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NEW LAMP FOR LIGHT CURABLE DENTAL COMPOSITES
I - PRELIMINARY RESULTS

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ABSTRACT

Nous avons testé une nouvelle lampe plasma APOLLO 95E fabriquée par DMDS (Dental Medical Diagnostic Systems) et récemment mise sur le marché français. Les premiers résultats de photopolymérisation de composites dentaires font apparaître, par rapport aux lampes traditionnelles utilisées en cabinet dentaire, des perspectives de gain de temps très appréciable pour le praticien. Les expériences conduites par photopolimérisation à compensation de puissance permettent de quantifier l'exothermicité de la réaction de réticulation et montrent qu'un temps d'exposition de 3 s avec la lampe APOLLO 95 E donnent des résultats supérieurs à 40 s d'exposition avec une lampe classique.

INTRODUCTION

La totalité des résines dentaires de composites photopolymérisables - composites 1ière , 2ième et 3ième génération, ciments verre ionomères - mettent en jeu des fonctions méthacrylates à travers les résines époxydes modifiées acrylates de Bowen (Bis-GMA), les uréthanes modifiées acrylates ou encore les silicones modifiées acrylates utilisées comme oligomères. Elles sont en général mélangées à des monomères monofonctionnels (MMA, HEMA) ou multifonctionnels (EGDMA, DEGDMA, TEGDMA, etc.) dans le but de diminuer leur viscosité. Ces fonctions méthacrylates sont très réactives et permettent, lors de leur réaction de polymérisation, d'assurer la formation d'un réseau tridimensionnel, réticulé et infusible. Cette réaction de réticulation confère à la matrice polymère ses propriétés mécaniques qui sont considérablement améliorées par la présence de charges minérales. Le photoamorceur, générateur de radicaux, généralement la camphoroquinone, absorbe dans le visible (lumière bleue) à 458 nm (1).

PROTOCOLE EXPERIMENTAL

Nous avons modifié notre photocalorimétre(2) - DSC classique à compensation de puissance surmonté d'une unité d'insolation (3ième génération) - en remplaçant la source lumineuse par la lampe plasma APOLLO 95 E ou la lampe classique ESPE. Le guide d'onde est fixé à une vis micrométrique au-dessus de la tête de mesure de l'analyseur enthalpique DSC, permettant de ce fait un réglage de l'intensité reçu par l'échantillon analogue. La lampe plasma APOLLO 95 E émet une lumière visible comprise entre 400 et 500 nm, de même que la lampe classique ESPE.

L'enthalpie mesurée est directement proportionnelle au nombre de fonctions acrylates mises en jeu dans la réaction de réticulation(3). Le coefficient de réactivité k est mesuré à partir de l'équation autocatalytique

$$R = -dC/dt = k\ C^m\ (1-C)^n$$

où C est le degré de conversion et m et n les ordres partiels de réaction, respectivement les réactions d'amorçage (m) et de propagation (n).

La résine testée est la Z100™ A2 de 3M(3). Son taux τ de résine a été mesuré par analyse thermogravimétrique TGA, soit τ[résine] = 19.09% (τ[charges] = 80.91%). La lampe plasma APOLLO 95 E dispose de quatre modes d'insolation: 1 s, 2 s, 3 s et mode Sc (5,5 s en deux flashs successifs). La lampe ESPE a été utilisée pendant 20 s et 40 s.

L'intensité lumineuse est fixée à $I = 10\ mW/cm^2$, les échantillons étant analysés à la température de 32°C ± 2°C.

RESULTATS EXPERIMENTAUX

Un exemple de thermogramme - **Figure 1**, et d'analyse cinétique - **Figure 2**, sont donnés pour la résine Z100™ A2 exposée 3 s à la lampe plasma.

Les résultats sont rassemblés pour différents modes d'insolation - **Tableau 1**, pour la lampe plasma APOLLO 95 E et - **Tableau 2**, pour la lampe classique ESPE.

On observe - **Tableau 1**, que les valeurs de ΔH et k augmentent avec le temps d'insolation pour être optimales pour le mode 3 s. Les temps d'induction quant à eux diminuent normalement - plus une réaction est rapide et plus court est le temps d'induction - excepté pour le mode Sc; ceci peut s'expliquer par le fait que l'on a affaire à deux flashs successifs de puissance variable qui ont pour effet d'élargir le pic exotherme (augmentation de l'enthalpie, ΔH = 137.9 J/g) et de diminuer la réactivité (k = 10.77 1/min).

Pour les échantillons soumis à la lampe ESPE on remarque - **Tableau 2**, qu'une augmentation sensible est observée quand on double le temps d'insolation mais les coefficients de vitesse restent beaucoup plus faibles que ceux observés pour la lampe plasma. Par contre les temps d'induction sont très nettement supérieurs à ceux observés pour la lampe plasma, traduisant le fait d'une plus faible réactivité.

CONCLUSION

En terme de réactivité, le composite dentaire soumis à une lampe plasma donne des valeurs cinétiques très supérieures à celles d'une lampe de photoréticulation classique et de plus pour des temps très courts, quelques secondes comparées à plusieurs dizaines de secondes d'exposition.

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Figure 1: Courbe DPC de l' échantillon Z100™ A2 soumis pendant 3 s à la lampe plasma APOLLO 95 E

Figure 2: Détermination du coefficient de vitesse pour l'échantillon Z100™ A2 soumis pendant 3 s à la lampe plasma APOLLO 95 E

MODE	**ΔH (J/g)**	**k (1/min)**	**Temps d'induction (s)**
1 s	82.6	9.99	2.6
2 s	109.5	12.87	2.5
3 s	127.3	15.32	2.4
Sc	137.9	10.77	2.9

Tableau 1: Echantillon Z100™ A2 soumis à la lampe plasma APOLLO 95 E

MODE	**ΔH (J/g)**	**k (1/min)**	**Temps d'induction (s)**
20 s	93.7	5.10	12.1
40 s	108.3	5.37	10.4

Tableau 2: Echantillon Z100™ A2 soumis à la lampe classique ESPE

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II – KINETICS AND PERFORMANCE

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Abstract

The new Apollo 95^E lamp manufactured by DMDS – Dental Medical Diagnostic Systems, and recently introduced into the French market, has been tested and evaluated on different photo-polymerisable dental composites.

The kinetic measures taken with a power compensation differential photo-calorimeter (DPC) show the advantages that this new lamp has in terms of reactivity and time saving.

Introduction

Photochemical procedures have greatly developed over the last 15 years and have had a great effect in industry (1). Odontology has also been effected experiencing the progressive replacement of amalgams by chemio-polymerisable resin composites and photo-polymerisation in dental reconstruction.

This slow evolution is due to the great simplicity in using a photochemical procedure and the important reactivity of the systems offered (2).

A photo-polymerisable composite consists of a photo-initiator that generates radicals, principally camphoroquinone, a resin constituted of oligomers multifunctional acrylates – principally Bis-GMA and mineral charge –silica and /or quartz. Under the effect of the luminous energy, the photo-initiator generates radicals that initiate the polymerisation of the functions of the acrylates, and propagate leading to the reticulation of the organic matrix.

In spite of the presence of charge – often about 80% - compared to the resin, the system hardens, giving a three dimensional, insoluble and infusible lattice.

In the case of dental composites, the initial milieu already has a significant viscosity due to the high percentage of charge. This indicates that the experimental conditions at the outset are not ideal for the practitioner because polymerisation and reticulation of the milieu are carried out in solid state, an even less favourable state than liquid for the reaction of the chain propagation.

Moreover, seeing that the reactions are brought to temperatures ~30°C, we are well under the Tg of the three-dimensional matrix which is formed, meaning the reaction is rapidly conducted to a vitreous milieu. These factors strongly contribute in restraining the propagation of the reactions, therefore reducing the reactivity of the system and have a direct incidence on the regularity of the formed lattice.

The reaction is made in a "hostile" milieu and therefore it is important to know if it is better to carry out a rapid reticulation or a slow photochemical reaction.

To answer, we suggest that we study the kinetic parameters "'de la prise en masse" (polymerisation and reticulation reactions) considering the enthalpic energy resulting from such reactions. The power compensation photo calorimeter (DPC) which couples the luminous source and the enthalpic analyser, is an ideal tool for measuring the exothermocity of a reaction induced photochemically (2, 3).

We present the comparative results on the dental composites exposed to a plasma lamp Apollo 95^E and a classic ESPE lamp.

Experimental protocol

1.1 Products

The following products were studied:

- Brillant Enamel B2 Y de Coltène, batch GJ 192
- Tétric A3 de Vivadent, batch 918027
- Z100 A2 MP Restorative, batch 8MC-2001-02 from 3M
- Hélio Progress from Vivadent
- Schein, batch 982G0417
- Solitaire A20, batch 30 from Kulzer

1.2 Method of Analysis

1.2.1 - TGA

The composites were studied by thermic gravimetric analysis TGA from Dupont. The samples were subjected to a temperature gradient of 5K/min, in a nitrogen atmosphere, and a temperature interval of 20-700°C. These analyses permit to determine the hardness ratio of the composite (or ratio of resin), essential for the kinetic study with the photo-calorimeter.

1.22 – DPC

The power compensation differential photo-calorimetric was modified in order to use either the plasma lamp, Apollo 95^E or the classic ESPE lamp as the luminous source.

1.23 - Units of exposure

1.23 -1 Apollo 95^E lamp

The Apollo 95^E 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 front panel keyboard is used for selecting the "curing" or "bleaching" mode and the time of illumination:

- 1s
- 2s
- 3s
- SC (step curing), a mode corresponding to half power for 1.5 s followed by full power during 4s, a total exposition of 5.5s.

The plasma lamp is manufactured by DMDS – Dental Medical Diagnostic Systems, Ltd.

1.23-2 Classic lamp

We have chosen the classic lamp commercialised by ESPE.

For the purpose the measure head of the DSC was shut in a hermetic box surmounted by a micrometric screw fixed to the housing for the wave-guide. This way the power discharged on to the sample to be analysed can be adjusted precisely at any moment.

Experimental Results

The dental composite is consists mainly of charges, acrylic oligomers, of a photo-initiator and additives. In reality the active phase consists only of an oligomer resin, which is responsible for the exothermicity of the reaction, observed during a polymerisation/reticulation of the resin. It is therefore important to know the charge ratio of the composite in order to correct the weight of the sample subjected to light.

The thermogravimetric analysis determines the ratio of charge minerals in each composite. An example of TGA analysis is given in **figure 1** for the Tétric sample from Vivadent, 83.06 % of charge (or 26.94 % of resin, the complement).

The results for the different composites are noted in **Table 1**. It can be noted that the Tétric is the most charged and Hélio the least.

The photocalorimetric analysis determines the kinetic parameters of the polymerisation/reticulation reaction, in particular the following parameters:

α - **the Enthalpy of the reaction – ΔH** expressed in Joules per gram of resin exposed to the insolation. This energy measured during the reaction is directly proportional to the functions that have reacted during the exposition. For instance the higher the reaction of the functions, the higher the reaction enthalpy. For example a mol of methacrylate releases during its first polymerisation an enthalpy of 13.6kcal/mol, that is 668.48J/g of methacrylate.

β **the coeffecient of velocity k** is expressed in 1/min. It is calculated using the velocity equation of an auto-catalytic system.

$$R = - dC/dt = k\, C^m(1-C)^n$$

Or C: is the conversion degree of the reaction,
m and n: part order of the reaction, initiation (m) and propagation (n) respectively.

In this equation the final reactions are ignored as we only consider the very beginning of the reaction.

γ **-the time of induction** expressed in seconds, is the time corresponding to the consumption of 1 % of the monomer. It is chosen this way in order to consider the reaction at the beginning therefore enabling easy comparison of one sample to another. The slower the time of induction, the higher the reactivity of the system.

An example of a exothermic graph line is given for the sample Brillant enamel B2 from Coltène exposed for 3s – **figure 2** and the calculation of the velocity coefficient – **figure 3**. All the results of the kinetic parameters obtained with the Apollo 95^E lamp are shown in **table 2** and for the classic lamp ESPE in **table 3**.

The samples that were subjected to the Apollo 95^E lamp show an increase in the reticulation of the resin when the system gradually passes from mode 1s to 2s or 3s even SC.

It can be said – **table 2** – that the optimum of the reaction is given either in the mode SC, either in the mode 3s.

Using the kinetic values, the resins can be classified by order of reactivity in each mode.

- **mode 1s**

Z100>Coltène>Tetric>Helio>Kulzer>Schein

- **mode 2s**

Z100>Coltène>Kulzer>Helio>Tetric>Schein

- **mode 3s**

Z100>Coltène>Tetric>Helio>Kulzer>Schein

- **mode Sc.**

Coltène>Tetric>Z100>Schein>Hélio

The composites can be listed into two groups independent of the exposition mode.

- the most reactive - from a photochemical point of view
  Z100, Coltène and Tétric

- the least reactive - from a photochemical point of view
  Hélio, Kulzer and Schein

The same remarks can be made for the samples reticulated by the classic ESPE lamp, i.e.

- for the same sample, the optimal values of the kinetic parameters are obtained through a exposure time of 40s or 60s. However, there are a few exceptions, in particular for Coltène, Hélio and Schein for which the maximum values of the velocity coefficient are obtained after 20s of exposure. As far as these composites are concerned, this surprising result could be explained by the fact that by rapidly obtaining the state of vitrification, the propagation of the chains, although not suppressed, is more difficult.

When comparing **table 2 and 3**, we can note the advantages of the kinetic performance of the Apollo 95^{E} lamp compared to those of the ESPE lamp. It can also be noted that if the reactional enthalpy have the same order of size **$\Delta H \approx 80 - 100$ J/g,** the velocity coefficient however is two to three times higher for the plasma lamp compared to the classic lamp. In the same way the values of time of induction – a value corresponding to the consumption of 1 % of the manomer – are definitely shorter, around 3 s compared to about 10s for the classic lamp.

These results confirm our preliminary results (4).

CONCLUSION

Our experiments based on the analysis of kinetic parameters i.e.: the enthalpic values of the reticulation reaction, the velocity coefficient, and the time of induction of the reaction, determined by power compensation photo-calorimetric, enable to confirm the great reactivity of the Apollo 95^{E} in comparison to the classic lamps used in Odontology.

Moreover, the Apollo 95^{E} enables the practitioner to save a considerable amount of time, just a few seconds compared to 20-40 seconds of insolation using a traditional lamp.

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Figure 1: Thermo-gravimetric Analysis TGA Tétric from Vivadent

Figure 2: Exotherm graph line by DPC for the sample Brillant Enamel B2 from Coltène exposed 3 seconds with the Apollo 95^E lamp.

Figure 3: Kinetic graph line which enables to calculate the velocity coefficient of the sample Brillant B2 from Coltène exposed 3 seconds with the Apollo 95^E lamp.

Composite	**Charge ratio**	**Resin ratio**
	%	%
Coltène	74.57	25.43
Tétric	83.06	16.94
Z100	80.91	19.09
Hélio	46.08	53.92
Schein	74.37	25.63
Solitaire	68.42	31.58

Table 1: Charge ratio (and resin) of the different composites analysed

Table 2: kinetic parameters – enthalpy, velocity coefficient and time of induction – of the different composites for several modes of insolation with the Apollo 95^E lamp.

Table 3: kinetic parameters – enthalpy, velocity coefficient and time of induction – of the different composites for several modes of exposure with the lamp ESPE.