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Development of dual-cured resin cements with long working time, high conversion in absence of light and reduced polymerization stress

André L. Faria-e-Silva^a, Carmem S. Pfeifer^b

^aAssociate Professor at Department of Dentistry, Federal University of Sergipe, Rua Claudio Batista s/n, 49060-100, Aracaju, SE, Brazil.

^bAssociate Professor at Department of Restorative Dentistry, Division of Biomaterials and Biomechanics, Oregon Health & Science University, 2730 SW Moody Ave, 97201, Portland, OR, USA.

Abstract

Objectives: This study evaluated the properties of experimental dual-cured cements containing thiourethane (TU) and low concentrations of p-Tolyldiethanolamine (DHEPT) and benzoyl peroxide (BPO) as chemical initiators.

Methods: BisGMA/TEGDMA-based dual-cured cement was formulated with 1.0 wt% DHEPT and 0.75 wt% BPO as initiators and used as control. The concentration of BPO was adjusted to 0.1 wt% in catalyst paste of experimental cements, and two base pastes containing TU and 0.5 wt% or 0.25 wt% of DHEPT were formulated. The rheological behavior and kinetics of polymerization of cements were assessed in the absence of light activation. The kinetics of polymerization was also evaluated for cements light-activated immediately or 5 minutes after the start of mixing. Polymerization stress, flexural strength and elastic modulus ($n = 5$) were also evaluated under these conditions.

Results: Cements with TU presented lower viscosity than the control, improved working time (0.25% DHEPT > 0.5% DHEPT) and higher conversion in the absence of light-activation.

Delaying the light-activation reduced the maximum rate of polymerization ($R_{p_{max}}$) but did not affect the conversion or stress. The addition of TU increased the $R_{p_{max}}$ and conversion, and reduced the stress when compared to the control, without affecting the flexural strength. Except for the control with delayed light-activation (highest values), the other experimental conditions yielded similar modulus.

Significance: Adding TU and using a low concentration of DHEPT/BPO resulted in dual-cured cements with longer working time, reduced polymerization stress and increased conversion even in the absence of light, with no significant effect on the mechanical properties.

Author to whom correspondence should be addressed. André L. Faria-e-Silva. Programa de Pós-Graduação em Odontologia, Rua Cláudio Batista, s/n, Sanatório, Aracaju, SE, Brazil. CEP 49060-100. Phone/ Fax: +55 79 3194-7220. fariaesilva.andre@gmail.com.

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Keywords

Dual-cure; Pre-polymerized additives; Polymerization stress; Resin cement

1. Introduction

Dual-cured resin cements are widely used to lute indirect restorations because they combine the advantages of light-activation, which allows for the on-command stabilization of the restoration, and of chemical-activation, which is necessary to ensure adequate polymerizations in regions not accessible to the light [1–3]. However, an increased concentration of redox initiators is necessary to ensure high conversion of the cement in those regions, which in turn reduces working time and increases the potential for discoloration, ultimately compromising the luting procedures [4]. Thus, some resin cements manufacturers have added primer/ adhesive solutions to be applied onto the substrate prior to the cement insertion to improve its chemical-activated polymerization [2,5,6]. The rationale is that co-initiators such as sodium sulfinic acid salts from these primer/ adhesives would increase the concentration of free-radicals to accelerate the redox-based polymerization of cements containing a low concentration of initiators (i.e., amines and benzoyl peroxide) [7]. However, despite allowing the use of cements with increased working time even when the light-activation is compromised, the faster cement polymerization obtained using this approach can impair the luting procedure in some clinical situations. One example is radicular post cementation [8].

Another important concern which remains over the adhesive cementation procedures is the polymerization stress. In addition to the volume of material and compliance of substrates, the cavity configuration factor (C-factor) also affects the stress developed during the polymerization of resin-based materials [9]. Therefore, resin cements are used in a critical scenario in terms of C-factor, since only the margins of the cement layer can deform and accommodate part of the polymerization stress. Prior studies have demonstrated that delaying the light-activation in dual-cure systems might reduce the polymerization stress by allowing part of the conversion to take place under less stringent diffusional limitations [10–15]. However, delaying the light-activation of the cement increases the chair time, and faster and simpler procedures are preferred by clinicians. Another approach for reducing the polymerization stress is to add chain transfers agents (i.e. thiourethane) into methacrylate polymerizations [15–17]. In fact, a prior study demonstrated the effectiveness of thiourethane in reducing the polymerization stress, but the dual-cured experimental resin cement containing this oligomer had short working time since the thiol moieties can also work as reducing agents and react with benzoyl peroxide [15]. Hence, the use of more efficient co-initiators for the chemically-activated reaction than the amine used in that prior study (ethyl 4-dimethylaminobenzoate) can allow for the addition of lower concentration of benzoyl peroxide to the catalyst paste and improve the cement working time.

Therefore, the aim of this study was to evaluate the rheological behavior, polymerization kinetics, polymerization stress, and mechanical properties of experimental dual-cured cements containing thiourethane and low concentrations of p-Tolyldiethanolamine (DHEPT)

and benzoyl peroxide as the redox initiator system. The hypothesis of the study was that adding thiourethane to experimental dual-cured cements with low concentrations of DHEPT and benzoyl peroxide would improve the working time and conversion, and reduce the polymerization stress of cement, without compromising its mechanical properties.

2. Material and Methods

2.1 Cement formulation

The control dual-cured resin cement was formulated using the monomers BisGMA (Bis-phenol A diglycidyl dimethacrylate) and TEGDMA (tri-ethylene glycol dimethacrylate) at a 2:1 mass ratio, all from Esstech (Essington, PA, USA). Fillers of 0.7- μ m silane-treated Barium glass (Esstech) were added at 60 wt%. Bis-acylphosphine oxide (BAPO) at 2.0 wt% was added as a photo-initiator to the base paste, and the amine DHEPT was also added to this paste at 1.0 wt%. The catalyst paste contained 0.75 wt% of benzoyl peroxide (BPO). The inhibitor (BHT [2,6-di-tert-butyl-4-methylphenol]) was added to both pastes at 0.1 wt%. DHEPT was obtained from TCI America (Portland, OR, USA) and the other initiators from SigmaAldrich (St. Louis, MO, USA). Those concentrations of amine and BPO were determined to obtain a working time around 5 minutes according to the results of a pilot study.

Prior to the formulation of experimental cements containing thiourethane, thiol-functionalized oligomers were synthesized by combining trimethylol-tris-3-mercaptopropionate (TMP) with 4,4'-Diisocyanato-methylenedicyclohexane (HMDI), according to previously reported methods [17]. Since the thiourethane can only be added to base paste [15], the oligomer was added at the concentration of 40 wt%, resulting in a 20 wt % thiourethane concentration after mixing base and catalyst pastes. The monomeric formulation of the catalyst paste was the same used for the control, but the proportion between BisGMA and TEGDMA was adjusted to 1:1 in the base paste to compensate for the increased viscosity caused by the addition of the oligomer thiourethane. For cements containing thiourethane, the concentrations of BAPO and BHT were the same used for the control. However, using the same concentrations of amines and BPO as in the control resulted in experimental cements with short working time, as demonstrated previously [15]. Therefore, a pilot study defined two base pastes containing thiourethane, which were formulated by adding DHEPT at 0.5 wt% or 0.25 wt% to be used with a catalyst paste with a reduced amount of BPO (0.1 wt%). These initiators concentrations were determined to obtain a dual-cured cement with working time similar to that observed for the control, and another with a longer working time. Therefore, the rationale for the different monomer and initiator concentrations for the experimental materials and the control was based in clinically-relevant aspects, rather than compositional uniformity.

2.2 Rheologic properties of the cements

Equal amounts of base and catalyst pastes of each cement were mixed and sandwiched between two 20 mm parallel acrylic disc plates, attached to a rheometer (DHR-1, TA Instruments, New Castle, DE, USA). The specimens were tested in oscillatory shear at a frequency of 1.0 Hz with 1.0% strain, using a gap of 300 μ m without any irradiation for 15

min ($n = 5$). The time elapsed between the beginning of the cement mixing and the start of data collection was standardized at 60 s, and this time was added to the results. The curve of the complex viscosity development as a function of the time was plotted and the working time calculated based on the tangent line touching the curve (Figure 1). The time for cements to reach the gel point was estimated based on the crossover between G' (storage modulus) and G'' (loss modulus), when the $\tan\delta$ was 1.0 (Figure 2).

2.3 DC and polymerization kinetics

Equal amounts of each paste were mixed and inserted in cylindrical silicone rubber molds ($n=3$; diameter=6 mm; thickness=0.8 mm), sandwiched between two glass slides ($n = 5$). Polymerization kinetics was monitored in an infra-red spectrometer (Nicolet 6700, Thermo Scientific, Pittsburgh, PA, USA) equipped with an InGaAs detector. Spectra were collected in real-time for 20 min, at 4 cm^{-1} resolution, 2 Hz acquisition rate. The monitoring of polymerization kinetics started 3 min after the beginning of cement mixing and was followed for 30 min in the absence of any light-activation. Polymerization kinetics of cements used at dual-cured mode was also monitored for 10 min after light activation. The light activation was performed with a LED-based unit (Elipar Deepcure-S, 3M ESPE, St. Paul, MN, USA) delivering approximately 1,450 mW/cm^2 to the surface of the specimen for 20 s, and the light-activation started immediately or after 5 min (delayed) from the beginning of kinetics measurement. Light intensity was checked daily using portable spectrometer-based instrument (CheckMARC, BlueLight Analytics, Halifax, NS, Canada). Degree of conversion (DC) was calculated based on the area of the methacrylate vinyl overtone at 6165 cm^{-1} [18]. The polymerization rate was calculated as the first derivative of the conversion vs. time curve. Polymerized specimens were stored dry for 72h and the degree of conversion was measured again.

2.4 Polymerization stress

Standardized mass of each paste of cements were mixed and placed over a silane-treated glass plate held to the Bioman device [19]. The tip of the of light-curing unit (Elipar Deepcure-S) was positioned under the glass plate into a cylindrical bolt. The cement was covered with a metallic rod (5.6 mm of diameter) treated with metal primer (Z-Prime Plus, Bisco Inc, Bisco, Schaumburg, IL, USA) placed 0.75 mm from the glass yielding a C-factor = 3.73. The time between the beginning of the cement mixing and to start the data collection was standardized in 3 min (the same of kinetics polymerization analysis) and the light-activation was performed for 20 s according to the protocols defined above. Polymerization stress development (in MPa) was followed in real-time for 20 min ($n = 5$).

2.5 3-point bending test

The dimensions of bars required by the International Organization for Standardization (ISO) specification 4049, which establishes the standards for performing the 3-point bending test for polymer-based dental materials were modified in this study to allow for a single exposure per sample. Mixed cements were inserted in rubber molds with $14 \times 2 \times 1$ mm, which still complies with the proportions that allow for the application of beam theory [20]. Specimens were then light-activated following the same conditions described previously. The delay time between to start the cement mixing and light-activation was also standardized accordingly.

The specimens were stored dry for 24h in dark containers, and then positioned in a 3-point bending device coupled to a mechanical testing system over two rods with diameter of 2 mm spanning 10 mm between them. A compressive load was applied to the center of specimen with a 2-mm of diameter tip and a crosshead speed of 1.0 mm/min until failure. The following equation was used to calculate flexural strength (σ_f) in MPa:

$$\sigma_f = \frac{3Fl}{2bh^2}$$

where F is the maximum load (N) exerted on the specimen, l is the distance (mm) between the supports, and b is the width (mm) and h the height (mm) at the center of the specimen.

The Elastic modulus (E) was calculated using the following equation:

$$E = \frac{F_1 l^3}{4bdh^3}$$

where F1 is the load (N) exerted on the specimen and d is the deflection corresponding to the load F1.

2.6 Statistical analysis

Data from all outcomes measured for the resin cements only chemically-activated were individually subjected to one-way ANOVA. Except for data of DC in the time when the light-activation was started (one-way ANOVA was used), data from cement used as dual-cured were analyzed by two-way ANOVA considering the factors “cement” and “light-activation protocol”. Student-Newman-Keuls Method was used for all multiple comparisons. Normal distribution and equal variance assumptions were assessed by Shapiro-Wilk and Levenès test, respectively. Data analysis was performed using the SigmaStat v.3.5 statistical software package (Systat Software Inc., Chicago, IL, USA) and a significance level of 95% was set for all analyses.

3. Results

Results for all outcomes measured for the resin cements chemically-activated only are shown in Table 1. Higher initial viscosity was recorded for the control and similar values of viscosity were measured for both cements containing thiourethane. The cements containing thiourethane had longer working time than the control, and the cement with 0.25% DHEPT had the longest working time. The time required for the chemically-activated only cements to reach G'/G'' crossover was similar. Regarding the kinetics of polymerization, the highest values of maximum rate of polymerization (Rpmax) were achieved by the control, and the cements containing thiourethane did not present difference between them. Similarly, both cements with thiourethane reached the Rpmax at similar and higher DC than that observed for the control (Figure 3). The cement with thiourethane and 0.25% DHEPT reached Rpmax earlier in conversion, and the other cements required similar times for the onset of deceleration. For both times of DC measurement (30 min and 72h), the control presented the

lowest values of conversion, without difference between the cements containing thiourethane.

Results for kinetics of polymerization of cements used in dual-cured mode are shown in Table 2. Regardless of the cement, delaying the start of light-activation reduced the R_{pmax} (Figure 4). For immediate light-activation, the control achieved lower R_{pmax} , without difference between the cements containing thiourethane. The cement containing thiourethane and 0.25% DHEPT had the highest values of R_{pmax} when the light-activation was delayed, and the control the lowest values. For delayed light-activation, the cement with thiourethane and 0.25% DHEPT achieved the lowest DC when the light-activation started, and similar values of DC were observed for the other cements. As expected, delaying the start of the light-activation increased the DC at R_{pmax} for all cements. For DC at R_{pmax} , cements containing thiourethane presented higher values than control for immediate light-activation. Conversely, highest values of DC at R_{pmax} were observed for the cement containing thiourethane and 0.5% DHEPT when the light-activation was delayed, without differences between the other cements. After 10 min or 72h, the cement control had the lowest values of DC and there was no difference between the materials containing thiourethane (Figure 5). Immediate activation resulted in higher DC for all cements after 10 min, but the difference between the light-activation protocols on DC was not significant after 72h.

For all cements, the light-activation protocol did not affect the polymerization stress (Table 3). Cements containing thiourethane showed similar and lower values of stress than the control. Both light-activation protocol and cement composition did not affect the flexural strength. The light-activation protocol only affected the elastic modulus for the control, which was more rigid (modulus increased by 23.6%) when the light-activation was delayed. For this light-activation protocol, the control achieved higher elastic modulus than those containing thiourethane. There was no difference between the elastic moduli of cements evaluated for immediate light-activation.

4. Discussion

An important challenge on the development of dual-cured resin cements is achieving a balance between convenient working time and high conversion in regions where light penetration is deficient, such as what is observed during the cementation of thick onlay restorations, or fiber posts into the root canal [1,21]. The chemical-activation of dual-cured cements progresses via a redox mechanism, usually reliant on a tertiary amine and benzoyl peroxide in the base and catalyst pastes, respectively. After mixing the pastes, the formation of amine radical cation and benzoylate anion yields a benzaloxo radical that starts the polymerization of the methacrylate-based cement [22]. Therefore, up to a certain threshold, improved conversion is expected by increasing the amount of these initiators, but this brings the caveat of shortened working time [4]. In the present study, both cements containing TU in the base paste showed higher DC in the absence of light-activation and longer working time than the control, despite the reduced amount of DHEPT and BPO added. Furthermore, the experimental cements containing TU presented reduced polymerization stress and

similar mechanical properties than those observed for the control, leading us to accept the hypotheses of the study.

The concentrations of DHPET and BPO in the control cement were defined through a pilot study which focused on standardizing the materials in terms of working time. It is acknowledged that this study design precluded standardization of BisGMA:TEGDMA ratios and initiator concentrations. However, it is important to highlight that the aim of this study was to potentially develop a material that would be clinically translatable, and to do that, it is necessary to improve its working time. This study shows, within its limitations, that by judiciously manipulating the composition, producing a commercially-viable thiourethane-containing material might be an achievable outcome. In fact, the cement containing 1.0 wt% DHEPT and 0.75 wt% BPO had working time close to 5 min, which is longer than that observed for most of the commercially available dual-cured cements [4,23]. The control cement reached DC of 62% after 30 min (67.8% after 72h), similar to the conversion observed for most commercial dual-cured cements [4,10]. These results were only possible by adjusting the concentrations of initiators of the experimental cements containing TU, since they led to fast polymerization when combined with higher concentrations of amine/BPO. It has been previously demonstrated that the thiol moieties are able to reduce the BPO, accelerating the polymerization reaction [15]. The mechanism for this acceleration relies on the fact that the generation of benzoyloxy radicals by redox reactions between thiol and BPO drastically increases in the presence of an amine reducing agent (such as DHPET) [24]. Therefore, TU was added only to the base paste, at 40 wt%, to obtain experimental cements with 20 wt% overall TU concentration after the mixing procedures. To improve the working time, the concentrations of initiators were gradually reduced in the pilot tests to obtain a working time similar to that observed for the control using 0.1 wt% BPO and 0.5 wt% DHEPT. Moreover, one additional base paste containing TU was also formulated to further improve the working time, by reducing the concentration of DHEPT in half (0.25 wt%). This last formulation yielded working time longer than 9 min without affecting the DC. An important observation is that all measurements were performed under ambient temperature ($\approx 25^{\circ}\text{C}$), but it is expected that the cements will be used by clinicians at increased temperatures, which will reduce the working time [4,23].

It is reasonable to correlate the working time with the rates of polymerization due to the concentrations of DHEPT and BPO. Indeed, the cement control containing the highest concentration of these initiators had shorter working time and higher R_{pmax} than the cements containing thiourethane. However, decreasing DHEPT content by half in cements with thiourethane increased the working time as expected, but did not modify the R_{pmax} . Interestingly, even though the working time was increased and R_{pmax} decreased, the experimental cement containing 20 wt% TU reached DC ($\approx 72\%$ after 30 min; $\approx 79\%$ after 72h) higher than the control in the absence of light-activation. Reduction in composite viscosity by increasing the content of monomers with low molecular weight (i.e. TEGDMA) tends to increase the R_{pmax} and the ultimate conversion [25]. However, the highest DC observed for cements with thiourethane cannot be attributed solely to their reduced viscosity since the values of R_{pmax} observed for these materials were approximately half of those from the control. Conversely, adding TU to the cements also increased the DC of dual-cured cements (for both light-activation protocols), but the R_{pmax} tended to increase slightly.

In the present study, we chose to use the single component photo-initiator BAPO to avoid any influence of the amine concentration over the light-activated polymerization reaction. Unlike the CQ/tertiary amine system, the mechanism of photo-initiation of BAPO is based on α -cleavage and does not depend on co-initiators to accelerate the reaction. The absorption maximum for BAPO lies in the visible spectrum between 365 and 416 nm ($\lambda_{\text{max}} = 371$ nm), which fits well with most poly-wave light-curing units currently available in the market [7,26]. The BAPO concentration of 2.0 wt% was chosen since it has been demonstrated that it results in high conversion even in the absence of any co-initiator [27]. Increased DC of materials containing TU was demonstrated in prior studies, and these findings have been related to the presence of pendant thiols leading to chain-transfer reactions to the vinyl. This delays deceleration to higher conversions, and ultimately increases final conversion [16,17,28,29]. The conversion at which the polymerization reaction reaches the R_{pmax} gives insight into the onset of deceleration, when both propagation and termination are restricted by the growing stiffness of the reaction medium [29]. If the reaction is allowed to progress further prior to the onset of more stringent diffusional restrictions, final conversion increases and polymerization stress decreases [31].

In the present study, indeed, cements containing TU (higher ultimate conversion) reached higher DC at R_{pmax} than the control as expected and previously demonstrated [15], but that was only observed when the cements were immediately light-activated. For delayed light-activation, the cement with TU and 0.25% DHEPT showed DC at R_{pmax} similar to the control. This was somewhat expected based on the fact that the photo-derived portion of the polymerization started when the polymers was already beyond 15–30% conversion. At that point, diffusional limitations are already high, though not at full vitrification [30]. It is important to note that the conversion at the time the light was turned on was also not statistically similar for all groups. The group containing TU and 0.25 wt% DHEPT had the lowest conversion at that point, most likely due to the lower amine concentration. Moreover, even though the R_{pmax} is achieved at similar values of conversion, the maximum rate is significantly lower for the control, followed by the materials containing TU plus 0.5 or 0.25 wt% DHEPT, respectively. Therefore, a complex interplay between the amine concentration and thiourethane-derived chain-transfer reactions ultimately determined the onset of deceleration. In any event, the presence of the thiourethane material was able to extend final conversion in relation to the control.

Several studies have demonstrated that delaying the start of the light-activation allows for at least partial volume accommodation prior to the onset of network stiffening, which leads to reduced stress overall [10–15]. A delay time of five mins was chosen in accordance with some prior studies evaluating delayed light-activation [10–14]. To this time, additional three minutes were added corresponding to the lag time between the start of cement mixing and crown seating in the clinical setting. This also conveniently allowed for the cements to be placed in the molds for IR tests. Regardless of the cement evaluated, however, delaying the light-activation was unable to affect the polymerization stress in the present study. Reductions on R_{pmax} ranged from 31 to 42%, and this reduction was directly proportional to the conversion (from 15 to 33%) of the cement at the time when the light-activation started. However, it has been demonstrated that more than 70% of overall stress occurs during the last 15% of resin-based material conversion, and that stress reductions are only

observed when at least one order magnitude lower rates are used [32]. In fact, similar rates of polymerization were recorded between the light-activation protocols at the final phase (vitrification stage) of conversion for all cements. Moreover, it is important to emphasize that any effect of delayed light-activation on stress only would be relevant in areas where the light penetration is sufficient to efficiently activate the polymerization reaction.

The absence of correlation between R_{pmax} and polymerization stress also holds for direct comparisons among cements. For either light-activation protocols, cements containing TU presented higher values of R_{pmax} than those observed for the control, but reduced polymerization stress values. Polymerization stress directly correlates with modulus development and volumetric shrinkage, which is closely related to DC [33,34]. Since the TU increases conversion, any potential reduction in shrinkage afforded by the addition of the high molecular weight oligomer is likely overshadowed. Therefore, the reduced stress obtained with the addition of TU is explained through difference on modulus development among the cements. The graphic of rate of polymerization as a function of DC show that the curves for materials containing TU start to decelerate at higher values of conversion than those achieved for the control. Deceleration of the rate of polymerization indicates that the material is reaching the vitrification stage, when radicals become trapped within the network [30,35]. The chain-transfer reactions with the addition of TU are chain-breaking and, as already mentioned, delay vitrification to higher conversions, giving opportunity for the reaction to progress further under lower constraint, which ultimately reduces stress [15–17,28,36,37]. The data for modulus development, which directly correlates to the level of constraint to polymerization, demonstrates not only a slower increase in stiffness for the materials containing TU, but also a much different modulus development profile. In this study, the conversion was not measured concomitantly with the modulus development, so the only indication for delayed network formation is the time at which each material reached tan delta values of 1 (crossover between G'/G''). While this is by no means a true measure of gel point, it can be clearly seen that the materials containing TU take an extra 200 s to reach that point.

The clinical procedures and performance of restorations luted with resin cements are strongly affected by viscosity and mechanical properties of the luting materials. In the present study, we used a different BisGMA/TEGDMA mass ratio for the cement containing TU (1:1) than that used for the control (2:1). The reduction on amount of BisGMA was justified because the addition of the oligomer TU significantly increases the viscosity of the cement, which could potentially impair the restoration seating or fiber post insertion. Indeed, combining reduced amount of BisGMA and addition of TU reduced the viscosity of cement. Unlike what is observed when the viscosity control is achieved by reduction on filler content, modifying the monomer composition here did not affect the flexural strength. Cement mechanical properties such as flexural strength and modulus affect the performance of restorations, with more rigid cements being able to strengthen the restoration [38]. All cements evaluated presented similar values of flexural strength (ranging from 114 to 125 MPa). In the present study, delaying the light-activation of the cement control resulted in highest values of elastic modulus, and no other difference was observed among the other experimental conditions. An interesting observation was that the highest elastic modulus (20% higher than the lowest modulus measured) was obtained by the only experimental

condition when the light-activation was performed after cement polymerization had reached G'/G'' crossover. It is important to note that the values of elastic modulus for all experimental conditions on par to those required to strengthen ceramic restorations [37]. It is also important to emphasize that the DC measured after 72 h for cements with TU ($\approx 90.0\%$) is higher than that usually measured for commercial dual-cured cements [4,11,21].

5. Conclusions

Within the limitations of this study, we conclude that the experimental dual-cured cements containing 20 wt% of thiourethane and low concentrations of DHEPT and BPO evaluated here had long working time, improved conversion, and reduced polymerization stress, without compromising the mechanical properties. Delaying the light-activation of dual-cured cements did not affect the conversion, flexural strength or polymerization stress development, and had limited effect on elastic modulus.

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Highlights

- The addition of thiourethane to dual-cured cements reduces their working time
- Low concentrations of redox initiators were required in cements with thiourethane
- High conversion was observed even in absence of light-curing for these cements
- Cements with thiourethane presented reduced polymerization stress
- The moment of light-activation did not affect cement properties and stress

Figure 1.

Viscosity development following the chemically activated polymerization of the experimental cements evaluated in the present study ($n=5$). The point where the tangent lines (blue) converge with the curves of viscosity indicate the moment when the viscosity started to increase more significantly, and was used to calculate the working time of the cements. Vertical dashed lines indicate the time when the light-activation of the cements was performed – orange and black lines for immediate and delayed light-activations respectively. The black area indicates the time between the start of cement mixing and the start of rheological analysis. TU – thiourethane. DHEPT - p-Tolyldiethanolamine.

Figure 2.

Development of $\tan\delta$ following the chemically activated polymerization of the experimental cements evaluated in the present study ($n=5$). The time when the curves cross the horizontal line ($\tan\delta = 1$) indicates that the material is achieving its gel point (elastic loss = storage modulus). TU – thiourehane. DHEPT - p-Tolyldiethanolamine.

Figure 3. Rate of polymerization as function of the degree of conversion for the cements chemically activated only (n=5). TU – thiourehane. DHEPT - p-Tolyldiethanolamine.

Figure 4.

Rate of polymerization as function of the degree of conversion for the cements according to the light-activation protocol ($n=5$). TU – thiourehane. DHEPT - p-Tolyldiethanolamine. LA: light-activation.

Figure 5.

Degree of conversion as function of the time for the cements according to the light-activation protocol ($n=5$). The black area indicates the time between the start of cement mixing and the start of rheological analysis. TU – thiourethane. DHEPT - p-Tolyldiethanolamine. LA: light-activation.

Table 1.

Average (standard deviation) for initial viscosity (Pa.s), working time (s), time to crossover between loss and storage moduli (G'/G'' , s) and kinetic parameters (maximum rate of polymerization, Rp_{max} in %/s and degree of conversion in % at several points) for the cements chemically-activated only (n = 5).

Cement	Initial viscosity (Pa.s)	Working time (s)	Time to G'/G'' (s)	Rp_{max} %/s	At DC (%)	At time (sec)*	DC (%) After 30 min	DC (%) After 72 h
Control	7.2 (0.4) ^A	284.9 (17.6) ^c	405.1 (27.6) ^c	0.31 (0.09) ^B	21.8 (1.8) ^B	440.2 (15.3) ^B	62.1 (1.5) ^B	67.8 (1.1) ^B
TU - 0.5% DHEPT	4.5 (1.0) ^B	372.7 (13.1) ^B	582.8 (28.0) ^B	0.16 (0.01) ^A	28.4 (2.5) ^A	461.3 (15.2) ^B	72.2 (0.4) ^A	79.2 (1.6) ^A
TU - 0.25% DHEPT	3.9 (0.4) ^B	571.1 (17.6) ^A	822.0 (16.8) ^A	0.14 (0.00) ^A	29.4 (1.6) ^A	619.0 (34.7) ^A	71.2 (0.7) ^A	79.8 (0.7) ^A
p-value**	< 0.001	< 0.001	< 0.001	0.001	< 0.001	< 0.001	< 0.001	< 0.001

* The time (180s) spent between the beginning of cement mixing and starting the polymerization kinetics measurement was added.

** Calculated by One-way ANOVA. Distinct letters indicate statistical difference ($p < 0.05$) at Student-Newman-Keuls Method.

Rp_{max} : Maximum rate of polymerization.

DC: Degree of conversion.

TU: Thiourethane.

DHEPT: p-Tolyldiethanolamine.

Table 2.

Average (standard deviation) for kinetic parameters (maximum rate of polymerization, R_{pmax} in %/s and degree of conversion in % at several points) for cements light-cured immediately or after 5 minutes (delayed) from the beginning of kinetics measurement (n = 5).

Cements	R _{pmax} (%/s)		DC (%)		At start of light-activation*		At R _{pmax}		After 10 min		After 72h	
	Immediate	Delayed	Immediate	Delayed	Immediate	Delayed	Immediate	Delayed	Immediate	Delayed	Immediate	Delayed
Control	15.4 (0.3) Ba	4.1 (0.9) Ca	27.3 (6.1) A	43.5 (2.6) Ba	26.8 (0.5) Bb	70.6 (0.7) Bb	71.7 (0.5) Ba	78.3 (1.2) Ba	78.1 (0.4) Ba			
TU - 0.5% DHEPT	17.3 (0.5) Aa	5.5 (0.4) Ba	33.2 (2.0) A	53.6 (2.0) Aa	31.2 (2.1) Ab	82.8 (0.4) Ab	83.4 (0.5) Aa	89.4 (0.8) Aa	89.4 (0.8) Aa			
TU - 0.25% DHEPT	17.2 (0.3) Aa	8.4 (0.5) Aa	14.9 (4.2) B	45.0 (2.5) Ba	31.1 (1.4) Ab	83.0 (0.7) Ab	83.5 (0.5) Aa	90.2 (0.6) Aa	89.6 (0.5) Aa			
P-value	*** Light-activation protocol: < 0.001; Cement: < 0.001; Interaction: < 0.001 ** Light-activation protocol: < 0.001; Cement: < 0.001; Interaction: 0.451 ** Light-activation protocol: 0.432; Cement: < 0.001; Interaction: 0.727											

* Measured only for the delayed light-activation.

** Calculated by two-way ANOVA.

*** Calculated by One-way ANOVA. Distinct letters (uppercase for column, lowercase for line) indicate statistical difference (p < 0.05) at Student-Newman-Keuls Method.

DC – Degree of conversion.

R_{pmax} – Maximum rate of polymerization.

TU – thiourethane.

DHEPT - p-Tolyldiethanolamine.

Table 3.

Average (standard deviation) for polymerization stress (MPa), and mechanical properties in flexure for the cements tested as a function of the light-activation protocol.

Cements	Polymerization stress (MPa) (n=5)		Flexural strength (MPa) (n=10)		Elastic modulus (GPa) (n=10)	
	Immediate	Delayed	Immediate	Delayed	Immediate	Delayed
Control	12.4 (1.5) ^{Aa}	11.4 (0.7) ^{Aa}	114.3 (28.3) ^{Aa}	115.5 (15.4) ^{Aa}	5.5 (0.9) ^{Ab}	6.8 (0.8) ^{Aa}
TU - 0.5% DHEPT	11.9 (1.8) ^{Ba}	10.1 (1.0) ^{Ba}	124.1 (14.1) ^{Aa}	125.3 (18.5) ^{Aa}	6.1 (0.4) ^{Aa}	5.8 (0.9) ^{Ba}
TU - 0.25% DHEPT	9.3 (1.3) ^{Ba}	9.9 (1.2) ^{Ba}	122.0 (12.1) ^{Aa}	114.5 (17.4) ^{Aa}	6.0 (0.9) ^{Aa}	5.6 (0.8) ^{Ba}
p-values *	Light-activation protocol: 0.517; Cement: 0.002; Interaction: 0.350.		Light-activation protocol: 0.134; Cement: 0.581; Interaction: 0.096.		Light-activation protocol: 0.360; Cement: 0.420; Interaction: 0.002.	

* Calculated by two-way ANOVA. Distinct letters (uppercase for column, lowercase for line) indicate statistical difference ($p < 0.05$) at Student-Newman-Keuls Method.

TU – thiourethane.

DHEPT - p-Tolyldiethanolamine.