

A Study of Localized Curing of Glass-Filled Composites Using Microhardness Measurements

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ABSTRACT: Extent of cure of hybrid composite systems is examined by conducting hardness measurements at different stages of the photopolymerization reaction and obtaining kinetic parameters that matched the experimental data. The materials are commercial dental composites based on bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane resins with different photoinitiator concentrations as well as filler particle sizes and combinations. Samples (five per group) were made using nylon molds (2.5×5 mm) of the tested composites. The samples were light cured with a constant-power light source for durations up to 20 s. After curing, all samples underwent Vicker's hardness testing of top and bottom surfaces. While there are significant differences in the polymerization behavior between the top and bottom locations for the tested composites, the corresponding growth exponent n , a kinetic parameter in the kinetic

theory, is very close in all cases. For the tested materials the coefficient factor k is much lower for the bottom surfaces compared with the top surfaces. This reduction in the value of k is more severe for the material with a higher concentration of the photoinitiator as well as a higher percentage of glass filler particles in the wavelength range affecting the photopolymerization. It is argued that a relationship between k and the irradiation intensity can be used to quantify the decay of irradiated light with its penetration into the composites. The comparisons can be used to draw preliminary conclusions on the parameters controlling the effective depth of cure in a hybrid composite. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 426–431, 2005

Key words: composites; curing of polymers; photopolymerization; kinetics; hardness

INTRODUCTION

Light-cured resin composites are in wide use as restorative dental materials. The majority of dental composites in commercial production use camphoroquinone as the photoinitiator, which is a diketone absorber of the irradiated visible light in the wavelength range of 400 to 500 nm to create free radicals that initiate the polymerization reaction.^{1–3} While the visible-light curable tooth-color composites offer clinical advantages to mercury-based silver amalgams in terms of esthetics,⁴ they also present drawbacks in a restorative filling operation, an important one being nonuniformity in the extent of cure. A combination of optical and photochemical effects limits the depth of penetration of irradiated light in the wavelengths responsible for the photoinitiation reaction. As a result, the time required for acceptable curing levels increases with an increase of distance below the irradiated surface of the exposed composite.

Low levels of curing in the interior section may lead to failure of a restoration and other effects such as

damage to the pulp tissue. Consequently, in clinical operations, there are specific guidelines on the thickness of a curing composite and the duration for the blue light irradiation for a more uniform cure. Knowledge of physicochemical parameters that control the depth of polymerization may lead to a better understanding of this complicated phenomenon. It should also help devise improved materials with different compositions and component concentrations to achieve a better restoration with optimal clinical factors such as exposure time and use of different lamps.⁵

Depth of cure and compressive strength of dental composites were measured by Jandt et al.⁶ using a conventional halogen light curing unit (LCU) and a light-emitting diode LCU to experimentally verify that light intensity in the range absorbed by camphoroquinone photoinitiator is the important parameter in the photopolymerization process. Using the Beer–Lambert law, Gatechair and Tiefenthaler⁷ assessed that intensity of absorbed light exponentially decayed with the distance from the exposed surface. However, this model may only be valid when scattering, reflection, and diffraction of light in the composite matrix are ignored and the results are applied in a narrow radiation power spectral range. For example, in hardness experiments with both macrofilled and microfilled

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composites, Atmadja and Bryant⁸ concluded that the microfilled composites had a much lower penetration depth. Nonetheless, there is no concrete information available on the depth of penetration of the curing light in terms of thermophysical properties of the composite.

Dewald and Ferracane⁹ examined four different methods to evaluate depth of cure and concluded that hardness testing and degree of conversion analysis were superior to optical and scraping methods. Infrared (IR) spectroscopy and differential scanning calorimetry (DSC) are two common methods for degree of conversion measurements. However, such experiments result in space-average values for the entire sample and no localized values could be obtained. By comparison, microhardness testing that can be performed on the top and bottom surfaces can provide information on the localized extent of cure at these two localized areas from which one can infer influence of the depth on dynamics of the photopolymerization reaction. Ultimately, such information may be used in the manufacturing of composites with better depth of cure properties. It should be added that reflectance-based IR spectroscopy could be a promising technique to determine the surface conversion; however, the authors are not aware of use of this technique in localized curing measurements.

The polymerization of polymer systems such as dental restorative copolymers with a mixture of bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (bisGMA) and triethylene glycol dimethacrylate (TEGDMA) is a complex chemical process that involves photochemical initiation, double-bond cross-linking reaction, and formation of polymer networks. A complete course of reaction starts with a growth phase because of a polymer branching mechanism that gives rise to an exponential reaction growth known as autoacceleration. The autoacceleration is generally followed by a slow reaction phase because of the reduction of the mobility of the radicals in the system and continuous depletion of nucleation sites that precedes the termination phase. Bowman and co-workers^{10,11} have proposed a pendant double-bond scheme for the chain reaction as well as a cross-linking kinetics model that matches their polymerization experiments, but contains a large list of model parameters that makes its use somewhat limited. The bulk isothermal rate of reaction model that depends on conversion has been used effectively by Maffezzoli and co-workers.^{12,13} Racz et al. showed that an analogy between the classical Avrami approach for phase transformations and the kinetic phenomena that occur during photocuring of polymer and copolymer resins gives rise to a simple algebraic two-parameter expression for the extent of cure versus time that matched cross-linking chemical conversion quite well.¹⁴ This expression will be used to appraise the hardness data

obtained for three polymer systems as the coefficient parameter, signifying that the reaction kinetics correlates well with the intensity of the curing light and the temperature.

In this paper, we perform Vicker's hardness experiments on three different commercial dental composites at successive time intervals. The data will be treated as extent of cure curves and will be matched with a photopolymerization kinetics model. It will be shown that the variation of the kinetic coefficients obtained in the comparisons can be related to key properties of the tested composites.

METHODS

Hardness experiments

Three commercial dental composites were used in preset light duration experiments that we refer to as sample A (*P60*, 3M ESPE Co.), sample B (Tetric Ceram, Ivoclar Vivadent Inc.), and sample C (Filtek A110, 3M ESPE Co.). Sample A is a BisGMA-based resin (roughly 50% TEGDMA) with 61% by volume filler particles of average 0.6- μm -size zirconia/silica filler system. The percentage of inorganic fillers in sample B is 50% by volume of particles in the range 0.04 to 3.0 μm with a mean average of 0.7 μm . Sample B consists of 20% TEGDMA. Sample C is another light-cured dental restorative composite with silica filler particles with an average size of 0.04 μm that constitutes 40% by volume of the material. It has a 70:30 bisGMA/TEGDMA composition. The data on the tested composites are provided by the manufacturers.

Samples (five per group) of each material were made using nylon molds of the tested composites. All samples, having a 5-mm diameter and a 2.5-mm thickness, were prepared over a Mylar strip placed on a flat glass surface. After composite placement on the molds, the top surface was covered with another Mylar strip and a glass slab was gently pressed over it to avoid air entrapment and reduce any possible effect of the oxygen-inhibited layer. The samples were light cured with a high-intensity quartz tungsten halogen light source (Virtuoso Phase II VLC, Den-Mat Corp.) on standard cure for durations of 3, 5, 10, 15, and 20 s. The intensity of the light was 900 mW/cm² tested with a Model 100 Curing Radiometer (SDS Kerr).

The different irradiation times used in this study were determined by first using the standard times recommended by the respective manufacturer. 3M ESPE recommends a curing time of 20 s with a standard light for sample A and Vivadent recommend a curing time of 40 s with a standard light for sample B. For the Virtuoso Phase II light it is suggested that a curing time of 5 s be used when a standard light would normally be used for 30–40 s. Increments of 5, 10, 15, and 20 s were used to test the level of cure at

these times to determine at which level was most similar to the standard light. However, for sample A, an additional group of 3-s curing time was added to simulate the “recommended” 5 s for 40-s ratio for the Virtuoso Phase II light. So, 3 s was used as a “recommended” time for the normal 20 s needed for the standard light. The 3-s time was determined with a laboratory timer.

After curing, the top surface of each sample was polished with 600-grit sandpaper to limit the effects of the oxygen-inhibited layer (Carbimet, Buehler Ltd.). Then hardness testing was carried out for the top and bottom surfaces within 5 min of the light-curing procedure. Vickers hardness was completed using a 50-g load for an indentation time of 30 s using a microhardness testing machine (Micromet 2103, Buehler Ltd.). Five readings were taken for each surface of each sample. The bottom:top hardness ratio was calculated as the percentage of cure of the average bottom surface hardness compared to the average top surface hardness. ANOVA, Student–Newman–Keuls, and a *t* test were used to evaluate the statistical significance of the results. Vickers hardness was used because it is the most used hardness method to test dental materials, including composites.

Kinetic model

For a polymerization reaction, the expression for the extent of cross-linking cure $X(t)$ can be written as an explicit function of time t ,

$$\frac{X}{X_m} = \frac{kt^n}{1 + kt^n} \quad (1)$$

X_m is the maximum fractional conversion and increases with an increase in the temperature at which the curing reaction occurs. k is a coefficient constant that depends on the temperature T during the cross-linking reaction and the intensity of the incident light I . The coefficient k is a thermally activated constant that for a given polymer or copolymer system that can be expressed as an Arrhenius-type equation of the form

$$k(T, I) = k_0(I)e^{-E/RT}. \quad (2)$$

This expression is valid for the special case in which the transformation occurs in the isokinetic range, i.e., where the characteristics of phase change remain constant. The pre-exponential k_0 in Eq. (2) is a constant that is dependent on the intensity of the incident light, E is activation energy for onset of nucleation that can be considered to be constant over a wide range, R is the gas constant, and T is the absolute temperature.

At low intensities of the incident light, the photoinitiation, a first-order reaction, may be the controlling reaction where the curing process depends on the initial population of the initiation component and therefore one can show that k is proportional to I , while at high intensities the polymerization, a second-order phenomenon, is the slow reaction resulting in k depending on $I^{1/2}$. Accordingly, one expects that¹⁴

$$\begin{aligned} k &\propto I && \text{when } I \text{ is low} \\ k &\propto \sqrt{I} && \text{when } I \text{ is high} \end{aligned} \quad (3)$$

For low intensive lights, the curing specimen temperature would remain relatively constant during the reaction. At high light intensities, the exposed material may have significant temperature changes, giving rise to changes in k . For these instances, a monitoring of the sample temperature is needed for a proper application of Eqs. (1) and (2). For the tested composites in this study, previous studies have indicated that the coefficient k is weakly dependent on the sample temperature and strongly dependent on I . Hannig and Bott¹⁵ measured temperature rise of 2-mm dental samples cured with various clinical lights. They report that conventional lights, such the one used in this study, will induce a maximum temperature rise of 5°C. Activation energies E for dental composites are such that this temperature rise will have a much lower impact on k than the incident light intensity I for the experiments reported in this paper.

The exponent n is a parameter largely influenced by the geometry of the curing matrix. The value that n takes in a polymerization reaction lends insight into the dimensionality of the growth mechanism, i.e., whether the nuclei are distributed in the volume, upon grain surfaces, or both. It also indicates whether kinetics of the phase transformation is dominated by the formation of new nuclei or by the growth and impingement of a finite number of previously formed nuclei.

A kinetic model for the extended volume fraction for polymers reveals that $n \approx 2$ for “thin” samples and $n \approx 3$ for “thick” samples. For thin samples, the chain polymerization occurs in a plane and for thick samples it occurs in a volume. One can also conduct a similar analysis for a homogeneous nucleation case for which the reaction frequency will be a function of time. For this case, n will be 3 and 4 for thin and thick samples, respectively. The presence of glass fillers in the polymer matrix is expected to reduce the dimensionality of the reaction; as a result, in practice for copolymers, the exponent n may assume values less than the corresponding values for polymers without glass fillers. The degree to which the exponent n can be influenced by the filler particles depends on factors such as filler concentration, filler geometry, and filler translucency.

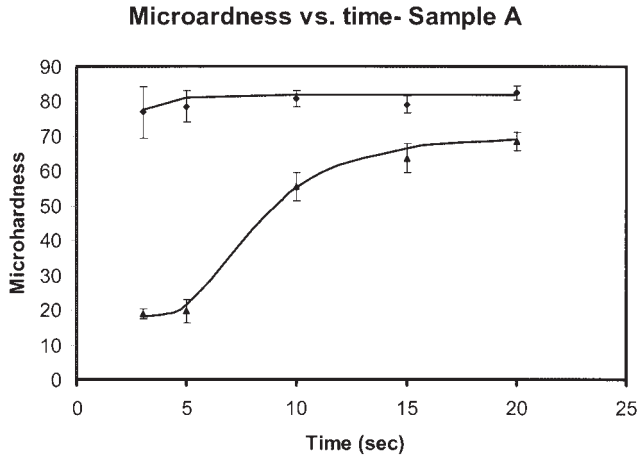


Figure 1 Localized curing of top and bottom surfaces for sample A. ▲ and ■ are the experimental data. Solid lines are theoretical curves.

The maximum conversion constant X_m is reached at large times. Depending on the composition of the composite, operating temperature, and the irradiation intensity, X_m can be less than the total conversion reached at the glass transition for the same temperature.¹¹ The lower values of X_m occur at lower temperatures and lower irradiation intensities and are associated with undesirable effects with a biomedical application of these composites. Low temperatures or low irradiation intensities can induce uneven cross-linking reaction that greatly diminishes the mobility of free radicals in the high-cross-linked segments of the composite and reduce the coefficient k and X_m .¹⁰

For comparisons in this paper, it will be assumed that the net change in mechanical properties of the composite is proportional to the extent of cure X . This assumption may be justified on the basis that properties such as surface hardness and modulus of elasticity are directly related to the number of cross-linked branched structures that make possible a net change in the matrix properties. An exception to this rule is the rheological properties of composite matrices that are known to exhibit more complex behavior.¹⁶ Recently, Orefice et al.¹⁷ have experimentally verified that a linear relationship between monomer conversion and the Vicker hardness exists for dental copolymers. Accordingly, the linear relationship between H , the Vicker hardness value, and the extent of cure X takes the form

$$H = H_i + \frac{H_m - H_i}{X_m} X, \tag{4}$$

where H_i is the hardness value for the uncured sample and H_m is the hardness when the extent of cure reaches its maximum value X_m .

RESULTS

Variation of Vicker’s hardness versus time for material samples A, B, and C is shown in Figures 1-3, respectively. Each figure contains our measurements of the top surface and the bottom surface and the sequence of experimental points indicate the evolution of localized curing at the two ends with respect to the irradiation. The experimental data in the figures show the average of the measurements. The data for average values for each group (a total of 25 readings per surface per group) in these figures have more scattering for exposure times below 5s and are more consistent for longer cured samples, as indicated by the error bars in the pictures for the data points. Nonetheless, the standard deviations obtained from our data are less than 6% of the corresponding average values in all the experiments. The best-fit theoretical curves obtained from Eqs. (2) and (4) are also included for comparison. To obtain the theoretical curves, the exponent n must be determined for each material and the coefficient k for each surface. Table I summarizes the values used to match the experimental data. In this table the coefficient k is expressed in units of $(1/s^n)$.

DISCUSSION

There are significant differences in the polymerization behavior between the top and bottom locations of the tested composites. The top surface of sample A reached cross-linking saturation within the first 5-s interval of the curing process. In the same curing step, Figure 1 indicates that the hardness of the bottom surface was virtually unaffected almost 5 s after the exposure reached the so-called autodeceleration¹⁸ phase of the photopolymerization reaction in about 10 s and the curing continued beyond 20 s. By com-

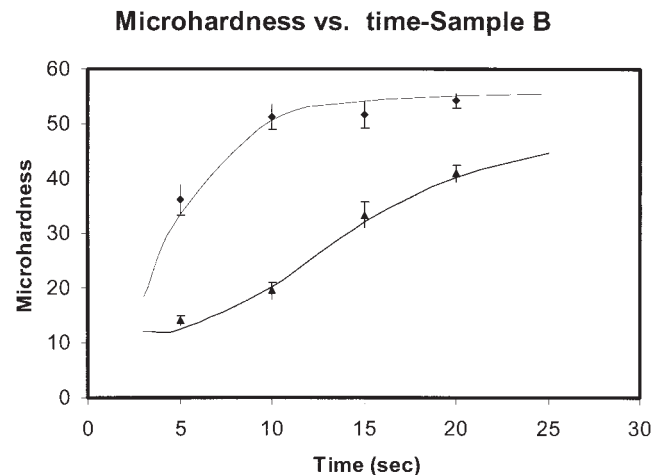


Figure 2 Localized curing of top and bottom surfaces for sample B. ▲ and ■ are the experimental data. Solid lines are theoretical curves.

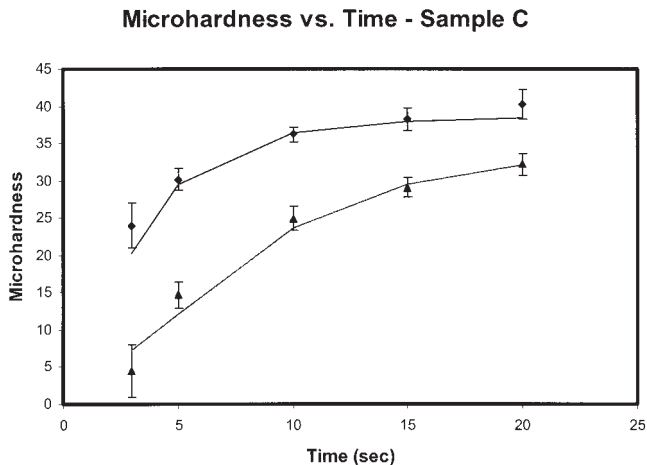


Figure 3 Localized curing of top and bottom surfaces for sample C. ▲ and ■ are the experimental data. Solid lines are theoretical curves.

parison, samples B and C exhibited slower polymerization reaction with the top surfaces reaching the curing plateau in about 20 s and bottoms continued to cure well beyond the exposure time of the experiments.

The materials under study are BisGMA-based resins with different TEGDMA concentrations. While they have different curing times, the theoretical curing curves reveal interesting similarities between the three composites. From Table I, it is evident that the exponent of photopolymerization reaction n is very close for the three composites. One may attribute the small difference between the values of n on differences on the filler particle geometries used in the composites. Additionally, while the coefficient k has different range of values for these composites, k_{bottom} is much less than k_{top} for all cases, reflecting slower rates of reaction for the bottom surfaces. The three tested materials all exhibit a photopolymerization induction time of 3 s for the top and the bottom surfaces.

The values for the coefficient k for P60 are consistently larger than the corresponding values for samples B and C. We have argued that the coefficient k depends on the localized irradiation intensity, temperature, and chemical composition of the composite. With the use of similar lighting source in our curing experiments, a value of 0.8 for sample A for the top surface versus 0.03 and 0.08 at the same location for samples B and C signifies use of a higher concentration of photoinitiator in P60, consistent with the data provided by the manufacturers. On the other hand, the ratio of k between top and bottom surfaces for the same material can be taken as an indication of the degree of pointwise irradiation intensity in a composite. According to Eqs. (3), a lower value for $k_{\text{bottom}}/k_{\text{top}}$ for the same sample means lower irradiation intensities, primarily in the effective wavelength range of the

photoinitiation reaction, for the bottom surface versus the top surface. In Table I, one finds that this ratio is almost one order of magnitude lower for sample A compared to samples B and C, indicating a much faster decay of irradiation intensity with depth for P60. A more quantitative assessment on degree of irradiation decay using the kinetic model used in this work requires a specific relationship between k and I for a composite. If the more plausible linear relationship is assumed, effective light in 2.5-mm P60 samples has declined by a factor of 80 versus a factor of 15 and 20 for the other tested materials under the same conditions. If k depends on $I^{1/2}$, the difference between the two materials on the rate of decay of effective irradiation intensity with depth would be even more dramatic. It is interesting to note that these results are in general agreement with the spectral measurements of Arikawa et al.¹⁹ on light transmittance for the dental composite at different thicknesses.

The difference between the rates of effective irradiation decay for the tested composites in this work can be attributed to two different mechanisms. The first is the absorption of irradiated light through the photoinitiation reaction. Compared to sample B, sample A has a higher photoinitiator concentration and consequently a higher decay rate. A second mechanism for the decay can be attributed to the size as well as the radiative spectral properties of the glass fillers used in the composites. When the particulate size is the same as the wavelength of the light, considerable opacity is enhanced because of a combination of reflection, refraction, and diffraction.²¹ Also, transmissivity is affected by the glass filler material²⁰ and this difference is specially pronounced in the wavelength 0.3- to 0.5- μm range in which the polymerization is initiated. Again, sample A has a higher percentage of filler glass particles with slightly higher concentration of sizes in 0.3- to 0.5- μm range than samples B and C, which contributes to faster decay to incident light in the copolymer matrix.

The significant variation in the value of k for top and bottom samples, to some extent, justifies the use of Eq. (1), which is derived for an isothermal reaction. The photochemical reaction of the materials used in this study is an exothermic reaction that can raise the temperature of the sample during the polymerization. This might give rise of an increase in the value of k by

TABLE I
The Kinetic Coefficients for Samples of the Tested Materials

Samples	A	B	C
n	2.8	2.5	2.3
k_{top}	0.8	0.03	0.08
k_{bottom}	0.01	0.002	0.004

as much as 50%.²² By contrast, variations in irradiation intensity can shift the coefficient k by several orders of magnitude²¹ that is encountered in this study and should support its principal conclusion.

CONCLUSIONS

Our comparisons between the kinetic model for photopolymerization and hardness experiments on three commercial dental composites have shown that the penetration of effective curing light density into a composite matrix is severely curtailed because of factors such as the concentration of the photoinitiator as well as the material, the size, and the size distribution of the filler particles in the composite. Sample A has exhibited a higher degree of light decay versus our other tested material because of a higher photoinitiator concentration and a higher percentage of particulates in the wavelength range most affected by the photoinitiation. An interesting question regards the relative importance of each of these factors in the overall light decay with depth of penetration. This latter part will require additional studies with more commercially available and laboratory-made composites, which the authors will be conducting in the future.

Finally, our successful comparisons between the photopolymerization kinetics model and the experimental data, and the fact that the three different tested composites showed very similar kinetic behavior, would suggest the utility of this model in interpreting curing data as well as the application of the hardness testing as an indication of extent of cure. Experiments on bulk-curing using existing techniques such as DSC or IR can provide additional information on the exponent n , while data on light transmittance characteristics of light-cured composites can be used to make a more detailed examination of the dependency of the

coefficient k on the effective irradiation intensity and their variations with depth.

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