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Alternative photoinitiator system reduces the rate of stress development without compromising the final properties of the dental composite

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ABSTRACT

Objectives. Stress development during the polymerization process continues to be a major factor that limits predictability and longevity of resin composite restorations. This study evaluated the effect of the photoinitiator type on the maximum rate of polymerization (R_p^{max}), stress development (final stress and maximum rate, R_{stress}^{max}), degree of conversion (DC) and cross-link density (CLD) of materials containing camphorquinone (CQ), phenylpropanedione (PPD) or CQ/PPD.

Materials and methods. R_p^{max} was evaluated via differential scanning calorimetry (DSC). Contraction force measurement was assessed with a single cantilever device for 5 min. The samples were subsequently tested by infrared spectroscopy (FTIR) to evaluate the DC. After, samples were soaked in ethanol to evaluate the swelling coefficient (α) as a way to estimate the CLD. The results were analyzed by one-way ANOVA and Tukey's test ($p = 0.05$).

Results. CQ showed the highest R_p^{max} and R_{stress}^{max}. PPD produced the lowest DC and the highest α. The mixture CQ/PPD produced statistically lower R_p^{max} and R_{stress}^{max} than CQ alone, but similar DC and CLD.

Conclusion. CQ/PPD reduced the R_p^{max} and R_{stress}^{max} without a reduction in DC and CLD. Therefore, the use of alternative photoinitiator systems could be a promising way to reduce the stress developed during the composite's polymerization without affecting the final properties.

1. Introduction

The stress development resulting from the polymerization process is the major drawback of dental composite restorations. Thus, special attention has been taken in order to develop techniques and materials that are able to reduce it [1].

The stress arises from multiple factors [2]. Basically, a volumetric shrinkage occurs simultaneously with elastic modulus development, as the length and the cross-link density (CLD) of the polymer chains increase [3,4]. In this way, the polymerization reaction, the material's formulation and the boundary conditions (bonding conditions, cavity configuration, and

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substrate compliance) all play essential roles in stress development and/or transmission to tooth structures [5–11].

In order to diminish the stress development in photoactivated composites, specific light exposure methods have been proposed as a way to reduce the rate of polymerization [12,13]. In theory, stress release by viscous flow before the vitrification stage would be allowed to occur without compromising the final polymer properties [14,15]. Therefore, initial light exposure at lower irradiance values might lead to the formation of a reduced number of polymer growth centers, reducing the reaction rate and decreasing stress development due to the increased opportunity for resin flow before the vitrification stage. However, there are contradictions about the proposed advantages: (i) the material's ability to flow (deformation) is questionable because the majority of the shrinkage stress is developed during and after the vitrification stage and, therefore, opportunity for polymer relaxation would be restricted for clinical time scales for light activation [11]; (ii) the final degree of carbon double-bond conversion (DC) tends to be lower when DC readings are performed during the stress evaluation, meaning that the lower stress would be resultant from lower DC [16], and (iii) the lower rate of polymerization decreases the cross-link density, resulting in greater softening in solvents [17,18] and/or lower final elastic modulus [19]. However, cross-linked dimethacrylate polymers have been characterized under controlled conditions and the polymer structure was not affected by the rate of polymerization [20].

Besides managing light exposure, changes in the resin composite formulation have also been tested to reduce contraction stress [1]. However, very little has been done regarding the photoinitiator system. Similar to the photoactivation protocols, the concentrations of camphorquinone (CQ, the most common photoinitiator) and inhibitors may be varied to reduce the rate of polymerization without affecting other properties [21]. Braga and Ferracane [22] tested experimental materials with different concentrations of inhibitor (2,6-Di-*tert*-butyl-4-methyl-phenol = BHT), and showed that increased inhibitor concentrations reduced the rate of polymerization and the shrinkage stress without significantly compromising the final DC. However, it must be noted that that in this study, the DC tended to be lower for mixtures containing higher amounts of BHT than those with lower content of the inhibitor and the specimens used for the spectroscopy measurements were cured under different conditions than those cured in the stress measuring device.

Recently, it was demonstrated that the addition of the photoinitiator phenylpropanedione (PPD), initially suggested to increase the polymerization efficiency and to reduce the yellowing effect provided by CQ [23,24], produced lower shrinkage and polymerization rates than CQ [25,26]. However, there is no evidence that the stress development is also reduced. Therefore, the objectives of the present investigation were: (1) to investigate the reaction kinetics of composites containing CQ, PPD and the mixture CQ/PPD, (2) to measure the polymerization stress development by these materials, and (3) to evaluate the resulting DC and the CLD. The CLD was assessed by measuring the swelling coefficient, α, in ethanol [18]. The hypothesis tested was that PPD alone or the mixture CQ/PPD produces lower maximum rate of polymerization (R_p^{max}) and maximum rate of stress (R_{stress}^{max}) development than CQ alone, without reduction in the final DC and CLD. Briefly, the R_p^{max} and the R_{stress}^{max} reveal the maximum speed of the polymerization reaction and the maximum stress development, respectively. Both parameters are directly related and are important to compare the different systems. It might be expected that the faster the material shrinks and acquires its elastic modulus, the faster it starts to generate stress within itself and the surrounding areas.

Table 1 – Photoinitiator systems tested in the present investigation (concentration in mol%). The co-initiator EDMAB was used at fixed concentration (1.2 mol%) for all groups tested.

Group	Photoinitiator type (concentration in mol%)
1 (control)	CQ (0.6)
2	CQ/PPD (0.3/0.3)
3	PPD (0.6)

2. Materials and methods

2.1. Composite preparation

Monomer mixtures of 2,2 bis[4-2(2-hydroxy-3-methacroyloxypropoxy)phenyl] propane (Bis-GMA, Esstech, Essington, PA, USA) and triethyleneglycol dimethacrylate (TEGDMA, Esstech) were prepared in the ratio of 50/50 by weight percentage (wt%). Two photoinitiators were used to make the resin photo-curable: CQ (Polysciences Inc., Warrington, PA, USA) and 1-phenyl-1,2-propanedione, PPD (Aldrich Chem. Co., Milwaukee, WI, USA). Ethyl 4-dimethylaminobenzoate (EDMAB, Avocado, Heysham, Lancashire, UK) was used as co-initiator and 2,6-Di-*tert*-butyl-4-methyl-phenol (BHT, Aldrich) was used as inhibitor at a constant amount (0.05 wt%). The percentage (in mol) of photoinitiator and co-initiator tested are shown in Table 1. The photoinitiator/co-initiator relationship at 1:2 was chosen after a pilot study. This relationship demonstrated the best properties (DC, hardness and solubility) when compared with 2:1, 1:1, 1:1.5, regardless of the photoinitiator type (CQ, PPD and the mixture CQ/PPD).

Resins were loaded with strontium glass fillers (4.0 μm average size; 3% silane level) (provided by Bisco Inc., Schaumburg, IL, USA) at a total content of 80 wt%. All the components were homogeneously mixed for 1 min at 1300 rpm (DAC 150 Speed Mixer, Flacktek, Landrum, SC, USA). All materials were prepared and handled under a yellow safe light, and used within 1 week after mixing.

2.2. Reaction kinetics characterization

A differential scanning calorimeter (DSC 7, PerkinElmer Inc., Wellesley, USA) was used to follow the polymerization reaction kinetics at a temperature of 25 ± 0.01 °C ($n = 3$). Ten milligrams (±0.1 mg) of resin composite was spread as a thin layer (≈130 μm) and polymerized in standard aluminum pans with three light exposures from a quartz-tungsten-halogen (QTH) light curing unit (LCU) (VIP, Bisco Inc., Schaumburg, IL, USA), the first designed to cure the specimen and the next two to determine the heat generated by the light application itself.

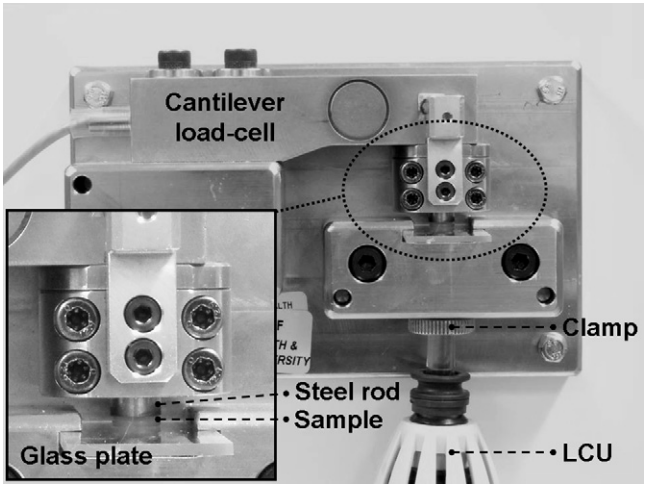

Fig. 1 – The Bioman stress measurement device.

The reaction kinetics were evaluated by recording the three thermograms under nitrogen atmosphere (20 psi) and constant water flow. The first peak represented the exothermic change generated by the composite polymerization plus the heat released from the LCU. The two following peaks represented only the heat released from the LCU. The heat of polymerization was determined by subtracting the average heat value of the two last peaks from the first peak value. Each exposure consisted of 40 s of light at 315 mW/cm^2. This value was measured through the DSC cap, which was positioned between the LCU and a power meter sensor (PM3/Powermax 5200, Molectron, Portland, OR, USA).

The DC at different times was determined from changes in heat release during the experiment. By registering the heat values and changes over time, conversion changes were calculated from the theoretical heat release per mole reacted from the carbon double-bond (56 kJ/mol) over the time course of the experiment. Therefore, the derivative DC/time was calculated as the rate of polymerization, the highest value in the spreadsheet was the R_p^{max} and the moment when it occurred was the peak-time of R_p^{max}. The parameters DC, R_p^{max}, DC at R_p^{max} and the peak-time of R_p^{max} were used to compare the formulations.

2.3. Stress development evaluation

The Bioman stress measurement device has been described previously in detail [9]. The system is based on a cantilever load-cell (500 kg) fitted with a rigid integral clamp (Fig. 1). The compliant end of the cantilever held a circular steel rod (10 mm diameter × 22 mm long) vertically and perpendicular to the load-cell axis. The counter-face consisted of a removable rigid glass plate that was held rigidly relative to the base-plate in a special clamp during measurement. The lower end of the steel rod was sand-blasted, and in contrast to the original methodology described by Watts et al. [9], the surface of the glass-plate opposing the steel-rod was only silanated (3M/ESPE Dental Products, St Paul, MN 55144, USA)) (instead of sandblasting + silanation). The composite was then introduced between the plate and vertical rod to form an uncured specimen-disk of 10 mm diameter and 0.8 mm thickness (which represents a bonded to non-bonded surface area, i.e. C-factor, of 6.25). The composite specimen was irradiated through its thickness dimension from below by the LCU (VIP) for 40 s at 800 mW/cm^2, as measured with the power meter.

The load-signal from the cantilever cell was amplified and the signal was acquired by a standard computer. The registered load (in Newton, N) was then divided by the disk area in order to obtain the stress values (MPa). Subsequently, as in previous studies [9,27], the raw stress data were treated by a "correction factor" of 4 in order to relate the present data to a low compliance system, such as a human tooth cusp. Measurements were performed during 5 min after the photoactivation procedure. Each group contained six samples ($n = 6$). Maximum stress, maximum rate of stress development (R_{stress}^{max}) and time when R_{stress}^{max} occurred (peak-time) were determined. Time zero was considered when the LCU was turned on.

After each evaluation, the Bioman clamps were removed and the set resin sample/glass-plate/metal piston was removed and carefully observed to verify if signs of any debonding were present. It is important to mention that detachments were rare and that these samples were excluded from the study.

2.4. Degree of carbon double-bond conversion measurements

Immediately after the stress development evaluation, the cured specimen was carefully removed from the *Bioman* and infrared spectroscopy (FTIR) was used to determine its DC. Five minutes were required to remove the sample from the *Bioman*, so the DC was evaluated around 10 min after the start of the photoactivation procedure.

Small chips of composite were removed with a scalpel from the surface of the sample and were placed on a KCl crystal for transmission spectroscopy (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 surface and an average DC value was calculated. This procedure was done for the two surfaces, the one that was in contact with the glass plate and the one in contact with the steel rod. The average of these two surfaces was considered for each sample to provide a more accurate representation of the cure through the specimen.

The paste of the uncured composite was similarly tested, where 40 μm (measured with a paper spacer) of the material was pressed directly onto the KCl crystal. DC was calculated with the following formula:

$$DC\,(\%) = 100 \times \left(1 - \frac{C = C_{cured}/Aromatic_{cured}}{C = C_{uncured}/Aromatic_{uncured}}\right)$$

2.5. Swelling coefficient determination

This methodology was modified from the original version described by Neumann et al. [18]. After DC analysis, the samples were immersed in absolute ethanol at room temperature until an equilibrium weight was reached. Then samples were

Table 2 – Mean values of degree of conversion (DC), maximum rate of polymerization (R_p^{max}), DC at R_p^{max} and peak-time at R_p^{max}.

Photoinitiator	DC (%)	R_p^{max} (%/s)	DC at R_p^{max} (%)	Peak-time of R_p^{max} (s)
CQ	62.11 (0.46)[a]	3.3 (0.1)[a]	12.24 (1.26)[a]	6
CQ/PPD	64.01 (2.34)[a]	3.0 (0.0)[b]	12.79 (1.24)[a]	7
PPD	59.58 (1.04)[b]	2.4 (0.1)[c]	14.37 (0.12)[a]	7

Numbers in parenthesis are standard deviations. Mean values followed by different letters in a column are significantly different ($p < 0.05$).

removed and the excess solution was quickly dried with blotting paper, before the samples were re-weighed. The swelling coefficient (α) values were calculated by the following formula:

$$\alpha = \left(\frac{M_{eq} - M_0}{M_0}\right)\left(\frac{1}{d_s}\right)$$

where M_{eq} is the mass of the saturated sample (polymer + solvent) after equilibrium, M_0 is the mass of the polymer before immersion and d_s is the density of the solvent (absolute ethanol = 0.789 g/mL).

2.6. Statistical analyses

The results were analyzed by one-way analysis of variance (ANOVA) and Tukey's tests ($\alpha = 0.05$).

Pearson's correlation tests and regression analyses were done to establish the relationships between: (a) maximum rate of polymerization (R_p^{max}) and maximum rate of stress (R_{stress}^{max}), (b) peak-time of R_p^{max} and peak-time of R_{stress}^{max}, (c) R_p^{max} and maximum stress, (d) DC (from samples removed from the Bioman) and maximum stress, (e) R_{stress}^{max} and maximum stress, (f) DC and α, and (g) R_p^{max} and α. The mean values of each group were used for comparison.

3. Results

3.1. Reaction kinetics characterization

Mean values of DC, R_p^{max}, DC at R_p^{max} and the peak-time reaction are shown in Table 2. The composite formulated with only PPD showed lower DC than the others. There was a significant difference among the R_p^{max} data produced by all groups, where CQ > CQ/PPD > PPD. There was no difference in DC at R_p^{max} among the groups; but the reaction peak-time for CQ occurred before those from CQ/PPD and PPD.

Table 4 – Mean values of DC obtained from the FTIR and swelling coefficients. Evaluation performed at the samples removed from the stress measurement device.

Photoinitiator	Degree of conversion (%)	Swelling coefficient (mL/g)
CQ	53 (1)[a]	0.004 (0.001)[a]
CQ/PPD	53 (1)[a]	0.005 (0.002)[ab]
PPD	47 (2)[b]	0.008 (0.002)[b]

Numbers in parenthesis are standard deviations. Mean values followed by different letters in a column are significantly different ($p < 0.05$).

3.2. Polymerization contraction stress development

The maximum stress, R_{stress}^{max} and peak-time at R_{stress}^{max} mean values are given in Table 3. Differences among the maximum stress values obtained from the different resin composites were not significant. However, the resin composite formulated with CQ produced the highest R_{stress}^{max} as well as the lowest reaction peak-time.

3.3. Degree of carbon double-bond conversion and swelling coefficients from the samples removed from the stress measurement device

Table 4 shows the mean values of DC obtained from the FTIR analysis and swelling coefficient after ethanol soaking. The composite formulated with PPD alone produced the lowest DC, while those formulated with CQ alone and the combination CQ/PPD produced statistically similar DC ($p < 0.05$).

The swelling test showed that the composite formulated with CQ produced lower swelling than that with PPD, while that with CQ/PPD produced intermediate values.

3.4. Correlations

The correlation tests showed high positive correlations between (a) R_p^{max} and R_{stress}^{max} ($r = 0.966$) and (b) peak-time of

Table 3 – Stress development measured in the Bioman. Mean values of maximum stress, maximum rate of stress (R_{stress}^{max}) and peak-time at R_{stress}^{max}.

Photoinitiator	Maximum stress (MPa)	R_{stress}^{max} (MPa/s)	Peak-time at R_{stress}^{max} (s)
CQ	4.69 (1.14)[a]	5.75 (1.18)[a]	2.21 (0.65)[b]
CQ/PPD	5.96 (1.14)[a]	4.09 (0.36)[b]	3.98 (0.45)[a]
PPD	6.10 (1.76)[a]	2.79 (0.80)[b]	5.03 (0.96)[a]

Numbers in parenthesis are standard deviations. Mean values followed by different letters in a column are significantly different ($p < 0.05$).

R_p^{max} and peak-time of R_{stress}^{max} ($r = 0.929$). A weak inverse correlation was found for (c) the DC and maximum stress ($r = -0.573$), while (d) the R_p^{max} and the maximum stress ($r = -0.934$) as well as (e) R_{stress}^{max} and maximum stress ($r = -0.811$) demonstrated a strong inverse relationship. DC and swelling coefficient ($r = -0.970$) (f), as well as (g) R_p^{max} and swelling coefficient ($r = -0.9704$), demonstrated a strong inverse relationship.

4. Discussion

The hypothesis tested, that alternative photoinitiator systems produce lower R_p^{max} and R_{stress}^{max} than CQ alone, without reduction in the final DC and CLD, was not rejected. PPD alone and the mixture CQ/PPD reduced the R_p^{max} and R_{stress}^{max}, but only the mixture CQ/PPD resulted in similar DC and CLD than CQ alone.

4.1. *Reaction kinetics*

The DSC results demonstrated that PPD alone produced the lowest R_p^{max} but also compromised the final DC (Table 2), while the mixture CQ/PPD reduced the R_p^{max} by 10% without compromising the final DC. These findings are probably related not only to the light absorption characteristics by the photoinitiator but also its characteristic photochemistry.

The correlation between the used photoinitiators and the VIP LCU has been described previously in detail [28]. Basically, the correlation between PPD and the VIP LCU spectra (named as the absorbed power density, PD_{abs}, in J/cm^3) is lower than that of CQ alone. Therefore, the presumption of Emami and Söderholm [26], that the reduced overlap between the PPD absorption spectra and the LCU emission spectra partially explains the lower reactivity of PPD formulations, is probably correct. However, the results obtained with the mixture CQ/PPD shows that some other factors might also play essential roles.

In the present investigation, the mixture CQ/PPD was tested at the same total concentration as each photoinitiator alone and produced lower R_p^{max} than CQ alone, thereby showing decreased reactivity. Since the aforementioned study [28] also demonstrated that the mixture CQ/PPD exhibited similar absorption from the VIP LCU as CQ alone, the lower reactivity might be attributed to other factors. Indeed, it was recently demonstrated that PPD produced a lower rate of polymerization than CQ even in a situation where the spectra of the LCU was better correlated with the PPD [29]. The authors attributed this effect to a lower quantum yield of PPD, despite another study [24] that showed a higher quantum yield for PPD when compared with CQ. Another hypothesis could be that the interaction of PPD with EDMAB might be less efficient than for CQ, which might reduce overall free-radical formation.

The process of initiation seems to be well established for CQ/amine systems. Basically, the absorption of light by CQ raises the molecule to an excited state, known as the "triplet-state", with a very short half-life. If the excited CQ interacts with an amine molecule, it results in an excited state complex, called an "exciplex". In this state, the CQ molecule can abstract a hydrogen atom from the tertiary amine, resulting in the formation of a free radical [30,31]. On the other hand, compared to CQ, there are few studies dealing with the PPD mechanism of free radical formation. Initially, it was supposed that the major route of free radical production by the PPD would be by direct cleavage of the C–C carbonyl bond species [32]. However, recent studies have shown that the polymerization efficiency of PPD is increased when higher levels of amines are used [29,33,34]. Consequently, these outcomes support the thesis that free radical formation from PPD proceeds mainly by a hydrogen abstraction mechanism, but the contribution by direct cleavage cannot be disregarded [33]. Therefore, questions remain concerning the mechanisms of free radical formation by PPD. As the efficiency of polymerization depends on the structure of each specific amine and the reactivity of the corresponding amine-derived radicals toward the initiation of monomer polymerization, additional studies are necessary to understand the influence of the amine structure on the process of generating free radicals by the PPD photoinitiator.

The photoinitiator type did not influence the DC at the R_p^{max}. Basically, the R_p^{max} occurred around 13% of conversion for all the tested groups. This phenomenon, known as the "gel effect", is characteristic of composites that become viscous very fast, making the rest of the polymerization reaction proceed by chain diffusion [11]. On the other hand, the peak-time of reaction was delayed when the composites were formulated with PPD or CQ/PPD ($\approx$1 s later than CQ). This behavior is characteristic of a slower reaction as a consequence of fewer free-radical centers and/or lower reactivity of the species [35].

4.2. *Stress development*

The results showed that the speed of stress development could be significantly reduced if the alternative photoinitiator systems were used. Basically, the use of PPD alone and/or CQ/PPD reduced the R_{stress}^{max} by about 51% and 29%, respectively, compared to CQ alone, whereas the peak-time of R_{stress}^{max} was delayed by about 56% and 44%, respectively. These outcomes are strongly correlated with the reaction kinetics, where a positive relationship was observed between the R_p^{max} and R_{stress}^{max}, as well as between the peak times at R_p^{max} and at R_{stress}^{max} ($r = 0.966$ and $r = 0.929$, respectively). This correlation exists because the rate of stress development is directly related to the polymerization reaction kinetics. Consequently, factors affecting free radical generation by the different photoinitiators will also affect reaction kinetics, and thus help to explain the slower stress development.

The correction factor was applied to the stress values to make the data fit a more conservative estimation of cuspal displacement and to compare the results of the current investigation with those obtained in a previously published study with the *Bioman* device [9]. The maximum stress values ranged between 3.55 and 7.86 MPa, which closely approximate the results obtained by Watts et al. [9], which ranged between 4.82 and 7.30 MPa (for Clearfil AP-X and Point-4, respectively) when using 0.8 mm thick specimens.

Though the maximum stress values registered during the 5 min testing period were not statistically different, the values tended to be higher for systems with lower DC, R_p^{max} and/or R_{stress}^{max}. These inverse correlations (DC and maximum stress, $r = -0.573$; R_p^{max} and maximum stress, $r = -0.934$; R_{stress}^{max} and maximum stress, $r = -0.811$) contradict previous find-

ings that stress development is dependent on these factors when tested in low compliance systems [16,22]. Maybe the greater deformation promoted by systems with higher DC and R_p^{max} resulted in more of the stress being absorbed by the system and therefore not measured as stress in the composite. Although all the aforementioned discussion is valid, it is important to highlight two facts: (1) there were no statistical differences among the groups and (2) the inverse correlations may be apparent because the mean values of each group (not considering standard deviations) were used in the calculations, and not the individual paired data as this is not possible since the measurements are made on different specimens.

Questions might remain about how a reduced R_{stress}^{max} with equivalent maximum stress would result in improved predictability and longevity of composites restorations. Though studies are needed to prove any theoretical benefit, it can be suggested that probably the lower R_{stress}^{max} would result in lower sudden change on the adhesive layer and tooth structure, decreasing the possibility of bonding failures.

4.3. *Degree of carbon double-bond conversion and swelling coefficients*

The FTIR readings and the swelling coefficient determinations of the samples removed from the *Bioman* were performed because it has been postulated that the methods used to reduce the stress development might affect the final DC [16] and/or the cross-linking density [17,19]. While the PPD alone produced a polymer with lower DC and higher swelling coefficient than CQ alone, the combination CQ/PPD did not compromise the final DC and/or the swelling coefficient, but it did decrease the R_p^{max} and R_{stress}^{max}. Therefore, the present outcomes are in agreement with the statement that polymer cross-link density is more dependent on the final DC than on the rate of polymerization [20], as CQ and CQ–PPD showed similar DC but different R_p^{max}.

Indeed, the CQ/PPD combination diminishes the rate of stress development, as well as delaying its peak-time, and without compromising the final DC and swelling coefficient when compared with CQ alone. Thus the mixture of both photoinitiators could be an interesting way to reduce the speed of reaction, and consequent stress, without compromising the final polymer structure.

5. Conclusions

The hypothesis was not rejected. Under the conditions used in the present investigation, composites formulated with the mixture CQ/PPD produced lower R_p^{max} and R_{stress}^{max} than that with CQ alone without compromising the final DC and CLD.

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