond between the matrix and the surface of these substances due to the presence of silanol groups on the filler surface. Therefore the interphase between the matrix and the filler is strong enough and both are directly linked by chemical bonds which reinforce the composite, especially during delamination.

We used to make a distinction between macro-fillers – average particle size between 30 and 10 μm - which include glasses, silicates and quartz and microfillers – average particle size between $7·10^{-3}$ μm to $4·10^{-2}$ μm - composed of fumed silica or fumed silicone dioxide. Actually the tendency is to have intermediate particle size range called hybrid composites which permit to be used indifferently for restoration of rear or front teeth.

2.1.4. Additives

Dental composites contain a variety of other components like:
- stabilizers or inhibitors such as substituted phenols or hydroquinones which help to prevent prepolymerisation of the monomers/oligomers;
- pigments like iron oxides;
- ultraviolet stabilizers to prevent discoloration from UV light;
- optical brighteners used to give the composite a fluorescence comparable to the natural tooth.

All these additives influence general or specific aspects of a composite. Proper selection of the components and careful balance are important.

2.2. Materials

The photoreactivity of commercial dental composites have been investigated under 2 types of visible light lamps.

2.2.1. Dental composites

The following light-curing composites have been studied:
- Silux Plus™ (3M) for anterior restoration
- Solitaire (3M)
- Tetric (Ivoclar Vivadent) for anterior and posterior restoration
- Tetric Ceram (Ivoclar Vivadent) for posterior region
- Z100™ MP A3 (3M) for posterior restoration
- Z100™ MP B3 (3M) for posterior restoration

2.2.1. Lamps

2.2.2.1. Classical lamp: we have chosen the lamp commercialized by ESPE. DSC head was in a hermetic box surmounted by a micrometric screw fixed to the housing for the wave guide. Time of exposure has been chosen for 20 and 40 s.

2.2.2.2. Apollo 95^E lamp: consists of a supply box containing the plasma lamp and a light guide. The light emits a visible light between 400 and 500 nm. The curing or bleaching time may be adjusted between 1, 2 and 3 s or SC (step curing) mode corresponding to 5.5 s of exposure in two times. The plasma lamp is manufactured by DMDS (Dental Medical Diagnostic Systems, Ltd.).

3. Results and Discussion

3.1. Photopolymerization

Upon exposition to halogen or plasma lamps, the photoinitiator system (camphorquinone and amine compound), generates free radicals which will initiate and propagate the reaction polymerization. As we have generally difunctional methacrylate monomers or oligomers, the system rapidly cross-links to form an insoluble and infusible three dimensional network system.

A number of analytical methods have been developed to determine accurately the degree of curing, particularly real-time methods which present the advantage to initiate the reaction and at the same time analyze the reaction upon UV radiation which transforms almost instantly (fraction of a second up to seconds) the liquid monomer film into a solid insoluble polymer.

One of these novel analytical methods – real-time technique – is based on the variation of the quantity of heat which results in polymerization or cross-linking reactions by using the principle of a differential scanning calorimeter and so-called photocalorimetry (DPC) [7, 8]. The advantage of this technique is to permit every one to monitor *in situ* the kinetics of ultrafast photopolymerization and to follow UV/visible curing reactions directly and continuously.

3.1.1. Differential photocalorimetry DPC [9, 10]

Calorimetry is a method of choice for monitoring in real time UV/visible curing reactions, which are highly exothermal processes. The sample and reference compartments of the DSC head are simultaneously exposed to visible radiation and the heat flow generated

by the polymerization reaction is directly recorded as a function of time (Fig. 5).

Our conventional DPC was modified by replacing the high pressure mercury lamp either by a conventional lamp, *i.e.* a halogen lamp from ESPE or by the Apollo 95[E] plasma lamp manufactured by DMDS – Dental Medical Diagnostic System. The light is focused on the DSC head (reference and sample sensors) *via* optical fiber (Fig. 6).
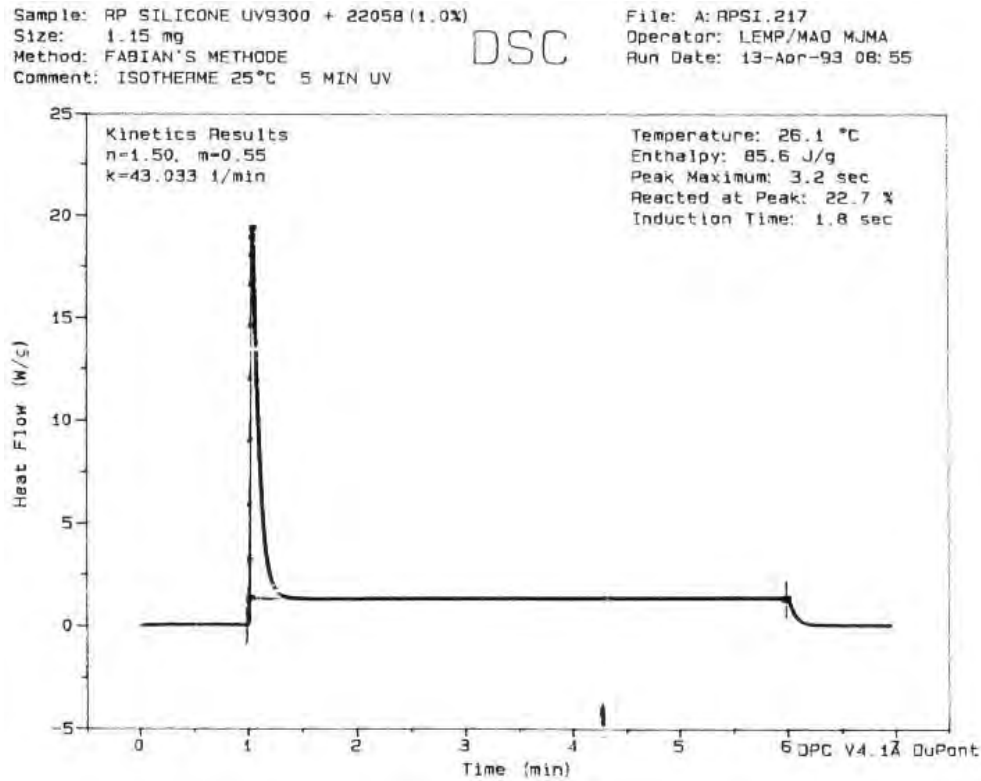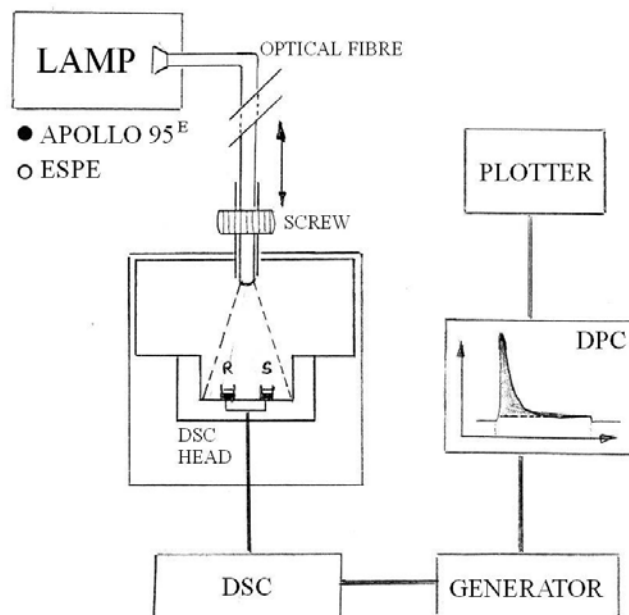

Fig. 5. DPC curve

Fig. 6. Scheme of the modified DPC used for investigation of dental materials

3.1.2. Kinetic model

The rate of polymerization R_p (mol/l/s) can be derived at any moment from the heat flow value dH/dt (J/mol/s), provided that the standard heat of polymerisation ΔH_0 (J/mol) is known for the monomer $[M_0]$ considered.

$$R_p = \frac{(dH/dt)\cdot[M_0]}{\Delta H_0} \qquad (1)$$

The total exothermic area gives a measure of enthalpy of the polymerization ΔH which, compared to ΔH_0, allows the degree of conversion of the cured polymer to be evaluated.

The rate coefficient k of photopolymerization can be evaluated according to the Sestak and Berggren equation [11]:

$$R_{p(T)} = da_{(t,T)}/dt = k_{(T)}\cdot a^m (1\text{-}a)^n \cdot [\text{-}\ln(1\text{-}a)]^p \qquad (2)$$

where: a – degree of conversion; k – rate coefficient; m, n, p – orders of the reaction: initiation, propagation and termination, respectively.

Assuming that at the beginning of the reaction we are far away from the termination reactions, we can neglect termination reactions and consider $p = 0$. We end up with the following simplified expression:

$$R_{p(T)} = da_{(t,T)}/dt = k_{(T)}ka^m (1\text{-}a)^n \qquad (3)$$

Beside the rate constant, other parameter important to consider in terms of photoreactivity is the *induction time* (IT) which is the time corresponding to 1 % of consumption of the monomer. In other words lower is the induction time, higher is the reactivity of the system.

3.1.3. Thermogravimetric analysis

Before doing kinetics on the dental composites, it is necessary to determine the quantity of filler present in each product. In fact only the resin, *i.e.* monomers or oligomers are photoreactive but not fillers.

Therefore different composites such as Silux Plus, Tetris and Tetris Ceram, Solitaire, Z100 MP A3 and B3 have been analysed by thermal gravimetric analysis TGA (Fig. 7) in view to determine the charge ratio (Table 1), the resin being only responsible of the light curable composites photoreactivity.
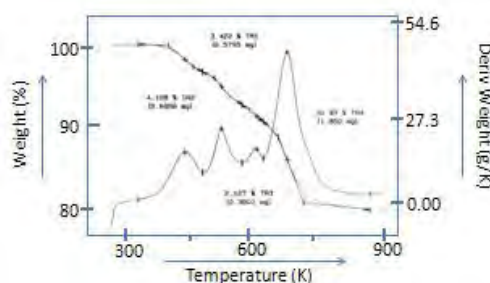

Fig. 7. TGA curve of Tetric

TGA results for different composites

Composite	Charge ratio, %
Silux Plus™	62.75
Solitaire	69.28
Tetric	79.41
Filtek™ Z250	82.17
Filtek™ P60	82.60
Z100™ MP A3	82.80
Tetric Ceram	83.14
Z100™ MP B3	83.38

3.2. Kinetic Results

Our experiments based on the analysis of kinetic parameters, *i.e.*: the enthalpic values of the crosslinking reaction, the rate coefficient based on autocatalytic model and induction time (time corresponding to 1 % of monomer conversion) are reported (Tables 2 and 3), respectively for the halogen lamp and the plasma lamp.

Table 2

DPC results for different composites – ESPE lamp mode 60 s

Composite	ΔH, J/g	k, 1/min	IT, s	Conv., %
Silux Plus™	13.1	0.99	36.6	18.4
Tetric	72	2.43	17.3	17.3
Z100™ MP A3	86	1.96	25.5	51.7
Tetric Ceram	86.4	1.89	33.7	51.8
Z100™ MP B3	64.5	1.55	31.7	36.8
Solitaire	22.8	0.92	49.7	49.7

Table 3

DPC results for different composites – Apollo 95[E] lamp mode SC

Composite	ΔH, J/g	k, 1/min	IT, s	Conv., %
Silux Plus™	35.7	6.76	5.2	50.2
Tetric	100.7	12.27	3.7	88.0
Z100™ MP A3	134.1	9.3	4.0	80.5
Tetric Ceram	138.8	12.34	4.0	81.6
Z100™ MP B3	126.9	9.61	4.7	72.4
Solitaire	100.1	4.59	6.9	45.9

The kinetic results confirm the great reactivity of the Apollo 95[E] plasma lamp in comparison with a classical halogen lamp used in odontology [12]. For example with Z100 MPA3 and using ESPE halogen lamp, kinetic parameters are respectively rate coefficient $k = 1.96$ 1/min, 25.5 s of induction time and 51.7 % of conversion compared to rate coefficient $k = 9.3$ 1/min, 4 s for induction time and 80.5 % of monomer conversion with plasma Apollo 95[E] lamp.

The difference is also illustrated by Figs. 8 and 9 for DPC thermograms, Figs. 10 and 11 for the rate of polymerization and Figs. 12 and 13 for the degree of conversion at different exposure times, respectively for the plasma lamp and the halogen lamp.

Moreover the Apollo 95[E] enables the practitioner to save a considerable amount of time, just few seconds compared to 20-40 seconds of insulation using traditional halogen lamp. Our results allow classifying the composites into two groups, independently of the exposition mode, in less and more photoreactive composites.
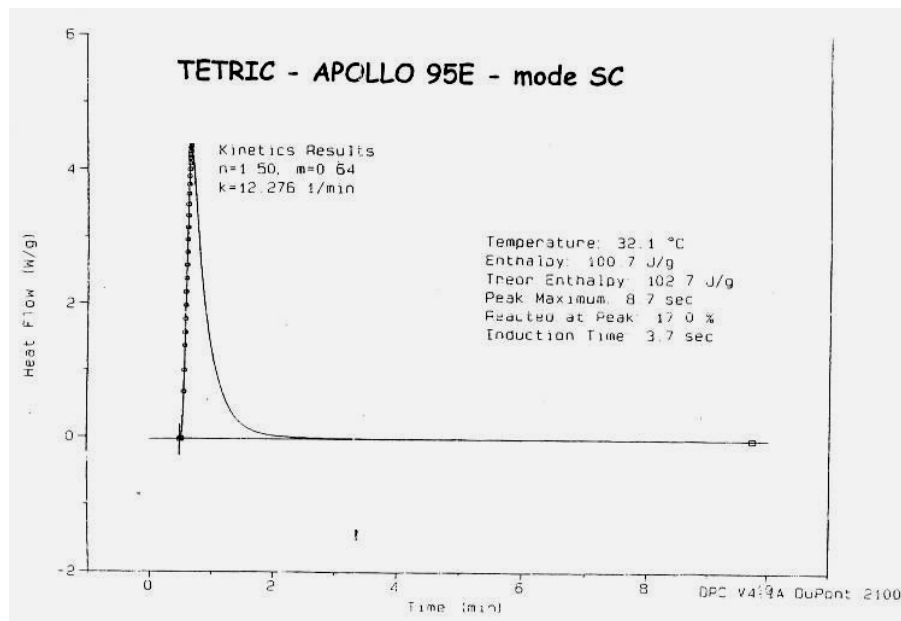

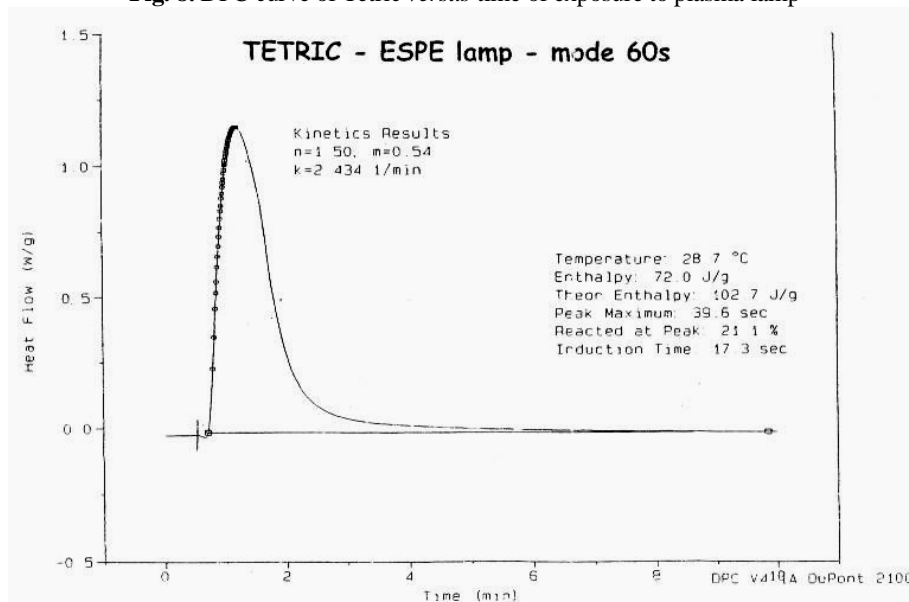**Fig. 8.** DPC curve of Tetric *versus* time of exposure to plasma lamp

Fig. 9. DPC curve of Tetric *versus* time of exposure to halogen lamp
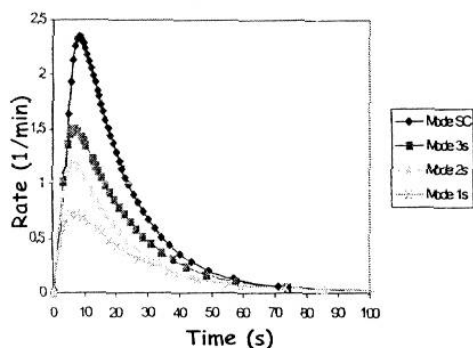
TETRIC - APOLLO 95E Lamp

Fig. 10. Rate of polymerisation of Tetric *versus* time of exposure to plasma lamp
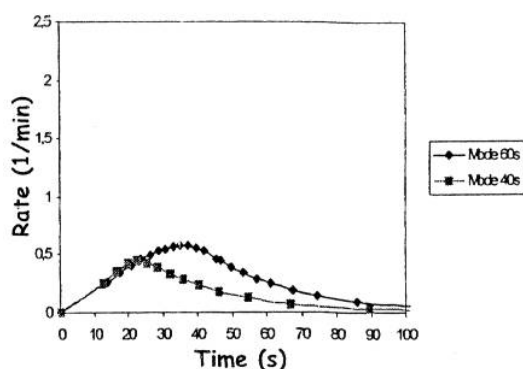
TETRIC - ESPE Lamp

Fig. 11. Rate of polymerisation of Tetric *versus* time of exposure to halogen lamp
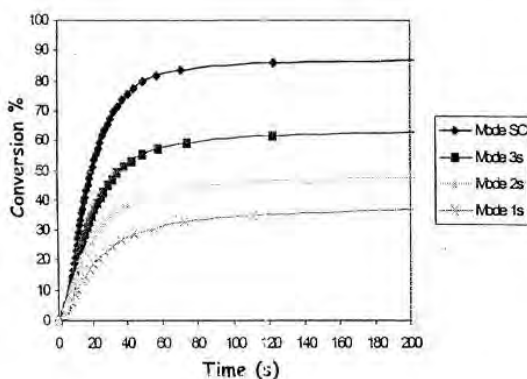
TETRIC - APOLLO 95E Lamp

Fig. 12. Conversion of Tetric *versus* time of exposure to plasma lamp
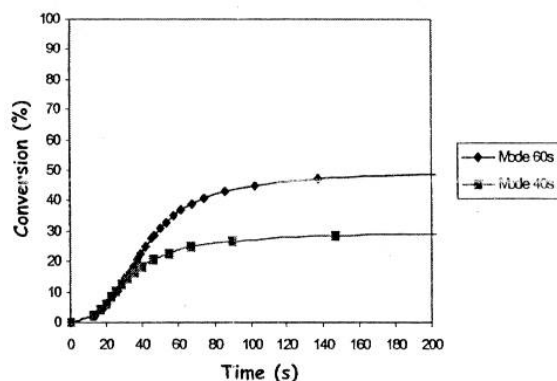
TETRIC - ESPE Lamp

Fig. 13. Conversion of Tetric *versus* time of exposure to halogen lamp

A recent study [13] has demonstrated that the new generation of curable dental composites with low shrinkage (3M™ Filtek™ Z250 and Filtek™ P60) has a higher energy of activation compared to older and conventional ones (3M™ P50 and Z100), *i.e.* :

- Ea = (10.69 ± 0.88) kJ/mol for 3M™ Filtek™ Z250
- Ea = (8.92 ± 1.25) kJ/mol for 3M™ Filtek™ P60
compared to
- Ea = (5.20 ± 1.13) kJ/mol for 3M™ Silux Plus™ [14]
- Ea = (4.94 ± 0.95)kJ/mol [14] or Ea = (4.62 ± ± 0.80) kJ/mol for 3M™ P50 [15]
- Ea = (3.22 ± 0.62) kJ/mol for 3M™ Z100 [15]

According to our DPC results we can conclude that a lower shrinkage leads to a reduced photoreactivity of the sensitive formulation, probably due to a larger free volume of the new reactants of the formulation.

4. Conclusions

Our experimental data based on kinetic parameters determined by phtocalorimetry DPC have shown the great reactivity of visible light curing composites exposed to Apollo 95^{E} lamp compared to the classical lamp from ESPE. In other words Apollo 95^{E} lamp allows the dentist to save a considerable amount of time, *i.e.* just a few seconds compared to 20–40 s using a traditional lamp. Moreover the degree of conversión is much higher with Apollo 95^{E} lamp which minimizes the concentration of monomer entangled in the network.

New systems recently developed and presenting a low contraction have been showing less photoreactivity than the oldest corresponding products.

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ФОТОЗАТВЕРДЖУВАЛЬНІ КОМПОЗИТИ ДЛЯ СТОМАТОЛОГІЇ – КІНЕТИКА ЗА ДОПОМОГОЮ ПЛАЗМОВИХ І ГАЛОГЕННИХ ЛАМП

Анотація*. Досліджено ряд торгівельних стоматологічних композитів, затверджуваних видимим світлом. За допомогою фотокалориметричного методу аналізу, з використанням двох різних типів ламп: звичайних (галогенових) та плазмових типу Аполлон 98^E проведено порівняння фотореактивності таких композитів. Визначено, що час затвердження композитів за допомогою плазмової лампи становить декілька секунд, у порівнянні з 20–40 с у випадку затвердження галогенними лампами. Показано, що нові композити мени фотореакційноздатні у порівнянні з попередніми системами.*

Ключові слова: *полімери для стоматології, композити, видиме світло, затвердіння полімерів, фотокалориметрія, кінетика, енергія активації.*