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Molar extinction coefficients and the photon absorption efficiency of dental photoinitiators and light curing units

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Dental photoinitiators;
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Quartz-tungsten-halogen (QTH);
Molar extinction coefficient;
Photon absorption

Summary *Objectives*. The light absorption of dental photoinitiators should correlate with the spectral emission profiles of dental light curing units compared on an equivalent basis. Spectral data of dental photoinitiators and light curing units can be used to define the photon absorption efficiency (PAE) obtained by integrating the product of the absorption and emission spectra in terms of photons. This parameter can be used to identify the best performance for photochemical process with specific photoinitiators.

Methods. The efficiency of two LED and one QTH lamps were tested comparing their performances with the photoinitiators camphorquinone (CQ); phenylpropanedione (PPD); monoacylphosphine oxide (Lucirin TPO); and bisacylphosphine oxide (Irgacure 819). Absorption and emission spectra of the photoinitiators and the LED (Ultrablue I and Ultrablue IS) and QTH (Optilux 401) LCUs were determined in the 360–550 nm range.

Results. CQ exhibited an absorption centered in the blue region and, although the maxima of PPD, MAPO, and BAPO were in the UV-A region, their absorption extended to the visible region. Power output maxima of the LCUs were at 467 (Ultrablue I), 454 (Ultrablue IS) and 493 nm (Optilux 401), and the total power densities were 170 ± 1, 470 ± 4 and 444 ± 4 mW/cm^2, respectively.

Significance. The use of the PAE allows a prediction of the most efficient photoinitiator/LCU systems. For similar photoinitiator concentrations, Lucirin and CQ are most efficiently photoinitiated by the QTH unit, whereas the high-power LED device is more efficient for Irgacure. PPD is photoactivated similarly by both LCUs.

Introduction

The resin matrix has an important influence on the chemical and physical properties of light cured

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resins. In the past four decades, no fundamental change occurred in the dimethacrylate formulations based on BisGMA.[1,2] The organic formulations also include photoinitiation systems that absorb light and take the molecules to excited states. From there, radicals or other initiating species start the conversion of the oligomer blend to a polymeric crosslinked network.[2,3]

Absorption requirements of dental photoinitiators should correlate with the spectral emission profiles of dental light curing units (LCU). The visible light photosensitizer camphorquinone (CQ) is widely used in dental resin and adhesive formulations.[2,4] CQ is a solid yellow compound with an unbleachable chromophore group, so that large amounts of CQ in resin formulations will lead to an undesirable yellowing, affecting the final aesthetic appearance of the cured material.[5–9] After light absorption between 400–500 nm (maximum at 470 nm) CQ is promoted to an excited triplet state that interacts with an electron- or proton donor molecule, like a tertiary amine, to generate free radicals.[2–4]

Since the light absorption process of the photoinitiators or photosensitizers is fundamental to improve the photochemical reaction efficiency, it is important to select compounds with absorption spectra that overlap with the emission spectra of the irradiation sources. Recently, manufacturers included different photoinitiators in the organic matrix to act alone, or synergistically, with CQ.[8] Compounds derived from acylphosphine oxides and α-diketones are used in adhesives and composite resins formulations to improve the polymerization kinetics and lessen the photoyellowing effects.[7,8,10,11] Unlike CQ, the absorption peak of these compounds is mainly in the near UV region (UV-A) and extends slightly into the visible region.[8,12,13] The generation of free radicals from these compounds will not be very efficient when using light-emitting diode (LED) sources, which do not have high emission intensity in this region, but probably might be efficient when the broad band emission of a quartz tungsten-halogen (QTH) light-curing unit is used.

The probability of light absorption by a molecule depends on its extinction coefficient (ε_λ),[12] and on the number of photons available that can be absorbed. Large values of ε indicate a high probability of absorption at a given wavelength, leading to large quantum yields of the initiating species and, consequently, improving the polymerization kinetics and overall conversion.[12,14] The efficiency of various visible light LCUs used with CQ-containing formulations was evaluated by Cook,[15] showing qualitatively the need of a good overlap between the emission of the lamps and the absorption spectrum of CQ. More recently, Stahl et al.[16] and Teshima et al.,[17] analyzed several LCU/photoinitiator systems by a method similar to that described in this work, but based on the energy output of the light sources, instead of the number of photons.

The aim of this study is to determine the molar extinction coefficient of four photoinitiators and the power density profiles of LED and QTH light curing units. The product of both spectra in terms of photons was integrated to calculate the photon absorption efficiency (PAE) of each LCU/photoinitiator pair, that can be used to evaluate the conditions for improving the photochemical process when using those photoinitiators.

Methods and materials

Absorption spectrophotometric analysis

The photoinitiators monoacylphosphine oxide or MAPO (Lucirin TPO, BASF), bisacylphosphine oxide or BAPO (Irgacure 819, Ciba-Geigy), phenylpropanedione (PPD, Aldrich) and camphorquinone (CQ, Aldrich) were used as received (Fig. 1). The solvent used was methyl methacrylate (MMA 99% HPLC, Fluka).

Solutions of the photoinitiators in methyl methacrylate were prepared taking into account the solubility of these compounds and are shown in Table 1. No hints of reaction of the solvent were observed after the spectroscopic measurements.

Absorption spectra were determined in the 200–600 nm range using a UV–Vis spectrophotometer (Hitachi U-2000), although only the visible and near UV range was of interest (360–550 nm), as this range reflects the emission of most QTH based curing units. The spectra were taken using a 1.0 cm pathlength quartz-cell. Absorption spectra were recorded for each photoinitiator and the ε_λ were calculated from the absorbance values in the original solutions, using the Beer–Lambert law

$$\mathrm{Abs}_\lambda = \varepsilon_{\mathrm{L/mol\ cm}}[c_{\mathrm{mol/L}}]L_{\mathrm{cm}} \quad (1)$$

where Abs is the absorbance at each wavelength, ε is the molar extinction coefficient, [c] is the concentration of the photoinitiator in the solution and L is the optical pathlength.

Emission spectrophotometric analysis

The LCUs used in this study were: (1) Optilux 401 (OPT, Demetron Inc., Danbury, MA, USA) a QTH unit

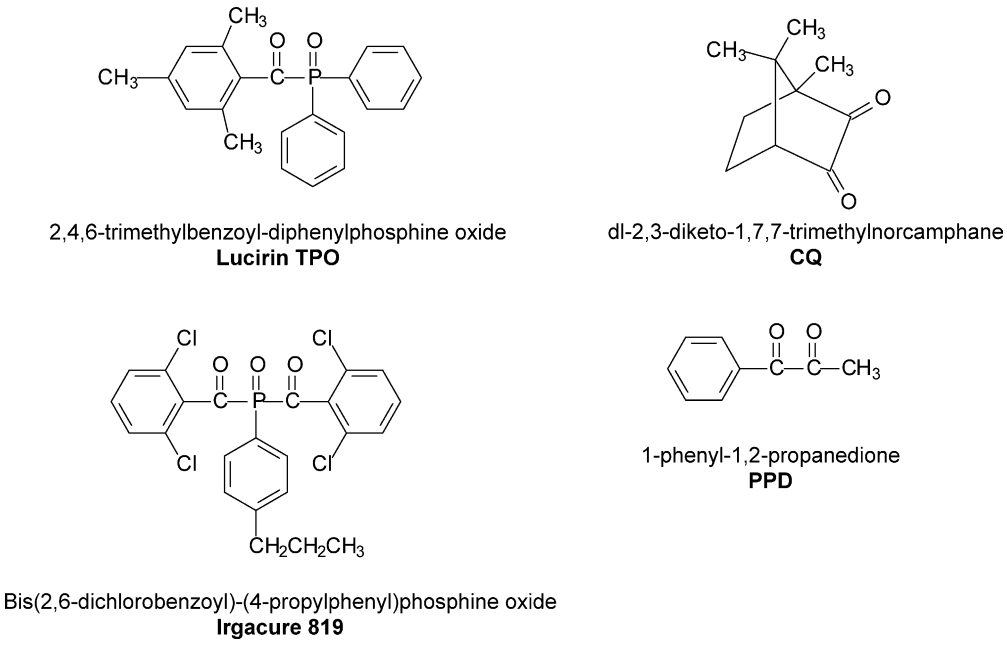

Fig. 1 Photoinitiators.

with a 13 mm straight light tip; (2) Ultrablue I (UBI, DMC Ltda, São Carlos, SP, Brazil) a cluster type LED unit; and (3) Ultrablue IS (UBIS, DMC Ltda, São Carlos, SP, Brazil) a high-power LED unit. Both LED LCUs used a turbo type light tip with 8 mm at distal end. Emission spectra of the LCUs were determined in the 360–550 nm range using a laboratory radiometer (Spectrometer 100, Labsphere Inc., Sutton, NH, USA) connected to an integrating sphere (LabSphere 2000, LabSphere Inc., Sutton, NH, USA). The properties of the ligth sources ae shown in Table 2.

The distal end of light tip was set at the sphere aperture where the total energy emitted was collected by an optical fiber cable and conducted to a grating that reflected the light beam to two groups of 1024 diodes able to select each wavelength emitted. The spectrometer was connected to a PC computer where the power output signals were obtained by the SLMA software (Version 3.9, LabSphere Inc., Sutton, NH, USA). All values were presented as spectral readings, in which the area under the curve was integrated to obtain the total power output between 360–550 nm. The spectrometer was calibrated using a National Institute of Standards and Technology (NIST, Gaithersburg, MD) light source.

Results

Fig. 2 presents the extinction coefficients, ε, for the photoinitiators between 360–550 nm. These spectra were calculated from the actual absorption spectra recorded with the concentrations shown in Table 1, using Eq. (1). The absorbance of the solutions were always below 0.6 and presented maximum peaks at different wavelengths, as shown in Table 1, together with the corresponding extinction coefficients. Although $\varepsilon_{\lambda max}$ of PPD, Lucirin TPO, and Irgacure 819 were in the UV-A region, their absorption profiles extend into the visible range (Fig. 2).

The ε values for both CQ and PPD are similar at 470 nm. For wavelengths up to 500 nm, ε_{CQ} presents the higher values, while at lower wavelengths ε_{PPD} is

Table 1 Properties and experimental conditions of the photoinitiators.

	FW	λ_{max} (nm)	ε_{max} (L/mol cm)	Concn used in this work	
				mol/L	Wt%
CQ	166.22	470	28 ± 2	8.31×10^{-3}	0.15
PPD	148.16	398	150 ± 10	2.47×10^{-3}	0.039
Lucirin	348.38	381	520 ± 10	0.99×10^{-3}	0.037
Irgacure	418.50	370	300 ± 10	1.03×10^{-3}	0.046

Table 2 Properties of the light curing units.

	Type	Distal end area cm^2	λ_{Max} nm	Power mW/cm^2	Photon flux 10^{19} photons/cm^2.s
OPT	QTH	1.03	493	445±5	1.44
UBIS	LED	0.38	454	470±5	1.54
UBI	LED	0.38	467	170±2	0.55

consistently higher than ε_{CQ}. In the near visible range (>400 nm) $\varepsilon_{Lucirin}$ and $\varepsilon_{Irgacure}$ were higher than ε_{CQ} up to 440 and 420 nm, respectively, and also higher than ε_{PPD} up to 408 nm. The extinction coefficient for CQ is within the same range as determined by Cook.[15]

Considering that the photopolymerization process is initiated by species originated from the absorption of light (photons) by the initiator, it seems more interesting to consider the number of photons emitted by the LCU than the energy. Therefore, the energy densities at each wavelength were converted to the number of photons per square centimeter (cm^2) and second (s) by dividing the power density by the energy of one photon

$$n_{ph\lambda} = W/h\nu = W\lambda/hc \quad (2)$$

were W is the energy output of the lamp; h, the Planck constant; λ, the wavelength; ν, the corresponding frequency; and c, the light speed. The emission spectra (in photon units) of all three lamps are shown in Fig. 3, and the values obtained by integrating over the whole radiation interval, the photon flow, is listed in Table 2.

Discussion

Assuming that the potential of photoactivation to initiate the polymerization reaction is proportional to the number of photons available at each wavelength and the probability of their absorption, it becomes apparent that two main factors will influence the photopolymerization efficiency. On one side, the spectral properties of the photolyzing radiation, which should ideally overlap with the absorption spectrum of the photoinitiator. On the other hand, the mechanism by which the polymerization process is launched by the excited photoinitiating species.

A very useful parameter to evaluate the first condition is the photon absorption efficiency, PAE, which measures the amount of photons actually absorbed by the photoinitiator when irradiated by a specific LCU. A similar procedure was used by Stahl et al.[16] and Teshima et al.,[17] with the difference that in the present evaluation the number of photons at each wavelength is used, instead of the energy output.

This parameter is obtained by integrating the product of the absorption spectrum of the initiator with the emission spectrum of the light source (plotted in terms of photons instead of energy). This calculation gives a better basis for analysing the performance of the photochemical processes, as it counts all photons at any wavelength that can be absorbed and excite the photoinitiator to a state that generates species that may initiate

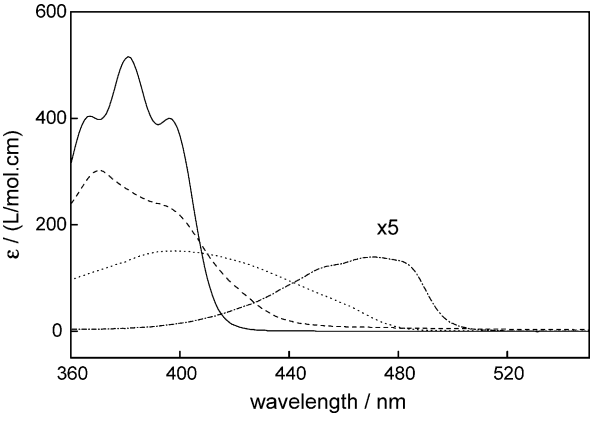

Fig. 2 Spectra of the photoinitiators.

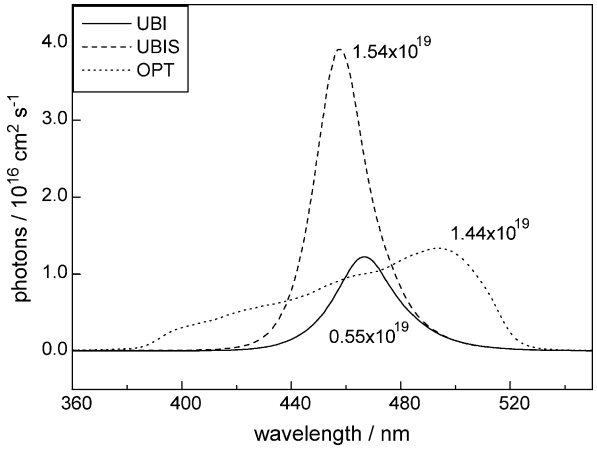

Fig. 3 Emission spectra of the LCUs, shown as number of photons per cm^2 and second.

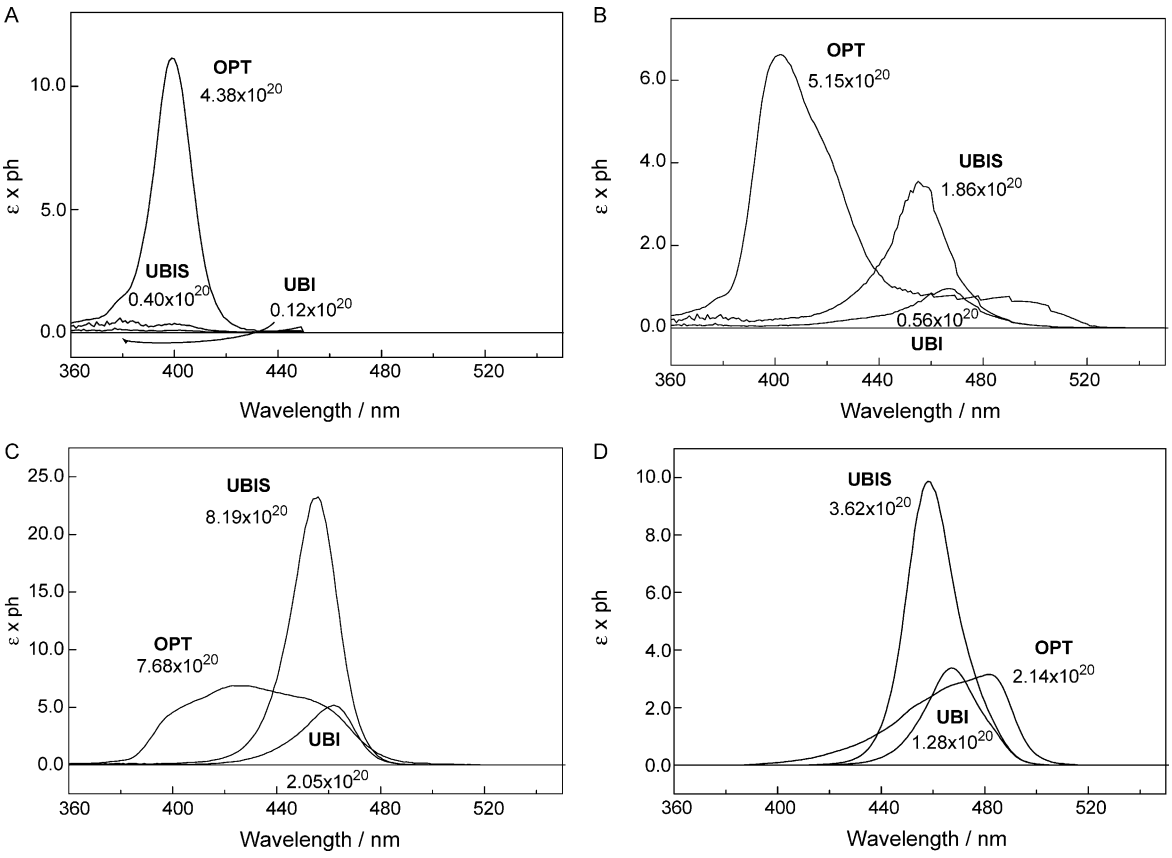

Fig. 4 Relative PAE for intiating systems containing the photoinitiators Lucirin TPO (A); Irgacure 819 (B); phenylpropanedione (C); and camphorquinone (D), with different LCUs.

the polymerization. Fig. 4(a-d) show, for each photoinitiator, the amount of photons absorbed at each wavelength from the output of each LCU. The integration of these curves corresponds to the PAE for the LCU/photoinitiator pairs, which are shown in Fig. 5.

All the photoinitiators, except CQ, showed the highest ε values at wavelengths near the UV-Vis limit, but the absorption profiles extended significantly into the visible range (Fig. 2). This pattern of absorption certainly allows the use of all of these photoinitiators in dental resin formulations, which might contain or not the conventional CQ/Amine system.

Although the near UV-Vis radiation emitted by most QTH LCUs has a relatively low output, the larger ε of some of the photoinitiators may compensate for this shortcoming. On the other hand, concentration adjustments and variable curing times might be used in order to obtain more efficient photopolymerization.

Analysis of the spectroscopic properties of PPD and CQ shows similar ε-values at 470 nm. Although equal extinction coefficients might suggest a similar behaviour for both photoinitiators, the photochemistry of each compound may deeply affect the generation of free radicals.[12] Sun and Chae[11] proposed that PPD could be more efficient than CQ in forming radical species by the photocleavage pathway, whereas for CQ the acting mechanism is an electron/proton transfer process. These authors observed higher values for flexural strength and VHN when PPD was used in a BisGMA based composite, photocured by a halogen source.

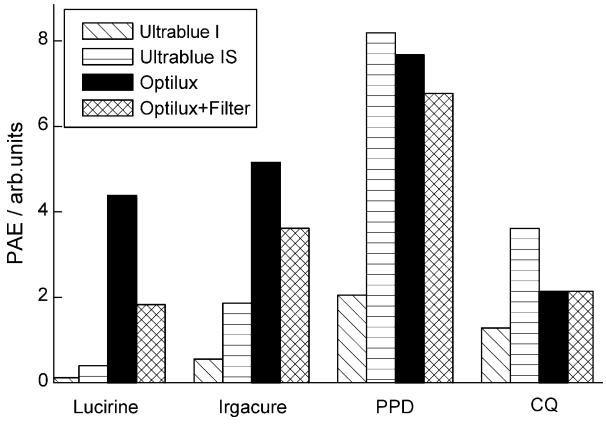

Fig. 5 Relative photon absorption efficiency for the LCUs and photoinitiators used in this work.

Park et al.[8] observed that equal amounts of CQ and PPD in an experimental unfilled resin (BisGMA/UDMA/TEGDMA) produced higher degree of conversion than CQ or PPD used separately. A complementary effect due to a wider absorption profile was suggested when both photoinitiators were used in the same formulation, so that this combination would absorb more of the available photons emitted by dental LCUs,[8,11] as can be observed in Fig. 2, where the conjunction of both photoinitiators will span over a wavelength range that practically overlaps with that of the halogen source showed in Fig. 3.

Due to the large variations of blue light radiation emitted by different types of LCUs, the polymerization pattern for a resin formulation containing acylphosphine oxide photoinitiators will depend on the irradiation device.[14,18-20] The narrow distribution of the spectral irradiance of LED LCUs, suggests that they seem not to be very appropriate to cure Lucirin TPO or Irgacure 819 resin formulations, as can be seen in Fig. 4(a) from PAE integrated values of 0.12 and 0.40, respectively, for Ultrablue I and Ultrablue IS. On the other hand, even with the band-pass filters mounted in most QTH LCUs, which usually allow only the passage of visible radiation between 400–515 nm,[4] these lamps present a much better overlap with the absorbance of Irgacure 819 or Lucirin TPO. An even better efficiency would be achieved with QTH units using the complete visible light emission in the 380–520 nm spectral range.[14,18-21] This indicates that the proper selection of the radiation source should be adapted for each photoinitiator/resin system to obtain a better curing performance.

Commercial composite resins containing Lucirin TPO are efficiently cured by QTH LCUs, when compared with a variety of CQ based ones.[16] However, when LED LCUs were used, despite the intensity of the emitted radiation, the hardness, the depth of cure and the flexural strength decreased by about 30%.[16,19,21] This effect probably occurred due to the lower output and narrow spectral band centered at 470 nm emitted by the first generation of LED LCUs (cluster type LED source), unable to excite the Lucirin molecule over all of its absorption range. This effect could also explain the highest percentage of unreacted monomers found in a NMR study of an experimental unfilled resin containing 0.5% of Lucirin TPO, compared with the same amount of CQ/Amine system when both were photocured by the same type of LED LCU.[22] Larger degrees of conversion were found when a the high power LED LCU was used to cure experimental resins containing Irgacure 819 in comparison with the photoactivation by a first-generation type LED unit.[14] It might be suggested that additionally to the higher output emitted by the UBIS LCU the shift of the maximum emission to lower wavelengths (454 nm), will imply in a larger availability of photons in the higher-energy absorption region of the photoinitiators, thus contributing to produce better conversion results and approaching those obtained by using a conventional QTH LCU. Additional improving of the efficiency could be ascribed to heating effects, as suggested by Lovell et al.[23]

Acylphosphine oxides undergo fast photolysis of the carbon-phosphorus bond, generating benzoyl and phosphonyl radicals, which are both very reactive and capable of initiating vinyl monomer polymerization.[25,24] The two carbonyl groups in the Irgacure 819 structure interact with the central phosphonyl group leading to a higher free radicals production efficiency than Lucirin TPO, as four reactive radicals could be generated from one molecule of Irgacure 819, compared to two obtained from Lucirin.[13]

It was found that only Irgacure 819 had synergistic effects on the degree of conversion of a BisGMA/UDMA/TEGDMA/BisEMA experimental resin when used with the camphorquinone/amine system.[14] No such effects were observed when Lucirin TPO or PPD were added. This effect was observed for photoactivation with the QTH LCU (Optilux 401) or the high power LED LCU (Ultrablue IS). Even with the lower emission of photons near the absorption peak of Irgacure 819, it could be assumed that the presence of this very reactive photoinitiator contributes to a more effective free radical generation mechanism when associated to the conventional CQ/Amine system.[14] This trend could also be explained from the PAE of Irgacure 819/Optilux and CQ/Ultrablue IS pairs in the present evaluation, where both systems showed the highest value among their group (Fig. 4(b) and (d)).

Fig. 6 shows the normalized PAE for the same systems as above. In this graph the values are normalized for energy output of the lamps and for wt% of the initiator. Thus, it is possible to compare the efficiency for lamps with different energy output, as well as take into account the concentration of the photoinitiator (as used in the formulation specifications). Here it can be observed that in terms of weight concentration, PPD is the more efficient initiator, mainly due to its low molecular weight when compared with the phosphine oxides. Another factor that contributes in this case is its good overlap with the LCUs. It can also be observed that the efficiencies for UBI and UBIS sources are very similar when normalized by energy

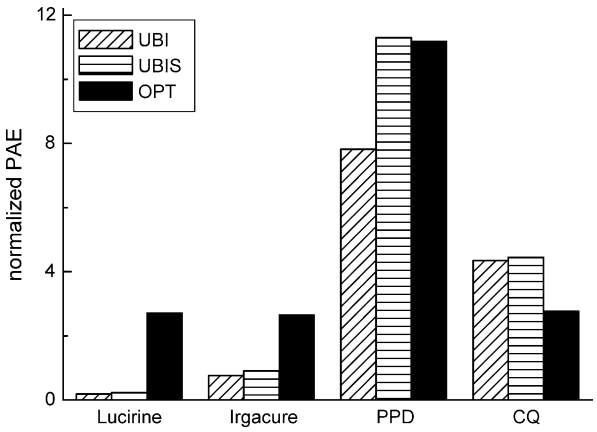

Fig. 6 Photon absorption efficiency (PAE) for various photoinitiators irradiated by different light sources, normalized for photoinitiator concentration (in wt%) and lamp energy output.

output, although UBIS is always somewhat more efficient due to the shift of the output to shorter wavelengths.

Conclusions

When comparing absorption values of photoinitiators on a molar extinction basis, all but CQ have significant absorption below 400 nm, remarkably higher than CQ. At 470 nm, PPD and CQ have equivalent molar absorbance, although PPD showed higher values below this wavelength.

Among the absorption profile of photoinitiators used in this study, resin formulations containing PPD and CQ seem to be more appropriate to be used for light curing, as they absorb a larger proportion of the photons in the range emitted by most LCUs. Due to its broader emission in the near UV-Vis range, Lucirin and Irgacure should be preferentially used with QTH LCUs, although the new high-power LED LCUs will also be efficient for Irgacure 819 when compared to a QTH lamp.

A parameter that takes account of the absorption properties of the photoinitiators, as well as the spectral output of the curing lamps, seems highly desirable in order to evaluate the real polymerization potential of a determined resin/LCU system. This lead us to define a photon absorption efficiency, which accounts for all the photons absorbed in a specific system that might initiate polymerization. Differences due to higher initiator concentrations or different lamp outputs can be taken into account by simply multiplying the PAE by the appropriate factors.

Moreover, manufacturers should inform the absorption profile of the dental resins on the product label or in the product data sheet, as well as the spectral band emitted by the LCU.[7]

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