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Influence of photoinitiator type on the rate of polymerization, degree of conversion, hardness and yellowing of dental resin composites

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ABSTRACT

Objectives. To evaluate the degree of conversion (DC), maximum rate of polymerization (R_p^{max}), Knoop hardness (KHN) and yellowing (*b*-value) of resin composites formulated with phenylpropanedione (PPD), camphorquinone (CQ), or CQ/PPD at different concentrations. The hypotheses tested were (i) PPD or CQ/PPD would produce less R_p^{max} and yellowing than CQ alone without affecting DC and KHN, and (ii) R_p^{max}, DC, and KHN would be directly related to the absorbed power density (PD_{abs}).

Methods. CQ/amine, PPD/amine and CQ/PPD/amine were used at low, intermediate and high concentrations in experimental composites. Photoinitiator absorption and halogen-light emission were measured using a spectrophotometer, R_p with differential scanning calorimetry (DSC), DC with DSC and FTIR, KHN with Knoop indentation; and color with a chromameter. The results were analyzed with two-way analysis of variance (ANOVA)/Student–Newman–Keul's test ($p < 0.05$). Correlation tests were carried out between PD_{abs} and each of DC, R_p^{max} and KHN.

Results. The PD_{abs} increased with photoinitiator concentration and PPD samples had the lowest values. In general, maximum DC was comparable at intermediate concentration, while R_p^{max} and KHN required higher concentrations. DC was similar for all photoinitiators, but R_p^{max} was lower with PPD and CQ/PPD. PPD produced the lowest KHN. Yellowing increased with photoinitiator concentration. PPD did not reduce yellowing at intermediate and/or high concentrations, compared to CQ-formulations. PD_{abs} showed significant correlations with DC, R_p^{max} and KHN.

Conclusion. PPD or CQ/PPD reduced R_p^{max} in experimental composites without affecting the DC. The use of PPD did not reduce yellowing, but reduced KHN. DC, R_p^{max} and KHN were dependent on PD_{abs}.

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1. Introduction

Camphorquinone (CQ) has been largely used as a photoinitiator since the introduction of visible-light activated resin composites. However, efficient this photoinitiator might be, its association with an electron/proton donor substance, usually a tertiary amine, may increase reactivity [1–3]. Absorption of light by CQ typically leads to the creation of two excited states: (i) the “singlet state”, which does not involve reversal of electron spin, and (ii) the “triplet state”, which is the one relevant to free radical formation and which has a very short half-life [4]. While in the triplet state, the CQ molecule may interact with an amine molecule and generate an excited state complex, the “exciplex”. Thus, the CQ abstracts a hydrogen atom from the tertiary amine resulting in free radical formation [2].

One factor that influences radical formation in CQ/amine systems is the concentration of the photoinitiators, which are known to vary among commercial brands [5,6]. There is evidence that higher concentrations of photoinitiators improve the degree of conversion (DC) and mechanical properties of the formed polymer [7–13]. Unfortunately, above a certain threshold, no benefits are observed [9,14] and may affect aesthetics due to CQ’s yellow color [10,11,15,16]. Although the yellowing might be reduced during the photoactivation process, part of the photoinitiator may remain unreacted due to insufficient irradiation [17] or other physical effects, such as the inner shielding effect [14]. Therefore, the restoration could still be yellowish and non-acceptable esthetically [17,18].

Studies have presented alternative photoinitiators (e.g., PPD) that could be used alone or in combination with CQ to reduce the “yellowing effect” in dental resins. The absorption peak of these molecules is at shorter wavelengths than CQ and they tend to be less yellow [2,16,19–21]. However, the literature on these alternative molecules is still poor and there is no consensus as to their potential for “yellowing” reduction or to the effect on the structure of the formed polymer.

The photoinitiator phenylpropanedione (PPD) has shown promising results as an alternative system for light-activation of dental resins. Besides the claimed advantage of less yellowing [16], PPD produces a lower rate of polymerization without affecting the final DC compared to CQ containing formulations [22–24]. It has been suggested that the rate of polymerization may affect polymerization stress development [25], but this is a matter of controversy [26]. The polymer formed at lower rates has been suggested to be more linear, although no consensus about this matter has been reached either [27–29]. Consequently, PPD formulations could be useful for reducing stress within the material and at the resin–tooth interface.

However, since the light curing units (LCUs) are optimized for curing CQ, and alternative photoinitiators absorb light at shorter wavelengths than CQ, these units may not be suitable for use with alternative photoinitiators [19]. Indeed, the low rate of reaction reported with the use of PPD has been related to lower light absorption [23]. One way to overcome this problem, as hypothesized by Neumann et al. [19], would be to increase the curing time or to design materials with higher concentrations of the alternative photoinitiators. However, there are only a few studies that deal with the influence of PPD concentration on the polymerization rate and on the structure of the resultant polymers [24].

Apart from the photoinitiator concentration and the irradiation protocol, certain characteristics related to the chemistry of the molecule itself can also affect curing initiation. The photoinitiator molecule must have a high molar extinction coefficient, which is defined as the absorption per unit length divided by the molar photoinitiator concentration of the solution. The best photoinitiators have high absorptions at low concentrations [2]. However, as previously mentioned, if the LCU does not emit sufficient light in wavelengths that are absorbed by the photoinitiator, then the polymerization process may be affected. Thus, considering solely the relationship between light emission and absorbance (since the chemical mechanism of free radical generation [20] as well as the optical properties [30] may also play a role in the process), it is the effective absorbed energy that influences the photoinitiation process [31]. For that reason, it is important to describe both the molar extinction coefficient as well as the absorbed power density (PD_{abs}) when studying different photoinitiator systems.

The objective of the present study was to evaluate the DC, Knoop hardness (KHN), maximum rate of polymerization (R_p^{max}), and the “yellowing effect” (assessed through the *b*-value of the CIELab color system) of resin composites activated by different photoinitiator systems. These parameters were studied as a function of different photoinitiator concentrations. PD_{abs} was studied to understand how well the LCU spectrum related to the photoinitiator’ absorption spectra and to check the correlation between the reaction kinetics and final polymer structure with the PD_{abs}. The hypotheses tested were that:

(i) PPD, by itself or combined with CQ, could promote comparable physical/mechanical properties as those achieved with the use of CQ alone, but with reduced “yellowing effect” and reduced rate of polymerization, and

(ii) R_p^{max}, DC and hardness are directly dependent on the PD_{abs}.

2. Materials and methods

2.1. Materials

The monomers 2,2-bis[4-2(2-hydroxy-3-methacroyloxypropoxy)phenyl] propane (Bis-GMA, Esstech, Essington, PA, USA) and triethyleneglycol dimethacrylate (TEGDMA, Esstech) were mixed in equal parts by weight. Two photoinitiators were used to make the resin photo-curable: CQ (Polysciences Inc., Warrington, PA, USA), 1-phenyl-1,2-propanedione, PPD (Aldrich Chem. Co., Milwaukee, WI, USA), and a combination of both in equal parts by weight. A tertiary amine, ethyl 4-dimethylaminobenzoate (EDMAB, Avocado, Heysham, Lanchire, UK), was added to produce a total photoinitiator to total amine ratio of 2:1 (by weight). Three concentrations were tested and named “Low”, “Intermediate” or “High” (Table 1). An inhibitor, 2,6-di-*tert*-butyl-4-methyl-phenol (BHT, Aldrich), was added at 0.05 wt.%.

Table 1 – Photoinitiator (Pt)/co-initiator (C) concentrations (in wt.%) used in the present study

	Concentration					
	Low		Intermediate		High	
	Pt (wt.%)	C (wt.%)	Pt (wt.%)	C (wt.%)	Pt (wt.%)	C (wt.%)
CQ	0.33	0.17	0.66	0.34	1	0.5
PPD	0.33	0.17	0.66	0.34	1	0.5
CQ/PPD	0.17/0.17	0.17	0.34/0.34	0.34	0.5/0.5	0.5

Concentration based on the total matrix resin weight. Note that the photoinitiator/amine ratio was kept constant (2:1) for all of the mixtures.

Inorganic silanated fillers of strontium glass and fumed silica in a 15:1 ratio by weight were added at 60 wt.%. All the components were mechanically mixed at 1300 rpm (DAC 150 Speed Mixer, Flacktek, Landrum, SC, USA) for 1 min to produce a homogeneous paste. All materials were prepared and handled under safe yellow light.

All photoactivation procedures were carried out with a quartz–tungsten–halogen (QTH) LCU (VIP, Bisco Inc., Schaumburg, IL, USA).

2.2. *Methods*

2.2.1. *LCU emission and photoinitiators absorption spectra readings*

The total LCU power output (mW), was measured with a power meter (Powermax 5200, Molectron, Portland, OR, USA). The irradiance (*E*), in mW/cm^2, was determined by dividing the power output by the area of the light guide. The power output measurement was repeated with the differential calorimeter cap used with the DSC to simulate the irradiance used inside the calorimeter chamber (Section 2.2.3). The VIP emission spectrum was determined in the 350–550 nm range using an integrating sphere (Labsphere Inc., North Sutton, NH, USA) connected to a spectrofluorometer (SPEX Fluorolog-3, Jobin Yvon Inc., Edison, NJ, USA).

Approximately 0.5 cm^3 of resin (before filler addition) was placed in a 1-mm thick, custom-made, glass-slide cuvette. Absorption spectra of the photoinitiators were measured using a UV–vis diode array spectrophotometer (Hewlett Packard 8452A, Palo Alto, CA, USA) over the range of 350–520 nm.

2.2.2. *Molar extinction coefficient and absorbed power density calculation*

The molar extinction coefficients (mm^{-1} mol^{-1} L) were calculated from the absorbance values using the Beer–Lambert law,

$$A(\lambda) = \varepsilon(\lambda)[c]l$$

where $A(\lambda)$ is the spectrophotometer absorbance at each wavelength, $\varepsilon(\lambda)$ is the molar extinction coefficient, [c] is the molar concentration of the photoinitiator and l is the optical path-length through the cuvette. Therefore, the molar extinction coefficient is

$$\varepsilon(\lambda) = \frac{A(\lambda)}{[c]l}.$$

The absorption coefficient $\mu_a(\lambda)$ has units of [1/cm] and is given by

$$\mu_a(\lambda) = -\ln(10)\varepsilon(\lambda)[c]$$

Absorbed power density (PD$_{abs}$):

The PD$_{abs}$ (in mW/cm^3) was calculated as

$$\mathrm{PD}_{abs} = \int E(\lambda)\mu_a(\lambda)d\lambda$$

where $E(\lambda)$ is the spectral irradiance of the LCU in (mW/cm^2)/nm emitted from the VIP LCU, $\mu_a(\lambda)$ is the photoinitiator absorption coefficient in cm^{-1}, and $d\lambda$ is a differential wavelength (nm). The $E(\lambda)$ values used for the PD$_{abs}$ calculation were those obtained when the light guide was positioned close to the power meter.

The $\varepsilon(\lambda)$ was calculated at each 2 nm wavelength interval to calculate PD$_{abs}$. Special attention was taken at the photoinitiators' absorption peaks, as demonstrated in Section 3.

2.2.3. *Differential scanning calorimetry*

Real-time polymerization was assessed by differential scanning calorimetry (DSC). Ten milligrams of composite (approximately 130 μm thick) were photoactivated in standard aluminum crucibles (Perkin-Elmer Inc., Wellesley, MA, USA) in the DSC chamber (DSC 7, Perkin-Elmer Inc., Wellesley, MA, USA) under nitrogen gas purge (20 psi) at 25 °C ($n = 3$). Each specimen was irradiated in the DSC three times. Each DSC thermogram comprised 40 s irradiance at 235 mW/cm^2. The peak in the first thermogram represented the exotherm generated by the polymerization of the material plus the heat generated by the LCU. The peaks in the next two thermograms represented only the heat generated by the LCU on the polymerized material (the second two thermograms were essentially equivalent and lower than the first). The area under each heat flow peak was integrated. The isothermal heat of reaction was obtained by subtracting the average of the peak areas in the last two thermograms from the area under of first peak [23,32]. Real-time DC was calculated by dividing the cumulative heat flow (registered at one data point per second) with the theoretical heat release per mole of reacted carbon double bonds (56 kJ/mol). The maximum rate of conversion (R_p^{max}) was found by taking the first derivative of the DC with respect to time.

2.2.4. *KHN and Fourier transformed infrared (FTIR) spectroscopy*

50 ± 0.5 mg of the experimental composite was applied and light activated in standard aluminum crucibles in the DSC

chamber under the same conditions as described above ($n = 3$). However, specimens were photoactivated with a single 40 s exposure.

As the samples exhibited a small concavity on their upper surface after the photoactivation procedure, KHN was measured on the bottom surface. Therefore, a razor blade was used to cut away the aluminum pans and expose the entire sample. To avoid any abrupt deformation of the sample – with consequent interferences in the KHN readings – the concavity was filled with slow-cure epoxy resin (Buehler epoxide, Buehler, Lake Bluff, IL, USA) and stored in dark containers at room temperature (25 ± 1 °C) for 24 h. Then, KHN measurements were taken with a 100 g load applied for 20 s (Kentron Hardness Tester, Torsion Balance Co., Clifton, NJ, USA). Five indentations per surface were averaged for each specimen. The same specimens were then used for the DC analysis. As the intention was to analyze hardness and DC under the same conditions, the FTIR measurements were also taken from the bottom surface. Therefore, small chips of resin composite removed with a scalpel from the surface of the sample were placed on a KCl crystal for transmission FTIR (DS20/XAD microscope, Analect Instruments, Irvine, CA, USA). Thirty scans were taken at 8 cm^{-1} resolution. Five measurements were made with chips removed from different regions of the sample and an average DC value was calculated. The paste of the uncured composite was similarly tested. DC was calculated from the ratio of the C=C peak from the methacrylate group to that of the unchanging C···C peak from the aromatic ring for the uncured and cured specimens using standard baseline techniques [33].

2.2.5. “Yellowing effect” level measurements

Specimens were prepared by placing the composite in a stainless steel mold (8.7 mm diameter and 1 mm thickness) sandwiched between Mylar strips. The composite was photoactivated for 40 s at 514 mW/cm^2, directly though the Mylar. The specimens were stored dry in a dark container for 24 h at room temperature (25 ± 1 °C). Then, the CIELab parameters were measured with a chromameter (Minolta, Corp., Ramsey, NJ, USA). The *b*-axis data was used to quantify the shift in yellow wavelengths, i.e., the higher the *b*-value, the higher the yellowing effect.

2.3. *Statistical analysis*

The results for each test were analyzed by two-way ANOVA followed by Student–Newman–Keul’s test (significance level of 5%). Pearson’s correlation tests ($p < 0.05$) were done to analyze the relationship between PD_{abs} and DC (from DSC and FTIR), $R_p^{\max}$ and hardness.

3. Results

3.1. *LCU emission and photoinitiators absorption spectra*

The VIP LCU irradiance (when set at 600) was approximately 510 mW/cm^2 when the light guide was positioned close to the power meter sensor. Because of the glass window and the distance between the light tip and the aluminum pan, the irradiance value decreased to roughly 230 mW/cm^2 in the DSC unit. The wide spectral range (364–520 nm) of the VIP is shown in Fig. 1a.

Fig. 1b shows the absorption coefficient as a function of the wavelength for the different photoinitiators. While CQ has a maximum absorption at 470 nm, the absorption peak for PPD occurred at 392 nm. The mixture CQ/PPD had an absorption peak at 452 nm.

3.2. *Molar extinction coefficient and PD_{abs}*

The molar extinction coefficient ($\varepsilon(\lambda)$) and PD_{abs} are presented in Table 2. Since the $\varepsilon(\lambda)$ is a constant, the value is independent of the concentration. As expected, a strong linear relationship was established between concentration and absorption for both photoinitiators (CQ, $r = 0.9992$; and PPD, $r = 0.9980$). The two photoinitiators (CQ and PPD) showed similar ε values (Table 2). On the other hand, the PD_{abs} increased with the concentration and PPD presented the lowest value, regardless of the concentration.

3.3. *Differential scanning calorimetry*

Table 3 shows the overall results for DC (DSC and FTIR), $R_p^{\max}$, KHN and yellowing.

Based on the DSC evaluation, the DC achieved with the intermediate and high concentrations of photoinitiator were greater than obtained with the low concentration for PPD and CQ/PPD. For CQ, the concentration did not affect the final DC. For a given concentration, there were no statistical differences among the tested photoinitiators. Conversely, the $R_p^{\max}$ increased significantly with the concentration, regardless of the photoinitiator. As for $R_p^{\max}$, the photoinitiators consistently ranked as follows: CQ > CQ/PPD > PPD.

Fig. 2 shows R_p curves obtained in real-time by the DSC method. The reaction peak-time (time at $R_p^{\max}$) occurred at approximately 6 s, with the exception of CQ at intermediate and high (5 s) concentrations. Instead of a defined peak, the $R_p^{\max}$ for PPD was observed between 6 and 10 s. The DC value at $R_p^{\max}$ was ≈15%, with the exception of PPD at low concentration (DC ≈ 7% at $R_p^{\max}$).

3.4. *KHN and DC*

The hardness values increased with the photoinitiator concentration, except for CQ which did not show significant differences between the intermediate and high concentrations (Table 3). Composites containing PPD had lower KHN than those containing CQ, regardless of the concentration tested. Composites containing CQ and the CQ/PPD mixture produced comparable KHN values only at the high concentration.

Intermediate and high concentrations produced higher DC, as determined by FTIR, than the low concentration in the CQ and PPD formulations. For the combination CQ/PPD, the increase in DC was ranked as: high > intermediate > low. For a given concentration, there were no statistical differences among the photoinitiator types, similar to what was shown with the DSC.

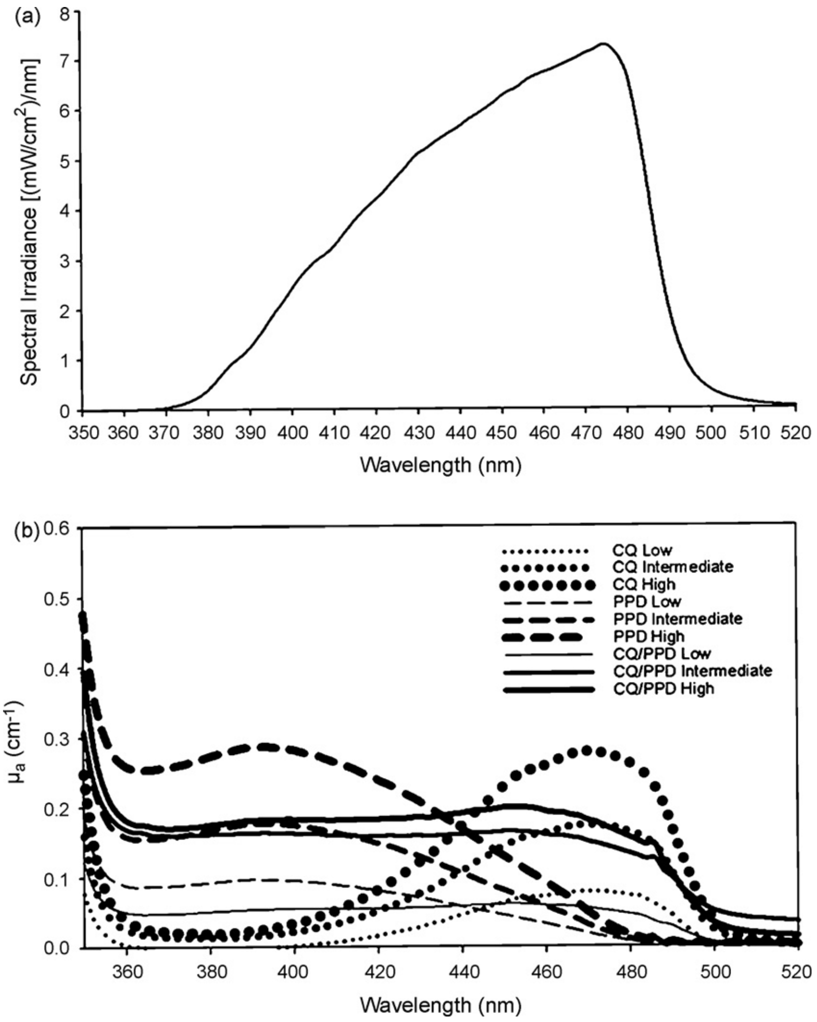

Fig. 1 – Spectral irradiance of the light curing unit (measured irradiance = 514 mW/cm^2) (a) and light absorption spectra of the different photoinitiator systems (b).

Table 2 – Molar extinction coefficients of the photoinitiators and absorbed power density from the VIP light curing unit

Photoinitiator	Concentration	$\varepsilon(\lambda)$ (mm^{-1} mol^{-1} L)[a]	PD$_{abs}$ (mW/cm^3)
CQ	Low	40.4	266
	Intermediate		517
	High		810
PPD	Low	37.3	197
	Intermediate		374
	High		601
CQ/PPD	Low	Not tested	253
	Intermediate		497
	High		800

[a] Molar extinction coefficient at the photoinitiators' respective absorption peaks: ε(468 nm) for CQ and ε(392 nm) for PPD.

3.5. *"Yellowing effect" level*

The yellowing effect always increased as the photoinitiator concentration increased, regardless of the photoinitiator type (Table 3). At low concentration, the samples containing PPD showed the lowest mean values for the *b* parameter. However, at intermediate and high concentrations, the samples containing PPD presented the highest yellowing effect. Samples containing CQ and CQ/PPD did not statistically differ at low and intermediate concentrations. At high concentrations, CQ/PPD produced greater yellowing than CQ.

3.6. *Correlations*

The Pearson's correlation tests demonstrated positive and significant relationships between PD$_{abs}$ and DC from the DSC

Table 3 – Results obtained for the variables tested: degree of conversion (DC) and maximum rate of polymerization (R_p^{max}) by the DSC method, Knoop hardness (KHN), DC by the FTIR method and *b*-value (“yellowing effect”)

Variable	Photoinitiator	Concentration		
		Low	Intermediate	High
DC (%)—by the DSC	CQ	62.19 (1.29) Aa	62.81 (0.74) Aa	65.13 (0.69) Aa
	PPD	56.76 (3.36) Ba	66.24 (4.73) Aa	67.77 (5.27) Aa
	CQ/PPD	60.52 (1.49) Ba	69.15 (6.01) Aa	68.97 (0.80) Aa
R_p^{max} (%/s)—by the DSC	CQ	3.1 (0.0) Ca	4.6 (0.1) Ba	5.2 (0.1) Aa
	PPD	1.7 (0.1) Cc	3.0 (0.1) Bc	3.8 (0.2) Ac
	CQ/PPD	2.1 (0.1) Cb	3.5 (0.1) Bb	4.6 (0.2) Ab
KHN (kgf/mm^2)	CQ	27.67 (0.75) Ba	36.66 (1.36) Aa	37.89 (0.79) Aa
	PPD	24.50 (2.08) Cb	30.30 (0.83) Bc	34.73 (1.37) Ab
	CQ/PPD	25.58 (0.11) Cb	32.59 (0.38) Bb	38.65 (1.01) Aa
DC (%)—by the FTIR	CQ	65.53 (2.50) Ba	73.50 (2.12) Aa	76.23 (1.72) Aa
	PPD	67.14 (2.34) Ba	72.28 (3.06) Aa	72.18 (1.90) Aa
	CQ/PPD	62.4 (0.92) Ca	71.11 (0.39) Ba	75.16 (1.91) Aa
Yellowing (*b*-value)	CQ	+1.5 (0.2) Ca	+4.3 (0.1) Bb	+7.1 (0.6) Ac
	PPD	+0.7 (0.2) Cb	+4.9 (0.2) Ba	+10.0 (0.7) Aa
	CQ/PPD	+1.7 (0.1) Ca	+4.0 (0.2) Bb	+8.1 (0.2) Ab

Values followed by the same lower case letter in the same column or by the same upper case letter in the same row are statistically equivalent ($p < 0.05$) according the Student-Newman-Keul’s test. *P*-values according the two-way ANOVA: DC (DSC): photoinitiator type (Pt), 0.170; concentration (C), <0.001 and interaction between Pt and C (Pt × C), 0.162. R_p^{max}: Pt, <0.001; C, <0.001 and Pt × C, 0.026. KHN: Pt, <0.001; C, <0.001 and Pt × C, <0.001. FTIR: Pt, 0.097; C, <0.001 and Pt × C, 0.050. Yellowing: Pt, <0.001; C, <0.001 and Pt × C, <0.001.

($r = 0.716$, $p = 0.030$), PD_{abs} and R_p^{max} ($r = 0.943$, $p = 0.000$), PD_{abs} and KHN ($r = 0.953$, $p = 0.000$) and PD_{abs} and DC from the FTIR ($r = 0.873$, $p = 0.002$).

4. Discussion

The purpose of the present study was to determine how different photoinitiator systems used at different concentrations, but at a constant photoinitiator/amine ratio, would affect DC, R_p^{max}, KHN and yellowing of experimental resin composites, and to describe the influence of the true light absorption (the power density absorbed) in the reaction kinetics (R_p) and final structure of the polymer (indirectly represented by DC and hardness).

As expected, DC, R_p^{max} and hardness tended to increase as the photoinitiator concentration was increased due to the greater amount of molecules available for reaction. This was probably due to the higher PD_{abs}, as demonstrated by the significant correlations between PD_{abs} and each of the variables, which is in agreement with previously reported data [9,25]. However, it has been shown that this relationship between concentration and efficiency may hold up to a certain threshold, above which excess CQ may decrease conversion. This effect has been related to either radiation attenuation through the film by CQ absorption through a phenomenon known as the inner shielding effect [3,14], or to high rates of primary radical termination, which in turn were caused by the high rates of initiation [8]. Indeed, it has been shown that the DC of an experimental resin composite increased as CQ concentration increased from 0.3 to 0.6 wt.% of the total resin matrix, and that above this limit, DC actually decreased [12].

The mechanism of free radical formation in polymers varies according to the photoinitiator system used. For instance, CQ and PPD present dissimilar behavior: while CQ operates by proton abstraction, PPD undergoes photo-cleavage and proton abstraction [21]. Moreover, the light absorption peaks for these photoinitiators occur at different wavelengths, and therefore, their combination produces a broader absorption profile. According to Park et al. [16], these two factors could help explain the synergistic effect observed when these molecules are combined in the same resin system. In the present study, both photoinitiators showed similar molar extinction coefficient values at their respective absorption peaks (ε(468 nm) for CQ and ε(392 nm) for PPD), but CQ presented higher levels of PD_{abs} than PPD when using the VIP as the LCU (Table 2). The LCU used in all experiments was a QTH type, with broad emission spectra, including the wavelength at which PPD is excited. Even so, CQ presented higher PD_{abs} compared to PPD and this can be explained by the lower spectral irradiance at 392 nm, where PPD has its absorption peak. The output from the quartz–tungsten–halogen light is a better match with CQ than with PPD.

Overall, for a given photoinitiator concentration, both DSC and FTIR showed that the photosensitive molecule used did not affect DC, in spite of the differences in the PD_{abs}. Thus, one can suggest that sufficient light energy was applied such that at these concentrations, each photoinitiator was operating at near maximum efficiency for this particular resin system. However, as far as R_p^{max} was concerned, statistically different values were obtained by each photoinitiator system and consistently ranked as CQ > CQ/PPD > PPD. This behavior is partially due to the fact that the VIP LCU had a less favorable spectral irradiance for PPD than CQ. This was true although CQ and CQ/PPD exhibited similar PD_{abs}. This can be explained, as previously mentioned, by the photochemistry of each photoinitiator. Although it seems that the major mechanism of free radical formation by the photolysis of PPD is the cleav-

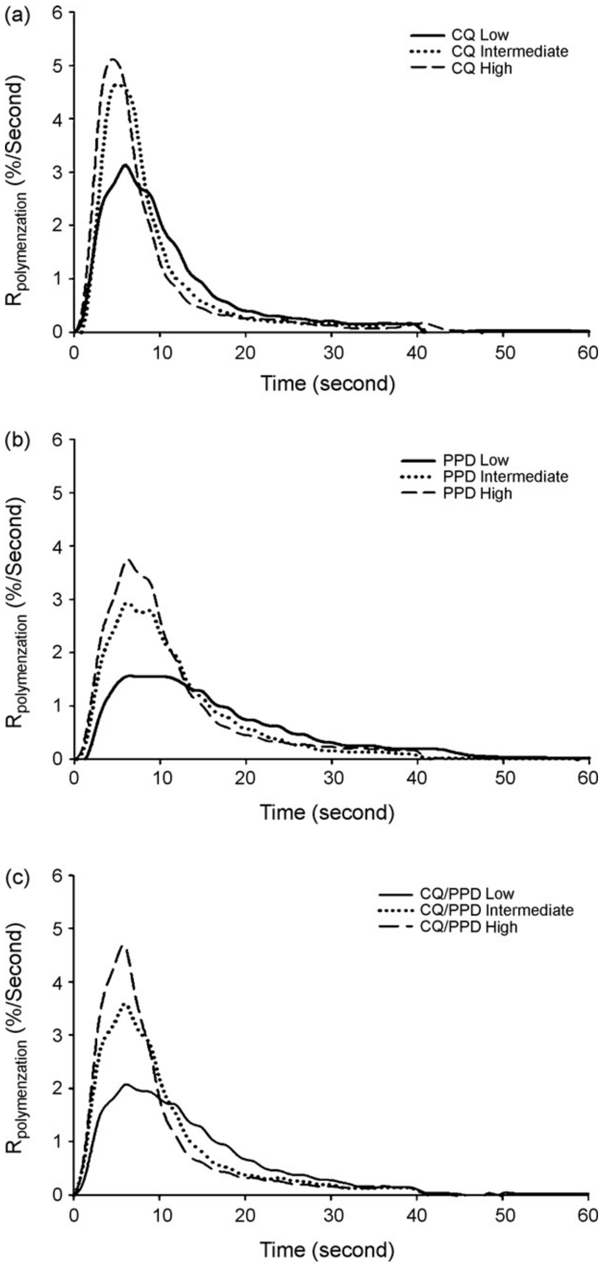

Fig. 2 – Rate of polymerization curves obtained by the photo-DSC. (a) Rate of polymerization as a function of time—CQ, (b) rate of polymerization as a function of time—PPD and (c) rate of polymerization as a function of time—CQ/PPD.

age of the C–C bond between the two carbonyls [16,21], the possibility that PPD reacts with a co-initiator has also to be considered [19]. However, based on the lower R_p^{max} observed in this study for the groups where CQ was not present, it can be speculated that the interaction between CQ and EDMAB was more efficient than that resulting from PPD [21]. A recently published study [34] demonstrated that the polymerization initiated by PPD progressed at a slower rate and exhibited lower DC than that initiated by CQ, even when the photon absorption efficiency for PPD was 40% higher than that for CQ, thus corroborating the results of the present study. More research needs to be carried out in order to determine the influence of the amine/photosensitive molecule ratio and to understand the actual interactions between the co-initiators.

The conversion curves obtained by DSC (Fig. 2) also revealed that R_p^{max} occurred earlier in time with an increase of CQ concentration, which was not observed for PPD and the combination CQ/PPD. One possible explanation for this fact is that PPD systems could be less reactive as a result of a less effective interaction with the co-initiator. On the other hand, the point in conversion where R_p^{max} happened was around 15% for all systems, with the exception of PPD at low concentration. This behavior is known as the "Trommsdorff effect", "Trommsdorff–Norrish effect" or, simply, "gel effect" [8,25]. At approximately 15% of conversion for this resin system, the polymer experiences a sudden increase in viscosity, which impairs mobility and leads to a rapid decrease in the termination rate constant. Therefore, as the reaction becomes diffusion controlled, it relies on chain propagation to go forward [35]. For the PPD formulation at low concentration, the R_p^{max} occurred over a range of conversions, causing the R_p^{max} curve to plateau (Fig. 2b). This behavior might offer some insight for explaining the lack of differences in DC among the photoinitiator types. While R_p^{max} for CQ peaked and dropped off dramatically, that of PPD, although being low, remained constant for about 4 s before dropping.

Although the DC assessed both by DSC and FTIR did not show differences among the photoinitiator types, composites formulated with PPD showed a trend toward the lowest KHN. Moreover, KHN values were statistically different among all levels of photoinitiator concentrations for the systems that presented the lowest R_p (PPD and CQ/PPD), unlike the CQ only groups, in which KHN values remained unchanged above the intermediate concentration. It has been suggested previously that the microhardness would be sensitive to even small changes in conversion that otherwise do not show any statistical difference [30]. This may be due to the fact that the hardness measurements consider the overall sample structure (as involves plastic deformation), while the FTIR readings were performed with 150 μm chips from the surface. It can also be speculated that, even though the final DC was the same, the polymer structure might have been affected by the rate of polymerization. In fact, it was observed that groups containing PPD only showed the lowest reaction rate at every concentration and also produced the lowest KHN values.

Whether rate of polymerization is correlated to network crosslinking is a matter of controversy in the literature [27–29]. It has been argued that if the point in conversion where R_p^{max} is achieved is low (as observed for the PPD groups), this is an indication that the reaction is prematurely decelerating [36,37]. However, this was expected to have been accompanied by lower conversion, which was not the case in the present study. This may point to the hypothesis that post-cure conversion for PPD groups is greater, as well as the aforementioned behavior of R_p^{max} remaining constant during a certain period of time.

Although a less crosslinked structure may be a liability, the fact that the reaction rate was lower for PPD or CQ/PPD groups may be an advantage from the standpoint of polymerization stress development [22,23]. There is evidence that reducing the R_p will cause polymerization stress to decrease [38], while maintaining adequate mechanical properties and low susceptibility to degradation in organic solvents [39]. However, as mentioned previously, this is a matter of controversy [27–29]. While there are no studies evaluating polymerization stress development with the use of alternative photoinitiators, preliminary tests by the authors of this study have shown promising results.

Color measurements revealed that for all systems, the increase in photoinitiator concentration was responsible for the higher *b*-values. Since all specimens were photoactivated at the same radiant exposure, this may indicate that unreacted species were present in the material. Other than produce the undesired yellowing effect, excess photoinitiator and products of their photolysis may leach out from the material into the saliva, with possible cytotoxic effects [12,40].

PPD produced lower *b*-value compared to the CQ or CQ/PPD systems, but only in the low concentration group. Although this may be an advantage in terms of color, this group exhibited the lowest mechanical properties. Also, as concentration increased, CQ presented lower *b*-values than PPD and CQ/PPD, indicating that its photobleaching ability is greater compared to that of the PPD molecule. Though it was not the aim of the present study to establish a relationship between PD_{abs} and photobleaching ability, it could be stated that the CQ photobleaches more than PPD due to the higher PD_{abs}. However, the present data do not agree with this hypothesis, since CQ alone and the combination CQ/PPD showed similar PD_{abs} with different photobleaching behavior. Thus, it is possible that the interaction between the photosensitive molecule and the co-initiator is the key. Consequently, it can be hypothesized that CQ presented a better interaction with EDMAB in addition to presenting a higher PD_{abs}, as observed in this study.

5. Conclusion

The first hypothesis was partially accepted. PPD and CQ/PPD were able to promote similar DC compared to that resulting from CQ only, and with lower maximum rate of polymerization. The use of PPD on its own resulted in lower KHN values and the yellowing reduction was only observed when PPD was used at low concentration, providing evidence that alternative photoinitiators might be used, but with care.

The second hypothesis was accepted. The correlation tests showed that the higher the PD_{abs} the higher was the DC, R_p^{max} and KHN. However, it seems that other variables, such as the reaction kinetics *per se* and the photoinitiator interaction with the co-initiator (as part of the photochemistry process), also play an important role.

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