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Influence of light-curing procedures and photo-initiator/co-initiator composition on the degree of conversion of light-curing resins

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Objective: The hypothesis that the degree and rate of conversion can be modified favourably by using different light-curing procedures and different photo initiator/co-initiator combinations was tested.

Method: A photo-initiator (0.02 mM/g resin); either camphorquinone (CQ) or 1-phenyl-1,2-propanedione (PPD), was mixed with bisGMA:TEGDMA (50:50 by weight). In addition, a co-initiator (0.04 mM/g resin); either N,N-dimethyl-p-aminobenzoic acid ethylester (DABE), N,N-cyanoethylmethylaniline (CEMA), or 2-dimethylaminoethyl methacrylate (DMAEMA), was added. These six combinations were subjected to three curing conditions (standard curing, soft-start curing or LED curing). The conversion levels (DC) were determined with differential scanning calorimetry (DSC). The DSC results were analysed using a general linear model (GLM) and Duncan's multiple range test and regular *t*-test.

Results: The fastest conversion initially was obtained by standard curing, followed by LED curing and soft-start curing. After 40 s of curing, conventional curing and soft-start curing produced a higher DC than LED curing. However, strong interactions occurred between the different variables (curing method, initiator and co-initiator). Initially, CQ was more efficient than PPD, but after 40 s, this difference was insignificant.

Conclusion: By using soft-start curing and an appropriate photo initiator/co-initiator combination it is possible to achieve slow curing and a high DC at within a curing time of 40 s.

Introduction

During the past few years, methods of light-curing dental composites have been discussed extensively in dentistry. By increasing the irradiance value of the light source, manufacturers of dental curing lights have been able to decrease the light curing time by developing more efficient light sources. At the same time, some researchers have claimed that the irradiance should be decreased and the cure time increased in an attempt to decrease polymerisation shrinkage stresses and retain sufficient curing [1–4]. Laser curing and arc plasma curing have been used to shorten the cure time [5, 6], while soft-start curing and stepwise curing have been used to decrease shrinkage stresses [3]. To increase useful light output and decrease heat generation during usage, light emitting diodes (LED) have been introduced during the past few years [7, 8]. However, the light-curing ability depends not only on irradiance value and spectral distribution of the light-source, but also on the light initiator/co-initiator systems. Therefore, proper combinations of light sources, cure times and photo initiator/co-initiator systems are major factors to optimise light curing of dental composites.

The optimal photo initiator/co-initiator concentration of a light curable dental composite depends on many factors such as solubility of these compounds in the monomer mixture, absorption characteristics of the initiator, photoreactivity (ability to form free radicals when the initiator and co-initiator react), the effects of these compounds on colour, the light-source/photochemical compatibility, and the biocompatibility of photo-chemicals [9]. Initiators absorb different wavelengths, and different light sources generate a variety of different wavelength ranges. The light source must generate a wavelength that the photo-initiator can absorb and which can trigger the photoreaction between the initiator and the co-initiator.

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Of different co-initiators, the most reactive ones are tertiary amines, followed by secondary amines, while primary amines are almost non-reactive. Tertiary amines interact easily with the light activated photo-initiator and form charge-transfer complexes (exciplexes) with the triplet excited carbonyl groups of the initiator. In these complexes, electron/proton transfer occurs with the formation of ketyl radicals and amine radicals [9–12]. The ketyl radicals and the amine radicals are responsible for the initiation of polymerisation, but the amine radicals are often more efficient. Efficiency of these radicals depends on the steric structure of the free radicals that must approach the reactive unsaturated carbon bonds of the monomer. Most amines have an optimum concentration.

With differential scanning calometry (DSC), one can determine the progression of the cure by measuring the heat generated during the polymerization reaction [13–20]. This heat is proportional to the overall extent of the polymerisation process, making it possible to study how different combinations of photo-initiator and co-initiator systems initiate and affect the final cure when different light curing methods are used.

We tested the hypothesis that the use of DSC and the optimal initiator/co-initiator system and curing protocol would control the reaction rate of the light curing process and still achieve a satisfactory degree of conversion of a dental resin.

Material and methods

Resin preparation

Monomer mixtures consisting of 50 wt% of bisGMA (2,2-bis[4-(2-hydroxy-3-methacrylyloxypropoxy)phenyl]propane) and 50 wt% of TEGDMA (triethyleneglycol dimethacrylate) were prepared. To these mixtures, 0.02 mM photo-initiator per gram bisGMA/TEGDMA resin was added. The photo-initiator was either camphorquinone (CQ) (1,7,7- trimethylbicyclo-(2,2,1)-heptane2,3dione) or 1-phenyl -1,2-propanedione (PPD). CQ was chosen because it is the most commonly used photo-initiator in dental composites and has a light absorption maximum at 468 nm. PPD was chosen because it is also used in some dental composites, despite its light absorption peak at 386 nm. Because of the latter, PPD is a better UV initiator than an efficient visible light photo- initiator. Both of these photo-initiators can be used without any co-initiator in light curable dental composites, but to decrease their concentrations they are used with different co-initiators. The reason is simply that too high of a photo-initiator concentration affects the colour of the dental composite. Therefore, to enhance the photo-initiator efficiency at lower concentrations, different co-initiators are added. The co-initiators used in this study with CQ or PPD were either DABE (N,N-dimethyl-p-aminobenzoic acid ethyl ester), CEMA (N,N-cyanoethyl methylaniline), and DMAEMA (2-(dimethylamino)ethyl methacrylate). An amount of 0.04 mM per gram of bisGMA/TEGDMA resin mixture of one of these co-initiators was used with one of the two photoinitiators. Consequently, a total of six different initiator/co-initiator combinations were prepared for our study. All chemicals with a purity of more than 98% were purchased from Sigma-Aldrich Chemie GmbH, Schnelldorf, Germany.

Experimental procedure

The curing kinetics of the six initiator/co-initiator combinations were studied with differential scanning calorimetry (DSC) adapted for photopolymerization measurements at a temperature of $36.00 \pm 0.01\,^{\circ}\mathrm{C}$. The DSC measurements were conducted with a Mettler Toledo DSC (Module 821^{e}, Mettler-Toledo GmbH, Switzerland). The experiments were performed under constant air flow.

To observe the effect of curing method on the kinetic cure behaviour of the experimental resin mixtures, the photo-polymerization experiments were carried out with three different curing methods. The first method (referred to as "standard curing") used a halogen light with an irradiance value of 850 mW/cm^2. The second method (referred to as "soft-start curing") used a halogen light starting with low irradiance ($<$100 mW/cm^2 for the first 5 s) and finished with high irradiance (850 mW/cm^2). The third method (referred to as "LED curing") used a light emitting diode (LED) lamp with an irradiance of 450 mW/cm^2. All of these curing procedures were performed for 40 s. The light source being used for standard and soft curing was an Ellipar Thrilight unit (3M ESPE, Seefeldt, Germany), while a Free Light unit (3 M ESPE) was used for the LED curing. A universal optical power meter (Melles Griot, Model #13 PDC 001, New York, USA) was employed to confirm the irradiance measurements. The irradiance distance was 9 mm from the composite surface and the light rod was placed exactly in the center of the sample inside the furnace.

Specimens consisting of 18–24 mg of the photo-curable experimental dental resin mixtures (corresponding to material thickness of 0.20–0.25 mm) were polymerized in 40 μL standard alumina-crucibles (ME-26763, Mettler-Toledo GmbH, Switzerland). When a specimen was placed in the DSC, it was first equilibrated at 36 °C for 5 min. For each experimental composition, six separate photo-polymerization experiments were performed inside the DSC unit. All materials were prepared and handled under safe yellow light before they were cured.

The cure kinetics of the tested materials was determined by recording four thermograms at 36 °C. The first peak represents the exotherm generated by the polymerization of the resin plus the heat released from the curing unit. The three following peaks represent light exposures of the initially cured specimen (Fig. 1) and are primarily caused by the irradiance exotherm of the curing unit. These three light exposures were similar in peak height, suggesting that not much additional curing occurred after the first light exposure (curing reaction).

According to [19, 20] the isothermal heat of resin polymerization can be determined by subtracting the average heat value of the three last peaks from the first peak value. The change in heat per time unit due to the polymerization reaction occurring under isothermal

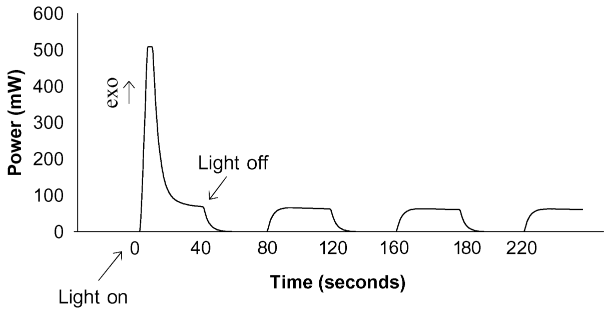

Figure 1 Isothermal DSC thermogram obtained during photocalorimetry at 36 °C using four light exposures.

conditions can be evaluated from DSC signal using a similar subtraction procedure.

The conversion levels at different times were determined by using changes in heat release during the experiment. By registering these heat values and their changes over time, conversion changes could be calculated from the theoretic heat release per mole reacted carbon double bond (56 kJ/mol) over the time of the experiment [21]. By use of this approach it was possible to determine the conversion level at different time intervals during our experiments.

Spectral distribution of the halogen and LED lamps were measured with an Avantes (Avantes BV. Eerbeek, Netherlands) AvaSpec-2048 fiberoptic spectrometer with a Sony 2048 pixel linear CCD. Grating # VA was set at 278-1100 nm with a resolution of 1.4 nm.

Absorption peaks for photo-initiators (CQ and PPD) were measured with Lambda 2S UV/VIS spectrometer Perkin-Elmer (registered trademark of E.Merck GmbH. Germany) with an operational range of 220 to 700 nm. Methanol with concentration of 99.8% was used as diluting agent for both photo-initiators (Fig. 2).

The irradiance of each curing method over time was measured with a universal optical power meter (Melles Griot, Model # 13 PDC 001, New York, USA). During these measurements, the distance between the light guide and the detector surface was less than 0.5 mm (Fig. 3).

Show in Fig. 4 are the plots of the heat generated over time for each light-curing method. The exotherm measurements were conducted by DSC on fully cured samples.

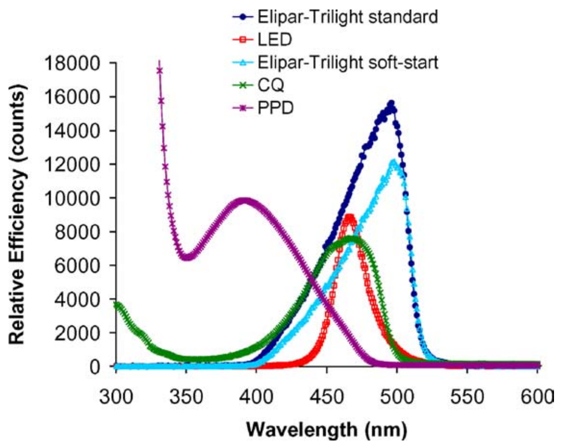

Figure 2 The spectrum distribution for curing units in comparison with absorption peak for photo initiators (CQ and PPD).

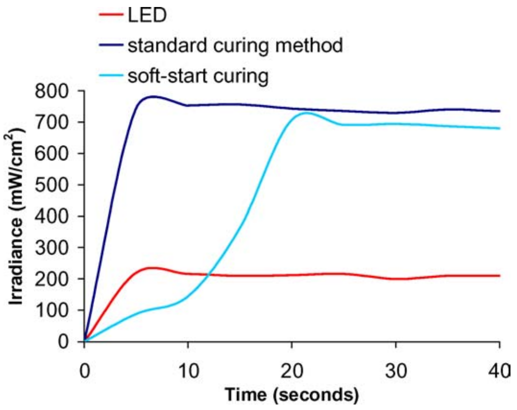

Figure 3 Irradiance values of the different curing methods over time.

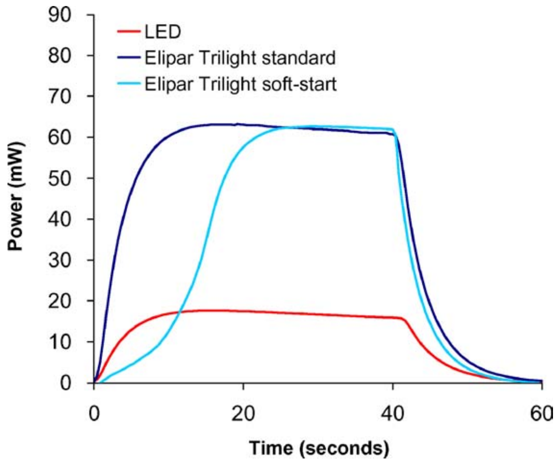

Figure 4 Heat generated by each curing method obtained from photocalorimetry experiments with DSC at 36 °C.

Statistical evaluation

The rate of polymerisation and the degree of conversion were compared between the different initiator/co-initiator combinations. These comparisons were performed by use of a general linear model (PROC GLM, SAS Institute Inc., Cary, NC, USA) to analyze how light source, initiator and co-initiator affected the rate of polymerisation and degree of polymerisation as a function of cure time. Interactions between light source, initiator and co-initiator were also compared, and individual differences among the groups were determined by use of Duncan's multiple range test.

Results

Tables I to III reveal how the degree of conversion (DC%) was affectd by each light initiator/co-initiator combination and each light source after 3, 10 and 40 s of light exposure. These tables reveal some clear trends. The PPD resins did not convert as fast initially as the CQ based resins. Of the different lights, soft curing resulted in a slower initial conversion rate than the other two curing systems (Tables I and II).

The GLM analysis conducted on the conversion levels generated after 3 s of light curing is shown in

TABLE I Degree of conversion values, expressed in percentages, for the different combinations of initiators/co-initiators at 3 s irradiation

Intiator/co-initiator combination	Curing methods		
	Standard	LED	Soft-start
CQ + DMAEMA	4.9 ± 0.6	4.6 ± 0.7	0.8 ± 0.2
CQ + DABE	9.7 ± 1.8	6.7 ± 2.5	1.9 ± 0.5
CQ + CEMA	7.0 ± 1.3	6.7 ± 0.7	0.8 ± 0.3
PPD + DMAEMA	2.4 ± 0.4	1.8 ± 0.3	0.1 ± 0.1
PPD + DABE	5.6 ± 0.6	3.3 ± 0.3	0.3 ± 0.1
PPD + CEMA	2.7 ± 0.6	1.6 ± 0.3	0.0 3 ± 0.1

The DC% values are given as mean values ± standard deviations.

TABLE II Degree of conversion values, expressed in percentages, for the different combinations of initiators/co-initiators at 10 s irradiation

Intiator/co-initiator Combination	Curing methods		
	Standard	LED	Soft-start
CQ + DMAEMA	41.5 ± 0.8	26.9 ± 0.2	10.9 ± 1.2
CQ + DABE	51.0 ± 4.5	41.3 ± 8.0	25.7 ± 3.3
CQ + CEMA	51.0 ± 2.3	40.1 ± 3.9	18.0 ± 2.3
PPD + DMAEMA	19.1 ± 0.9	9.6 ± 1.0	4.2 ± 0.7
PPD + DABE	42.8 ± 2.2	20.7 ± 0.9	10.1 ± 0.9
PPD + CEMA	24.7 ± 3.1	11.6 ± 0.8	3.2 ± 1.2

The DC% values are given as mean values ± standard deviations.

TABLE III Degree of conversion values, expressed in percentages, for the different combinations of initiators/co-initiators at 40 s irradiation

Intiator/co-initiator combination	Curing methods		
	Standard	LED	Soft-start
CQ + DMAEMA	73.0 ± 1.8	60.1 ± 4.2	63.5 ± 5.0
CQ + DABE	72.8 ± 2.4	68.8 ± 4.2	73.9 ± 2.9
CQ + CEMA	72.7 ± 2.5	66.1 ± 4.7	75.0 ± 5.2
PPD + DMAEMA	72.4 ± 1.9	52.7 ± 4.0	68.6 ± 2.2
PPD + DABE	77.2 ± 1.9	63.4 ± 2.0	73.0 ± 3.5
PPD + CEMA	77.4 ± 1.2	58.8 ± 0.9	70.7 ± 2.0

The DC% values are given as mean values ± standard deviations.

TABLE IV The GLM analysis conducted on the conversion levels generated after 3 s of light curing

Source	DF	Type I SS	Mean square	*F* value	Pr > F
Initiator	1	212.2403704	212.240307	128.92	<0.0001
Co-initiator	2	88.5664500	44.282250	26.90	<0.0001
Light	2	430.9679167	215.4839583	130.89	<0.0001

Table IV. As seen from the table, the light source was the most important variable closely followed by the initiator. Duncan's multiple range test showed that of the three light sources, standard curing yielded a significantly highest conversion value and soft-start curing produced the lowest. The degree of conversion for the LED-cure was intermediate, significantly lower than standard curing and significantly higher than soft-start curing. Duncan's multiple range test also revealed that of the two initiators, CQ was significantly more efficient than PPD. Of the co-initiators, DABE was the most efficient and DMAEMA the least efficient. Statistically significant differences existed among all three co-initiators.

TABLE V The GLM analysis conducted on the conversion levels generated after 10 s of light curing

Source	DF	Type I SS	Mean square	*F* value	Pr > F
Initiator	1	8854.70341	8854.70341	410.49	<0.0001
Co-initiator	2	3371.31682	1685.65841	78.14	<0.0001
Light	2	12882.03717	6441.01859	298.59	<0.0001

TABLE VI The GLM analysis conducted on the conversion levels generated after 40 s of light curing

Source	DF	Type I SS	Mean square	*F* value	Pr > F
Initiator	1	47.097615	47.097615	2.75	0.1004
Co-initiator	2	825.952919	412.976459	24.10	<0.0001
Light	2	3055.855735	1527.927868	89.17	<0.0001

The GLM analysis conducted on the conversion levels generated after 10 s of light curing is shown in Table V. As seen in this table, the most important variable after 10 s of curing was the initiator, followed by the light source. After 3 s of curing, CQ was still more efficient than PPD, and standard curing gave the highest conversion values and soft-start curing the lowest values. Of the three co-initiators, DABE remained the most efficient and the DMAEMA the least efficient.

The GLM analysis conducted on the conversion levels generated after 40 s of light curing is shown in Table VI. After 40 s, the initiator choice had no significant impact on conversion. At this time, the light source was the most important variable, followed by the co-initiator. Of the three light sources, standard curing gave the highest conversion value and LED-curing the lowest. There were significant differences among all three lights. Regarding the co-initiators, they were still in the order DABE, CEMA and DMAEMA. At this time interval there were no significant difference between DABE and CEMA, while DMAEMA yielded significantly lower conversion values.

To determine the conversion levels after 40 s, interactions between initiators, co-initiators and lights were also evaluated by PROC GLM. This analysis revealed significant interactions between all variables, interactions that were strongest between initiator and light, followed by interactions between initiators and co-initiators. Duncan's multiple range test was also used to determine where statistically significant differences existed for each light cure method after 40 s for each material. The results of this analysis are shown in Table VII. As shown in the table, PPD ∗ DABE and PPD ∗ CEMA cured with standard curing yielded the highest conversion, while PPD ∗ CEMA and CQ ∗ DMAEA cured with LED-curing produced the lowest conversion. Standard curing is associated with high conversion levels, followed by the soft-start curing approach, while LED curing in general was associated with low conversion levels.

Shown in Fig. 2 are the spectral distribution curves generated by the halogen and LED lamps and a relative comparison of the absorption peaks of the two photoinitiators (CQ and PPD). The LED lamp emitted the most favourable spectral distribution for activation of both CQ and PPD. The heat generated from each of

TABLE VII Degree of conversion levels (in percentages) of the individual initiator/co-initiator, light curing method combinations

Initiator	Co-initiator	Light source	DC%	Statistical group
CQ	DMAEMA	STANDARD	73.0 ± 1.8	BC
CQ	DMAEMA	LED	60.1 ± 4.2	HI
CQ	DMAEMA	SOFT-START	63.5 ± 5.0	GH
CQ	DABE	STANDARD	72.8 ± 2.4	BCD
CQ	DABE	LED	68.8 ± 4.2	DEF
CQ	DABE	SOFT-START	73.9 ± 2.9	ABC
CQ	CEMA	STANDARD	72.7 ± 2.5	BCD
CQ	CEMA	LED	66.1 ± 4.7	FG
CQ	CEMA	SOFT-START	75.0 ± 5.2	AB
PPD	DMAEMA	STANDARD	72.4 ± 1.9	BCDE
PPD	DMAEMA	LED	52.7 ± 4.0	J
PPD	DMAEMA	SOFT-START	68.8 ± 2.7	EF
PPD	DABE	STANDARD	77.2 ± 1.9	A
PPD	DABE	LED	63.4 ± 2.0	GH
PPD	DABE	SOFT-START	73.0 ± 3.5	BC
PPD	CEMA	STANDARD	77.4 ± 1.2	A
PPD	CEMA	LED	58.8 ± 0.9	I
PPD	CEMA	SOFT-START	70.7 ± 2.0	CDE

The DC% values are given as mean values ± standard deviations.

the three light curing methods is shown in (Fig. 4). The LED lamp generated only a third of the heat compared with the other two curing methods. Data presented in Fig. 4 are based on one single heat measurement per light source.

Discussion

The results presented above clearly show that different initiator/co-initiator combinations affect the polymerization rate. The results also show that different curing methods affect the degree of conversion, both initially and after 40 s of curing (Tables I to III).

Since polymerization is initiated by a reaction between a diketone and an amine [22], the mechanism through which the ketone and the amine interact will affect free radical formation. Another important factor is the photo activation efficiency of the photo initiator, which explains why light sources and initiators were the most important variables affecting conversion after 3 and 10 s (Tables IV and V). Each of the used light sources had high output in the range of the absorption peak of the CQ, while their light output that overlapped the PPD peak was less pronounced. As a consequence, a larger number of CQ molecules were activated and consumed earlier in the curing process than what occurred for PPD. This would explain why there was a significant difference between CQ and PPD after 3 and 10 s, thereby favouring a higher conversion of the CQ-containing resins. However, as the light exposure continued after 10 s, more and more of the PPD molecules were activated, while most of the CQ molecules had already been consumed. As a result, the conversion of the PPD-containing resins caught up. After 40 s there was no significant difference between the mean conversion values for CQ and PPD.

The findings that PPD reacted more slowly than CQ without compromising the final degree of conversion values suggest that PPD-containing resins remain in their viscous stage for a longer time period during curing, and that such a delay may allow for more plastic flow during initial curing. An increase in plastic flow during this time period should decrease initial shrinkage stress development in bonded restorations [23]. This possibility needs to be investigated further because of its clinical significance.

The light spectrum distribution and its distribution with the absorption peak of the photo-initiator are important factors to consider. The spectral distribution of the light generated by the three curing methods and the absorption spectra of CQ and PPD can partially explain the cure behaviour (Fig. 2). As seen in the figure, the peak intensities are different as a function of wavelength of the two initiators. The halogen lamp has also a broader spectral distribution than the LED source, and some of the halogen generated light falls outside the absorption peaks of the initiators. The PPD has an absorption peak just below 400 nm, but it continues to absorb some light almost up to 500 nm. Because of the lower absorption ability of PPD in the ranges where the three lamps have their light emission peaks, the probability for photo-initiation of PPD is lower than it is for CQ, since CQ has an absorption peak at 467 nm, making it more favourable for the lamps with emission peaks in the range of 470 to 500 nm. Thus, without considering the spectral distribution of the light source and the light absorption ability of the photo-initiator, one cannot properly explain the cure behaviour of the photo/co-initiators.

Of the three light sources, the normal use of the halogen light was most efficient, while the LED light was the least efficient after 40 s of cure. After 3 and 10 s of light curing, the soft-start curing yielded the lowest conversion. These findings can be explained by considering when energy output rather than irradiance values when we evaluate the results. During the first 10 s of the light curing, soft- start curing transfers the least light energy to the resin (Fig. 3). As a consequence, the conversion level is also lowest for soft-start curing within the first 10 s (Tables I–III and Fig. 3). However, at the end of the curing time (40 s), the LED lamp has released light energy not exceeding that of soft-start curing, while standard curing has released the most energy. This is further confirmed if we assume that both standard curing and soft-start curing releases more heat during use than the LED unit (Fig. 4), and that the higher heat also facilitates molecular mobility and higher conversion [24–26].

A simple relationship between irradiance and exposure time (= light energy) is an oversimplification of predicting the conversion level of light-cured composite, because irradiance values vary at different wavelengths and that the irradiance value recorded with most light meters represent the integrated irradiance over a certain wavelength region, often between 450–500 nm [27]. In addition, manufacturers use different light initiators, which suggest that a light source with high irradiance value may still not generate a significantly larger number of photons to activate a specific photo-initiator.

When comparing the influence of the three co-initiators, a key variable to consider is the ease with which the different co-initiators release protons during the activation/initiation process. Of these three co-initiators, DABE was the most efficient co-initiator at the beginning of the curing process (Table I), DMAEMA was the least efficient, while CEMA was intermediate in efficiency. Of the three compounds, DABE exhibited the greatest ability to donate protons while DMAEMA revealed the lowest proton-donating ability [28].

As reported in many research articles, stresses that develop in bonded light-curable dental composite are closely related to the conversion of the double bonds [29–31]. When resin composites are cured, a high degree of conversion is needed to optimise wear resistance, but conversion increases the final contraction. In the present study, the conversion of resins containing different initiator/co-initiator combinations reveals that it is possible to control cure rate and still achieve a high final degree of conversion. To achieve such control, one must consider light irradiance and how the light interacts with different photo initiators. By combining different initiator/co-initiators/curing methods, lower polymerization rates can be achieved while the final conversion is still very high. The benefit of this regimen is that by lowering the conversion rate it should be possible to decrease the shrinkage stress developed at the critical composite-tooth interface of bonded composites. At the same time, despite a slower initial conversion, one can still achieve conversion levels as high as those yielded at faster curing procedures. Because the goal of this study was not to prove that each initiator/co-initiator/light curing method combinations generated different stress levels in bonded composites, we cannot claim that such a stress decrease will occur. However, our findings quite clearly show that more research is needed to support our suspicion that with the optimal initiator/co-initiator/curing method combination, well cured and relatively stress-free restorations can be produced.

Conclusion

By using soft-start curing and appropriate photo initiator/co-initiator combination it is possible to achieve slow curing and high DC within a 40 s. That was best achieved by use of soft-start and PPD/DABE.

PPD was not as efficient as CQ during the beginning of the curing process, but at 40 s there was no significant difference in conversion between the two photo initiators. Of the co-initiators, the most efficient one was DABE, at least initially, while DMAEM was the least efficient co-initiator.

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