Energy dependent polymerization of resin-based composites
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Chapter 3

Energy dependent polymerization of resin-based composite.

Introduction

The understanding of methacrylate-based polymerization of dental restorative materials is becoming increasingly important. This is due to a number of factors including the recent introduction of non-traditional curing sources (e.g. plasma arc lamps and lasers), curing techniques that promote a reduction in polymerization stress, and claims of curing resin-based composite (RBC) in thickness significantly greater than has been historically advocated. In all of these instances, the extent of polymerization (conversion) is a desired parameter to characterize since it relates to ultimate mechanical and dynamic mechanical properties [1], hardness and monomer solubility [2], fracture toughness [3] and wear [4].

Conversion of methacrylate functionalized dental restorative materials via photoinitiated polymerization is dependent upon several parameters. Monomer formulation has been shown to impact conversion of unfilled resins [1,5,6] and resin-based composite [7]. Even with the most reactive monomers, the fraction of reacted functional groups is significantly less than unity due to the highly cross-linked structure of the developing polymer. Increasing temperature increases the molecular mobility with a subsequent increase in conversion [8,9]. Conversion is also dependent upon the rate of polymerization and the exposure time. Since the former is impacted by the radiant intensity absorbed by the photoinitiator, the irradiance of the curing source and its spectral distribution become critical variables [10]. The efficiency of the photoinitiating system and oxygen quenching also affect the polymerization rate [10] and hence, the conversion. This inhibition is particularly noted at the outer surface of materials incorporating acrylate and methacrylate resins. Of all these variables, the irradiance of the light source and the exposure time are of

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particular interest since they, in practice, are amenable to manipulation by
the clinician.

The exposure time and intensity dependence on conversion of resin-based
dental materials or their conversion dependant properties has been a topic
of much investigation. Rarely, however, has the interdependence of
intensity and exposure time on conversion been explored. Of particular
interest is determining the conversion of acrylates and methacrylates
polymerized under conditions of equivalent radiant energy (dose) by
adjusting the irradiance (power density) and exposure time. Establishing a
reciprocal relationship between these two parameters would add
significance to the analysis of conversion as a function of radiant energy
rather than as two separate variables. The post-vitrification
polymerization of hexanediol diacrylate using differential scanning
calorimetry and FTIR has been reported [11]. In one set of experiments,
similar conversion for thin film samples measured via FTIR was reported
when maximally polymerized with equivalent doses using a UV source.
The exposure conditions, however, were well outside the range
encountered in dentistry (from over seven minutes up to 125 hours). For
bulk-cured dental RBC materials, similar depths of cure utilizing a
scrape-back method and similar conversion profiles from FTIR
measurements were found when cylindrical samples were polymerized
with equivalent doses [12]. Finally, equivalent fracture toughness, flexural
strength, and modulus values were found for four RBC materials when
equivalent doses were applied [13]. Although equivalent conversion with
an equivalent dose was inferred from these two studies, it was
demonstrated only through a limited range of conversions [12] or under
exposure conditions that are assumed to yield near maximum properties
[13].

It was the intent of the present study to explore the energy dependency on
conversion of resin-based composite by measuring conversion via FTIR
at doses sufficient to span the full conversion range and to examine the
reciprocal relationship between power density and exposure time at
selected points within this range.

**Methods and Materials**

The materials evaluated are identified in Table 1 and their composition
described in Table 2. All contain Bisphenol A diglycidyl ether dimethacrylate (Bis-GMA) together with one or more other dimethacrylate diluents.

**Table 1. Materials Investigated**

<table>
<thead>
<tr>
<th>Material</th>
<th>Code</th>
<th>Shade</th>
<th>Manufacturer</th>
<th>Lot no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heliomolar® radiopaque</td>
<td>HL</td>
<td>A3</td>
<td>Vivadent Schaan, Lichtenstein</td>
<td>AO2845</td>
</tr>
<tr>
<td>3M™Silux Plus™ Anterior Restorative</td>
<td>SP</td>
<td>U</td>
<td>3M Dental Products St. Paul, MN USA</td>
<td>8EL</td>
</tr>
<tr>
<td>XRV™ Herculite®</td>
<td>XR</td>
<td>A3</td>
<td>Kerr Corporation Orange, CA USA</td>
<td>712399</td>
</tr>
<tr>
<td>3M™ Z100™ Restorative</td>
<td>Z</td>
<td>A3</td>
<td>3M Dental Products St. Paul, MN USA</td>
<td>8WR</td>
</tr>
</tbody>
</table>

**Table 1. Material Composition (Bis-GMA: Bisphenol A diglycidyl ether dimethacrylate; TEGDMA: Triethylene glycol dimethacrylate; UDMA: Urethane dimethacrylate; DDMA: Decadiol dimethacrylate; Bis-EMA: Ethoxylated bis-phenol A dimethacrylate)**

All data obtained from manufacturer literature except as indicated.

<table>
<thead>
<tr>
<th>Code</th>
<th>Monomers</th>
<th>Fillers</th>
<th>Filler size</th>
<th>%Filler content</th>
</tr>
</thead>
<tbody>
<tr>
<td>HL</td>
<td>Bis-GMA, UDMA, DDMA</td>
<td>Colloidal Silica, copolymer, ytterbium trifluoride</td>
<td>0.04-0.2μm (range)</td>
<td>78/59 (wt/vol)</td>
</tr>
<tr>
<td>SP</td>
<td>Bis-GMA, TEGDMA</td>
<td>Colloidal Silica, copolymer</td>
<td>0.04μm (avg.)</td>
<td>56/40</td>
</tr>
<tr>
<td>XR</td>
<td>Bis-GMA*, TEGDMA*</td>
<td>Colloidal Silica, Barium-aluminum boro silicate</td>
<td>0.6μm (avg.)</td>
<td>67/46</td>
</tr>
<tr>
<td>Z</td>
<td>Bis-GMA, TEGDMA</td>
<td>Zirconia silicate</td>
<td>0.6μm (avg.)</td>
<td>84.5/66</td>
</tr>
</tbody>
</table>

* Reference [14]

**Conversion Profiles**

Transmission FTIR was utilized to determine monomer conversion as a function of radiant energy. Specimens were prepared by forming a thin film of composite (approximately 50 to 75 microns) between polyester film (25 micron) and a KBr plate. This assembly was placed on a slab of composite of the same type being measured and irradiated with a tungsten halogen curing light (3M™XL 3000 Curing Lamp, 3M, St. Paul, MN, USA). The radiation energy of the curing lamp at full output was

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determined using a power meter (Power Max 500D Laser Power Meter, Molelectron Detector Inc., Portland, OR, USA) integrating the radiant power with respect to time over the interval of zero to 30 seconds (a constant irradiation time of 30 seconds was chosen to determine the curing profiles). Bandpass filters were used to limit the measured bandwidth between 400 and 500nm. Power density was determined by dividing the measured power by the cross sectional area of the light guide. Because of the limited response time of the above meter when determining the light output immediately after being switched on, a second power meter was used (351 Power Meter, UDT Instruments, Baltimore, MD, USA) to measure the power output of the curing lamp during the first five seconds. This data was then included in the determinations of the integrated energy after cross calibration of the two meters. Attenuation was achieved by neutral density filters placed between the light guide and the KBr plate. The attenuation factor of the filters together with the KBr plates were determined using the latter power meter (351 Power Meter) and the aforementioned curing lamp. The spectral output of the curing lamp with and without filtering was recorded with a spectroradiometer to ensure that the filters attenuated the spectral output without changing the spectral distribution. Infrared spectra were recorded with a Magna 550 FTIR spectrometer (Nicolet, Madison, WI, USA) using 32 scans at a resolution of 4cm\(^{-1}\). Spectra were collected at five minutes from start of cure and 24 hours post-irradiation. A background spectrum of the polyester film was made prior to each sample spectrum. Conversion was calculated from the decreasing absorbance of the methacrylate carbon double-bond vibration at 1638cm\(^{-1}\) using as an internal reference the aromatic skeletal absorbance from Bis-GMA at 1582cm\(^{-1}\). Integrated areas of both peaks were determined using a standard baseline technique. After the five-minute measurement was complete, samples were stored at room temperature in nitrogen until the 24-hour spectra were recorded. Each test condition was run in triplicate.

\textit{Power density / exposure time reciprocity}

Reciprocity was examined for materials XR and Z at four applied energy levels. A series of samples prepared as above were irradiated with equivalent doses by adjusting the exposure time and power density. This process was accomplished by determining the exposure time required to yield a desired energy level through integration of the unattenuated lamp
output and accounting for a filtering factor. Spectra were recorded after five minutes from start of irradiation and again after 24 hours. Conversion was determined using the same method described above. Results within each energy level were analyzed with one-factor ANOVA and compared for differences using Fisher Protected LSD at a .05 significance level. Each test condition was run in triplicate.

Results

Figure 1 shows the unattenuated power output of the curing lamp. As with many tungsten halogen curing devices, the power decays after reaching a maximum output shortly after being switched on. An alternative would have been to let the power stabilize before initiating exposure. It was the intent of the present investigation, however, to operate the lamp as it would be used in practice. Figures 2 through 5 show conversion as a function of radiant energy at five minutes and 24 hours for the four materials evaluated. The abscissa has been split to increase the resolution of the data at low energies. It is also instructive to compare the curing profiles between materials by expressing the conversion as a percentage of the maximum 24-hour conversion. This is shown in Figures 6 and 7 for the 5-minute and 24-hour measurements respectively. These two figures show the full data collected. Although no statistical differences within a material were measured over the upper three-quarters of the exposure energy range, a trend towards maximum conversion with increasing power density is seen. Finally, Tables 3 and 4 show conversions obtained at equivalent energy doses for materials XR and Z. Statistically significant differences between means (p=.05) within an energy level are identified with letter designation for both the 5-
Figure 2. Heliomolar – conversion vs. applied energy. Each point represents an average of three measurements.

Figure 3. Silux Plus – conversion vs. applied energy. Each point represents an average of three measurements.

Figure 4. Herculite XRV – conversion vs. applied energy. Each point represents an average of three measurements.

Figure 5. Z100 – conversion vs. applied energy. Each point represents an average of three measurements.
**Figure 6.** Five-minute curing profile: five-minute conversion values are shown relative to the maximum 24 hour conversion.

**Figure 7.** 24-hour curing profile: 24-hour conversion values are shown relative to the maximum 24 hour conversion.

minute and 24-hour values. There appears to be a slightly greater range for the 5-minute measurements compared to the 24-hour values within a given dose, though this is not true for all groups. The 24-hour values show quite similar conversion at a given dose for the four levels.
Table 3. Conversion at equivalent radiant energy for material XR (mean values designated with the same superscripts are statistically equivalent, \( p=0.05 \)). \( n=3 \) per group

<table>
<thead>
<tr>
<th>Energy (mJcm(^{-2}))</th>
<th>*Exposure time (s)</th>
<th>Conversion (%)</th>
<th>5 Minute</th>
<th>24 Hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>3931</td>
<td>7</td>
<td>47.7(0.8) (^a)</td>
<td>60.3(1.4) (^a)</td>
<td></td>
</tr>
<tr>
<td>3931</td>
<td>30</td>
<td>48.7(1.2) (^a)</td>
<td>60.7(1.0) (^a)</td>
<td></td>
</tr>
<tr>
<td>3931</td>
<td>70</td>
<td>50.6(0.9) (^b)</td>
<td>61.8(0.5) (^a)</td>
<td></td>
</tr>
<tr>
<td>3931</td>
<td>158</td>
<td>51.9(0.6) (^b)</td>
<td>61.0(0.5) (^a)</td>
<td></td>
</tr>
<tr>
<td>1724</td>
<td>6</td>
<td>44.7(0.9) (^a)</td>
<td>57.5(1.5) (^a)</td>
<td></td>
</tr>
<tr>
<td>1724</td>
<td>13</td>
<td>45.6(0.3) (^a)^(^b)</td>
<td>58.1(0.3) (^a)^(^b)</td>
<td></td>
</tr>
<tr>
<td>1724</td>
<td>30</td>
<td>46.6(0.7) (^c)^(^d)</td>
<td>58.7(1.0) (^a)^(^b)</td>
<td></td>
</tr>
<tr>
<td>1724</td>
<td>67</td>
<td>48.0(0.7) (^c)^(^d)</td>
<td>59.2(0.7) (^b)</td>
<td></td>
</tr>
<tr>
<td>1724</td>
<td>120</td>
<td>49.2(0.9) (^d)</td>
<td>59.2(0.7) (^b)</td>
<td></td>
</tr>
<tr>
<td>314</td>
<td>3</td>
<td>36.2(0.4) (^a)</td>
<td>46.6(0.9) (^a)^(^b)</td>
<td></td>
</tr>
<tr>
<td>314</td>
<td>6</td>
<td>35.8(0.4) (^a)</td>
<td>45.8(1.0) (^a)</td>
<td></td>
</tr>
<tr>
<td>314</td>
<td>12</td>
<td>37.4(0.8) (^b)^(^b)</td>
<td>46.2(1.8) (^a)</td>
<td></td>
</tr>
<tr>
<td>314</td>
<td>21</td>
<td>38.0(0.5) (^c)^(^d)</td>
<td>46.0(1.4) (^a)</td>
<td></td>
</tr>
<tr>
<td>314</td>
<td>40</td>
<td>38.8(0.5) (^c)</td>
<td>48.1(1.8) (^a)^(^b)</td>
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</tr>
<tr>
<td>314</td>
<td>86</td>
<td>39.8(0.4) (^d)</td>
<td>48.8(1.4) (^b)</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>8</td>
<td>13.8(2.3) (^a)</td>
<td>14.6(2.5) (^a)</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>14</td>
<td>13.0(1.3) (^a)</td>
<td>13.2(2.5) (^a)</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>30</td>
<td>11.8(1.2) (^a)</td>
<td>11.3(2.6) (^a)</td>
<td></td>
</tr>
</tbody>
</table>

\(^*\) determined from integration of unattenuated power output and a filtering factor to yield the desired energy.
Table 4. Conversion at equivalent radiant energy for material Z (mean values designated with the same superscripts are statistically equivalent, p=0.05). n=3 per group.

<table>
<thead>
<tr>
<th>Energy (mJ/cm²)</th>
<th>*Exposure time(s)</th>
<th>Conversion (%)</th>
<th>5 Minute</th>
<th>24 Hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>3931</td>
<td>7</td>
<td>37.2(0.7)</td>
<td>48.5(0.7) a</td>
<td></td>
</tr>
<tr>
<td>3931</td>
<td>30</td>
<td>39.5(0.9) b</td>
<td>50.3(0.9) b</td>
<td></td>
</tr>
<tr>
<td>3931</td>
<td>70</td>
<td>40.4(1.0) b c</td>
<td>50.3(1.0) b</td>
<td></td>
</tr>
<tr>
<td>3931</td>
<td>158</td>
<td>41.7(0.7) c</td>
<td>51.6(0.7) b</td>
<td></td>
</tr>
<tr>
<td>1724</td>
<td>6</td>
<td>34.7(1.4) a</td>
<td>45.0(1.1) a</td>
<td></td>
</tr>
<tr>
<td>1724</td>
<td>13</td>
<td>35(0.2) a</td>
<td>45.7(0.5) a b</td>
<td></td>
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<tr>
<td>1724</td>
<td>30</td>
<td>36.5(1.3) a b</td>
<td>46.9(1.1) b</td>
<td></td>
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<tr>
<td>1724</td>
<td>67</td>
<td>37.4(0.9) b</td>
<td>46.8(0.03) b</td>
<td></td>
</tr>
<tr>
<td>1724</td>
<td>120</td>
<td>37.3(0.7) b</td>
<td>46.7(1.4) a b</td>
<td></td>
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<tr>
<td>314</td>
<td>3</td>
<td>24.6(0.8) a b</td>
<td>31.8(1.5) a b</td>
<td></td>
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<tr>
<td>314</td>
<td>6</td>
<td>24.2(1.0) a</td>
<td>30.6(1.3) a</td>
<td></td>
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<tr>
<td>314</td>
<td>12</td>
<td>26.5(1.3) c</td>
<td>34.4(1.7) b c</td>
<td></td>
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<tr>
<td>314</td>
<td>21</td>
<td>26.4(0.5) a b c</td>
<td>33.5(1.2) b c</td>
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<td>314</td>
<td>40</td>
<td>27.1(1.7) c</td>
<td>35.5(1.2) c</td>
<td></td>
</tr>
<tr>
<td>314</td>
<td>86</td>
<td>26.4(1.8) a b c</td>
<td>35.3(2.2) c</td>
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<tr>
<td>113</td>
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<td>11.5(0.8) b</td>
<td>12.6(0.6) a</td>
<td></td>
</tr>
</tbody>
</table>

* determined from integration of unattenuated power output and a filtering factor to yield the desired energy.
Discussion

Consistent with previous studies on dental resins [1] and resin based composite [7] a limiting conversion was found at maximum intensity. This result is characteristic of highly crosslinked polymers in which the developing network severely restricts the mobility of the reacting constituents. It is also apparent from the figures that significant conversion occurs post-irradiation in the interval between five minutes and 24 hours. For each material, the extent of the "dark-cure" is consistent throughout the plateau extending into the "knee" of the curing profile. This additional cure from five minutes to 24 hours represents, depending upon the material, as much as 19 to 26% of the final conversion. Below the knee of the curing profile, the dark-cure measured within this interval decreases though it is still measurable even at very low intensities. Due to the lag between the end of exposure and the first measurement (four and one-half minutes) the full extent of post-irradiation conversion is not represented throughout the curing profile. Though data was not collected within this time interval at low conversion, supporting experiments have shown the additional cure to be as much as 35% when measured from the end of a 30 second exposure for material Z when converted maximally (unpublished data). Approximately 37 and 62 percent of this occurs within the first five and 60 minutes respectively. Post-irradiation conversion for RBC inlay materials from measurements made immediately after irradiation and 24 hours later have been reported [15]. Additional conversion approaching 30 percent relative to the final measurement was found for some of the materials when polymerized maximally. Although the post-irradiation polymerization of resin-based composite has been described previously via hardness measurements [16], a non-linear correlation with conversion [2] prevents a direct comparison. These previous experiments are in agreement with the results of this study that extensive post-irradiation polymerization does occur over the first twenty-four hours.

As noted previously, the conversion within an increment of a given thickness of material will be related to the efficiency of the photoinitiating system, the intensity at the increment and the irradiation time. Figures 6 and 7 reveal similar curing profiles when conversion is represented relative to the maximum 24-hour conversion. While this was not predicted, it might be understood, in part, by considering the widespread use of photoinitiating systems based on camphorquinone.
(CPQ) and tertiary amines. While no attempt was made to identify the specific amine present in all the materials investigated, manufacturer's data, together with gas chromatographic results, revealed that all materials use CPQ. Below the knee of the curing profile, a greater range in fractional conversion between the materials is noticed at a given energy. Structural differences in the dimethacrylate monomers used in these materials may account for this effect either through differences in chemical reactivity due to steric or polar differences [17], or to pendant group mobility [18]. The differences noted may also be due, in part, to filler composition through a radical termination mechanism [19].

The influence of power density on the extent of conversion is readily illustrated through its relationship to the polymerization rate. With continuous illumination, the rate of free radical polymerization of acrylates and methacrylates follows a characteristic pattern throughout the course of the reaction due to diffusion limitations on the reacting species. This pattern is manifested early in the reaction by a decrease in the radical termination rate and a concurrent increase in the radical concentration. As a consequence, the rate of polymerization accelerates (autoacceleration) through a maximum despite a decreasing monomer concentration. After having passed through this maximum, the rate begins to decrease due to continuation in monomer consumption. As the network develops further, the rate of radical propagation eventually becomes diffusion limited and the polymerization rate decelerates, often towards a limited conversion in the presence of unreacted monomer and a significant population of radicals. Decreasing power density will decrease the rate of polymerization and shift the maximum rate to longer times [20]. Provided the irradiation time is not limited, conversion will continue through to its diffusion limited maximum. If irradiation is terminated while propagation is chemically controlled, the final conversion will be reduced from its maximum. The severity of this reduction is observed in Figure 7 where the rapid descent in conversion is observed to occur over a relatively narrow applied energy range relative to the full exposure. The conversions measured in this interval (0-500mJ/cm²) suggest that the rate of propagation has not yet come under appreciable diffusional control [6] and incomplete conversion results from terminating the reaction during the chemically controlled phase of propagation. A significantly greater energy expenditure is required for a much smaller change in conversion near the knee of the curing profile and into the plateau. This result is expected due to the greater diffusional limitations present at increased conversion.
In the previous discussion, it was noted that in order to increase conversion with lower power density, longer exposure times are required. Tables 3 and 4 reveal that increasing the exposure time under conditions of declining intensity such that the total energy remains constant has resulted in similar conversion. This result was consistent throughout the curing profile for both materials. Similar results were noted under conditions producing maximum conversion for a multifunctional diacrylate [11]. In the aforementioned study, while increased conversion was noted at the lowest intensities, this result occurred using extremely long exposure times (greater than twelve hours) and was explained from kinetic theory as being due to the dependency of kinetic chain length on intensity. In the present investigation, the exposure time was considerably less. Except as indicated in Tables 3 and 4, equivalent conversion at 24 hours was found at the doses investigated. Exceptions were generally found only at the shortest exposure times. Inadequate resolution of the measured lamp power (Figure 1) within the first ten seconds, during which it is changing most rapidly, is a likely contributing factor. For example, a single half-second temporal error will result in an approximate 25% error in integrated energy at an exposure time of 3 seconds. A consistent underexposure error of this magnitude in this timeframe is not unrealistic considering the procedure used to measure the energy. At 30 seconds, this magnitude of temporal error results in negligible error in integrated energy. The differences noted within a group are not expected to be a result of temperature increase at extended exposure times as photoinitiated copolymerization of acrylates between KBr plates has been shown to be isothermal [9]. It is presumed, in the present case, that a single KBr plate will yield similar conditions. Despite these slight differences in conversion, the reciprocity between exposure time and power density from a practical standpoint is amply demonstrated.

The observation of reciprocity for these materials extends the significance of the curing profiles since any combination of exposure time and power density within the range investigated will reproduce a similar curve. At the surface of bulk-cured RBC isolated from air, it is expected that the profile will be directly applicable in predicting the final conversion from the power density and exposure time. Insufficient conversion at this surface generally is not a concern since nearly maximum conversion can be achieved with relatively low power density and short exposure times (e.g. a ten second exposure with an incident
irradiance of 200mW/cm² is sufficient to achieve 90 percent of the maximum conversion—Figure 7). This profile is also expected to pertain within the depth of a composite where decreasing light intensity will shift the energy for a given exposure time toward the lower part of the curve. The decrease in energy will mirror the exponential decay of intensity with depth and will be composition dependent. Ideally, the transmission properties of light through RBC in conjunction with the conversion profile are sufficient to describe the percent conversion with depth. Preliminary data suggests this hypothesis to be true, and further work is in progress to verify this. Non-isothermal polymerization may limit the applicability of estimating conversion from a curing profile generated under presumed isothermal conditions.

Conclusion

Very similar curing profiles for four, commercially available, photoinitiated resin-based composite materials were observed when thin films were exposed to decreasing power density. Conversion at distinct points along this conversion profile can be duplicated with equivalent applied energy, which documents the reciprocal relationship between power density and exposure time over a timeframe of practical interest. The significance of these results is that given the curing profile for a resin based composite and its transmission properties for a curing light, the conversion at any point within the material can, in theory, be determined for any applied dose.
References


