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## ABSTRACT

The potential for maximizing conversion of room-temperature, photoactivated resin composite in the oral environment is limited. Pre-heating composite prior to light-curing is hypothesized to increase monomer conversion and reduce the duration of light exposure. Composite temperature was controlled at between 3°C and 60°C prior to exposure with a conventional quartz-tungsten-halogen curing unit: 5, 10, 20, or 40 sec. Monomer conversion was calculated from infrared spectra at 0 mm (top) and 2-mm-deep surfaces 5 min after light initiation. A strong, positive correlation existed between temperature and monomer conversion: top  $r^2 = 0.999$ , 2 mm  $r^2 = 0.998$ . Conversion ranged from 31.6% (3°C) to 67.3% (60°C). The duration of light exposure, reduced by 50 to 75% with pre-heated composite, yielded the same or significantly higher conversion ( $p = 0.001$ ) than with control (22°C, 20 sec). Both hypotheses were accepted: Pre-heating composite prior to photoactivation provides greater conversion requiring reduced light exposure than with room-temperature composite.

**KEY WORDS:** resin composite, monomer conversion, curing temperature, light exposure duration.

# Monomer Conversion of Pre-heated Composite

## INTRODUCTION

Polymerization of photo-activated restorative dimethacrylate-based materials exhibits incomplete conversion of double-bonds (from 50 to 75%), leaving a significant proportion of methacrylate groups unreacted (Cook *et al.*, 1984), depending upon monomer and filler composition, initiator system, and light-curing procedure (Peutzfeldt and Asmussen, 2004). This reaction is self-limiting, principally arising from the increase in system viscosity and the resulting dramatic decrease in reactive species mobility imposed by the rapid formation of a highly cross-linked polymeric network (Ferracane, 1985; Watts, 1992).

Incomplete conversion results in residual, unreacted monomer. This material and unreacted photoinitiator (and its photoreactive products) can be leached into saliva, possibly producing allergic reactions or stimulating growth of bacteria around restorations (Carmichael *et al.*, 1997; Hansel *et al.*, 1998; Nie *et al.*, 1998; Reichl *et al.*, 2002). Unreacted monomers also act as plasticizers, reducing restoration mechanical strength and increasing swelling (Nie *et al.*, 1998; Lovell *et al.*, 1999). Oxidation of unsaturated methacrylate groups can also be responsible for composite color change (Ferracane *et al.*, 1985), as well as result in formaldehyde formation, which has an allergic potential (Øysæd *et al.*, 1988).

The extent of polymerization in resin composites is expressed as the degree of conversion of monomeric C=C bonds into polymeric C-C bonds (Ruyter and Svendsen, 1978; Watts, 1992). Conversion extent affects both physical and mechanical polymer properties (Ferracane, 1985; Rueggeberg and Craig, 1988). Increasing conversion produces higher surface hardness, greater flexural strength and modulus, improved fracture toughness, enhanced diametral tensile strength, and higher wear resistance (Lovell *et al.*, 2001a). However, mechanical properties are very dependent upon polymer network formation, which is not equivalent to conversion (Ferracane, 1985). Network formation occurs during polymer chain propagation and includes a mixture of linear, crosslinked, and entangled, interpenetrating chain segments, the totality of which determines material properties. Crosslink density is associated with increased mechanical properties and stability. However, polymers having similar conversion values may have different crosslink density (Peutzfeldt and Asmussen, 2004). Thus, conversion alone may not prove to be a predictor of restoration performance.

Polymerization temperature also affects monomer conversion and, thus, polymer properties (Bajaj *et al.*, 1977; Bausch *et al.*, 1981; Lovell *et al.*, 2001b). Radical mobility increases with temperature, and additional polymerization ensues as a result of lowered system viscosity (Bausch *et al.*, 1981; Maffezzoli *et al.*, 1994; Cook *et al.*, 1997; Nie *et al.*, 1998; Lovell *et al.*, 1999, 2001b).

The relationship between conversion and temperature has been studied in a wide range of model resin systems (Nie *et al.*, 1998; Lovell *et al.*, 1999,

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2001a,b) and a few commercial products (Bausch *et al.*, 1981; Trujillo *et al.*, 2004). However, little is known about the effect of pre-heating on conversion at different depths and light exposure durations of a commercial composite.

A new commercial device (Calset™, AdDent Inc.)(AQ) pre-heats dental resin composite to 54° or 60°C prior to placement. Ideally, pre-heating would increase composite flow, which, in turn, would improve adaptation of uncured resin to prepared tooth walls, and potentially reduce microleakage. We found that some

**Table 1.** Mean (SD) Composite Conversion 300 Sec Following Light Initiation: Effects of Composite Temperature, Exposure Time, and Surface<sup>a</sup>

	Composite Temperature (°C)	Exposure Duration (sec)	Conversion (%)	
			Top Surface	2-mm Depth
R	3	40	35.6 (0.2)	34.3 (0.6)
		20	35.4 (0.1)	31.6 (0.6)
	10	40	40.8 (0.5)	39.7 (0.5)
		20	40.3 (0.6)	36.9 (0.2)
RT	20	40	47.6 (0.3)	46.6 (0.3)
		20	47.6 (0.5)	44.9 (1.5)
	(control)*	40	48.8 (0.3)	47.5 (1.5)
		20	48.7 (0.7)	45.8 (1.4)
	22	10	47.6 (0.6)	37.6 (1.1)
		5	45.7 (0.6)	32.6 (2.1)
	25	40	51.3 (0.7)	49.8 (0.4)
		20	50.8 (0.7)	47.9 (0.2)
		10	49.2 (0.5)	41.3 (0.3)
	27	40	52.1 (0.6)	50.2 (0.5)
		20	50.9 (0.3)	49.0 (0.9)
	30	40	52.1 (0.9)	52.0 (1.0)
		20	52.8 (0.6)	51.0 (0.9)
		10	52.2 (0.3)	44.1 (1.2)
	40	40	58.4 (0.6)	57.3 (0.7)
		20	58.0 (0.5)	54.7 (0.7)
10		55.6 (0.4)	47.5 (2.0)	
5		55.0 (0.5)	44.8 (1.6)	
54	40	64.2 (0.3)	63.3 (0.7)	
	20	64.4 (0.2)	61.2 (1.2)	
	10	62.9 (0.5)	58.9 (0.6)	
	5	62.3 (0.7)	52.1 (1.9)	
60	40	67.3 (0.7)	64.1 (2.0)	
	20	66.3 (0.4)	63.0 (1.5)	
	10	65.4 (0.4)	60.4 (1.1)	
	5	64.3 (0.8)	54.5 (2.4)	

<sup>a</sup> n = 5 specimens per experimental group.

\* Control, room temperature, and manufacturer-recommended light exposure duration.

R = refrigerated; RT = room temperature.

commercial composites demonstrated reduced film thickness upon heat application before photoactivation (unpublished observations), indicating flow enhancement from pre-heating. The benefits of pre-heating composites may have an impact on daily restorative procedures as well, with the application of shorter light exposure to provide conversion values similar to those seen in unheated conditions. Also, pre-heating may significantly increase monomer conversion above levels seen with current methods, possibly enhancing restoration properties.

This study investigated the effects of composite pre-polymerization temperature and duration of light exposure on monomer conversion of a commercial resin composite. It was hypothesized that (1) temperature elevation increases monomer conversion on the top and at 2-mm depths, and (2) pre-heated composite requires reduced light exposure to achieve conversion similar to that seen with conventional exposure with composite at room temperature.

## MATERIALS & METHODS

### Specimen Preparation

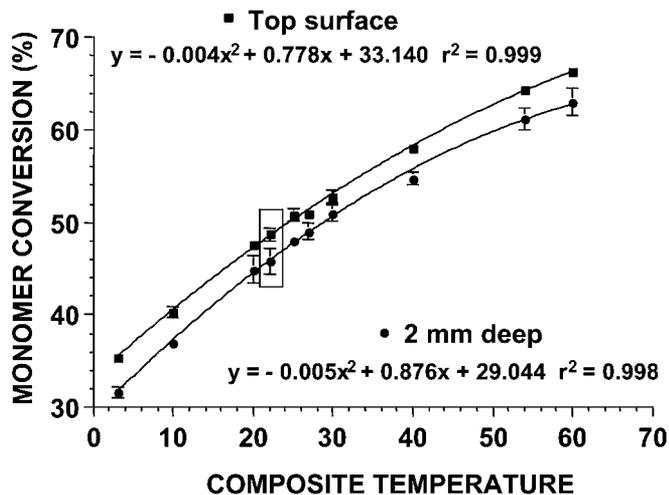
A commercially available, photo-activated hybrid resin composite was used (Esthet•X, shade A2, lot #030221, Dentsply/Caulk, Milford, DE, USA). According to the manufacturer, the resin matrix consists of a BIS-GMA adduct (adduct of 2,2-Bis[4-2-hydroxyl-3-methacryloyloxypropoxy]-phenyl]propane with hexamethylene diisocyanate), Bis-EMA(AQ) (2,2-Bis[4-(2-methacryloyloxyethoxy)-phenyl]propane), and TEGDMA (triethylene glycol dimethacrylate). This specific material was selected because we found that it had greatly reduced viscosity when heated (unpublished observations). A temperature-controlled stage of a diamond-attenuated total reflectance (TCS-ATR) unit (Heatable Golden Gate ATR, MkII, SPECAC Inc., Smyrna, GA, USA) was used. A custom-made chilling device was fabricated to facilitate temperature control below room temperature. Composite curing temperatures tested were: 3°, 10°, 20°, 22° (control), 25°, 27°, 30°, 40°, 54°, and 60°C.

Brass rings (6-mm diam, 2 mm high) were filled with uncured composite and placed on the TCS-ATR, covered with a sheet of clear plastic matrix (0.08 mm, type D Mylar, Du Pont, Wilmington, DE, USA), and pressed to force the paste to conform to the ring dimensions. This arrangement enabled conversion of the bottom, 2-mm-depth surface to be determined. We simulated monomer conversion at the top composite surface by placing a small amount of uncured composite on the TCS-ATR, covering it with a Mylar sheet, and pressing it into a flat, thin layer (approximately 150 μm) by applying digital pressure on a microscope slide. Specimen thickness was measured by means of a digital caliper after polymerization.

A pilot study determined that 30 sec was sufficient to warm or cool composite to stage temperature. A conventional quartz-tungsten-halogen light-curing unit (Optilux 501, Demetron/Kerr Co., Orange, CA, USA) was used to photocure the composite for 5, 10, 20 (control), or 40 sec, with the light guide held 1 mm from the top surface (Table 1). Spectral irradiance was determined with the use of a laboratory-grade spectral radiometer (DAS 2100, Labsphere, N. Sutton, NH, USA) having a 3-inch integrating sphere and calibrated against a NIST-traceable source. The irradiance of the light-source measured 630 mW/cm<sup>2</sup> between 350 and 600 nm.

### Monomer Conversion

Infrared spectra were collected between 1680 and 1550 cm<sup>-1</sup> at a rate of one-per-second with the use of a Fourier transform infrared



**Figure 1.** Relationship between composite conversion at 20-second exposure and various temperatures and surfaces. n = 5 specimens per experimental group; vertical bar = ± standard deviation; box = control (22°C).

spectrometer (FTS-40, Digilab/BioRad, Cambridge, MA, USA) at 2-cm<sup>-1</sup> resolution. The first 4 collected scans served to supply the infrared spectra of the uncured resin. On the 5th recorded scan, composite was light-activated, while spectra continued to be collected for 300 additional sec. Five replications were made for each test condition. Monomer conversion was calculated from infrared spectra at both 0 mm (top) and 2-mm depth, by standard methods that utilize changes in the ratios of aliphatic-to-aromatic C=C absorption peaks in the uncured and cured states (Ruyter and Svendsen, 1978; Ferracane and Greener, 1984; Rueggeberg *et al.*, 1990).

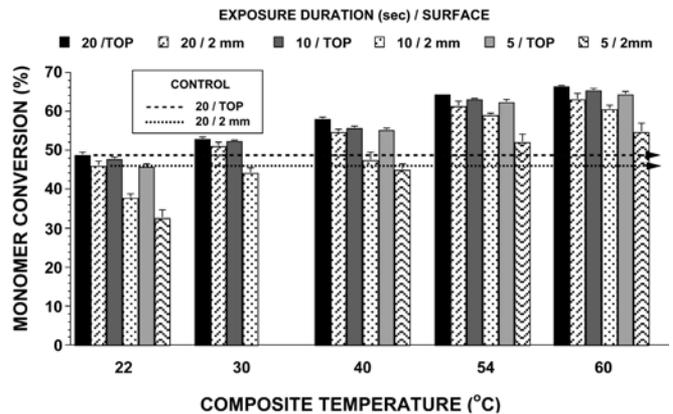
**Statistical Analyses**

Student's *t* test compared conversion values between top and bottom surfaces for a given temperature and light exposure duration. Student's *t* test and one-way analysis of variance (ANOVA), followed by Tukey's test, identified conversion differences regarding light exposure duration. Conversion values of pre-heated conditions at each surface were compared with those of the control (22°C/20 sec) by a one-way ANOVA, followed by Dunnett's one-tailed *t* test. Regression analysis determined the correlation between monomer conversion and composite temperature. All statistical testing was performed at a pre-set alpha of 0.05.

**RESULTS**

**General Trends**

Increased composite curing temperature produced elevated monomer conversion (Table 1). At a 20-second light exposure (top surface), conversion ranged from 35.4 to 66.3% (3°C to 60°C, respectively) and from 31.6 to 63.0% at 2-mm depth—an increase in relative values of 87% (top) and 99% (bottom). For all light exposure durations at each temperature, top-surface conversion exceeded that at 2 mm (*p* < 0.05). When samples were exposed for 20 or 40 sec, top-surface composite conversion was equivalent and similar throughout the temperature range. At 2-mm depth, however, conversion at 20 sec of exposure was lower (*p* < 0.05) than that at 40 sec for temperatures of 3°, 10°, 27°, and 40°C. When different light



**Figure 2.** Composite conversion of pre-heated conditions relative to control values. n = 5 specimens per experimental group; vertical bar = ± standard deviation.

exposures were compared at a specific temperature, conversion values at 20 sec were always greater than those at either 5 or 10 sec of exposure, regardless of surface (*p* < 0.05). Regression analysis between monomer conversion and temperature (20 sec of light exposure) showed a very good fit according to a second-order polynomial (Fig. 1). Monomer conversion increased steadily with composite temperature for both surfaces.

**Effects of Composite at Room Temperature and Above**

Composite temperature, light exposure duration, and surface had large effects on conversion values (Fig. 2). Statistical comparisons indicated that all pre-heated conditions exhibited equal or greater conversion values than the control (Table 2). Use of only a five-second exposure (¼ recommended duration) on pre-heated composite at 54° or 60°C resulted in greater conversion (52-64%) than when a 40-second exposure (twice the recommended duration) was used with room-temperature composite (48%).

**Table 2.** Statistical Comparison of Conversion Values Relative to Control (22°C/20 sec)

Composite Temperature (°C)/ Light Exposure Duration (sec)	Composite surface	
	Top	2 mm
22/10	<	<
22/5	<	<
30/20	>	>
30/10	>	=
40/20	>	>
40/10	>	=
40/5	>	=
54/20	>	>
54/10	>	>
54/5	>	>
60/20	>	>
60/10	>	>
60/5	>	>

Statistical significance level: *p* < 0.05.  
< less than control; = equivalent to control; > greater than control.  
n = 5 specimens per experimental group.

## DISCUSSION

The first hypothesis was validated: Composite temperature prior to photo-polymerization significantly affected conversion at the top and bottom surfaces for all light exposure durations tested. Relative to control (22°C, 20 sec), top-surface conversion decreased 27% (3°C) and increased 36% (60°C), while at 2-mm depth, conversion decreased 31% (3°C) and increased 38% (60°C). This conversion increase with temperature agrees with work where experimental resin formulations were used (Lecamp *et al.*, 1997; Nie *et al.*, 1998; Lovell *et al.*, 1999, 2001a,b). The reasons for increased conversion are based on many factors. Increased temperature decreases system viscosity and enhances radical mobility, resulting in additional polymerization and higher conversion (Nie *et al.*, 1998; Lovell *et al.*, 2001b). The collision frequency of unreacted active groups and radicals increases with elevated curing temperature when below the glass transition temperature (Bausch *et al.*, 1981). Furthermore, as composite temperature is raised, additional free volume increases, giving trapped radicals increased mobility, resulting in further conversion. This explanation assumes that the free volume available to radicals is not evenly distributed, but exists in packets of various sizes, which cannot be redistributed (Nie *et al.*, 1998).

The second hypothesis was also confirmed: Equivalent conversions are attainable with the use of reduced light exposure in pre-heated composite. Light exposure duration could be reduced by 50 to 75% and still attain conversion the same as, or higher than, that of the control. Fewer radicals are formed with decreased light exposure, but their mobility is enhanced as a result of decreased system viscosity, resulting in greater conversion.

Absolute conversion values of the control (top, 48.7%; 2 mm, 45.8%) may be lower than many reported values for Bis-GMA/TEGDMA-based materials (Ferracane and Greener, 1984; Asmussen and Peutzfeldt, 2001). This reduction may be due to the fact that specimens tested in the present work were examined by real-time ATR, and those tested with thin film transmission are typically tested 24 hrs subsequent to cure. Considering the additional, dark-cure conversion of the aged specimens, one would expect their conversion values to be greater than those tested immediately (Johnston *et al.*, 1985).

Increased conversion is also expected to result in greater crosslinking and, therefore, may yield better mechanical properties (Ferracane *et al.*, 1997; Lovell *et al.*, 2001b). However, polymer mechanical properties are also highly dependent on network formation characteristics, which are not equivalent to conversion in these materials. The extent of property enhancement with conversion increase due to pre-heating is still unknown.

An interesting finding was the poor conversion values observed at decreased temperatures. Based upon these results, care should be taken in the use of composite stored in the refrigerator. The need to bring cooled composite to at least room temperature prior to placement is thus demonstrated.

Elevated temperatures of 54° and 60°C were specifically chosen because these values are provided by the Calset™ device. Little difference in conversion was found between these values; perhaps the additional heating is not necessary. In contrast, once composite is pre-heated, there is a time delay between dispensing it from a syringe or compule, placing it into a preparation, contouring, and subsequent light-curing. It is

likely that heated composite cools rapidly, reducing the heat benefit. But even if pre-heated composite cools below 54°C (perhaps to 30° or 40°C), benefits may still be seen (in terms of conversion) in comparison with those attained when the composite was at room temperature. If composite cools to 40°C, it is possible to use only a 10-second exposure and attain better conversion than at 20 sec at 22°C. Also, the results of the current study were obtained *in vitro*, and composite conversion may not behave similarly in a clinical scenario. While laboratory studies show improved composite conversion, no data are available regarding temperature change of pre-heated composite when placed *in vivo*; this aspect is currently under investigation.

Only a single brand and shade of composite were tested in this study. While specimen temperature prior to photo-polymerization correlated well with conversion for this particular material (Fig. 1), an absolute temperature value cannot be used to predict an absolute conversion value for other resins. The degree of conversion may vary from brand to brand and from shade to shade. Direct extrapolation of relationships observed in the present study to all other composites may not be valid, because of differences in filler composition and chemistries. However, these general trends observed were also found in another investigation (Trujillo *et al.*, 2004). The reader also needs to consider potential concerns related to intrapulpal temperature change when placing pre-heated composite, and studies are currently under way to investigate this issue.

In conclusion, monomer conversion significantly increases with temperature when a commercially available, photo-activated resin composite is pre-heated prior to polymerization. Pre-heated composite allows for reduced light exposure duration, resulting in similar or better conversion than when the composite is irradiated at longer exposures at 22°C.

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