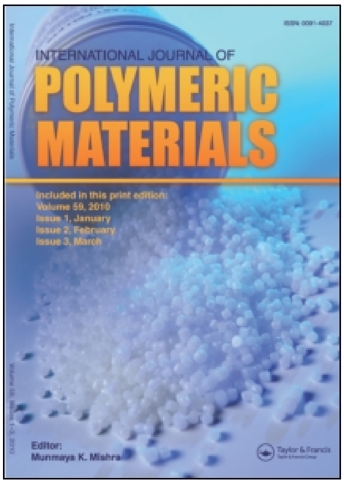

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Photopolymerization of "dual-setting" α-tricalcium phosphate cements

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PHOTOPOLYMERIZATION OF "DUAL-SETTING" α-TRICALCIUM PHOSPHATE CEMENTS

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Photo-cured "dual setting" cements based on α-tricalcium phosphate (α-TCP) as Solid Component, S, and a mixture of water soluble acrylic monomers as Liquid Component, L, were prepared. The monomers employed were acrylamide (AA), 20 wt./vol. %, and N,N′-methylenebisacrylamide (MBAA) 0.4 wt./vol. %, both dissolved in a 2.5 wt./vol. % Na_2HPO_4 aqueous solution. Polymerization of these systems was initiated photochemically under the action of visible light (wavelength in excess of 400 nm) and using camphorquinone as photoiniator.

During the kinetic study of the photopolymerization of L it was found that the amide groups present in the monomer structures acted as co-initiator, and efficiently photoreduced the camphorquinone. The addition of N,N-dimethyl aminobenzyl alcohol (DMOH) as co-initiator produced a retarding effect on the polymerization. This phenomenon was explained in terms of chain transfer.

It was also found that the photo-cured mechanism of L does not obey a simple free radical polymerization scheme since it does not fit in with the well known kinetic expression for "ideal" photo-initiated polymerization.

The kinetic study of the photopolymerization of cements was carried out at different irradiation intensities (from 0.70 to 1.37 mcal/s) and varying the filler content from 47.6 to 71.4 wt.-%. It was established that the photopolymerization rate rises linearly with the L/S ratio used. This result was satisfactory explained on the basis of the Mesophase Theory.

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Keywords: calcium phosphate bone cement, dual-setting, α-tricalcium phosphate, photopolymerization, acrylamide, N,N′-methylenbisacrylamide

INTRODUCTION

Setting and hardening of conventional calcium phosphate bone cements (CPBC) are the result of one or several hydraulic reactions involving dissolution of the calcium phosphate phases initially present in the cement powder, and precipitation of new less soluble ones in the mixing liquid. The entanglement of microcrystals of precipitated calcium phosphates is responsible for the mechanical strength in these CPBCs [1–3].

Among the different systems of CPBCs reported those based on α-$Ca_3(PO_4)_2$ are interesting because the product of the reaction of hydraulic setting (Eq. (1)) is calcium-deficient hydroxyapatite (CDHA) which closely resembles biological apatite naturally occurring in bone tissue in terms of solubility, stoichiometry and biological behavior [3, 4].

$$3\ \alpha - Ca_3(PO_4)_{2(s)} + H_2O \rightarrow Ca_9(HPO_4)(PO_4)_5OH_{(s)} \qquad (1)$$

The main handicaps of conventional CPBCs are: their relatively low strengths; their instability in the presence of biological fluids in the implantation site; and their setting times, which are occasionally inadequate for clinical applications [5].

At the beginning of the 90's, the so called "dual-setting" glass ionomer cements (GIC) or "compomers" were introduced in dentistry. They overcame the disadvantage of large setting time and solubility, and low initial strength, of conventional GICs. The basic modification differentiating the "dual-setting" GIC from those produced in the conventional way is the introduction of acrylic monomers such as hydroxyethyl methacrylate, ethyleneglycol dimethacrylates, and Bis-GMA, and, latterly, acrylic moieties in the chain of the polycarboxylic acid. The acrylic derivatives employed are able to polymerize under the action of "blue" light in the presence of a photo-active red-ox pair, such as camphorquinone/tertiary amine. In this way, in "dual-setting" GIC, two setting reactions proceed in parallel. One is the conventional acid-base reaction between the inorganic glass and the polycarboxylic acid, which produces a tridimensional network consisting of polycarboxylic chains and bi- and trivalent metallic cations. The other is the polymerization of acrylic derivatives, which also yield a tridimensional polymeric network. The result of both reactions is the formation of two parallel and interpenetrating networks that provide a cement with a lower solubility, shorter setting time, and a greater strength [6].

Taking into account the above considerations, in previous works we developed a "dual-setting" α-TCP-based CPBC [7–9]. This consisted of a powder composed of α-TCP, precipitated hydroxyapatite (HA), and ammonium persulphate (AP). The mixing liquid contained acrylamide (AA), N,N′-methylenebisacrylamide (MBAA) and N,N,N′,N′-tetramethylethylenediamine (TEMED), all dissolved in aqueous Na_2HPO_4. The monomers (AA, MBAA) and the initiating red-ox system (AP, TEMED) were those employed in gel-casting technology because of their ability to polymerize into a crosslinked hydrogel network [10].

In this new "dual-setting" CPBC two setting reactions proceed after mixing the powder and liquid components. One is the conventional hydraulic reaction represented in Eq. (1), and the other is the polymerization of the acrylic monomers. The hydrogel-like network resulting from polymerization reinforces the inorganic entanglement of CDHA microcrystals. The "dual-setting" α-TCP-based CPBC showed higher strength than conventional ones whereas the phase composition and microstructure were the same.

Bearing in mind the well recognized advantages of photo-cured systems over self-cured systems, namely a larger shelf-life and longer handling time during application [11], we decided in this work to develop a photo-cured "dual-setting" α-TCP-based CPBC, and to study the kinetic characteristics of its photo-initiated polymerization.

EXPERIMENTAL

Syntheses of α-TCP

α-TCP was synthesized by the solid-state reaction between $CaCO_3$ (QP, Probus) and $Ca_2P_2O_7$. $Ca_2P_2O_7$ was previously prepared by heating $CaHPO_4 \cdot 2H_2O$ (RP, Carlo Erba) at 550° for 2 hr. Equimolar amounts of $CaCO_3$ and $Ca_2P_2O_7$, were previously mixed and pulverized by ball-milling in anhydrous acetone. After drying, the resulting mixture was heated in a platinum crucible at 1400°C for 24 hr. and quenched in air. The product was ball-milled in anhydrous acetone to a mean particle size of 14 µm (Mastersizer S). The X-ray diffraction pattern (Siemens D5000; $CuK\alpha_1$, 2°/min) of the resulting product showed the presence of α-TCP (JCPDS 29-0359) as the only crystalline phase.

Composition of the Liquid Component (L) of the Cements

As was mentioned in the introduction to this article, the addition of water-soluble monomers to L, which are able to polymerize "*in situ*" *via* free radicals, can significantly improve some of the important properties of the CPBC's. The monomers employed were acrylamide (AA), 20 wt./vol. %, and N,N′-methylenebisacrylamide (MBAA) 0.4 wt./vol. %, both supplied by Aldrich. The former was used as a mono-functional monomer and the latter as a bi-functional crosslinked monomer. Both monomers were dissolved in a 2.5 wt./vol. % Na_2HPO_4 aqueous solution.

These monomers, as well as their concentrations, were selected on the basis of the results of previous works [9]. To this monomer composition the camphorquinone (CQ, supplied by Aldrich), 2.5 wt./vol. %, was added as photo-initiator for the photo-curing process. It is well known that CQ, which shows a maximum absorption at 470 nm, in conjunction with a tertiary amine (co-initiator), and upon irradiation, forms, *via* a charge transfer mechanism, the corresponding exciplex, whose decomposition leads to the production of amino radicals capable of initiating the polymerization process of acrylic structures. As a result, this initiating system (CQ-amine) is widely used in a variety of dental materials [12] because of its ability to carry out efficient setting or polymerization "*in situ*" of dental formulation under the action of visible light. Only wavelength in excess of 400 nm are permitted by International Regulation Organizations for use in the oral cavity.

Taking into account the potential capability of the amide groups present in both monomers, to play the role as co-initiator in CQ photo reductions, kinetic studies were carried out in the presence, as well as absence, of a tertiary amine. In the former case N,N-dimethylaminobenzyl alcohol, 0.5 wt./vol.%, was employed for this propose.

Measurement of Photopolymerization Kinetics

The kinetics of photopolymerization were monitored by photocalorimetry with the aid of a differential scanning calorimeter (Perkin Elmer, model DSC-4, USA) modified to permit irradiation of samples within the calorimeter chamber. The ends of a twin light-conducting fiber were inserted into the cover of the DSC aluminium block by drilling holes directly above the sample and the reference holders, so that the exit windows of each optical fiber were located 3 mm above the base of the DSC pan. A detailed description of the modified differential calorimeter can be found in previous publications [13, 14]. In our current work the twin-branch flexible light guides (each 50-cm length) are terminated with a ferrule connector which is plugged into the light guide socket of a cold light source (Schott KL-1500, Germany). This irradiation source allows direct regulation of the intensity of light in graduated stages by means of a brightness control. Installation of neutral filters in the filter holder, or on the focusing attachment of the instrument, extends the range of intensity control. In order to avoid the heating effect of the photo-curing source, and to isolate the 470 nm wavelength, a solid heat filter (Schott, KG-1) and a 470 nm violet filter (Schott VG-9) were placed into the filter holder.

The DSC calibration, data processing, determination of incident and absorbed light intensity, as well as complementary details, have been described elsewhere [13, 14]. All polymerizations were carried out at 37°C, being approximately the temperature of the human body. The quantity of each Liquid Component sample was 20 μL, measured accurately using a Hamilton 25 μL syringe. In the case of composites, samples of about 60 mg were accurately weighed and spread as a layer over the base of the 6.5-mm diameter aluminium DSC pan.

All the polymerization experiments were performed in a open pan to avoid the difference between the values of I_0 emitted by the lamp and the I_0 which actually reaches the sample. Taking into account the possibility of the solvent used in these systems (water) being evaporated during the experiment, all runs were initially performed in the absence of light.

In this way a base line reading was established for each experiment, which then permitted correction of the resulting thermogram. In the case of composites these "dark runs" were carried out for all ratios of L/S studied in order to subtract the possible contribution to the thermal effect of polymerization by the heat produced as a result of hydraulic setting. Examples of this procedure are shown in Figure 1.

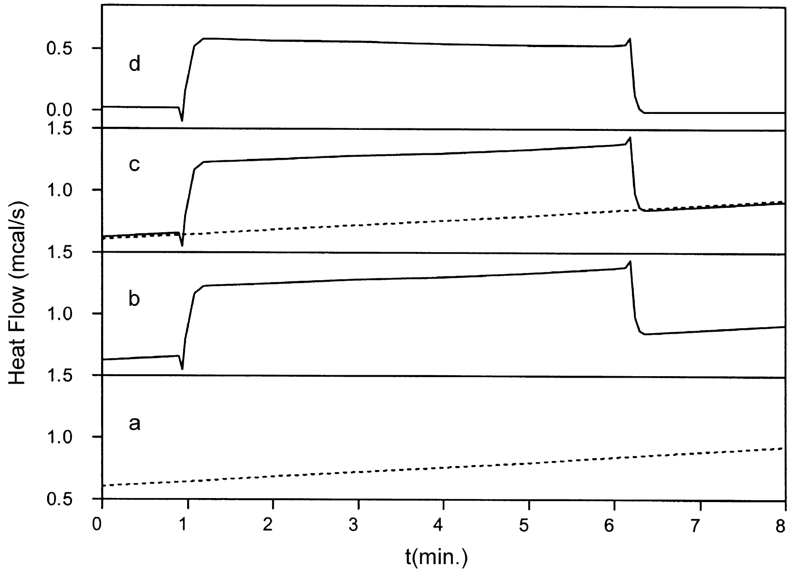

FIGURE 1 Correction procedure of the thermograms. (a) thermogram of L without DMOH "in dark"; (b) the same as (a) but with 5 min. irradiation; (c) correction of thermogram for base line; (d) corrected thermogram.

From the above corrected thermograms the heat evolved at different times of polymerization were calculated. Using the values of the total heats of polymerization (81.5 kJ/mol for AA and 82.7 kJ/mol for MBAA) [15] and also the contribution of each monomer to the total thermal effect according to their molar fraction in the feed, the evolution in real time of percent and/or molar conversion of monomer mixtures under irradiation could easily be determined.

RESULTS AND DISCUSSION

Photopolymerization of the Liquid Component

Polymerization experiments were carried out at different light intensities, both in the presence and absence of DMOH, in order to determine the influence of the incident light intensity (I_0) and the presence of co-initiator upon the kinetic parameters of the photo-curing of L. Typical kinetic "curves" obtained for both systems are shown in Figure 2. It is clearly seen that in the time range studied (from 0 to 350 s) the conversion increases linearly with irradiation time, as to be expected for the polymerization of diluted monomer mixtures.

From the linear part of the graph obtained for conversion *vs*. time, and using linear least squares fit, the rates (Rp) and the quantum yield of polymerization (ϕ_p) were calculated. This quantum yield, which shows the amount of monomer transformed to polymer per photon absorbed, was obtained as the ratio of the conversion degree (mol) to the energy absorbed (einstein).

All experimental conditions and data obtained, together with the calculated parameters are displayed in Table 1, where $C_{5\,min.}$ is the conversion determined after 5 minutes of polymerization and R is the correlation coefficient.

As can be observed, both Rp and conversion increase by increasing the incident light intensity in irradiating intervals between 0.22 – 1.39 mcal/s while the values of ϕ_p remain almost constant in the large range of Io (from 0.59 to 1.39 mcal/seg). This last fact indicates that the efficiency of the use of light energy for polymerization of these systems is practically the same over the whole range of irradiation intensities studied, *i.e*., for each mol (einstein) of energy absorbed the same amount of monomer is transformed into polymer.

On the other hand, it can be clearly seen that all the above parameters are larger for a system without DMOH, which could imply that the amide groups present in the structure of the monomer component (AA and MBAA) are able to play a role as co-initiator for efficient photo-reduction of CQ. In addition, the excess of amine (in systems with DMOH) provokes the effect of retardation of polymerization. Similar behavior was reported by Cook [16] who observed that excess of amine acted as a retarder when the tetramethyl

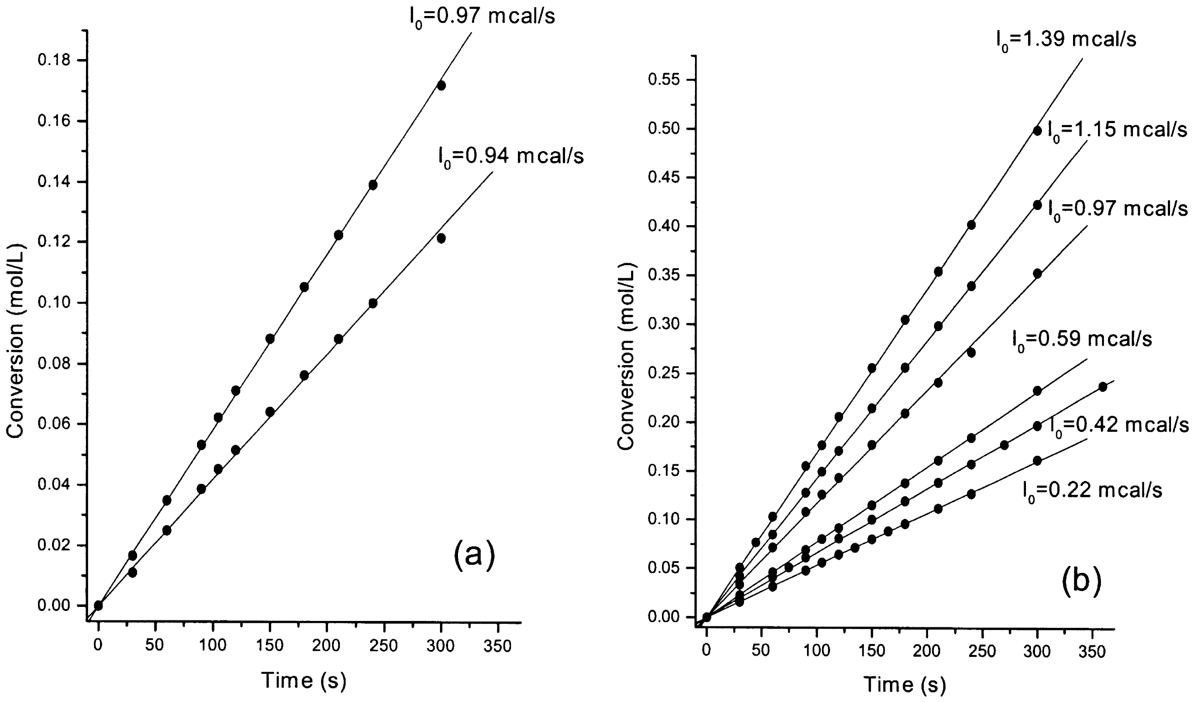

FIGURE 2 Kinetic curves of the photopolymerization of L. (a) with DMOH; (b) without DMOH.

TABLE 1 Results of the study of photopolymerization of L

I_0 (*mcal/s*)	R_P. 10^4 (*mol/L·s*)	*Corr. Coef.* *R*	Φ_P	$C_{5\,min.}$ (%)
Without co-initiator				
0.22	5.36 ± 0.01	0.99990	21.72 ± 0.04	5.70 ± 0.01
0.42	6.63 ± 0.02	0.99989	13.43 ± 0.04	7.05 ± 0.02
0.59	7.74 ± 0.02	0.99995	10.55 ± 0.04	8.23 ± 0.03
0.97	11.70 ± 0.07	0.99944	10.16 ± 0.06	12.45 ± 0.07
1.15	14.20 ± 0.02	0.99997	10.22 ± 0.02	15.11 ± 0.02
1.39	16.90 ± 0.05	0.99988	10.27 ± 0.03	17.98 ± 0.05
With co-initiator (0.5% m/v DMOH)				
0.74	4.17 ± 0.03	0.99921	4.61 ± 0.04	4.44 ± 0.04
0.94	5.82 ± 0.02	0.99981	5.05 ± 0.02	6.19 ± 0.02

amine was used as co-initiator for a Bis-GMA and triethylene glycol dimethacrylate (TEGDM) blend. Cook explained the dual action of the amine in accelerating polymerization at low levels, and of retarding polymerization at high concentration, in terms of chain transfer where the rate of addition of amine radical to monomer is much slower than the rate of propagation reaction. So, something similar might occur in the current system and it could equally be related to retarding effect of the excess of amine.

In order to elucidate some phenomenological characteristics of the process of photopolymerization of this system, Rp against incident light intensity was plotted (Fig. 3). As can be seen there exists a linear relationship (with correlation coefficient 0.9933) between both parameters. This suggests that the photo-cured mechanism of L does not obey a simple free radical polymerization scheme since it does not fit in with the well known kinetic expression for "ideal" photo-initiated polymerization:

$$\mathrm{Rp} = \mathrm{Kp/Kt}^{0.5}[\mathrm{M}](\varphi_1 \mathrm{Ia})^{0.5} \tag{2}$$

where:

$\mathrm{Ia} = \mathrm{Io}\ (1 - 10^{-\varepsilon \mathrm{cl}})$
Kp and Kt are the propagation and termination rate constants
c is the concentration of the absorbing species (mol/1)
ε is the extinction coefficient of the photo-initiator at 470 nm (1/mol.cm)
φ_1 is the quantum yield of initiation
1 is the thickness of the irradiated layer (optical path length)

So, Eq. (2) indicates that in the case of "ideal" polymerization the overall rate of process, Rp, should be directly proportional to the square root of the incident light intensity. This does not occur in the system we describe. In fact, the relationship between Rp and the square root of Io, which is shown

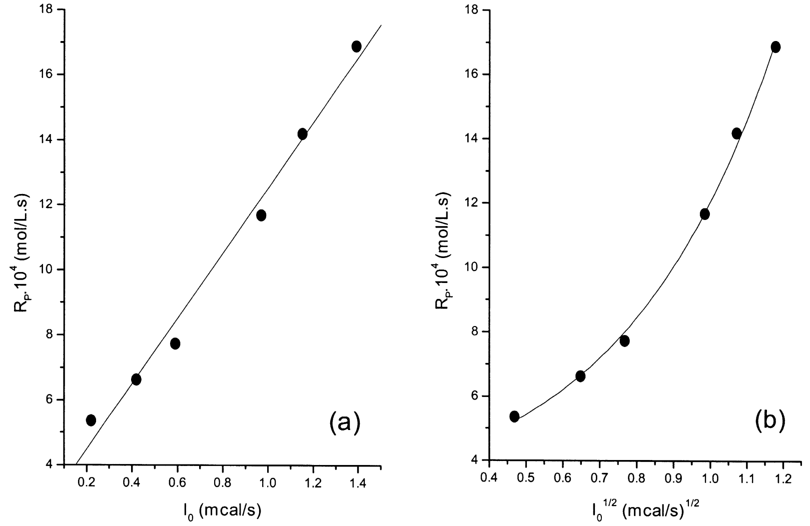

FIGURE 3 Dependence of the rate of photopolymerization of L without DMOH, on: (a) the intensity of incident light, I_0; (b) the square root of I_0.

in Figure 4, can be satisfactory adjusted to the exponential fit (correlation coefficient 0.9987) according the following expression:

$$Y = Yo + Ae^{x/t}$$

where:

$Yo = 2.5 \pm 1.0$
$A = 0.90 \pm 0.41$
$t = 0.42 \pm 0.06$

This result clearly indicates that in the polymerization mechanism of L some "complicating" steps such as degradative transfer, which can alter the overall kinetic equation, should be considered.

Kinetic Study of Cement Polymerization

To assess the influence of the α-TCP concentration and the incident light intensity on the photopolymerization of resulting cements, samples of these composites were prepared using L without co-initiator and varying the filler content from 47.6 to 71.4 wt.% which corresponds to the following ratios of L/S: 1.1 and 0.4 mL/g respectively. The irradiation intensity was varied from 0.70 to 1.37 mcal/s. It should be stressed that the selected interval of filler content permits the resulting composites to be obtained as manageable

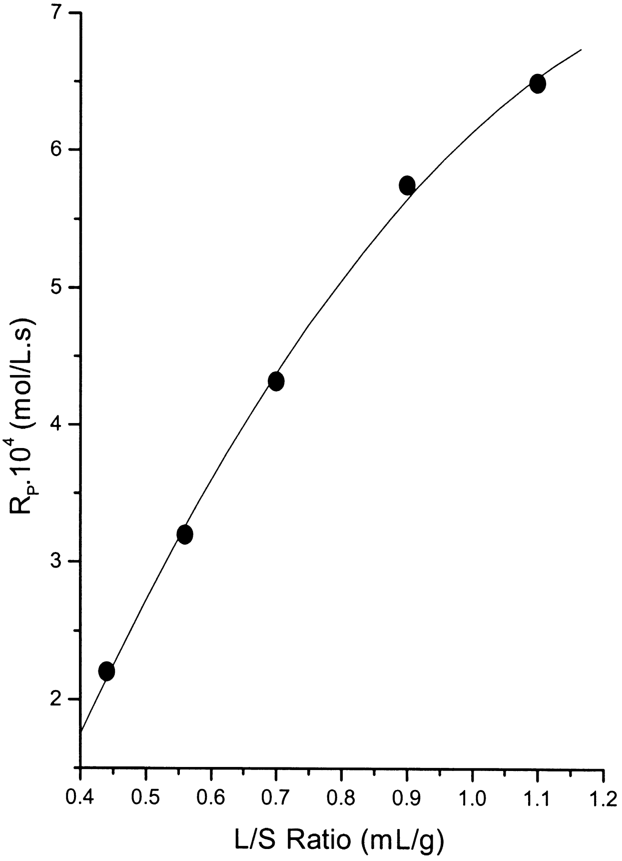

FIGURE 4 Dependence of the rate of photopolymerization of "dual setting" cement on L/S ratio. $I_0 = 1.30$ mcal/s.

homogeneous pastes without segregation during handling. Moreover, a concentration of S of 71.4 wt.% corresponds to the maximum admissible filler content, while a value lower than 47.6 wt.% gives unstable viscous suspensions. In order to verify the possible influence of the contribution of the heat of hydraulic setting upon the exothermic effect of polymerization, calorimetric studies were initially carried out in the absence of irradiation, as was described above (see EXPERIMENTAL). As can be seen in Figure 1 no calorimetric effect, which might be ascribed to the above mention process, was detected.

The results of the kinetic study of the photopolymerization of the above cements are summarized in Table 2, where it may be observed that, for all composite formulations studied, all calculated parameters (Rp, ϕ_p and conversion) increase with increase of incident light intensity. On the other

TABLE 2 Results of the study of photopolymerization of "dual setting" cements

L/P Ratio (*mL/g*)	I_0 (*mcal/s*)	$R_P \times 10^4$ (*mol/L·s*)	*Corr. Coef.* *R*	Φ_P	$C_{10\,min}$ (%)
0.44	1.31	2.18 ± 0.03	0.99975	0.34 ± 0.01	0.88 ± 0.01
0.56	1.01	1.43 ± 0.01	0.99954	1.55 ± 0.01	3.10 ± 0.01
	1.37	3.88 ± 0.05	0.99960	2.83 ± 0.01	7.92 ± 0.03
0.70	0.70	2.08 ± 0.06	0.99920	2.83 ± 0.01	4.46 ± 0.02
	0.99	2.82 ± 0.02	0.99991	2.62 ± 0.01	5.35 ± 0.02
0.90	0.93	3.37 ± 0.03	0.99986	4.10 ± 0.02	7.81 ± 0.03
	1.22	5.54 ± 0.04	0.99975	5.92 ± 0.02	14.75 ± 0.06
1.10	1.35	6.83 ± 0.03	0.99993	6.47 ± 0.03	18.01 ± 0.07

hand, an increase of filler content (diminution of ratio L/S from 1.1 to 0.44 mL/g) causes an appreciable decrease of all of these parameters. The profile of dependence between Rp and L/S is shown in Figure 4 where the values of Rp were normalized to Io = 1.30 mcal/s according to the experimentally found dependence between both parameters. These results are in accordance with those observed in the photopolymerization of composites based on Bis-GMA/TEGDM and hydroxyapatite, where a diminution of Rp with filler content was observed [17]. In order to explain the observed phenomenon, the authors turned to the three-layer model applicable for particulate composites (TLMPC) [18] (or Mesophase Theory).

According to this model, three different and distinguishable phases are present in the composite: the filler or inclusions, the matrix and the mesophase. The main element of this model is the third phase, a hybrid lying between the two other phases, where transition phenomena between the properties of the two phases occur. This hybrid characterizes the effectiveness of interaction between filler and matrix. The mesophase represents a zone of imperfections surrounding the inclusions (in our case the particles of α-TCP), and is considered to consist of a homogeneous and isotropic material of finite thickness. Mesophase properties, such as viscosity and density, are usually higher than in the bulk of the matrix; this might produce a lower molecular mobility, and thus a decrease in Kp value and in the corresponding Rp. With this in mind, it is logical to suppose that with increase of filler content, more L occurs in the mesophase, and it seems that the mesophase content reaches a maximum at L/S = 0.44 mL/g. Assuming a lower Rp in the mesophase because of its higher viscosity and lower molecular mobility (which produces a decrease in k_p value) the observed inverse correlation between filler content and Rp values can be explained.

CONCLUSIONS

Dual setting CPBC's based in α-TCP were prepared and studied, in which the polymerization reaction of water soluble acrylic monomers is initiated photochemically. During the study of the photopolymerization of the Liquid Component of these cements it was found that the amide groups present in the monomer structures of AA and MBAM act as co-initiator, and efficiently photo-reduce the camphorquinone. The addition of DMOH as co-initiator produces a retarding effect on the polymerization. This phenomenon may be explained in terms of chain transfer, assuming that the rate of addition of the monomer to the amino radical is much less than that of propagation.

The rate of photopolymerization of the Liquid Component rises linearly with the intensity of incident light, which indicates a deviation from the "ideal" behavior of linear radical polymerization as a consequence of the phenomena of crosslinking and degradative transfer present in the system.

In the case of cement pastes the photopolymerization rate rises linearly with the ratio of L/S used. This result is in agreement with those obtained from other studies carried out by the current authors on systems consisting of Bis-GMA/TEGDM/hydroxyapatite, which were satisfactory explained on the basis of the Mesophase Theory.

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