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J Dent Res 85(1):38-43, 2006

ABSTRACT

Temperature affects the polymerization behavior of dimethacrylate-based materials. This study describes the influence of pre-polymerization temperature and exposure duration on polymerization kinetics of a commercial dental photo-activated composite at the top and at 2-mm depth. We used the temperature-controlled stage of a diamond-attenuated-total-reflectance unit to pre-set composite temperature between 3° and 60°C. Composite was light-exposed by a conventional quartz-tungsten-halogen curing unit for 5, 10, 20, or 40 sec. Real-time conversion, maximum conversion rate (R_p^{\max}), time to achieve R_p^{\max} , and conversion at R_p^{\max} were calculated from infrared spectra. Composite pre-warming enhanced maximal polymerization rate and overall monomer conversion (top significantly greater than 2 mm). Time when R_p^{\max} occurred did not change with temperature, but occurred sooner at the top than at 2-mm depth. Conversion at R_p^{\max} increased with temperature, allowing more of the reaction to occur prior to vitrification than at room temperature.

KEY WORDS: resin composite, kinetics, polymerization rate, monomer conversion, curing temperature.

Received June 7, 2004; Last revision August 29, 2005; Accepted September 15, 2005

Polymerization Kinetics of Pre-heated Composite

INTRODUCTION

Photo-activated polymerization of dimethacrylate-based materials is based on free-radical formation and leads to a strong, cross-linked network. The reaction kinetics of these multifunctional monomers used for dental restorations is a multifaceted process exhibiting complex features such as autoacceleration, autodeceleration, limited final conversion, cyclization, and radical trapping. This complex behavior arises from the decrease in mobility of reaction media by network formation as polymerization proceeds, leading to the onset of autoacceleration from the very beginning of polymerization (Andrzejewska, 2001). This phenomenon, also called the gel effect, corresponds to a sudden increase in reaction rate (R_p), despite the monomer's being consumed. It is generally accepted that autoacceleration occurs due to changes in the termination mechanism that becomes diffusion-limited, causing a reduction of the termination rate constant (k_t), and a consequent increase in the concentration of free-radicals. Polymerization rate reaches its maximum value (R_p^{\max}), and then the reaction proceeds with decreasing rate (autodeceleration), as propagation also becomes diffusion-controlled. Decreased R_p during autodeceleration is attributed to reduced mobility of both monomer and unreacted pendant double-bonds, and decreasing dissociation efficiency of photo-initiators in the viscous media (cage effect) (Cook *et al.*, 1997; Lecamp *et al.*, 1997; Lovell *et al.*, 1999, 2001a; Nie *et al.*, 1999; Andrzejewska, 2001; Sideridou *et al.*, 2002). Upon continued reaction and crosslinking, mobility is reduced further, and the system becomes even more entangled and viscous until the reaction stops due to polymer vitrification. The onset of vitrification occurs when the increasing glass transition temperature (T_g) of the reaction mixture reaches the polymerization temperature. The reaction rate will undergo a significant decrease after vitrification, and the reaction becomes very slow as it is controlled by the diffusion of the reactive species. The diffusion-controlled effect, which produces a slow-down of the polymerization process, will also determine the final degree of conversion (O'dian, 1982).

The R_p^{\max} occurs close to the point where reaction diffusion (in which radical pairs meet by a series of random chain propagation steps) starts to dominate over the translational/segmental diffusion termination mechanism (Cook, 1992). The temperature at which polymerization occurs affects the conversion process and polymer properties (Bajaj *et al.*, 1977; Bausch *et al.*, 1981; Cook, 1992; Cook *et al.*, 1997). Increased temperature enhances both radical and monomer mobility, resulting in higher overall conversion and R_p^{\max} (Cook, 1992; Lovell *et al.*, 2001b).

Temperature has been shown to have a significant effect on final conversion values of commercial dental resin composites. Pre-heating a microhybrid composite to 54° or 60°C produces higher conversion, allowing for reduced exposure duration up to 75%, while still attaining conversion values similar to those achieved with the longer exposure recommended for room temperature (Daronch *et al.*, 2005). Attainment of high conversion values by short exposure times implies a more rapid photopolymerization at

elevated temperatures. Such high reaction rates may result in elevated stress formation and hasten development of the vitrification point, proving detrimental to the integrity of the resin/tooth interfacial bond (Uno and Asmussen, 1991; Sakaguchi and Berge, 1998). However, increased conversion of composite from being pre-heated may also result in enhanced restoration properties (Lovell *et al.*, 2001b). Thus, it is important that one evaluate the kinetics of composite curing within a range of clinically relevant temperatures to understand factors that may affect the eventual success of a restoration.

This study investigated kinetic polymerization parameters at the top (irradiated) and 2-mm depth of a commercial composite as a function of pre-polymerization temperature and light-exposure duration. We tested the hypotheses that temperature increase (1) would increase maximum conversion rate (R_p^{\max}) and final conversion, (2) would reduce the time to achieve maximum conversion rate (t_{\max}), (3) would increase conversion attained at R_p^{\max} , and that (4), at a given temperature, R_p^{\max} at the top surface would be greater than at the bottom depth, but that t_{\max} would occur sooner at the top than at 2-mm depth.

MATERIALS & METHODS

Specimen Preparation

A commercial, photo-activated hybrid resin composite was used (Esthet•X, shade A2, lot # 030221; Dentsply/Caulk, Milford, DE, USA). Detailed experimental set-up and data collection have been previously described (Daronch *et al.*, 2005). In summary, composite was placed into a 2-mm-high brass ring on the temperature-controlled stage of a diamond-attenuated-total-reflectance unit (Heatable Golden Gate ATR, MKII; SPECAC Inc., Smyrna, GA, USA). Composite pre-cure temperatures were 3°, 10°, 20°, 22° (control), 25°, 27°, 30°, 40°, 54°, and 60°C. The latter two values are similar to those used in a commercial composite pre-heating device (Calset™, AdDent Inc., Danbury, CT, USA). The 3°C value represented refrigerator storage temperature. The upper composite surface was exposed with a conventional quartz-tungsten-halogen light-curing unit (Optilux 501; Demetron/Kerr Co., Orange, CA, USA) for 5, 10, 20 (control: manufacturer-recommended exposure for a 2-mm-thick increment), or 40 sec. We obtained spectra representing top surface values by pressing composite into a thin film ($\approx 150 \mu\text{m}$) on the pre-heated stage and photocuring as above. Curing unit irradiance was 630 mW/cm² between 350 and 600 nm, measured with a laboratory-grade spectral radiometer (DAS 2100; Labsphere, N. Sutton, NH, USA). Infrared spectra between 1680 and 1550 cm⁻¹ were collected at both 0-mm and 2-mm composite depths for 305 sec at a rate of 1 scan/sec, in a Fourier transform infrared spectrometer (FTS-40; Digilab/BioRad, Cambridge, MA, USA). Monomer conversion was determined 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 Øysæd, 1982; Ferracane and Greener, 1984; Rueggeberg *et al.*, 1990).

Data Analysis

Calculation of polymerization kinetics followed methods previously described (Rueggeberg *et al.*, 1999). Infrared spectra yielded information on conversion rate (first derivative of real-time conversion), maximum conversion rate (peak value in 1st

derivative, R_p^{\max}), time to achieve R_p^{\max} (t_{\max}), and conversion at maximum rate.

Statistical Analyses

Two-way analysis of variance (ANOVA)/Dunnett's two-tailed *post hoc t* test compared conversion values with those attained at 22°C for a 20-second exposure (control). One-way ANOVAs were also performed with the independent variable being temperature or depth. Comparisons were performed for each kinetic parameter. Individual unpaired, one-tailed Student's *t* tests were performed at each temperature between top and bottom parameter values. One-way ANOVA/Tukey's test detected differences in kinetic parameters with respect to exposure duration at a given temperature and surface. All statistical testing was performed at a pre-set α of 0.05.

RESULTS

Overall Observations

Control R_p^{\max} (22°C/20 sec) at the top was 13.8%/sec, reached after only 2.0 sec of light exposure; whereas, at 2-mm depth, R_p^{\max} was 7.3%/sec, reached at 2.8 sec (Table). The most extreme heated condition (60°C/5 sec) exhibited R_p^{\max} of 24.2%/sec (top), occurring after 2.0 sec, and 9.8%/sec (2-mm depth), reached after 3.6 sec. Control monomer conversion when composite reached R_p^{\max} was 16.2% (top) and 11.2% (2 mm), and 28.2% (top) and 19.5% (2 mm) when pre-heated (60°C/5 sec). Composite cured at 3° and 10°C exhibited lower R_p^{\max} and conversion at R_p^{\max} than did the control.

Real-time Conversion

At 20-second exposure, conversion significantly increased with temperatures above control (Fig. 1). Most of the reaction occurred within the first 10 sec. Top surface conversion was always significantly greater than at 2-mm depth at any given pre-heated temperature. Final conversion at 300 sec increased approximately 35% between control and extreme pre-heated conditions (54 and 60°C).

Maximum Conversion Rate

R_p^{\max} increased with temperature, and statistical differences were detected between values at 3°, 30°, 40°, 54°, 60°C, and control (22°C) for both composite surfaces (Table, Figs. 2A-2D). Top surface values exceeded those of the bottom at each temperature. Pre-cure composite temperature and R_p^{\max} followed an Arrhenius-type relationship. We determined the activation energy (E_a) at R_p^{\max} with a 20-second exposure between 3° and 60°C by plotting the natural log of conversion rate vs. inverse temperature (Lovell *et al.*, 1999). The slope of the linear regression represented E_a : 15.6 kJ/mol (Fig. 2E).

Time into Exposure of R_p^{\max} (t_{\max})

The t_{\max} ranged from 1.8 sec (40°, 54°, and 60°C/top surface) to 4.4 sec (3°C/2-mm depth), occurring significantly sooner at the top than at 2-mm depth for all temperatures and exposure durations (Table). Temperature increase diminished t_{\max} most noticeably at 2-mm depths. This reduction, however, was not statistically significant when compared with those of the control.

Conversion at R_p^{\max}

Conversion at R_p^{\max} increased with temperature, being significantly greater on the top than at 2-mm depths for all

Table. Mean (SD) of Kinetic Parameters for Composite Polymerization: Effects of Temperature, Exposure Duration, and Surface^a

	Composite Temperature (°C)	Exposure Duration (sec)	R_p^{\max} (%/sec)		Conversion at R_p^{\max} (%)		t_{\max} (sec)	
			Top Surface	2-mm Depth	Top Surface	2-mm Depth	Top Surface	2-mm Depth
R	3	40	7.1 (1.1)	3.7 (0.2)	9.3 (3.0)	6.1 (1.1)	2.2 (0.4)	3.4 (0.5)
		20	6.1 (0.8)	3.7 (0.6)	8.3 (3.8)	8.5 (1.2)	2.4 (0.5)	4.4 (0.5)
	10	40	10.4 (0.7)	4.8 (0.7)	11.8 (1.7)	8.6 (1.0)	2.0 (0.0)	3.0 (0.0)
		20	8.5 (1.3)	4.6 (0.7)	9.7 (2.0)	7.8 (3.1)	2.2 (0.4)	4.0 (0.7)
	20	40	12.4 (1.4)	6.6 (1.0)	17.0 (2.1)	10.0 (4.1)	2.0 (0.0)	2.6 (0.9)
		20	13.1 (0.9)	6.4 (0.4)	15.5 (0.7)	10.0 (4.6)	2.0 (0.0)	2.6 (0.9)
RT	(control)*	20	11.8 (1.6)	6.5 (0.8)	14.4 (2.2)	11.6 (3.2)	2.0 (0.0)	2.8 (0.8)
		20	13.8 (1.3)	7.3 (0.9)	16.2 (1.9)	11.2 (1.7)	2.0 (0.7)	2.8 (0.4)
RT	22	10	13.0 (1.4)	5.0 (0.6)	18.4 (2.7)	8.6 (1.8)	2.2 (0.4)	3.6 (0.5)
		5	13.7 (1.0)	5.1 (0.9)	17.4 (2.5)	9.0 (2.5)	2.0 (0.0)	3.8 (0.8)
	25	40	12.9 (1.1)	7.5 (0.2)	21.2 (1.2)	10.5 (3.2)	2.0 (0.0)	2.4 (0.5)
		20	13.4 (1.2)	6.9 (0.9)	20.0 (2.9)	10.5 (3.0)	2.2 (0.4)	2.6 (0.5)
		10	14.9 (1.6)	5.4 (0.2)	18.2 (2.1)	10.0 (3.2)	2.4 (0.5)	3.6 (0.5)
	27	40	13.4 (1.2)	6.6 (0.5)	22.6 (1.2)	7.6 (1.1)	2.0 (0.0)	3.0 (0.0)
		20	14.1 (2.9)	7.7 (0.3)	19.0 (2.2)	11.6 (3.0)	2.4 (0.5)	2.4 (0.5)
	30	40	15.6 (0.9)	7.8 (0.8)	22.2 (1.1)	12.1 (3.0)	2.0 (0.0)	2.6 (0.5)
		20	15.4 (2.8)	8.3 (1.0)	15.6 (3.1)	10.5 (2.6)	2.0 (0.0)	2.2 (0.4)
		10	15.0 (1.8)	6.3 (1.1)	19.0 (1.8)	10.9 (2.2)	2.0 (0.0)	3.2 (0.4)
	40	40	19.1 (2.2)	9.1 (0.5)	25.0 (2.2)	14.3 (3.5)	2.0 (0.0)	2.6 (0.5)
		20	18.1 (2.6)	9.6 (0.3)	20.6 (3.5)	13.1 (3.4)	2.0 (0.0)	2.2 (0.4)
		10	15.3 (1.9)	6.4 (1.0)	19.3 (4.6)	13.3 (4.6)	2.0 (0.0)	3.8 (0.8)
		5	16.3 (1.8)	7.0 (0.9)	22.0 (4.2)	10.4 (2.2)	1.8 (0.4)	3.0 (0.7)
	54	40	21.4 (1.1)	11.4 (1.0)	26.5 (1.6)	13.2 (2.2)	1.8 (0.4)	2.0 (0.0)
		20	21.3 (1.9)	11.1 (0.6)	26.4 (4.6)	14.2 (3.2)	2.2 (0.4)	2.2 (0.4)
		10	18.9 (0.8)	11.6 (0.9)	26.8 (4.2)	15.7 (4.8)	2.2 (0.4)	2.2 (0.4)
		5	22.1 (1.0)	10.5 (1.7)	27.8 (2.7)	14.3 (1.9)	2.0 (0.0)	3.0 (0.0)
	60	40	23.6 (0.8)	11.7 (1.8)	28.2 (3.8)	16.2 (2.0)	1.8 (0.4)	2.3 (0.4)
		20	22.1 (1.7)	10.8 (1.0)	25.0 (3.8)	21.2 (2.0)	2.0 (0.0)	3.0 (0.0)
		10	22.2 (1.8)	11.9 (0.6)	27.3 (3.4)	18.4 (6.7)	2.0 (0.5)	2.6 (0.5)
		5	24.2 (1.8)	9.8 (1.1)	28.2 (3.7)	19.5 (5.3)	2.0 (0.0)	3.6 (1.1)

^a n = 5 specimens per experimental group.

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

R Refrigerator temperature; RT Room temperature.

temperatures and exposure durations (Table, Figs. 3A-3D). Conversion at R_p^{\max} was 8.3% at 3°C, as opposed to 28.2% at 60°C (top).

Effect of Exposure Duration on Kinetic Parameters

For most test conditions, exposure duration did not have a significant effect on kinetic parameters when compared at a specific temperature. However, at 2-mm depth, t_{\max} at 10 sec (40°C) or 5 sec of exposure (54° and 60°C) occurred later than at 20 sec of exposure. Also, at 2-mm depth, 10- and 5-second exposures produced significantly lower R_p^{\max} than did 20-

second exposures at 22° and at 40°C.

DISCUSSION

This study demonstrated the strong influence of composite temperature on polymerization kinetics of a dental restorative composite. The first and third hypotheses were validated. Temperature increase dramatically improved molecular mobility, increasing collision frequency of reactive species, and allowing for further monomer conversion before the onset of autodeceleration. Increase in R_p^{\max} with temperature was

expected, and was in agreement with published reports (Cook, 1992; Watts, 1992; Nie *et al.*, 1999; Lovell *et al.*, 2001b; Trujillo *et al.*, 2004). Increased molecular mobility allowed propagation to continue for a longer time without becoming diffusion-controlled, increasing conversion at R_p^{max} . Furthermore, temperature rise improved the segmental mobility of the polymer chain, postponing the change in the termination mechanism from one diffusion-controlled to one controlled by reaction diffusion (Cook, 1992; Andrzejewska, 2001; Scott *et al.*, 2002). In this way, more monomer could convert into polymer prior to vitrification. The glass transition temperature of the reacting mixture increases as monomer conversion rises, so greater final limiting conversion can be achieved at higher polymerization temperatures.

The kinetic constants for dimethacrylate polymerization exhibited an Arrhenius-type behavior (*e.g.*, large increase in reaction rate with small temperature increase) (Billmeyer, 1984; Lovell *et al.*, 2001b). Apparent activation energy at R_p^{max} (15.6 kJ/mol) was similar to that reported by others using dimethacrylates (15.5 kJ/mol; Lecamp *et al.*, 1997), diacrylates (13.5 KJ/mol; Scherzer and Decker, 2000), and methylmethacrylate (17.1 kJ/mol; Odian, 1982), and was within the range expected for reaction-diffusion-controlled termination and for translational diffusion (Scott *et al.*, 2002). It should be noted that the Arrhenius plot for the rate data taken at constant conversion presents a more complex behavior (Figs. 2F, 2G). Quite similar trends were observed by Cook (1992) and Scott *et al.* (2002). At lower temperatures and higher conversions, the polymerization rate becomes considerably slower as the propagation,

Figure 2. Conversion rate with time at the top surface and at 2-mm depth, at selected temperatures and exposure durations: (A) 40 sec, (B) 20 sec, (C) 10 sec, and (D) 5 sec, (E) natural log of R_p^{max} as a function of inverse temperature. A linear fit to the data was used to determine the activation energy (15.6 kJ/mol). (F) Natural log of conversion rate as a function of inverse temperature and monomer conversion at the top surface and (G) at 2-mm depth. For A-D, data at each one-second time point represent the mean of 5 replications; coefficient of variation ranged from 3.1 to 17.6%.

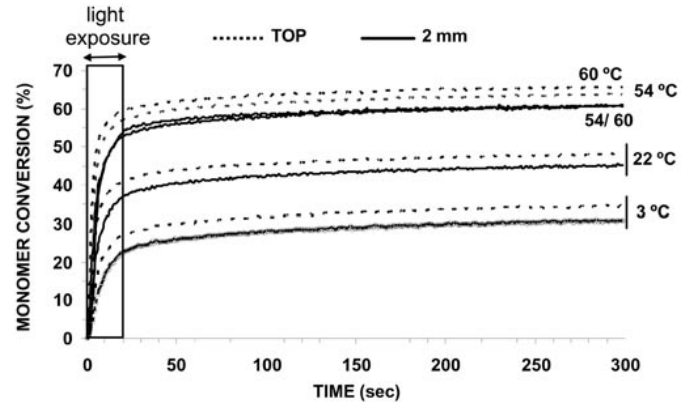
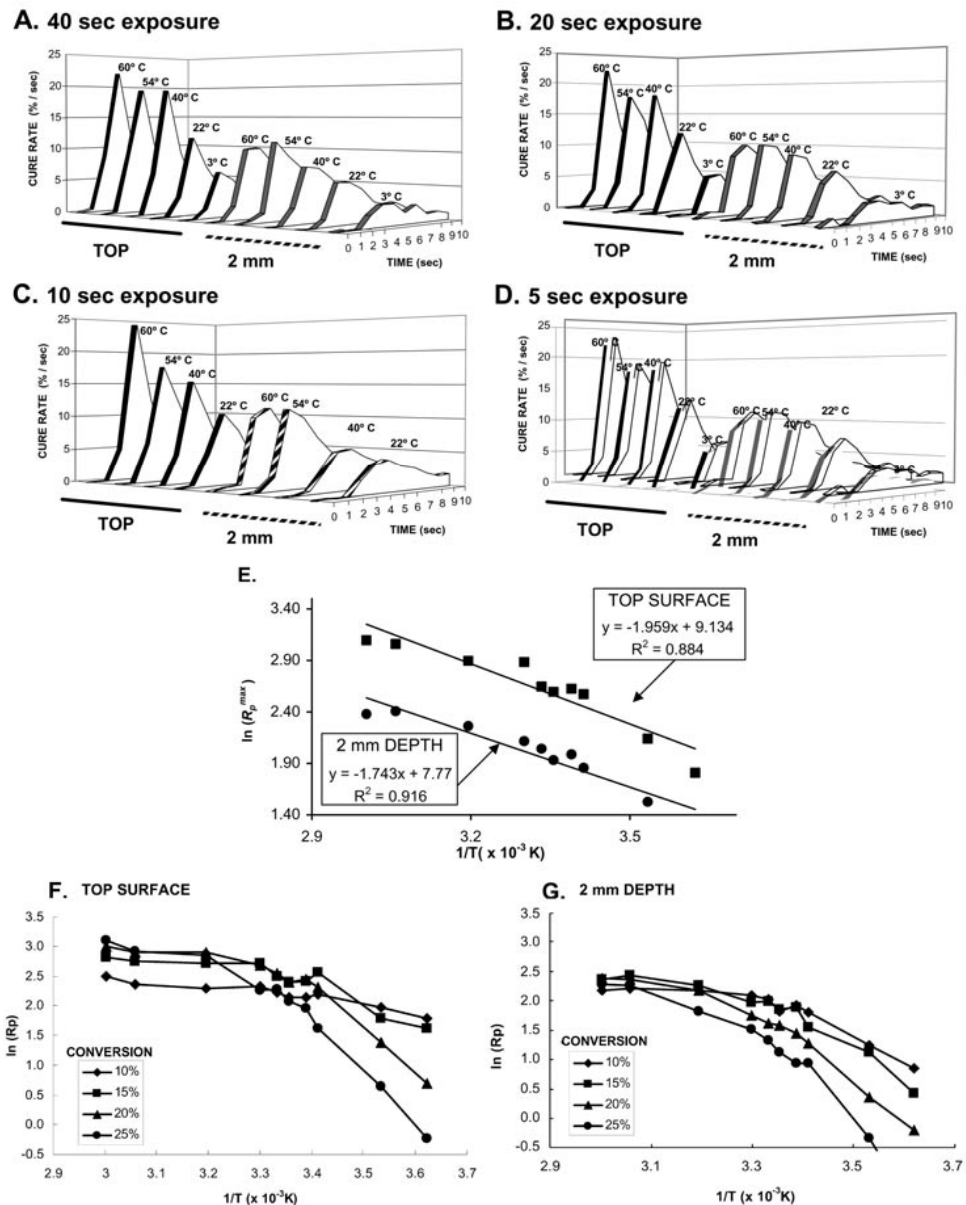


Figure 1. Conversion with time at the top surface and at 2-mm depth with 20-second exposure duration at pre-selected composite temperatures. $n = 5$ specimens per experimental group. Coefficient of variation ranged from 0.3 to 3.0%.



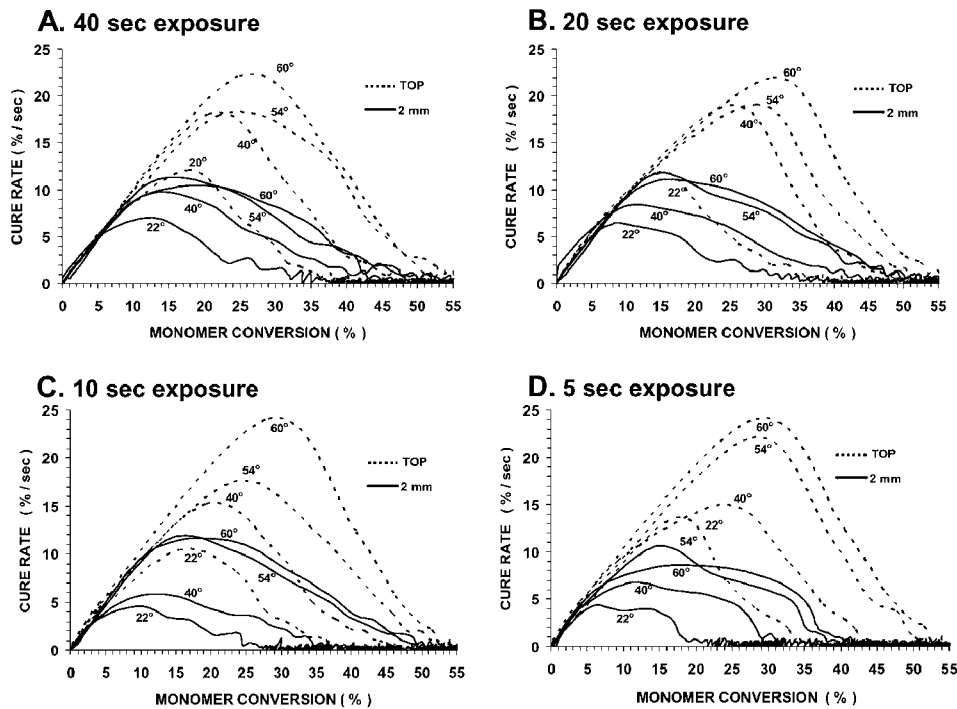


Figure 3. Conversion rate as a function of monomer conversion obtained at the top surface and at 2-mm depth for various temperatures and exposure durations: (A) 40 sec, (B) 20 sec, (C) 10 sec, and (D) 5 sec. Each datapoint represents mean of 5 replications; coefficient of variation ranged from 6.0 to 36.4%.

termination, and initiation steps become diffusion-controlled, due to a decrease in molecular mobility.

Composite reacts quickly once light exposure is initiated (Fig. 2). The t_{\max} occurred before 5 sec of light exposure at 2-mm depth, and even sooner—under 3 sec—at the top surface. At a given surface, as temperature increased, t_{\max} slightly decreased. This change, however, was not statistically significant. Thus, the second hypothesis was rejected. This finding is in agreement with those of others (Maffezzoli *et al.*, 1994; Nie *et al.*, 1998). However, other studies also found that t_{\max} can increase or remain almost constant (Cook, 1992) or decrease with reduction in temperature (Cook, 1993). Thus, this effect seems to be dependent on the system nature and on the experimental conditions used. Final conversion increased with temperature, and its dependence on exposure duration has been established (Daronch *et al.*, 2005). The effect of exposure duration on kinetic parameters is clinically relevant in the context of the use of short exposures (5 or 10 sec) when composite is pre-heated. At a given temperature and surface, R_p^{\max} and t_{\max} should not be dependent on exposure duration. As long as the duration of light exposure exceeds the occurrence of R_p^{\max} , kinetic parameters would not be affected. Exposures shorter than this critical time would result in lower conversion, yielding poorer properties. Some commercial light-curing units advocate exposure durations of only 1 to 3 sec, possibly not fulfilling this requirement. In the present study, we measured conversion on the top surface and at 2-mm depth, which is the maximal accepted thickness for placement of composites (Rueggeberg *et al.*, 1994). We achieved equivalent cure at 2 mm in less exposure time with increased temperature. It should be noted, though, that while elevated cure temperatures can facilitate reduced irradiation time for the

same conversion, the depth of cure will probably be less, based on the logarithmic relationship between the depth of cure and irradiation dose (Cook and Standish, 1983).

The fourth hypothesis was upheld. At a given temperature, R_p^{\max} was greater and t_{\max} occurred sooner at the top surface than at the bottom. These results are based on factors affecting photo-initiation and the ability of light to penetrate: Radiation is attenuated and initiation is delayed at greater depths (Cook and Standish, 1983). Therefore, irradiance at the bottom surface will always be lower than at the top. Temperature can affect the reaction rate by influencing rates of propagation and termination. However, the increase in cure temperature has a minimal effect on the decomposition rate of photoinitiators, since it is light rather than heat that leads to radical formation (Trujillo *et al.*, 2004). The effect of low temperature on composite polymerization was significant. When composite was

polymerized at 3°C, system viscosity was apparently so great that R_p^{\max} occurred at less than 10% conversion, and final conversion was limited to values below 35%. These results stress that refrigerator-stored composite should be allowed to reach room temperature prior to clinical use.

The results of this study demonstrate that pre-warming composite enhances conversion without hastening the time at which maximum cure rate occurs at the top and at 2-mm depth. This enhancement is probably attained by increased molecular mobility resulting from the temperature increase and, thus, the postponement of diffusion-controlled propagation, reaction-diffusion-controlled termination, and autodeceleration, thereby allowing the system to reach higher limiting conversions before vitrification. As a result, a more highly crosslinked polymer network and improved mechanical and physical properties may be anticipated from composites when they are pre-heated to temperatures above that of the room.

ACKNOWLEDGMENTS

The assistance and dedication of Ms. Linda Moss and the talents of Mr. Don Mettenburg are greatly appreciated. This research was supported by CAPES Brazil (grant 03/48031) and by The Medical College of Georgia School of Dentistry. The authors thank Dentsply/Caulk for supply of composite. This paper is in partial fulfillment of requirements for the PhD degree for Dr. Márcia Daronch, University of São Paulo, São Paulo, SP, Brazil.

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