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The effect of specimen temperature on the polymerization of a resin-composite

Richard B. Price^{a,*}, J.M. Whalen^b, Thomas B. Price^c, Christopher M. Felix^d, John Fahey^e

^a Department of Dental Clinical Sciences, Dalhousie University, Halifax, Nova Scotia, Canada

^b Department of Chemistry, Dalhousie University, Canada

^c Student, Faculty of the Environment, University of Waterloo, Canada

^d Department of Dental Clinical Sciences, Dalhousie University, Canada

^e Halifax, Canada

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ABSTRACT

Objective. To use rapid scan FT-IR and Knoop microhardness to determine the effect of specimen temperature on the rate and extent of polymerization of a dental resin.

Methods. Two-millimeter thick specimens of shade A2 Tetric EvoCeram were light cured for 20 s at 22, 26, 30, and 35 °C. The IR spectrum was obtained at the bottom of the specimens at a rate of 3 measurements per second for the first 5 min, and then again 2 h later. The Knoop microhardness was measured at the bottom of the samples in the region where the IR spectrum was recorded at 5 min and 2 h after light curing. Data were statistically analyzed using mixed model ANOVA (with Fisher's PLSD) to examine the effect of temperature, time and their interaction. The rate of conversion was determined using first differences and smoothed using a cubic spline procedure.

Results. The bottom surfaces of the samples light cured at 22, 26, 30 and 35 °C were all significantly different from each other ($p < 0.05$). The higher temperature resulted in higher degree of conversion and Knoop microhardness values, and faster maximum rate of polymerization, which also occurred sooner. One second after the light was turned on, the rate of conversion was 106% faster at 35 °C than at 22 °C ($p = 0.003$). Regression analysis showed a positive linear correlation between the degree of conversion and Knoop microhardness ($r^2 = 0.93$).

Significance. A relatively small difference in temperature can have a large and significant effect on the rate and extent of polymerization of dental resin. Consequently laboratory studies comparing the performance of resins should be conducted at clinically relevant temperatures.

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1. Introduction

Light-cured resin composites are widely used in dental restorations. These resins are polymerized by a light-curing

unit (LCU) and the degree of conversion (DC) of dental resins can be determined using Fourier Transform-Infrared Spectroscopy (FT-IR) [1–5]. In addition, Knoop microhardness has been shown to be a reliable method to determine how well a resin is cured [6] and a good correlation has been reported

* Corresponding author. Tel.: +1 902 494 1226; fax: +1 902 494 1662.

E-mail address: rbprice@dal.ca (R.B. Price).

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between the Knoop microhardness and both the DC [5,7] and the Young's modulus [6].

The overall rate of polymerization of unfilled resins is determined by the rates of the initiation, propagation and termination phases of the reaction. The rate constant for initiation (k_i) is independent of temperature, whereas the rate constants for both propagation (k_p) and termination (k_t) increase with temperature according to the Arrhenius dependence [8]. Using typical activation energies for propagation and termination, it has been estimated that the overall polymerization rate for unfilled dimethacrylate based resins will increase by 1.90% for each 1 °C rise in temperature [8]. However, the rate of polymerization of filled dental resins is further accelerated by the Trommsdorf effect, wherein the marked increase in the viscosity of the filled resin material during gelation decreases the mobility of large polymer radicals. This effectively reduces the termination rate constant k_t at a given temperature and accelerates the reaction [8].

Kinetic studies of unfilled dimethacrylate resins using calorimetric techniques [9–11] have shown that for a given resin composition and light intensity, increasing the temperature up to 50 or 60 °C results in greater extent of conversion as well as an increased maximum conversion rate. Daronch et al. [1,12] and Trujillo et al. [13] explored the effect of pre-heating commercial filled resin composites using infrared methods. In the 2006 study by Daronch et al. [1] irradiation of Esthet X shade A2 with a QTH source emitting 630 mW/cm² showed a marked increase in extent of conversion at the top and bottom surfaces of 2-mm thick samples when temperatures of the resin were increased from 3 °C to 60 °C. Similarly Trujillo et al. [13] observed an increase in immediate and final conversion values for three commercial resin composites using three different curing lights, when the temperatures of the resins were increased from 23 °C to 54.5 °C. Atai and Watts concluded in their study that shrinkage strain rate of a light curing resin composite increases at 45 °C compared to 23 °C [14]. Similar conclusions were reported by Elhejazi when the temperature was raised up to 60 °C [15]. Kitzmüller et al. also reported higher strain values at 37 °C compared to room temperature for dual-curing resin cements [16]. These results confirmed that the basic temperature dependency observed in the earlier kinetic studies [9–11] is relevant to commercial resin composites and resin cements.

The majority of dental research on resin polymerization, shrinkage and bond strengths has been conducted at room temperature, e.g., the ISO 4049 test for depth of cure [17] stipulates that the temperature of the resin should be 23 ± 1 °C. Since resin polymerization in the mouth occurs neither at room temperature nor above 37 °C but at between 30 °C and 35 °C [18,19], it is expected that the rate and extent of resin polymerization in the tooth will be different from that occurring at room, or higher temperatures, e.g., above 37 °C. Consequently resin properties that are affected by the polymerization rate, such as bond strengths to the tooth [20], shrinkage, or internal stresses within the restoration [14–16], may be affected by relatively small changes in the resin temperature. This interaction may affect the conclusions of these studies because different resin based composites may react very differently when the temperature of the experiment is changed from room to typical intra-oral temperatures [16].

The aim of this study was to examine the photocuring of a common commercial resin (Tetric Evoceram shade A2) in the temperature range of 22–35 °C. Reflectance infrared spectroscopy (measuring DC) and Knoop microhardness were used to monitor polymerization. The temperature range was chosen to evaluate the rate and extent of resin polymerization carried out at room temperature and at representative intra-oral temperatures [18,19]. A rapid infrared scan rate was used to monitor the DC at the bottom surface of the resin during the crucial initiation and gelation stages. The Knoop microhardness of the vitrified resins was correlated with the DC at 5 min and at 2 hours. Knoop microhardness was correlated with the DC of the vitrified resins at 5 min and 2 h.

The hypotheses tested were that:

1. The degree of conversion, rate of polymerization and Knoop microhardness, will all be greater at representative intra-oral temperatures compared to room temperature.
2. Within the range of conversion studied, there will be a positive linear correlation between the degree of conversion and Knoop microhardness measurements made at the same location.

2. Materials and methods

The same lot number of shade A2 Tetric Evoceram (Ivoclar-Vivadent Amherst, NY, USA) resin composite was used throughout the study. Samples of this resin composite were prepared in 2-mm thick aluminum rings that had a 6-mm diameter internal hole, directly on a temperature controlled Attenuated Total Reflectance (ATR) element (Golden Gate, Specac, New Brunswick, NJ, USA) attached to an infrared spectrometer (Tensor 27, Bruker, Billerica, MA, USA). The ring was filled with the resin composite and, using a flat microscope slide, a 50 μm thick Mylar Matrix Strip (Patterson Dental, St. Paul, MN, USA) was pressed down over the uncured resin to produce a flat surface. The slide was removed and resin composite and the ring were left on the heated ATR plate in the dark for 5 min to allow the temperature of the resin composite on the ATR plate to stabilize at 22, 26, 30, or 35 °C. The 5 min time interval was based on a pilot study where the temperature at the top and bottom of the resin composite was measured using a fast response tissue implantable T-type thermocouple (IT-23, Physitemp Instruments, Clifton, NJ, USA) and found to be the same as the heated ATR element after 5 min. The resin composite was then light cured at a distance of 0-mm from the end of the light guide for 20 s using a SmartLite IQ² curing light (Dentsply, York, PA, USA). The light output from this unit was recorded using a laboratory grade spectroradiometer (USB 4000, Ocean Optics, Dunedin, FL, USA) connected to an integrating sphere (FOIS-1, Ocean Optics) and analyzed using SpectraSuite software version 5.1 (Ocean Optics). This system was calibrated using a National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) referenced light source (Ocean Optics, LS-1-Cal-Int). The light output was checked three times throughout the experiment and the mean ± standard deviation (SD) irradiance values were 750 ± 8 mW/cm². Thus all samples received 15 J/cm².

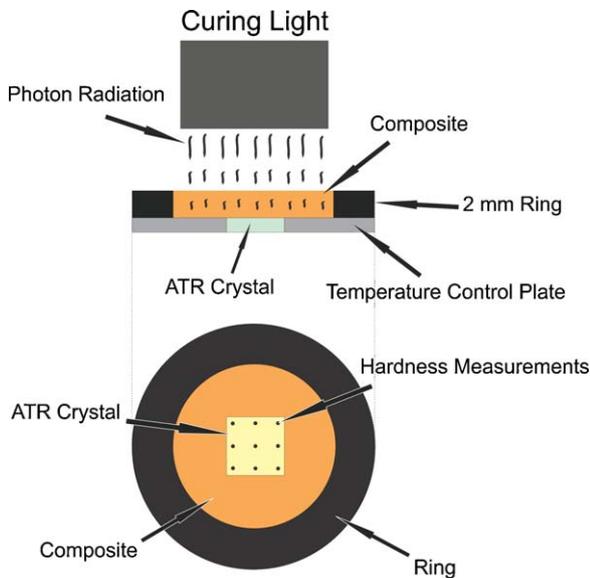


Fig. 1 – Location where the nine Knoop microhardness readings were made on the bottom surfaces in the region of the ATR crystal.

Rapid scan Attenuated Total Reflectance Fourier Transform-Infrared Spectroscopy (ATR FT-IR) was used to determine the DC at the bottom of the resin composite as it polymerized. For three resin specimens made at each temperature (22, 26, 30, and 35 °C), the spectral window of 1200–1680 cm^{-1} was sampled at intervals of 0.33 s for 5 min. For each spectrum at a given time, the DC was calculated from the ratio of the integrated areas of the peaks at 1608 cm^{-1} (aromatic C=C) and 1638 cm^{-1} (aliphatic C=C) [5,21,22]. Five minutes after light curing the resin, the specimens were removed from the ATR plate, the Mylar strip was removed from the top surface and immediately nine Knoop microhardness readings were made in close proximity to the location of DC recording (Fig. 1). The 6 mm diameter hole in the metal ring allowed at least a 1-mm buffer of resin composite between any hardness measurement and the metal ring. This 1-mm buffer minimized any effect the mold may have had on resin polymerization [23]. Three additional specimens were made at each temperature, and these specimens were left on the ATR plate for 2 h before making the DC and then the microhardness measurements. The microhardness measurements were made using a Knoop indenter that applied a 50-g load for 10 s (HM-123 Mitutoyo Canada Inc., Mississauga, ON, Canada). This hardness tester was pre-programmed to measure nine Knoop microhardness values across a 3 × 3-mm matrix pattern with a 1.5 mm pitch in the same area where the DC had been recorded (Fig. 1). A total of 27 Knoop microhardness measurements were made at each temperature and at each time interval. The Knoop microhardness at the bottom of the resin specimens, as well as the polymerization rates and final DC recorded at the bottom of the specimens were compared at curing temperatures of at 22, 26, 30, and 35 °C. A total of 24 samples were made (4 temperatures × 3 repetitions × 2 time intervals) in a random order of temperatures. Analyses of variance (ANOVA) followed by Fisher's PLSD post hoc

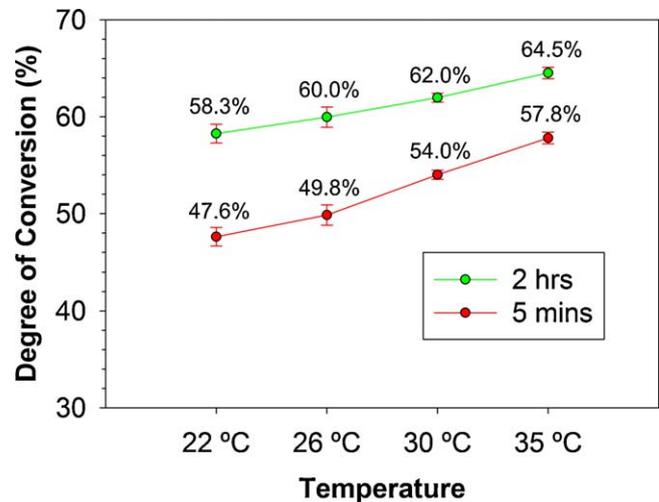


Fig. 2 – Effect of initial temperature of the resin on mean (\pm SD) degree of conversion measured at the bottom of the specimens at 5 min and 2 h after light curing.

multiple comparison analyses were carried out for DC and hardness to study the effect of temperature at a preset alpha of 0.05. A mixed model ANOVA was carried out to examine the effect of temperature, time and their interaction. The rate of conversion was determined using first differences and smoothed using a cubic spline procedure [24].

3. Results

At 5 min and at 2 h, the bottom surfaces of the samples that had been light cured at 22, 26, 30 or 35 °C were all significantly different from each other ($p < 0.05$). The higher temperature resulted in higher degree of conversion and Knoop microhardness values, and a faster maximum rate of polymerization, which also occurred sooner. Analysis of the results from the three repeats showed that a small round-to-round variability was present, but this was explicitly accounted for in the statistical models used. Table 1 reports the one-way ANOVA showing the highly significant effect of temperature on the DC at 5 min. Fig. 2 shows that after 2 h there was a meaningful and significant increase in DC at 35 °C; the mean \pm SD for the resins light cured at 22 °C was 58.3 \pm 1.0% and for the resins cured at 35 °C the DC was 64.5 \pm 0.6%.

The Knoop microhardness at the bottom increased as the temperature of the resin increased from 22 °C to 35 °C. Table 2 shows that at 2 h after light curing, the Knoop microhardness values at the bottom of the specimens were significantly greater when the initial temperature of the resin was increased. Fig. 3 illustrates the effect of temperature on Knoop microhardness. Two hours after light curing there was a meaningful and significant increase in mean \pm SD Knoop microhardness at the bottom from 30.9 \pm 1.4 to 43.8 \pm 0.4 KHN_{50gf} as the temperature of the resin was increased from 22 °C to 35 °C.

Fig. 4 illustrates that at all temperatures, even though the curing light was on for 20 s, the majority of the polymerization was completed in the first 10 s, as evidenced by a plateau

Table 1 – One way ANOVA showing effect of temperature on degree of conversion at 5 min.

DC @ 5 min	DF	Sum of squares	Mean square	F-value	p-Value	λ	Power
Temperature	3	183.311	61.104	95.148	<.0001	285.445	1.000
Residual	8	5.138	0.642				

Table 2 – One way ANOVA showing effect of temperature on Knoop hardness at the bottom 2 h after light curing.

Bottom KHN @ 2 h	DF	Sum of squares	Mean square	F-value	p-Value	λ	Power
Temperature	3	932.483	310.494	172.663	<.0001	517.990	1.000
Residual	32	57.544	1.798				

Table 3 – Mixed model ANOVA showing the effect of time and temperature and their interaction on the rate of polymerization.

Effect	Numerator DF	Denominator DF	F-value	Pr > F
Temperature	3	3	9.06	0.0120
Time	45	88	63.45	<0.0001
Temperature \times Time	135	264	1.55	0.0014

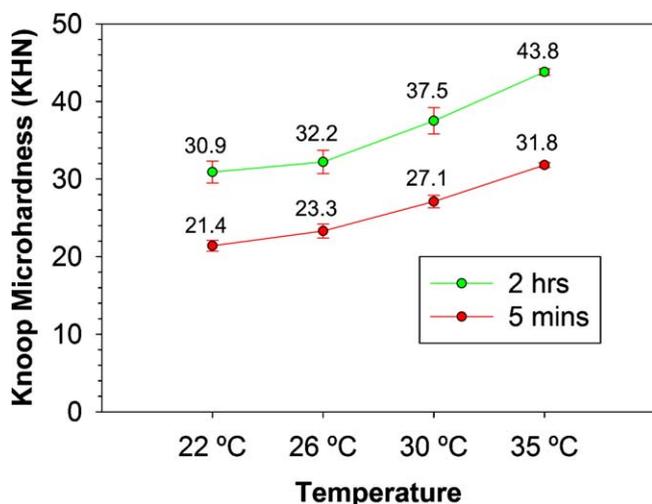


Fig. 3 – Effect of initial temperature of the resin on mean (\pm SD) Knoop microhardness measured at the bottom of the specimens 5 min and 2 h after light curing.

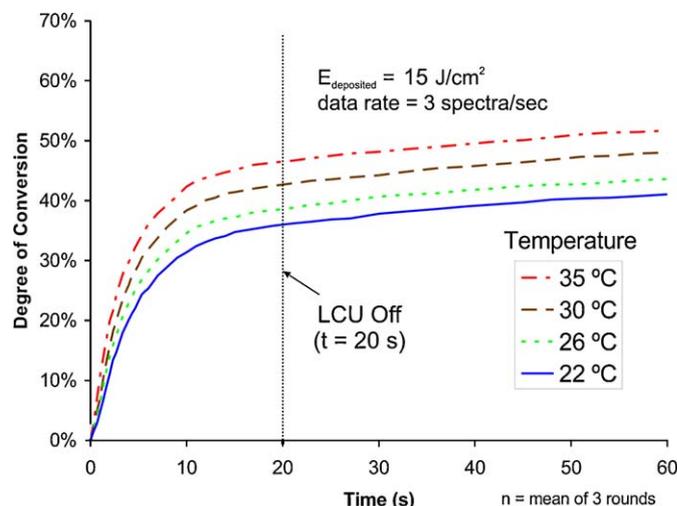


Fig. 4 – Effect of initial temperature of the resin on the degree of conversion in the first 60 s.

signifying the transition within the resin from a rubbery state to a glassy state. The mixed model ANOVA reported in Table 3 shows that temperature, time and their interaction were all significant factors on the rate of polymerization. Fig. 5 shows the smoothed cubic spline fit of the conversion rate averaged over the three rounds as a function of time at each temperature. Individual components of the test for interaction in the mixed model ANOVA showed the most significant effects occurred within the first second ($p < 0.0001$). When the temperature of the resin started at 22 °C, the maximum rate of polymerization (R_p) was 7% per second and this occurred at ~ 1.7 s. When the resin started at 35 °C, the maximum rate of polymerization was 12% per second and this occurred at ~ 0.7 s. For the time interval ending after the first 1/3 s, the conversion rate was 79% faster when the initial temperature of the resin was increased from 22 °C to 35 °C ($p = 0.046$). At 1 s after the LCU was turned on, there was a 106% increase in the conversion rate when the starting temperature was increased from 22 °C to 35 °C ($p = 0.003$). At 2 s, there was a 50% increase in the conversion rate when the starting temperature was

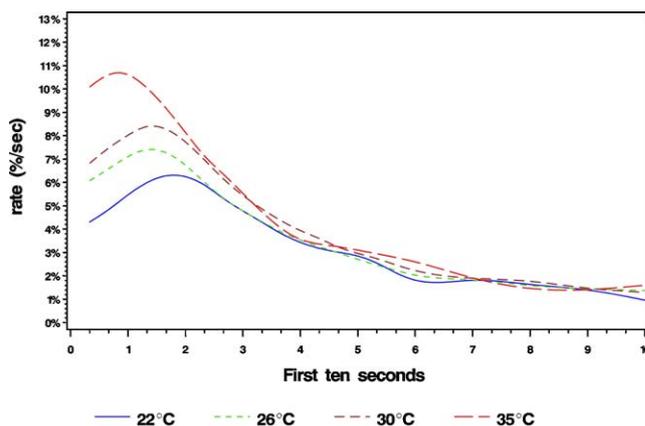


Fig. 5 – Effect of initial temperature of the resin on the rate of conversion versus the first 10 s of the reaction. Each smoothed line is the mean of three repetitions.

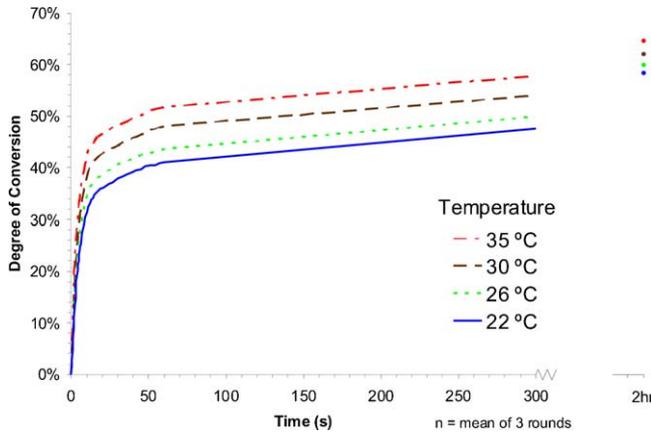


Fig. 6 – Effect of initial temperature of the resin on the degree of conversion from 0 to 300 s and the final DC at 2 h.

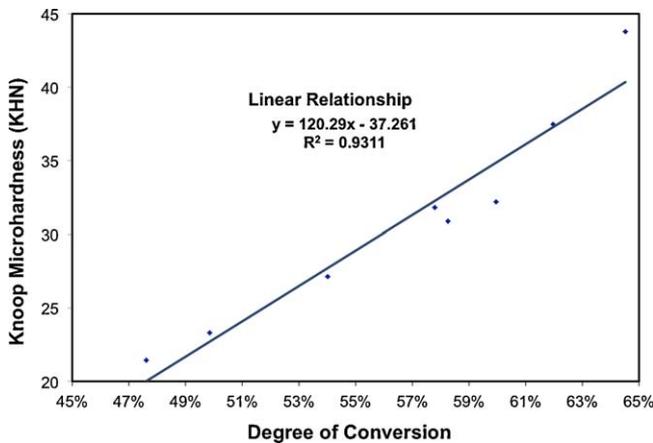


Fig. 7 – Regression analysis between mean degree of conversion and mean Knoop microhardness at the bottom of the specimens obtained at each temperature and at both times (mean values at the 4 temperatures × 2 times).

increased from 22 °C to 35 °C, but this was not a significant difference ($p=0.16$). Thereafter, the initial temperature of the resin did not have an effect on the rate of conversion, but it did have an effect on the amount of conversion. Fig. 6 illustrates how the degree of conversion after the initial very active phase increased with temperature and time, up to the final recording at 2 h. Fig. 7 shows the mean DC and Knoop microhardness values obtained at the bottom of each cured sample at each temperature and at both times (8 values based on the mean values at the 4 temperatures × 2 times). There was a strong positive linear correlation (r^2 value of 0.93) between the mean DC and Knoop microhardness measurements recorded at the same location.

4. Discussion

The bottom surfaces of the samples light cured at 22, 26, 30 and 35 °C all had significantly different DC and Knoop microhardness values from each other ($p<0.05$). Resin polymerization occurs rapidly within the first 2 s after the LCU is turned on

and the ability to make three measurements a second using real time ATR FT-IR is an improvement on previous reports that were based on one scan per second [1,12]. The first hypothesis was proven to be correct as the degree of conversion, rate of polymerization and Knoop microhardness at the bottom of the sample were all significantly increased by starting to light cure the resin at simulated intra-oral temperatures compared to room temperature.

The volume of resin contained within the 2-mm high, 6-mm diameter ring (0.057 mm^3) was similar to the volume of resin in a large restoration in a molar tooth. The shapes of the %DC versus time curves (Figs. 4 and 6) are typical for bulk polymerization of dimethacrylate resins [25–27]. The smoothed four curves in Fig. 5 illustrate the maximum rate of polymerization (R_p^{max}) occurred at each temperature. The time when this occurs corresponds to the transition between autoacceleration and autodeceleration regimes, as is described elsewhere [9,26]. These figures show that the R_p^{max} and the DC increase as the initial starting temperature increases, which is also consistent with an Arrhenius dependence of rate constants for propagation (k_p) and termination (k_t) [8,11]. The overall polymerization rate is controlled by a competition between propagation (which increases the rate) and termination (which decreases the rate), and the rate of reaction decreases after R_p^{max} as the monomer is consumed. Auto-acceleration of the rate due to a reduction of k_t occurs due to the Trommsdorf effect. The increase in viscosity as the polymer network is formed results in drastically reduced diffusion and mobility of large polymer radicals. This effectively reduces the termination rate constant k_t at any given temperature [8] and shortens the time at which the maximum rate of polymerization (R_p^{max}) occurs. Fig. 5 highlights the first 10 s of the reaction as the resin composite undergoes a transition from liquid monomers to a rubbery state (liquid monomer combined with polymer). The plateau region illustrated in Fig. 6 signifies that a substantially reduced rate of polymerization occurs when the network has reached the glassy state, after this point the rate of polymerization is controlled by diffusion of the molecular species [25]. Interestingly, Figs. 5 and 6 show that after 5 seconds and up to at least two hours the rate of polymerization remained essentially the same for all starting temperatures.

Using experimental resins light cured with much lower irradiance values, Cook [10] showed that a faster initial rate of polymerization resulted in greater final degree of conversion because the excess free volume of the polymer allowed greater macromolecule mobility and therefore a greater extent of reaction. This is entirely consistent with our observations since a higher extent of the reaction (DC), shown in Figs. 4 and 6, occurred when the initial reaction rate was greater. Several authors have noted that the rate of polymerization increases with initial viscosity of the monomers [25,28] and commercial dental resins often have a higher viscosity than experimental blends of unfilled monomers. As a result, the rates of polymerization of commercial resin based composites can be higher than unfilled monomers owing to the Trommsdorf effect, wherein the termination rate constant is effectively reduced by the decreased mobility of macroradicals during gelation (e.g., k_t is not constant with temperature) [8]. This complex interplay of propagation and termination rates is illustrated in Fig. 5. When the initial temperature of the resin

is increased by only a few Celsius, the value of R_p^{\max} increases and occurs much sooner. This observation is consistent with an overall increase in the rate of the complex polymerization process as the temperature increases [8].

It should be noted that the times of maximum rate of polymerization (t_{\max}) for the Tetric Evoceram A2 used in this study ranged from 2.3 s at 22 °C to 0.7 s at 35 °C. These values of t_{\max} occurred sooner than those observed for the photopolymerization of Esthet•X (Dentsply, Milford, DE) at similar temperatures (2.6 s at 20 °C and 2.2 s at 40 °C), but these results were based on data collected at one scan per second [1]. This difference in t_{\max} may be due to the faster scanning rate of 3 scans per second, or may be because the polymerization of Tetric Evoceram occurs at a faster rate than Esthet•X. Further studies using a wider range of resins and irradiance values are required to determine at what time t_{\max} occurs.

The second hypothesis that there would be a positive linear correlation between the DC and Knoop microhardness measurements recorded in the same region of the specimens was also proven. Fig. 7 shows that, within the range of DC and Knoop microhardness values recorded in this study, there was an excellent positive linear correlation between the DC and Knoop microhardness with an r^2 value of 0.93. This supports previous studies that have also shown a good correlation between degree of conversion and the Knoop microhardness of dental resins [5,7] and supports the use of Knoop microhardness as a means to evaluate the polymerization of dental resins [6]. While it has been suggested that directly underneath the overlying Mylar strip there is a resin rich layer [29] that must be removed before hardness testing [30], closer examination of this article shows that there was no significant difference in the Vickers Hardness values recorded on unfinished specimens that had been cured through the Mylar and specimens that had been polished with 400 grit silicon carbide paper followed by 30 and 15 μm diamonds [30]. This treatment would have removed all of the top layer of the resin. Only those specimens that had been polished through a series of 400, 600, 1200 and 2000 grit silicon carbide papers and then finally with 1 μm aluminum oxide slurry were significantly harder than the unfinished surfaces. This additional polishing of the specimens may have produced enough thermal energy to cause additional polymerization of the resins. For this reason, the resin specimens in the present study were not polished prior to hardness testing and instead were tested immediately after they were removed from the heated ATR plate.

4.1. Research, clinical implications, study limitations

Although this study used only one commercial resin composite, the results were completely as expected and have implications when interpreting laboratory studies that have polymerized dental resins at room temperature. The ISO 4049 test for depth of cure [17] stipulates that the resin should be at 23 ± 1 °C, but this temperature can be ~ 12 °C less than mouth temperature [18,19]. The results of this study show that at 1 s, there was a 106% increase in the conversion rate for one popular commercial resin composite when the initial temperature of the resin was increased from 22 °C to 35 °C. As reported by Atai and Watts, the shrinkage strain rate of a light curing resin composite increases with increasing temperature [14].

A similar result has been reported for some dual curing resin cements [16]. The faster rate of polymerization shown in Fig. 5 may increase the rate of stress build up within the resin and at the resin–tooth interface. This may negatively affect the longevity of the bond to tooth structure. Therefore, it is recommended that laboratory studies comparing the performance of resins, or the effect of different LCUs on resin photopolymerization, should be conducted with the resin at a clinically relevant temperature. Further studies are required to study the complex interaction of small changes in temperature on the rate and extent of polymerization of a range of commercial dental resins with different viscosities and photoinitiator systems.

5. Conclusions

Under the conditions of this study, the bottom surfaces of the samples light cured at 22, 26, 30 and 35 °C were all significantly different from each other ($p < 0.05$). It was concluded that small changes in the initial temperature of the resin significantly affect the final degree of conversion, the Knoop microhardness, the rate of polymerization and the time at which the maximum reaction rate occurs. One second after the light was turned on, the conversion rate was 106% faster ($p = 0.003$) when the initial temperature of the resin was increased from 22 °C to 35 °C. Within the range of DC and Knoop microhardness values recorded in this study, there was a positive linear correlation between the degree of conversion of the resin and the Knoop microhardness ($r^2 = 0.93$). This supports the use of Knoop microhardness as a useful measurement parameter.

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