Energy dependent polymerization of resin-based composites
Halvorson, R.H.

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Chapter 4

An energy conversion relationship predictive of conversion profiles and depth of cure for resin-based composite.

Introduction

A number of methods have been explored to characterize depth of polymerization of photoactivated resin-based composite (RBC) and understand the variables involved. The "scrape-back" technique (Cook, 1980) is perhaps the simplest of such methods and essentially delineates a polymerization boundary beyond which the resin is either grossly underpolymerized or completely unpolymerized. The length of the remaining composite has a logarithmic dependence for both the intensity of the light source and exposure time for UV (Cook, 1980) and visible light (Cook & Standish, 1983) polymerized RBC. The logarithmic relationship was predicted using a mathematical model for depth of cure based on the rate of initiation of free radical polymerization and incorporates the exponential attenuation of light intensity through composite thickness. This attenuation severely limits the length of the scrape-back sample that can be obtained as revealed in a study reporting only a modest increase in length (< 25%) upon doubling the exposure time (Ruyter and Øysed, 1982). It has also been shown that similar depths of cure (scrape-back) are obtained when the product of the irradiance and the exposure time is kept constant (Cook, 1982; Nomoto, Uchida, & Hirasawa, 1994). It was suggested that the depth of cure corresponds to the minimum amount of energy required to initiate polymerization.

To determine polymerization throughout composite requires more extensive methods such as hardness measurements (Cook, 1980; De Lange, Bausch & Davidson, 1980) or infrared spectroscopy (Eliades, Vougiouklakis & Caputo, 1987; Dewald and Ferracane, 1987). These techniques generally reveal a rapid decrease in hardness or conversion of methacrylate double bonds beyond a certain depth. Consistent with studies utilizing the scrape-back technique, the irradiance of the light source, the exposure time and light transmission of composite are significant variables that affect the hardness or conversion profile (i.e. variation with depth). It has been shown that similar conversion profiles (via FTIR) were obtained when an RBC was exposed under reciprocal irradiance-exposure time relationships (Nomoto & others, 1994). This suggests that the conversion at any point within the RBC is dependant upon the radiant energy available at that point. It is therefore useful to construct the relationship between the conversion of photopolymerized RBC and the exposure energy (the energy-conversion relationship or ECR). This has been performed for various commercial RBC in a thin film via transmission FTIR together with confirmation of the reciprocal nature of irradiance and exposure time (Halvorson, Erickson & Davidson, 2002). This ECR is applicable toward the goal of predicting conversion at the surface of photopolymerized RBC given the irradiance and time of exposure. Similarly, prediction of conversion at any point within an RBC may be accomplished from an ECR for bulk curing and knowledge of the light transmission of the RBC. The transmission curves are readily determined radiometrically and it should be possible, based on prior work, to define a unique ECR by measuring the conversion versus depth for a single shade of RBC at maximum irradiance. This data, combined with the transmission data can relate conversion to energy thereby providing the ECR.

The goals of the present investigation were to 1) determine the energy dependent conversion relationship (ECR) of commercial RBC and confirm that this describes a reciprocal relationship between irradiance and exposure time, 2) show that this relationship, together with transmission properties, can be use to predict the conversion profile for various exposure energies and RBC opacities, and 3) define a critical exposure energy that is predictive of scrape-back length for various exposure energies and RBC opacities.
Methods and Materials

Energy conversion relationship

Two small particle hybrid resin-based composites of similar shade (A3.5) were examined to construct the ECR’s: XRV™ Herculite® (Kerr Corp., Orange, CA, USA) and 3M™Z100™ Restorative (3M, St. Paul, MN, USA). The composition of these RBC materials has been described previously (Halvorson & others, 2002). Cylindrically shaped samples were prepared by packing RBC into a split stainless steel mold with an approximate 6mm diameter by 16mm length. The mold was assembled to include two stainless steel wedges positioned along the length of the mold, on opposite sides, with their internal edges protruding into the cylinder approximately one-half millimeter and their outside edges extending outside the sides of the mold. Two machine screws held the assembly in place during the packing and polymerization phase. Transparent polyester film was placed over the ends of the cylinder to confine the composite within the mold. The mold was then placed on a white background and positioned directly under and the 7mm diameter light guide of a tungsten-halogen lamp (3M™XL 3000 Curing Lamp, 3M, St. Paul, MN, USA) with a nominal power density of 600mWcm⁻². This lamp was checked periodically throughout the experiment to monitor any deviations in its output. Samples were exposed for thirty seconds (18Jcm⁻²) and kept in the dark at room temperature for 24 hours. The screws were than removed and one of the wedges was gently tapped with a hammer, splitting the sample lengthwise down its center. The two halves were then separated, carefully teasing the unpolymerized end of the sample apart with a scalpel.

To determine conversion with depth, microscopic specimens were dissected with a scalpel at selected intervals down the length of each half using a binocular microscope. The microscopes reticle was used to determine the depth along the cylinder at which the specimen was dissected and its lamp was filtered to prevent additional polymerization. Dissection was confined to approximately the central third of the sample. Conversion of the dissected specimens was measured using transmission FTIR microspectroscopy. Specimens were placed on a KBr disc and measured in transmission with a Nic-Plan™ Microscope combined with a Magna-IR® 750 spectrometer (Nicolet, Madison, WI, USA) coadding 90 scans at a resolution of 4cm⁻¹. Three cylinders were prepared and analyzed for each group with three to five specimens measured at each depth from...
each cylinder. Conversion was determined by measuring the decreasing absorbance of the methacrylate carbon double-bond vibration at 1638 cm\(^{-1}\) using as an internal reference the aromatic skeletal absorbance from Bis-GMA at 1582 cm\(^{-1}\). Integrated areas of both peaks were determined using a standard baseline technique. The radiation energy density of the curing lamp was determined using a power meter (Power Max 500D Laser Power Meter, Molelectron Detector Inc., Portland, OR, USA) integrating the radiant power density over the thirty second exposure time. Power density was determined by dividing the measured power by the cross sectional area of the light guide.

The transmittance \(T = \frac{P}{P_0}\) at thicknesses for each RBC shade was determined by polymerizing the respective materials in 6mm diameter stainless steel molds of various lengths. The polymerized sample together with its mold was placed on the detector of a power meter (351 Power Meter, UDT Instruments, Baltimore, MD, USA) centering the light guide of the curing lamp over the mold and in contact with the sample. The power measured in this fashion \(P\) was divided by the unattenuated power \(P_0\) obtained by placing the light guide in direct contact with the detector head. A minimum of three replications was done for each condition and a mean value was determined. Transmission as a function of thickness was determined by regression analysis of the data. Small errors may be introduced by using only transmission data from cured composite but the benefits in simplifying the analysis justify this procedure. The energy exposure at depths \(E_d\) where FTIR specimens were dissected was determined from the incident energy \(E_0\) and the transmittance \(E_d = \%T_d x E_0\). This permitted conversion to be related to energy and thereby define an ECR for the Z100 and Herculite RBC materials.

**Predicted conversion profiles**

Predicted conversion profiles were obtained by determining the energy density transmitted to various depths from the transmittance curves and the incident energy density. The corresponding conversions obtained from the Z100 ECR were plotted as a function of depth to yield the predicted conversion profiles. Profiles for Z100, shades A1, A3.5 and CY were predicted at various exposure conditions (see Figure 4). The curves were experimentally verified by FTIR microspectroscopy using methods described above.
Scrape-back length: measured and predicted

Identical molds as that described above for FTIR sampling (without wedges) were used to determine the depth of cure via the scrape-back technique. The samples were prepared as described above and exposed to the curing light at various energy densities. After 24 hours at room temperature, the molds were disassembled and the poorly polymerized material gently scraped off with a rigid plastic spatula. Three replicates were prepared and the length along the cylinder axis was measured to the nearest 0.01mm. Average scrape-back lengths for Herculite and Z100 (A3.5 shade) exposed to 18 Jcm\(^{-2}\) were used to define a critical energy density associated with the scrape-back lengths utilizing the transmission data and incident energy density. The critical energy density together with transmission data was subsequently used to predict scrape-back lengths for other materials and curing conditions. Conversions at the scrape-back lengths were determined from the ECR for the critical energy density.

Results

Conversion profiles as measured with FTIR microspectroscopy for shade A3.5 of Herculite and Z100 at an exposure energy of 18Jcm\(^{-2}\) are shown in Figure 1. Maximum conversion for Herculite is greater than for Z100 and reflects differences in the formulation of these two RBC materials.

Although both materials are designated as A3.5 shades, there is a greater depth of cure for Z100 because of its lower opacity (see Figure 2). Figure 2 shows the percent transmittance curves for the materials investigated and describes the expected exponential decrease in energy with depth. Regression analysis reveals an exponential relationship between transmittance and depth with the attenuation coefficient defined by the
slope of the line and \( R^2 \) values very close to 1.000. Using the regression equations and the incident light energy density, the energy density at depths corresponding to the measured conversion in Figure 1 was calculated and ECR’s were plotted as shown in Figure 3. In this comparison, the conversion for both materials has been expressed relative to their maximum measured conversion and it is apparent that the ECR curves on a relative conversion basis are very similar.

**Figure 2.** Percent transmittance versus depth. H:Herculite, Z:Z100.

**Figure 3.** Energy conversion relationship (ECR) for Herculite and Z100 derived from their respective conversion profiles and transmittance curves. Conversion is expressed relative to the maximum 24 hour conversion.

**Figure 4.** Predicted conversion profiles (solid lines) for the indicated shades and exposure conditions for Z100 together with experimental values from FTIR analysis. Legend: (incident energy density,mJ/cm² / irradiance,mWcm² / exposure time,s).
Using the ECR for Z100 together with transmittance curves and the incident energy density, conversion profiles for Z100 shades A1, A3.5 and CY were predicted as shown in Figure 4. Experimental values obtained by FTIR microspectroscopy are also shown in Figure 4 and depict a reasonably good fit to the predicted curves. The variability of the experimental values is similar to the variability of the average values for the conversion profiles depicted in Figure 1, and is greatest at the steepest portion of the curve. The precision of the predicted curves will be affected mostly by the precision represented in the conversion profile for Z100 (Figure 1) from which the ECR was derived.

The scrape-back lengths and exposure conditions for shade A3.5 of both materials are shown in Table 1. Comparison of conversion profiles in Figures 1 to their respective scrape-back values in Table 1 reveal that the latter are several tenths of millimeters shorter than the extrapolated depth at zero conversion and that conversion at the scrape-back depth is approximately 20 percent for Herculite and 22 percent for Z100. These conversions represent a local exposure of approximately 32 mJcm\(^2\) for each of the materials as determined from the ECR. This energy density will be defined as the critical scrape-back energy density. Figure 5 presents a photograph of material Z100-A3.5 prepared as described for sample dissection after 24 hours together with the corresponding conversion-depth profile from Figure 1. To enhance the contrast between cured and uncured material, the split sample has been stained with a dye (Astra Blue) that has an affinity for the dimethacrylate monomers (de Gee, ten Harkel-Hagenaar, Davidson, 1984). The scrape-back length and associated conversion (Table 1) are indicated in the figure. Beyond the scrape-back depth, a region exists that exhibits very low cohesion and terminates as a granular appearing zone with a gelatinous consistency. The terminus of this zone, at approximately 6.7mm, corresponds to the extrapolated depth at zero conversion. The corresponding energy density was determined from the ECR to be 21mJcm\(^2\).

<table>
<thead>
<tr>
<th>Material</th>
<th>Scrape-back length (mm)</th>
<th>Conversion at scrape-back (%)</th>
<th>Energy density (mJ/cm(^2))</th>
<th>Irradiance (mW/cm(^2))</th>
<th>Exposure time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Herculite-A3.5</td>
<td>5.27 (0.07)</td>
<td>20</td>
<td>18,000</td>
<td>600</td>
<td>30</td>
</tr>
<tr>
<td>Z100-A3.5</td>
<td>6.19 (0.10)</td>
<td>22</td>
<td>18,000</td>
<td>600</td>
<td>30</td>
</tr>
</tbody>
</table>
Figure 5. Sample of Z100 A3.5 exposed with 18,000mJcm² (600mWcm²/30s) prepared as described for specimen dissection and FTIR analysis (24 hours). Sample has been stained with a dye (astra blue) that has an affinity for dimethacrylate monomers. The conversion profile for Z100-A3.5 depicted in Figure 1 and exposed under identical conditions is shown for comparison.

Table 2.
Predicted and experimental scrape-back lengths.

<table>
<thead>
<tr>
<th>Material</th>
<th>Scrape-back length (mm)</th>
<th>Energy density (mJcm²)</th>
<th>Irradiance (mWcm²)</th>
<th>Exposure time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Predicted</td>
<td>Experimental</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-A3.5</td>
<td>NA</td>
<td>5.27 (0.07)</td>
<td>18,000</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>5.30</td>
<td>5.29 (0.04)</td>
<td>18,000</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>4.33</td>
<td>4.21 (0.08)</td>
<td>6160</td>
<td>560</td>
</tr>
<tr>
<td></td>
<td>4.33</td>
<td>4.30 (0.10)</td>
<td>6160</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>4.33</td>
<td>4.31 (0.14)</td>
<td>6160</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>2.16</td>
<td>2.14 (0.08)</td>
<td>560</td>
<td>28</td>
</tr>
<tr>
<td>Z-A3.5</td>
<td>NA</td>
<td>6.19 (0.01)</td>
<td>18,000</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>6.19</td>
<td>6.29 (0.19)</td>
<td>18,000</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>5.07</td>
<td>5.06 (0.16)</td>
<td>6160</td>
<td>560</td>
</tr>
<tr>
<td></td>
<td>5.07</td>
<td>5.14 (0.13)</td>
<td>6160</td>
<td>310</td>
</tr>
<tr>
<td></td>
<td>5.07</td>
<td>5.16 (0.09)</td>
<td>6160</td>
<td>170</td>
</tr>
<tr>
<td></td>
<td>2.54</td>
<td>2.54 (0.01)</td>
<td>560</td>
<td>28</td>
</tr>
<tr>
<td>Z-A1</td>
<td>8.23</td>
<td>8.09 (0.08)</td>
<td>18,000</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>5.50</td>
<td>5.31 (0.02)</td>
<td>2430</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td>3.50</td>
<td>3.27 (0.12)</td>
<td>560</td>
<td>28</td>
</tr>
<tr>
<td>Z-CY</td>
<td>5.27</td>
<td>5.26 (0.10)</td>
<td>18,000</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>4.45</td>
<td>4.31 (0.04)</td>
<td>7110</td>
<td>355</td>
</tr>
<tr>
<td></td>
<td>2.20</td>
<td>2.10 (0.06)</td>
<td>560</td>
<td>28</td>
</tr>
</tbody>
</table>
Predicted scrape-back lengths are shown in Table 2 together with experimentally derived values. Predicted values were determined using the critical scrape-back energy (32mJcm$^{-2}$). The good agreement between the predicted and measured values suggests that the critical energy is unique for both RBC materials and applies to varying shades of material and curing conditions. Figure 6 shows predicted curves relating scrape-back length and exposure energy for Z100 shades A1, A3.5 and CY. Measured scrape-back lengths for selected exposure energies are superimposed. Corresponding results for Herculite are shown in Figure 7. The experimental scrape-back values are in good agreement with the predicted curves and verify the logarithmic dependence between scrape-back length and exposure energy.

**Figure 6.** Predicted scrape back lengths (solid lines) as a function of the incident energy density together with experimental values for the indicated shades of Z100.

**Figure 7.** Predicted scrape back lengths (solid line) as a function of the incident energy density together with experimental values for Herculite A3.5.

Figure 8 shows conversion profiles, each for an incident energy density of 18Jcm$^{-2}$ but with different incident irradiance and time of exposure for Z100-A3.5. The excellent overlap of these two profiles confirms a reciprocity relationship between irradiance and time. Similar
confirmations of reciprocity are seen in Table 2 where similar scrape-back lengths are observed when total energy density is conserved. One-factor ANOVA showed that the scrape-back values obtained with constant energy densities were equivalent.

**Figure 8.** Conversion profiles for Z100 A3.5 produced from samples exposed with equivalent doses.

**Discussion**

In this study, predicting the extent of polymerization of RBC material throughout its thickness has been reduced to a set of variables by considering the energy-conversion relationship, the light transmitting properties of the RBC and the applied radiant energy. The results have shown that an ECR, derived from a single shade of RBC, can be used to predict conversion profiles for a range of shades at various exposure conditions. Specifically, the ECR describes the local energy density required to obtain a given normalized conversion at any depth in the material, independent of shade and reflects the combined polymerization efficiency of the monomer composition and photoinitiating system. The ECR has previously been described for other commercial RBC’s using a thin film technique that predicts surface conversion (Halvorson & others, 2002). Predicting conversion within RBC using the thin film technique, however, is limited to exposure conditions that yield near maximum conversion. This limitation is possibly due to an inhibition mechanism and requires further investigation. Both techniques are consistent, though, in describing similar ECR’s across different RBC compositions and both confirm reciprocity between time and irradiance. The similar ECR’s are likely a consequence of the widespread use of resins based on the dimethacrylate, Bis-GMA and photoinitiator consisting of camphorquinone and amine.
For a given chemistry, the ECR suggests that transmission properties of the RBC ultimately determine the conversion profile and depth of cure. This is shown by the transmission curves for Z100 (Figure 2) and the predicted and experimental conversion profiles obtained with an 18 Jcm\(^2\) exposure (Figure 4). The significance of similar ECR’s across materials is shown for Herculite A3.5 and Z100 CY, where identical scrape-back lengths at an 18 Jcm\(^2\) exposure are predicted from their nearly identical transmission curves (Figure 2). The regression equations in Figure 2, describing the exponential decrease in percent transmittance with depth, conform to the Lambert Law (Christian, 1977) and represent the combined effects of reflection, scattering and absorption. Analysis of the regression equations revealed that surface reflected radiation, identified by the y-intercept, is as much as 38 percent of the incident radiation. Thus, the maximum fractional conversion, observed in Figure 3 (relating to surface measurements in Figure 1), correspond to energy densities significantly less than the 18 Jcm\(^2\) incident energy. This loss is considerable, though less than that measured for similar commercial RBC’s in another study (Watts & Cash, 1994). The effect of shade on attenuation reveals the expected result for Z100, showing progressively decreasing attenuation from the darkest (CY) to the lightest (A1) shade corresponding to a progressive change in opacity. However, shade designations, per se, are not necessarily a predictor of the relative curing potential (Ferracane & others, 1986; Matsumoto & others, 1986). Similar shade designations of various commercial materials may show substantial differences in attenuation and depth of cure due to differences in opacity (Shorthall, Wilson & Harrington, 1995) as indicated in Figure 1 for the A3.5 shades of Z100 and Herculite.

The value of the ECR as a predictive tool relies on the dose dependent conversion and the reciprocal nature of irradiances and exposure time. The dose dependency has previously been described from a kinetic model of the free radical polymerization of methacrylates that relates depth of cure to the product of the intensity and exposure time (Cook, 1980; Cook, 1982). Support for reciprocity in the present investigation is noted in the scrape back-values for the A3.5 shade of Herculite and Z100 light-cured with different irradiances and exposure times to yield total exposures of either 18 Jcm\(^2\) or 6160 mJcm\(^2\) (Table 2) and with depth profiles for Z100 A3.5 shown in Figure 8. The latter compares the data in Figure 1 for Z100 A3.5 with the experimental data of the same material in Figure 4 where a sixty percent reduction in irradiances has been compensated with
an equivalent increase in exposure time. These results verify similar findings obtained for thin films over a multiple dose range (Halvorson & others, 2002). Additional evidence for the reciprocal irradiance/exposure time relationship has been presented for bulk-polymerized specimens (Nomoto & others, 1994, Miyazaki & others, 1996).

The usefulness of the ECR in predicting conversion profiles for various shades of RBC and various incident curing exposures is demonstrated by the results shown in Figure 4. The predicted conversion profiles are in reasonably good agreement with the measured values. An implicit assumption in predicting profiles for various shades of material is that there are no changes in the formulations of monomer content or photoinitiator levels. This is generally a good assumption for commercially available materials.

The extent of cure at the terminus of the scrape-back sample has generally been considered to be significantly less than the maximum attained conversion. In studies characterizing the hardness or conversion profile through RBC, extrapolated depths at zero hardness or conversion were felt to correspond favorably to the length remaining after gently removing the uncured material (Cook, 1980; Nomoto & others, 1994). Under a kinetic model (Cook, 1980), the exposure energy at this depth relates to the minimum energy required to initiate polymerization. However, in the present study, the scrape-back length corresponds to approximately 20 percent conversion and a related unique critical scrape-back energy of 32mJcm⁻². This length obviously does not identify the minimum required polymerization energy. The latter can be identified by the split sample shown in Figure 5 where the sample terminates at a clearly visible delineation. This length corresponds to an energy density of approximately 21 mJcm⁻² for all the materials investigated. The different results between the present and above referenced studies with respect to the extent of cure at the scrape-back terminus are, perhaps, related to a small inaccuracy in extrapolating conversion to the zero point (Nomoto & others, 1994) and to the definition of the scrape-back conversion in the kinetic model (Cook, 1980). It is expected that even with great care to keep it intact, the gelled material, identified in Figure 5, will be readily lost during scrape-back. It is likely that the scrape-back length is determined by a degree of polymerization where sufficient mechanical properties are developed to resist moderate abrasive forces, and in this study this is characterized to be about 20-22 percent.
conversion. The scrape-back measurements have also demonstrated that the scrape-back length is logarithmically related to the exposure as shown in Figure 6 and 7 where the predicted cures and experimental values are in good agreement. This is reflective of the logarithmic attenuation of light intensity and its affect on free radical generation as described by the model referenced above (Cook, 1980).

Though the minimum cure required for maintenance of acceptable clinical performance of an RBC material is not known, a recommendation has evolved, based on comparative analysis of scrape-back, hardness, solubility and sorption measurements (Fan & others, 1986). From these measurements, the depth at one-half the scrape-back length corresponded to the depth at which the relative solubility started to increase and was marginally less than the depth corresponding to 80% of the maximum knoop hardness. The current ISO standard also defines an acceptable cure depth as one-half the scrape-back length as measured immediately after curing (International Organization for Standardization, 2000). In the present study, this value corresponds to approximately 90% of the maximum measured conversion at 24 hours for the materials investigated here. It should be noted that the test method defined by this standard was modified in the present investigation to conform to the sample preparation for FTIR analysis. Scrape-back lengths determined using a 4mm diameter mold as per the standard have been observed to be around ½ mm shorter than values described in this report (personal observation). Similar mold effects have been reported previously (Fan & others, 1984). While mold geometry may impact scrape-back length, the cohesion at the scrape-back length is expected to represent a unique conversion independent of mold geometry. As shown, this conversion is approximately 20% for both materials and is expected to be similar for other RBC’s formulated with similar chemistry.

Some results of this investigation are expected to be dependent upon certain experimental conditions. Light transmission through the composite is likely to include interactions with the walls of the metal mold. In this investigation, such interactions are equalized by using the same mold materials and geometry throughout. Consequently, predictions from the described ECR’s would be accurate only for samples prepared in similar molds; for different molds, new transmission curves would be needed for use with the ECR. The reaction temperature will impact the final conversion that is attained in free-radical polymerization of RBC
(Maffezzoli & others, 1994). Hence, ECR's derived from samples prepared at different temperatures may not correspond to those described here. The impact of different reaction temperatures may be minimized, however, by expressing the conversion relative to the maximum attained conversion as in Figure 3. However, it is expected that conversion at scrape-back will be unaffected by these experimental factors. Finally, ECR's derived from samples cured with plasma arc lamps or devices based on light emitting diodes may be different due to radiated heat associated with the former and possibly greater polymerization efficiency of the latter.

**Conclusion**

This study has shown that an energy-conversion relationship can readily be determined that is predictive of the conversion profiles for a family of RBC materials under variable light-curing conditions. It has further been confirmed that depth of cure is logarithmically related to the energy of exposure and that reciprocity between time and irradiance pertains. From these results it is suggested that scrape-back lengths are correlated with about 20 to 22 percent conversion.
References


