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Use of near-IR to monitor the influence of external heating on dental composite photopolymerization

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Summary *Objectives*: This study was conducted to determine the effect of modest external heating on the photopolymerization kinetics and conversion of commercial dental composite restorative materials.

Methods: A transmission-mode, real-time near-infrared spectroscopic technique was used to monitor the photopolymerization process in the composite materials at various temperatures between 23 and 70 °C. Several light curing units, differing in spectral output and power densities were compared at the different cure temperatures. Several significantly different commercial composites were compared for their response.

Results: Regardless of the curing light or composite material used, photopolymerization at a moderate curing temperature of 54.5 °C resulted in significantly higher immediate and final conversion values compared with room temperature photocuring. Contrary to the room temperature cured materials, at the elevated cure temperature the extent of post-cure was minor and different curing lights produced very uniform conversion values within a given material. The time required to reach a given level of conversion, established as full conversion with the room temperature cure, was reduced typically by 80–90% using the elevated curing conditions. Complementary kinetic studies confirmed the effect of cure temperature on increasing the polymerization rate in dental composites as significant.

Significance: Increasing the temperature of composite resin within potentially biologically compatible limits can significantly influences resin polymerization. These increased rates and conversion could lead to improved properties of composite restorative materials.

Introduction

Warming of uncured composite restorative materials can potentially improve the handling properties during placement in a cavity preparation. Increased flow, better adaptation to the cavity wall, and for very stiff composites, easier placement, can all be realized. Recently a commercial device has been introduced[1,2] that can be used chair-side by the dentist to warm a composite for immediate delivery to the cavity preparation at temperatures in the range of approximately 50–60 °C. Upon delivery, the composite would begin cooling to reach thermal equilibrium with the surrounding tooth structure,

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which has been reported to range between room temperature and body temperature (37 °C), typically about 30 °C.[3] The ambient tooth temperature can depend upon location in the mouth, respiration of the patient and use of a rubber dam. Any thermal insult to reach the pulp would further depend on the thickness of remaining dentin and the thermal diffusivity of the tooth,[4-6] as well as the cavity preparation geometry,[7] and the temperature of the composite at the time of delivery. Depending on the time interval between composite placement and introduction of the curing light, the use of a heated composite offers the potential for intra-oral photocuring of restorative materials at moderately increased temperatures.

Composite restoratives establish highly cross-linked networks and under normal curing conditions achieve approximately 45–70% conversion. The comonomers and photoinitiators used, the filler particle size and type, and the interactions between monomers and filler all affect the rate of polymerization and the degree of conversion that can be attained.[8] The light source can also significantly impact the ability to polymerize the composite. The intensity of the light and the bandwidth of the light output could modify the response of the material. Conventional quartz–tungsten–halogen (QTH) lights have a broad bandwidth output, which is filtered to deliver blue light in the region of about 400–500 nm. The higher intensity xenon–plasma–arc lights (XPA) may have a narrower bandwidth, and the lower intensity light-emitting diodes (LED) typically provide a relatively narrow spectrum output. The design of the lights and filtering systems attempts to target the visible light absorption range of the most common visible light photoinitiator used in dentistry, camphorquinone, which has an absorption maximum at 460–480 nm. The various light sources can have different effects on composite curing based not only on the photoactivation of camphorquinone but also potentially through other photoinitiators with different peak absorption ranges in the visible light region.[9]

It is well known that the rate of polymerization, the resulting cross-linking density, and the ultimate degree of conversion of dimethacrylate-based monomers and resins can be enhanced by raising the temperature at which the photopolymerization is conducted.[10,11] These parameters will affect clinically important functional properties of the set composite. Prior real-time photopolymerization studies, which have included cure temperature as a variable, have been conducted primarily on unfilled di(meth)acrylate monomers and have relied primarily on photo-differential scanning calorimetry (photo-DSC) as the analytical tool.[12-19] In limited studies, thermal effects on the photopolymerization of diacrylate or dimethacrylate monomers has been examined by real-time mid-IR spectroscopy using thin films.[18,20] In one study, the effect of temperature on the photopolymerization kinetics of unfilled dimethacrylate resins was monitored by a near-IR (NIR) technique.[21] The use of NIR spectroscopy to measure conversion in dental resins has been validated in comparison with more traditional mid-IR techniques.[22] The use of NIR has the particular advantage that silica-based fillers are essentially transparent in this spectral region (14,000–4000 cm^{-1}) and thus, the technique appears appropriately suited for the study of highly filled dental composites.

The limited prior work focused on monitoring thermally assisted photocuring of dental composites, which involve comonomer mixtures and include particulate filler, has relied on DSC methods.[23-25] With dental composite formulations, the majority of studies related to thermal effects have focused on post-cure heating of materials to improve the final conversion and mechanical properties. It was shown that polymers with higher glass transition temperatures (T_g) could be prepared if the photopolymerization was conducted at an elevated temperature rather than photocuring at ambient temperature and then applying a post-cure heating cycle.[26] A linear relationship between photocure temperature and polymer T_g has been demonstrated over a curing temperature range of ambient to 90 °C for an ethoxylated bisphenol A dimethacrylate monomer.[15] Extra-oral photopolymerization of inlay and onlay composite materials is typically conducted at elevated temperatures in light-curing ovens to maximize the conversion that can be achieved. Again DSC analysis, which is restricted to very small specimen size (typically 1–10 mg), is the only technique that has been used to simulate the simultaneous interaction of temperature and light in dental composite materials.[27]

The focus of this investigation is to extend the use of NIR spectroscopy to examine the effect of modestly elevated photocuring temperatures on the dynamic polymerization of composite materials and to determine some practical limitations, which might be anticipated in its application to clinical dentistry.

Materials and methods

Materials

Three commercial restorative composite materials were used in this investigation: a microfill (M)

(Filtek A110, A3 dentin shade, 3M ESPE, St. Paul, MN, USA), a hybrid (H) (Herculite XRV, A3 enamel shade, Kerr, Orange, CA, USA) and a 'condensable' hybrid (C) (Surefil, shade B, Caulk, Milford, DE, USA). The light sources employed to cure the dental composites were three dental curing lights: a conventional QTH light (QHL 75, Caulk: output 380-510 nm with $\lambda_{max} = 490$ nm), a LED unit (Elipar FreeLight, 3M ESPE: output 430-500 nm with $\lambda_{max} = 470$-475 nm), and a XPA light (PAC) 1000, American Dental Technologies: output 430-500 nm with $\lambda_{max} = 470$-475 nm). These light sources were previously characterized with a spectroradiometer (Ocean Optics 1000 Dunedin, FL, USA) and a power meter (Ophir Wilmington, MA, USA), and the diameter of the light guide measured with a micrometer (Mitutoyo Tokyo, Japan). In addition, a 100 W high-pressure mercury arc lamp, (MAL) (Novacure, EFOS, Mississaugua, Ontario, Canada) was used with a bandpass filter to provide an output from 325 to 500 nm. Over this spectral region, the mercury arc lamp output is approximately evenly divided between a series of emission bands centered around 365 nm in the UV and isolated bands at approximately 405 and 435 nm in the visible region with some weaker emissions in the range of 450-500 nm.

Measurement of polymerization conversion

The composite pastes were placed in a Delrin ring (inner dimensions: 1.25 mm thick by 12.5 mm diameter) on a glass cover slip. A Mylar film was placed over the composite paste and pressed flat to the Delrin mold with a microscope slide to produce a uniform specimen dimension. The top glass slide and the Mylar film were then removed to leave the upper surface of the composite exposed to the atmosphere and subsequent photopolymerizations were conducted in this configuration.

Both dynamic and static measurements of methacrylate monomer conversion in the composite materials during and after photopolymerization were accomplished by transmission NIR analysis using a FT-IR spectrophotometer (Nexus 670, Nicolet Instrument Corp., Madison, WI) equipped with a white light source, an extended range potassium bromide beam splitter and a MCT-A detector. NIR spectra over the range of 4500-7000 cm^{-1} were acquired in all cases.

An initial high-resolution static spectrum of the unpolymerized composite paste allowed analysis of the peak area of the fully resolved methacrylate =C-H first overtone absorption centered at 6165 cm^{-1}. Parameters for acquisition of the static spectra were 32 scans at 4 cm^{-1} resolution. Without altering the specimen, the data collection parameters were modified to reduce the number of scans per spectra to two, allowing dynamic series data to be rapidly acquired during the photopolymerization process. The series spectra collection extended over a range of 300 s including an initial 15 s baseline interval prior to the onset of irradiation from one of the light sources. A high-resolution static scan of the polymerized material was run at 7 min from the start of polymerization to allow calculation of an 'immediate' conversion value.

With the commercial dental curing lights, the maximum irradiation intervals were dictated by the internal programming of the particular light. The QTH light provided a 60 s irradiation interval; the LED, 40 s; and the XPA, 10 s. With the short irradiation interval and high output intensity of the XPA light, the spectral data acquisition rate was increased to accommodate the more rapid curing process. The change from 4 to 8 cm^{-1} resolution in this case allowed the dynamic spectral acquisition rate to be increased from approximately 0.8-0.2 s intervals.

The photocured composite discs were stored in the dark for 3-5 days at room temperature to ensure that the post-cure process was essentially complete.[26,28-30] The specimen was carefully repositioned in the NIR and another static spectrum was collected on the aged composite. The area of the methacrylate =C-H absorbance peaks in the 'final' and 'immediate' spectra were ratioed to that obtained from the original uncured specimen spectra to obtain the respective conversions and to determine the extent of post-cure as the difference between the immediate and final conversion values.

Effect of curing temperature, light source and light intensity

For the study of the effect of curing temperature, specimens were placed in a temperature cell in a horizontal sampling accessory unit attached to the FT-IR (Fig. 1). This accessory uses a four-mirror arrangement to convert the horizontal NIR beam to a vertical path as it transmits through the specimen and then back to its horizontal path to reach the detector.[31] This approach allows the irradiation source to be applied nearly normal to the specimen surface from above. The light guide tips from the various curing units were clamped and placed in the horizontal accessory with a separation of less than 1 cm between the light tip and the specimen surface. While not advised for clinical applications, this separation was required here to keep

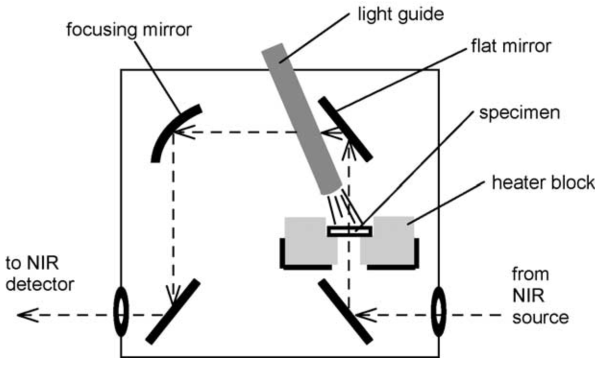


Figure 1 Schematic of the NIR horizontal sample accessory, which includes the heater block and light guide access. The unit mounts in the IR sample chamber. The composite specimen is supported on a glass slide recessed into the cylindrical opening of the heater block.

the light tip out of the path of the NIR beam. This experimentally imposed configuration significantly attenuates the irradiance that is actually delivered to the specimen. The exact separation between the light guide and the specimen was measured for each light and this configuration was reproduced with a radiometer (Model 100, Demetron Research Corp., Danbury, CT) in place of the sample to determine the effective visible light intensity reaching the specimen surface. Irradiance values delivered to the composite specimens were: LED = 95 mW/cm^2, QTH = 165 mW/cm^2 and XPA = 500 mW/cm^2. The output intensities of these respective lights measured directly at the tip of the light guide were 240, 610 and 1890 mW/cm^2 and thus, the irradiance used here was only 26–40% of the potential from these lamps. For the MAL light, three different specimen irradiance levels were chosen for the study: 250, 600 and 1000 mW/cm^2. The aperture control available on the MAL light was used in conjunction with the physical separation between the light guide and the specimen to control the irradiance level. These measured visible light intensities are comparable to those commonly encountered with various commercial dental photocuring units. Even though the filtering of the MAL light allowed a spectral output of 300–500 nm, the radiometer by which the irradiance level was measured is filtered only to detect the 400–500 nm range. However, since camphorquinone has very limited absorptivity in the 300–400 nm region,[32] the photo-activity can be assumed to originate predominantly from the visible light output of the MAL light. The irradiance (400–500 nm) reaching the specimen surface can be coupled with the irradiation intervals to provide the following energy densities: LED = 3.8 J/cm^2; QTH = 9.9 J/cm^2; and XPA = 5.0 J/cm^2, assuming constant output levels.

The temperature cell used in the FT-IR relied on circulation of a temperature regulated ethylene glycol/water mixture through an aluminum block for coarse control. This was coupled with a Peltier cell that allows for heating or cooling to achieve very precise control over the temperature. The composite specimens were kept inside the temperature cell for 3 min to allow the temperature to stabilize. By use of a thermocouple embedded into a composite test specimen placed in the heated block, it was found that the specimen equilibrated to the desired temperature within this time.

The three composite materials were polymerized at room temperature (defined as 22.7 ± 0.2 °C) and 54.5 °C with the commercial dental curing lights and only material M was photocured at room temperature, 37, 54.5 and 70 °C with the MAL light source. The 54.5 °C value was selected to match the output of the composite pre-heating device.[1,2] Triplicate specimens of each material were used with all combinations of curing units, light intensities and temperatures.

Effect of storage at elevated temperature

In addition to the examination of the effect of cure temperature on final conversion and rate of polymerization, the effect of composite storage at elevated temperature was also evaluated. Syringes or unidose tips of the commercial composite materials were placed in an oven at 54.5 °C for up to 8 h. Disc-shaped specimens (1.25 mm × 12.5 mm) were prepared for NIR analysis of conversion at room temperature by photopolymerization with the MAL light at an irradiance of 600 mW/cm^2. The immediate conversion values obtained for the materials stored at elevated temperature were compared with conversion in the same control composites stored at room temperature before polymerization.

Measurement of temperature rise

Duplicate specimens of the material M composite paste were prepared in a 1.25 mm thick × 12.5 mm diameter Delrin mold bounded by clamped glass slides. At the time of composite placement, a thermocouple was embedded in the center of the specimen. The specimens were equilibrated either to room temperature or 54.5 °C in the same temperature control unit used for the NIR studies. Photopolymerizations were conducted with the same commercial dental curing lights and irradiance levels used in the NIR cure monitoring experiments described in Section 2.3. The irradiation intervals also matched those previously used with the exception that a 10 and 40 s irradiation were evaluated for the QTH light, rather than the 60 s interval. The maximum temperature reached during photopolymerization was recorded and the differential between the maximum and baseline temperatures were used to calculate the temperature rise during polymerization. Each specimen and thermocouple were left undisturbed until the specimen temperature returned to the baseline value. The irradiation process was then repeated and the secondary temperature rise determined on the cured composite to ascertain the thermal contribution from the light.

Statistical analysis

The conversion data obtained for the commercial composite materials photopolymerized with the dental curing lights were analyzed by a three-way ANOVA to examine the interactions between all factors (material/light/cure temperature) followed by one-way ANOVA using a Student–Newman–Keuls multiple comparisons test to specifically examine the effect of cure temperature on each material. Curve fitting on all the conversion versus time plots was done with a sigmoidal equation (Hill, SigmaPlot, ver. 8.0, SPSS). Data from the MAL studies of irradiance versus cure temperature were examined with two-way ANOVA. The rate versus conversion plots were obtained using the derivative of the fitted conversion versus time data (SigmaPlot). The analysis of storage conditions data was conducted using one-way ANOVA.

Results and discussion

A transmission NIR spectroscopic method was used to obtain the immediate and final conversion values from static spectral data as well as the real-time photopolymerization kinetics of the commercial composite materials. Stansbury and Dickens have described the static NIR analysis of unfilled dental resins[22] and the potential advantages of this approach compared with traditional mid-IR methods based on either transmission or reflectance modes. Benefits of the NIR method include nondestructive analysis, accommodation of thick specimen geometries, no purge requirements, and most notably for the study of dental composites, tolerance of silica-based substrates or fillers. Glass and quartz are essentially transparent over the NIR spectral range; therefore, transmission of these wavelengths through composites can be significant since signal attenuation occurs primarily by light scattering rather than absorption. In this current investigation, the NIR method is extended to include dynamic conversion monitoring in highly filled composite materials.

The stability of the monomers, as represented by material M, at elevated temperatures was evaluated by monitoring the NIR series spectra acquired at 70 °C, which is the upper limit of temperatures used in this study, for 15 min without irradiation. From this, it was demonstrated that no thermally induced polymerization occurred during this period. Ban et al. have previously shown that in the short-term, either unactivated or photoinitiator-activated dimethacrylate monomers do not undergo spontaneous thermal polymerization until temperatures of 140–200 °C.[33] Typical dimethacrylate dental monomers have also been found to have very limited volatility over the range of temperatures examined here.[34] There is still a concern that under prolonged heating, certain low molecular weight components of the photoinitiator system can be volatilized and thus, compromise any subsequent photopolymerization.[20] While composite packaging would mitigate issues of volatility, to examine the potential impact of these possible effects in dental composites, the room temperature photopolymerization of the various composites was evaluated after extended storage of the materials at 54.5 °C. After 8 h storage at the elevated temperature, only material H exhibited a clearly reduced ($p < 0.05$) immediate conversion compared with control samples that had been stored at room temperature prior to photocuring. A fresh sample of material H was re-tested with a 4 h storage interval at 54.5 °C. Under these conditions, no significant decrease in immediate conversion was noted for either material compared with the controls stored at room temperature ($p > 0.05$). Among the composite materials evaluated here, the decreased thermal stability of material H may be correlated with its greater photopolymerization reactivity. These preliminary data suggest some practical limitations on the extended storage of composites at elevated temperatures prior to photopolymerization.

The effect of temperature on immediate and final conversion for the three composite restorative materials was evaluated using three commercial curing lights (LED, QTH and XPA) at two different temperatures (room temperature and 54.5 °C). Fig. 2 represents the average conversion values calculated from the static NIR spectra. The elevated cure temperature clearly increases the values of both immediate and final conversion for all the materials with all of the curing lights tested. Also evident is the limited post-cure that occurs following photopolymerization at the higher temperature.

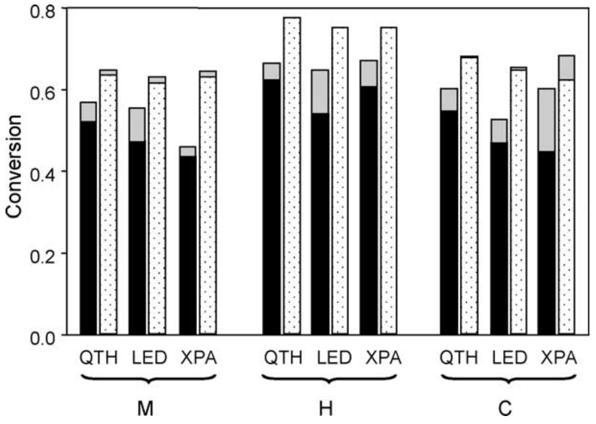


Figure 2 Static NIR determinations of immediate and final conversion in photopolymerizations of commercial composite materials (M, H and C) using three different curing lights (QTH, LED and XPA) and two different cure temperatures (room temperature = dark bars and 54.5 °C = white bars). Gray segments on the tops of the bars represent the additional conversion or post-cure that occurred over the 3–5 day storage interval.

To examine the interactions between all the factors (material/light source/cure temperature) an analysis of variance of conversion results (immediate and final) for each material was conducted with three-way ANOVA. This was followed by one-way ANOVA using Student–Newman–Keuls multiple comparison test to specifically examine the effect of cure temperature on each material. The three-way ANOVA analysis of the immediate conversion results indicates significant differences among materials M and H as well as H and C ($p < 0.05$), but not between M and C. In a comparison of the effect of the different lights on immediate conversion (pooling all materials), the QTH light produced significantly higher values compared with the LED and XPA lights. No difference in immediate conversion was noted between the LED and XPA lights. As was mentioned before, there was a clear difference in the immediate conversion between the room temperature and elevated temperature conditions for all lights and all materials. Similar results were obtained from the three-way ANOVA using final conversion values for all materials except that there were no differences based exclusively on the light source.

The one-way ANOVA focused on each of the materials showed the following general pattern: (a) at room temperature, final conversion was significantly greater than immediate conversion; (b) at the elevated cure temperature, there was no significant difference between the immediate and final conversion values; (c) immediate conversion was significantly higher at elevated temperature than at room temperature; (d) the immediate conversion obtained with elevated cure temperature was in general, significantly greater than the final conversion achieved with room temperature polymerization. The only exceptions to these trends were with the XPA light: for material M where the immediate and final conversions attained at room temperature were not different; and for material C, where the final conversion obtained at room temperature was similar to the immediate conversion produced at 54.5 °C. This latter case was also the only example in which a significant difference was observed between the immediate and final conversions obtained at the 54.5 °C cure temperature.

In this study, material H had the highest conversion values and even these relatively high values obtained during room temperature curing were significantly enhanced with the elevated temperature curing process. Unlike the ambient temperature polymerizations, where within a given material significant differences were noted in the conversion levels depending on the light source, the use of the higher cure temperature produced very consistent immediate and final conversion results regardless of the curing unit used. It is expected that both ambient and elevated temperature photopolymerizations could produce conversion values that would be scaled modestly higher if the full power densities of the various light sources were used rather than the reduced irradiance intensities provided due to the experimentally imposed distance between the specimen and the light tip.

With increasing temperature, the viscosity of the dimethacrylate resins decreases and thus, the flow properties of composite pastes are considerably enhanced. However, because of the random nature of diffusion processes, thermal effects on diffusion-based reaction rates are, in general, relatively low. The increase in cure temperature has a minimal effect on the decomposition rate of photoinitiators since it is light rather than heat energy that leads to radical formation with an activation energy of zero.[35] Because of this, a fairly low apparent activation energy is associated with photopolymerization processes and these reactions are known to be relatively insensitive to temperature compared with thermally initiated polymerizations. The photoinitiator efficiency, particularly in the case of the two-component camphorquinone/tertiary amine initiator system, may be slightly enhanced by the reduced resin viscosity. Thus, while the reaction rates are expected to be modestly affected by the temperature range investigated here, the enhanced mobility at higher temperatures of both monomer and polymer can produce the significant effect of delaying the vitrification point to higher conversion. The thermally induced physical changes to resin viscosity and diffusional effects have been discussed by other authors.[20,36]

Efficient termination reactions typically eliminate active radical sites rapidly in mobile polymer systems. However, in highly cross-linked, glassy polymers, such as those used as dental resins, some proportion of the radicals generated throughout the polymerization process are trapped within the heterogeneous network and can persist for extended periods.[37] At these longer time scales, trapped radicals can encounter residual monomer or pendant groups resulting in additional conversion or post-cure. The large majority of the post-cure process is complete within hours but a measurable increase in conversion continues over days and weeks. DSC-based analyses lack the sensitivity to monitor even the relatively early stages of post-cure, whereas nondestructive IR-based spectroscopic techniques can be conveniently applied to follow the subtle increases in conversion over very long intervals through repeated measurements on individual specimens. The NIR conversion results obtained here demonstrate that for a given resin/filler system, post-cure levels typically are proportionally greater when a moderate level of the initial conversion is achieved. If the initial conversion is too low, then sufficient mobility exists such that the active radical concentration rapidly decreases through efficient diffusional termination and the post-cure potential may be limited. However, it is clear that for room temperature polymerizations, the initial conversion is not the only factor controlling post-cure. Differences in the selected photoinitiators and their concentrations as well as the different lights used would be expected to affect not only the overall number of radicals produced, but also the radical population at various stages of conversion, which may be important in the post-cure process.

Since these dimethacrylate-based network polymers become vitrified as the polymeric T_g increases with conversion beyond ambient temperatures, the mobility decreases to the point that the potential for post-cure is also quite limited. In the case of room temperature irradiations, which always gave significantly lower immediate conversions than the analogous elevated temperature photopolymerizations, significant post-cure ($p < 0.05$) was seen in all but one case (material M cured with the XPA light). When curing at the elevated temperature, the mobility constraints that evolve with conversion are delayed and substantially higher initial conversions were achieved. However, when the composites were returned to room temperature and stored, no significant post-cure was observed (except for material C with the XPA light) because of the even greater restrictions imposed on mobility by the higher initial conversions. Material H, which exhibited the highest conversion overall, showed no measurable post-cure conversion increase when cured at 54.5 °C. When the effect of the higher cure temperature is evaluated in terms of the percentage increase in conversion over all curing lights used, materials M, H and C show increases of 32.5 ± 11.7, 29.1 ± 8.6 and 33.5 ± 8.7% for immediate conversion and 22.5 ± 15.1, 13.2 ± 3.2 and 17.0 ± 6.5% for final conversion, respectively.

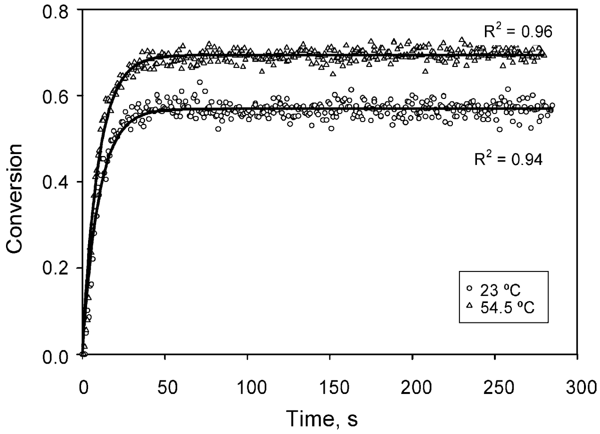


Figure 3 Conversion as a function of irradiation time for LED photopolymerizations at room temperature and 54.5 °C for material H. Data points represent triplicate runs with solid lines provided from the regression fit.

Fig. 3 shows an example of a typical plot of conversion versus time generated with the real-time NIR. In this, the replicate conversion/time data has been fit by a sigmoidal equation with the R^2 values for these fits to the overall data in the range of 0.88–0.96. As shown in Fig. 4, the dynamic

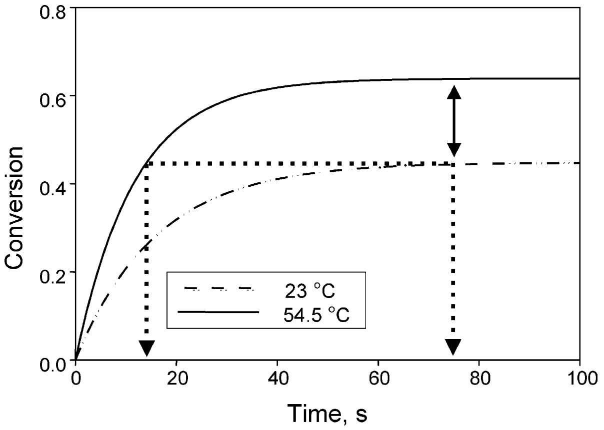


Figure 4 Representative fitted photopolymerization kinetic profiles for a composite photocured at two temperatures. The approximate beginning of the plateau region (the 2% offset of the end of the dynamic room temperature conversion) is shown at approximately 75 s as well as the equivalent elevated temperature conversion at about 15 s.

conversion data can be used to compare relative photopolymerization profiles. In order to make reasonable comparisons using the dynamic scans, an approximate beginning plateau region was identified for the room temperature plot as the 2% offset value (98% of the 'final' value) based on the conversion at the 285 s end point. The time required for the conversion to rise to this offset value during room temperature polymerization was determined from the dynamic data and compared with the time required for the analogous elevated temperature photopolymerization to reach this equivalent conversion. The corresponding reductions in the time required to reach equivalent degrees of conversion at the two temperatures are illustrated in Fig. 5 for all material and light combinations. The time to reach comparable conversion levels with the higher cure temperature was decreased by 80–92% compared with room temperature photocuring, except for the 50% time reduction observed in the case of material M photocured with the XPA light. At room temperature, limiting conversions were reached most quickly with the XPA light probably because of the higher irradiance involved and the irradiation interval only extended to 10 s. From the combined results provided in Figs. 2 and 5, it is clear that at room temperature, material H achieves its relatively high conversion levels in the shortest time intervals and thus, exhibits the highest overall photo-reactivity. The data in Fig. 5 once again illustrates that the elevated cure temperature provides very uniform photopolymerization behavior, regardless of the composite material or the light source used. In all materials and with all lights, the conversion at the plateau region of the room temperature polymerization was reached in less than 20 s at the elevated temperature.

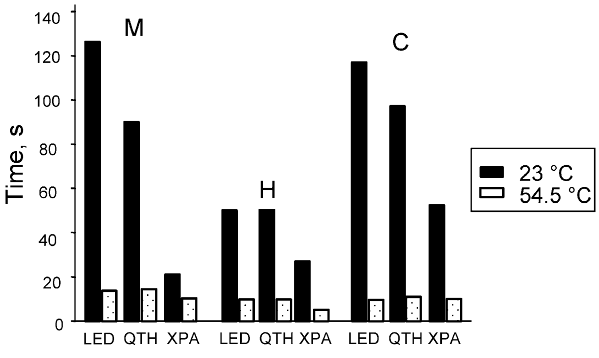


Figure 5 Time differential for various composite materials and light source combinations to reach equivalent conversion between the 2% offset of the dynamic conversion limit achieved during room temperature cure (dark bars) and the analogous polymerization conducted at 54.5 °C (white bars).

The previous survey of results was followed by a more detailed examination using one material (M) and a single light source (MAL, equipped with a filter to provide light in the visible region). This lamp was selected to provide uniform wavelength output over a wide range of light intensities with aperture and shutter control of the irradiation. Visible light irradiances at the specimen surface were set at either 250, 600 or 1000 mW/cm^2 and the cure temperatures evaluated were room temperature, 37, 54.5 and 70 °C. In Fig. 6, the effects of a combination of light intensity and cure temperature on immediate conversion are summarized. For any given temperature, the immediate conversion increases with irradiance; although, the relative change between 250 and 600 mW/cm^2 is much greater than the increase observed between 600 and 1000 mW/cm^2. Over the temperature range examined here, as the cure temperature is increased, there is a linear increase in the immediate conversion achieved for all the light intensities used with the effect being greatest at the lowest light intensity. The slopes from the linear regressions (in units of percent conversion/°C) for 250, 600 and 1000 mW/cm^2 are 0.36 ± 0.03, 0.28 ± 0.01 and 0.23 ± 0.03, respectively. This convergence of conversion results at the higher temperatures implies that a more homogeneous conversion can potentially be attained throughout an entire composite increment cured at elevated temperatures.

The dynamic photopolymerization data generated from the NIR series spectra can be evaluated in a number of forms. A derivative of the standard plots of conversion as a function of time was obtained to provide the polymerization rate (R_p), which can then be plotted as a function of conversion (Fig. 7). This form provides a very convenient means to compare the effects of different polymerization conditions on

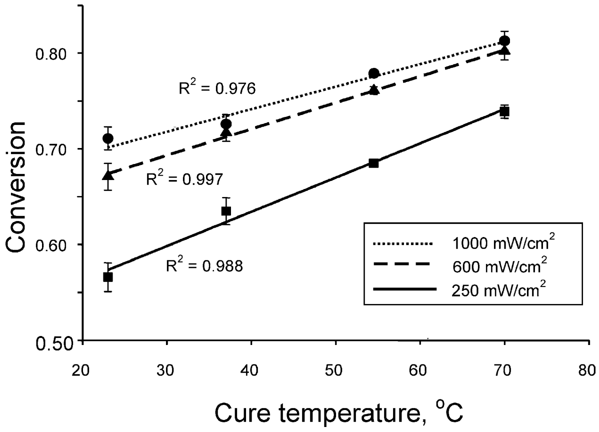
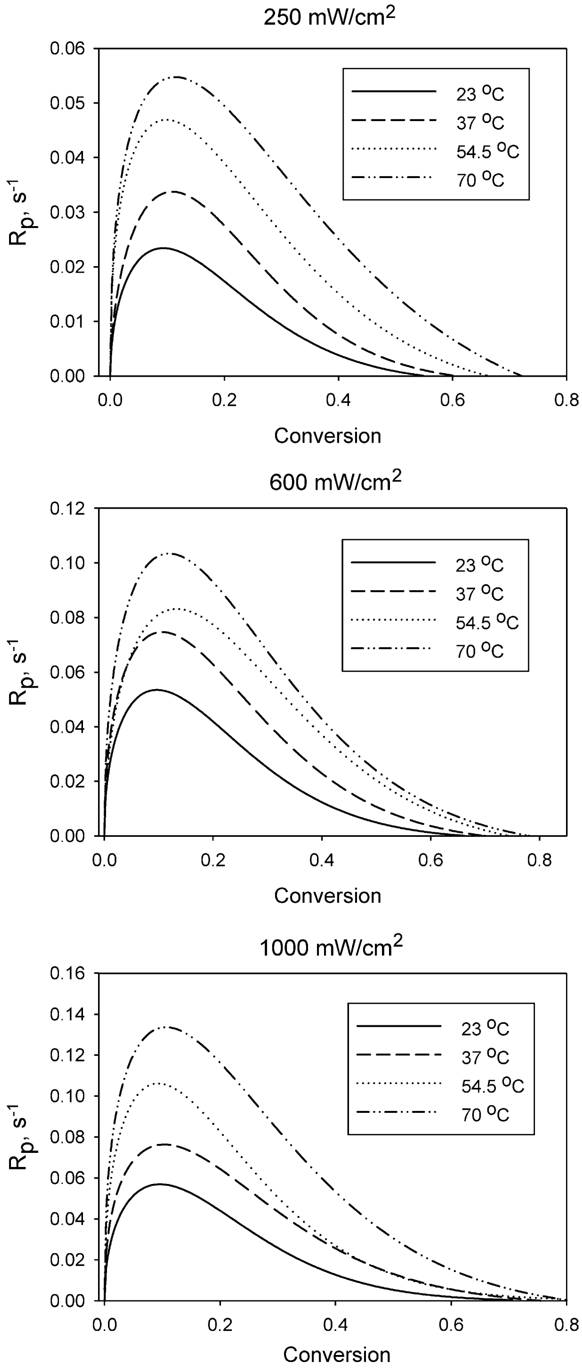


Figure 6 Effect of irradiance (MAL source) on immediate conversion as a function of photocure temperature.


250 mW/cm2

600 mW/cm2

1000 mW/cm2

Figure 7 Polymerization rate of material M as a function of double bond conversion for various photocure temperatures. Separate plots represent results obtained at different irradiance levels with the MAL source.

reaction kinetics. The data can be normalized based on the concentration of the reactive groups in the resin or composite; however, since the current example uses only a single composite material (M), nonnormalized data can be fairly presented. The kinetic data demonstrate that the maximum rate of polymerization ($R_{\text{p max}}$) occurs over a fairly narrow range of conversion (9–13%) and is significantly affected by both light intensity and cure temperature. Over the temperature range investigated here, there is a good linear correlation between $R_{\text{p max}}$ and cure temperature, regardless of the irradiance with R^2 values of 0.993, 0.963 and 0.998 for the photopolymerizations conducted at the 250, 600 and 1000 mW/cm^2 irradiance levels, respectively. The dependence of $R_{\text{p max}}$ on irradiance was nonlinear with the highest cure temperatures (54.5 and 70 °C) providing good fits to the classical square root intensity dependence[35] (linear regressions with $R^2 = 0.995$ and 0.994, respectively; Fig. 8), while the lower temperature polymerization results fit even lower order dependencies. The practical meaning of these results is that a modest increase in cure temperature can have a more significant impact on the polymerization reaction rate compared with relatively large changes in light intensity. As examples, the rate maxima obtained with 250 mW/cm^2 irradiance at 54.5 and 70 °C are approximately equal to the maximum rates achieved with room temperature polymerizations at 600 and 1000 mW/cm^2, respectively.

While conducting the NIR analyses of the photopolymerization reactions, it was evident that both the temperature and the state of the composite material (uncured or cured) influenced the signal transmission. This is not surprising since it is well known that light transmission through composites is affected by the refractive index mismatch between the resin and filler phases. While the filler refractive index remains constant, the optical properties of the resin change as it is converted from monomer to polymer.[9,38,39] Because the coefficient of thermal expansion of the resin is much greater than that of the filler, the refractive index of the resin is also more sensitive to changes in temperature.

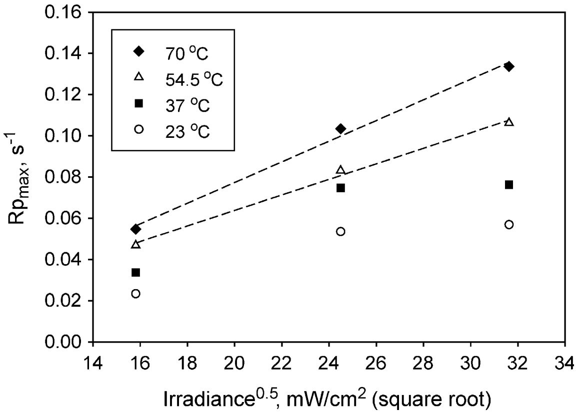


Figure 8 Square root dependence of irradiance (250, 600 and 1000 mW/cm^2 from MAL source) on maximum rate of polymerization of material M at various photocure temperatures. Linear regressions are shown for 54.5 and 70 °C data.

To quantify these effects, the signal intensity of the NIR white light source transmitted through the uncured composite materials was monitored at a fixed level of gain. At room temperature, the maximum signal values for materials M, H and C were 3.86, 3.31 and 2.55, respectively, while at 54.5 °C, the signal strength was significantly reduced in each case by 74, 13 and 25%, respectively. The large decrease in NIR signal transmission through the uncured microfilled composite at the elevated temperature can be explained in part, by the relatively high proportion of resin in this material. For material M, the route mean square assessment of the signal to noise increases from 0.09 to 0.31 over the range of room temperature to 70 °C. On the other hand, as photopolymerization proceeds, the NIR signal transmission efficiency improves considerably. This would be anticipated since increased temperature lowers the resin refractive index, while the densification that accompanies resin polymerization alters refractive index in the opposite direction. So fortuitously, the sensitivity of the NIR analysis technique increases as the methacrylate double bond concentration it monitors is decreasing.

The polymerization of composite restorative materials is an exothermic process with the extent of the thermal excursion dependent on the composite composition, specimen geometry as well as the intensity and wavelength of the irradiation source. In addition to the reaction exotherm, the photocuring units contribute varying amounts of energy in the form of heat. Several prior investigations have determined the range of the temperature rise associated with different combinations of composite material and light activation unit.[40-43] Some of these studies have relied on thermocouples situated either at the center of the composite or at the bottom surface interface to simulate the temperature rise that would be conveyed to dentin in a dental restoration. High-resolution infrared cameras have also been used to analyze temperature gradients set up during composite photopolymerization. In other investigations, the thermal effects during photocuring have been monitored through an intervening buffer of dentin to indicate practical temperature rise experienced in the pulp chamber. Thermal insult to the pulp can be a significant concern in composite photopolymerization[44-46] and the use of elevated curing temperatures may further exacerbate this problem. Therefore, a preliminary examination of the temperature rise associated with both the photopolymerization reaction and the various light sources was conducted at ambient and elevated cure temperatures.

As shown in Table 1, for every case examined, the extent of the temperature rise observed during the photopolymerization process was greater at the elevated cure temperature. This is consistent with the combined observations of higher conversion and increased polymerization rate at elevated cure temperatures. It should be emphasized that this temperature differential is measured in the center of the composite mass and therefore, represents the maximum thermal excursion. The effective thermal change that would be experienced clinically at the restoration–dentin interface would be a combination of the initial cure temperature and some proportion of the temperature rise accompanying the polymerization. Significantly higher irradiance values would result from placement of the curing light tip at the composite specimen surface and this would undoubtedly result in a higher temperature rise due to both a more compressed exothermic reaction and additional direct heating due to radiant energy from the various lights. The most notable

Table 1 Temperature rise during photopolymerization and during post-cure irradiation of composite restorative (material M) at two cure temperatures.

Light/irradiation time[a]	Maximum temperature rise (°C)[b]		ΔT (°C)[c] (significance, $p < 0.05$)[d]
	23 °C cure temp.	54.5 °C cure temp.	
QTH/10 s	3.40 (0.14)	5.10 (0.14)	1.70 (+)
	0.70 (0.00)	0.55 (0.07)	−0.15 (−)
QTH/40 s	6.00 (0.00)	6.15 (0.07)	0.15 (−)
	1.95 (0.07)	1.65 (0.07)	−0.30 (−)
LED/40 s	5.17 (0.21)	5.55 (0.21)	0.38 (−)
	0.83 (0.07)	1.15 (0.07)	0.32 (+)
XPA/10 s	5.50 (0.14)	7.55 (0.35)	2.05 (+)
	3.95 (0.07)	4.25 (0.07)	0.30 (−)

[a] The irradiance associated with each light was matched to that used in the NIR experiments.
[b] Standard deviation in parentheses, $n = 2$.
[c] Differential between maximum temperature and initial cure temperature.
[d] Result of *t*-test.

differences in the temperature rise data are the 10 s irradiations with the XPA and QTH lights; however, no significant differences were seen for the 40 s irradiations with the LED or QTH lamp at the different cure temperatures. The post-cure irradiations show the radiative heating effects of the lights alone on the composite in the order of XPA > QTH > LED, which correlates with in vitro results of pulp chamber temperature change during composite polymerization.[44,45] The LED was the only light that produced a significantly greater post cure heating effect at the elevated temperature, possibly the result of a small but significant amount of additional photopolymerization during the second irradiation cycle.

It is generally accepted that pulp vitality may potentially be compromised by temperature rises of greater than about 5 °C from the baseline level of approximately 32–34 °C.[47] While the temperature increases provided in Table 1 were within the polymerizing or cured composite paste, the temperature rise in the pulp associated with the placement of a pre-heated composite is expected to be substantially less. In an independent evaluation from another laboratory, a class V cavity preparation with 1 mm remaining dentin thickness was placed in extracted teeth ($n = 3$). The roots were submerged in a thermostatically controlled water bath and perfused with water at 1.25 μl/min to simulate physiological conditions in the pulp chamber. Upon placement of the composite preheated to 54.5 °C, the temperature rise recorded by a thermocouple situated in the pulp chamber was only 2.4 ± 0.3 °C.[48] Such a temperature rise would suggest that the composite could be placed with relative safety. Additional thermal excursion would be produced by polymerization exotherms and radiation-induced heating. The impact of these thermal sources combined with the heat from the warm composite, though ameliorated by the insulation effects of the remaining dentin thickness and the continuous cooling of the composite after placement, still needs to be investigated. Further studies with full irradiation intensities would be warranted. In addition, studies to determine the influence of elevated photocuring temperatures on composite physical and mechanical properties as well as on depth of cure, shrinkage and shrinkage stress development are currently in progress.

Conclusions

The exposure of composite resins to elevated temperatures, limited to a range that may be biologically compatible has significant effects on the polymerization kinetics. Both rate and conversion increases have been demonstrated with several commercial composite formulations and with different curing light sources. The data identify a more significant effect of increased composite temperature than increased irradiance over these ranges of clinical applicability studied. Both direct thermal effects on reaction kinetics and viscosity effects may contribute to these results. The increased storage temperature for up to 4 h has been demonstrated to have no significant deleterious effect on the conversion. NIR spectroscopy has been demonstrated to be a very effective analytical technique to monitor the photopolymerization process in dental composite materials.

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