Energy dependent polymerization of resin-based composites
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Chapter 1

Introduction

Growth in the use of resin based composite (RBC) as a direct restorative material continues to increase to the extent that, in some markets, its use rivals that of amalgam [1]. Esthetic demands together with pressure to limit mercury exposure, either directly or environmentally, have been offered as reasons for the increased growth [2]. Increased confidence in RBC performance may be driving growth, as well, due to improvements in physical properties and bonding procedures [3]. In comparison to the placement of amalgam, however, restoration with RBC is considered to be more technically challenging and time consuming. Isolation of the field with rubber dam and strict compliance with the bonding protocol are necessary to optimize the seal between enamel and dentin and the restorative material. Careful placement of the RBC is required to ensure complete adaptation to the cavity and to maintain approximal contacts, both of which will limit possible foci for plaque accumulation. Due to limitations in RBC depth of light curing, incremental placement with a separate cure of each increment is typically recommended. The time expense is significant during this phase especially with less translucent composites. Finally, contouring the restoration within the limits of the RBC’s operatory light stability and finishing and polishing add to the complexity of the restorative procedure.

Decreasing the complexity and time commitment of placing an RBC is a strategy that has not gone unnoticed by manufacturers and the profession. Light curing technologies have been introduced to the dental profession with claims that significantly shorter cure times are possible than traditionally recommended. Of interest are plasma arc lamps whose power output has been reported to be as great as four times that of a typical tungsten-halogen lamp [4]. Claims of curing composite with exposures one-tenth of the recommended manufacturers cure time have been made with these more powerful lamps [5]. Curing lamps based on light-emitting diodes (LED) and lasers are available for curing RBC. Their polymerization efficiencies have been suggested to be greater than traditional tungsten-halogen lamps [6], though considerable confusion surrounds this topic. Increasing the increment depth that can be placed and cured is another strategy that has been promoted [7,8]. The advantage
of such strategies remains to be fully substantiated in light of potential negative consequences arising from insufficient cure.

Other strategies exist that are diametrically opposed to the rapid cure described above. There is evidence that curing at lower polymerization rates moderates polymerization stress [9] and may help preserve marginal integrity [10,11,12]. This is the basis for curing lamps designed to emit a gradual increase in intensity (ramped or slow-start) [12], or to deliver a short, low intensity pulse followed by a delay before final curing is commenced (pulse activation) [13]. It is also the basis for the reported improved marginal continuity found with the through-the-tooth, threesited curing technique [14,15]. Investigations designed to explore the reaction rate/stress relationship, whether purely by instrumental means or simulated clinical models, must recognize the impact that conversion may have on the results.

A greater understanding of the parameters that affect the extent of cure of RBC materials would help optimize the potential benefits associated with the above claims and minimize the potential misuse of these materials. A valuable starting point begins by evaluating the extent of cure of RBC cured by traditional means on an energy basis. Once developed, this relationship can be applied towards predicting the extent of cure provided other material and lamp parameters are known. This chapter is intended to provide an overview of those parameters that are critical for predicting cure throughout photoinitiated RBC.

**Determining extent of cure: conversion**

The term conversion is used to express the percentage of carbon-carbon double bonds reacted during polymerization of the matrix resins. Its characterization is frequently accomplished with spectroscopic methods such as Fourier transform infrared spectroscopy (FTIR). For methacrylate resins, the absorption most commonly analyzed is the carbon-carbon double bond at 1638cm⁻¹. During polymerization, this absorption decreases as the carbon-carbon double bonds react via free radical addition. Comparing the relative peak heights or areas of this absorption at a desired time after initiation with that of the uncured sample allows calculation of the conversion.

Cured RBC materials typically show a limited conversion of network
polymers caused by severely restricted reactant mobility; maximum conversion between 43 and 73 percent via infrared spectroscopy has been reported [16,17,18,19]. In large part, the diffusional constraints are contributed by the highly viscous, difunctional methacrylate, Bis-GMA, the presence of which helps to moderate polymerization shrinkage. Diluents, with viscosities up to five orders of magnitude less than that of Bis-GMA are incorporated to facilitate admixing filler and optimize mechanical properties—the latter brought about, in large part, by increased conversion. The increased mobility conferred by diluents incorporated within parameters common to dental resins can increase conversion by $2^{1/2}$ times over that of pure BisGMA (from 26% to 66% for 50/50 Bis-GMA/TEGDMA [20]. Structural differences among diluents probably contribute to the variation in conversion noted above due to differences in segmental motion of the pendent methacrylate (unreacted methacrylate attached to the polymer network) [21].

The relative reactivity of silane and matrix methacrylates may impact the conversion when determined via infrared spectroscopy. Methacrylate functional silane, typically processed with the filler to enhance adhesion with the matrix resin, also contributes to the measured absorbance at 1638 cm$^{-1}$. Under certain conditions, the silane methacrylate may not appreciably react and its contribution to the overall carbon-carbon double bond absorbance may be great enough to artificially depress the calculated matrix conversion.

It is not necessarily true that RBC materials with higher conversion will exhibit higher mechanical properties. Instrumental factors such as resolution of silane/matrix methacrylate, as mentioned above, may limit such a correlation as may filler particle size distribution and loading [22]. The chemical nature of matrix methacrylates may also confound a conversion-mechanical property correlation. For example, increasing the concentration of the diluent, TEGDMA, relative to Bis-GMA, over a range of unfilled formulations, was found to decrease the measured flexural strength despite an expected positive correlation with conversion [23,24]. This discrepancy is, perhaps, explained from a kinetic model that predicts that TEGDMA in a binary composition with Bis-GMA will decrease the cross-link density of the polymer [25]. This result has been related to the relative flexibilities of TEGDMA and Bis-GMA pendant methacrylate groups—greater flexibility of the TEGDMA pendant methacrylate increases the probability that it will form a primary cycle
with itself, which is not expected to contribute to increased mechanical properties. Monomers with greater flexibility than TEGDMA may have a more pronounced impact with respect to the amount of primary cycles.

**Factors affecting conversion of RBC**

*Reciprocity*

It has been suggested that a trade-off exists between intensity and exposure time such that similar cures can be obtained as long as their product remains constant [26]. Little systematic documentation for reciprocity has been offered, however. Verifying this relationship over the full range of cure is the required first step in predicting extent of polymerization from the applied radiant energy.

It is not apparent from the customary analysis of theoretical kinetics of free radical polymerization that intensity and exposure time will predict a reciprocal relationship for RBC materials. The rate of polymerization initiated from monochromatic radiation within an incremental thickness has been theoretically described for linear chain reactions [27,28]. Under this scenario it is assumed that termination of free radicals occurs via a bimolecular process. The differential equation (1) reveals that the rate of monomer consumed is related to the rate at which primary free radicals are produced (proportional to $\Phi I_a$), the rate of addition of monomer and pendant groups to the growing chain or network (described by the rate constant for propagation, $k_p$), and the rate at which the radicals terminate (described by the rate constant for termination, $k_t$).

$$ R_p = -d[M]/dt = k_p[M](\Phi I_a/k_t)^{0.5} $$

(1)

In the preceding, $I_a$ is the light intensity absorbed by the photoinitiator, $\Phi_i$ is the initiation quantum yield or the number of primary free radicals generated per photon absorbed and [M] equals the time dependent monomer concentration. The conversion can be obtained by integrating equation (1) with respect to time:

$$ Conversion = \{M_o - M_f\}/M_o = 1 - \exp[-k_p k_t^{0.5} (\Phi I_a)^{0.5}] $$

(2)

where $M_o$ and $M_f$ represent the initial and final monomer concentration respectively. It is obvious that equation (2) would not predict conversion
dependency upon a reciprocal relationship between intensity and time considering the half-order dependence on intensity ($I_t$). Experimentally, half-order intensity dependence is observed with monomers forming linear polymer structures, such as methylmethacrylate, in accordance with classical kinetics. With multifunctional monomers deviation from half-order intensity with respect to the rate of polymerization has been reported. Studies exploring photoinitiated kinetics of hexanedioldiacrylate (HDDA) demonstrated that the rate of polymerization was dependent upon $I^{0.7}$ [29] while studies with other multiacrylate resins revealed a dependence of $I^{0.85}$ [30]. Other studies with HDDA have shown that the exponent was dependent upon conversion, increasing from $I^{0.65}$ to $I^{0.97}$ at 15.3 and 53.5 percent conversion respectively [31]. To account for the deviations from theoretical kinetics based on bimolecular termination exclusively, a kinetic description incorporating unimolecular termination, where the intensity exponent is unity, has been described [30].

$$R_p = \alpha \frac{k_p}{k_t^{0.5}} [M][\Phi I_a]^{0.5} + (1 - \alpha) \frac{k_p}{k_t'} [M][\Phi I_a]$$

(3)

For multifunctional methacrylates, the contribution of unimolecular termination to the rate equation is significant as the reduction in reactant mobility during network formation leads to an increased concentration of trapped radicals [32]. As the polymer becomes more cross-linked, the proportion of radicals terminating via a first order process increases [33], which explains the increasing intensity exponent observed at higher conversion [31]. Experiments with real time infrared spectroscopy (RTIR) have attributed the deviation in the termination exponent to the effects of the dark cure polymerization [34]. Since the dark cure phase of RBC polymerization is appreciable, the contribution from a first order termination mechanism is expected to be significant. Consequently, predicting conversion solely from equation 2 would lead to errors. Although radical trapping commences at very low conversion and continues throughout the dark cure phase, there is not sufficient evidence to conclude that, for dental resins, unimolecular termination would dominate bimolecular termination to the extent that the overall rate of polymerization (and conversion) would be directly proportional to light intensity ($\alpha = 0$ in equation (3)).

A theoretical kinetic model has been proposed that predicts a depth of cure dependency for RBC on the product of the incident intensity and
exposure time [35]. The model incorporates the rate of free radical initiation at depths below the surface considering that significant polymerization will only occur after inhibiting molecules have been consumed by initiating radicals (inhibition model):

$$D = \frac{1}{\varepsilon} \log_{10} \left( \frac{2.303 \Phi X_0 t}{\varepsilon} \right)$$  \hspace{1cm} (4)$$

where D equals the depth of cure, ε equals the RBC attenuation coefficient and $X_0$ equals the initial inhibitor concentration. In this model, depth of cure was associated with either the depth at zero hardness or the "scrape-back" length. Experimental results were observed to support the theoretical model. This included evaluation of scrape-back lengths, obtained from samples exposed over a range of curing conditions, that supported the predicted reciprocal relationship between intensity and exposure time [36].

**Transmittance and reflectance**

At the surface of RBC exposed to air during light curing, polymerization is suppressed via oxygen quenching of primary and polymeric free radicals. This suppression occurs even though the absorbed light is at a maximum. Typically, this underpolymerized layer is removed during finishing. At depths below the surface, light penetration becomes dependent upon scattering and absorption effects. The relationship describing light attenuation throughout depth of RBC conforms to the Lambert Law [28]:

$$\text{Transmittance} = \frac{I}{I_0} = e^{-b\ell}$$  \hspace{1cm} (5)$$

where I is the intensity penetrating to a depth, $\ell$, below the surface, $I_0$ represents the intensity entering the sample and $b$ is the naperian absorption coefficient. In base-ten, the Lambert law becomes:

$$\frac{I}{I_0} = 10^{-a\ell}$$  \hspace{1cm} (6)$$

where $a$, the specific absorptivity of the RBC material (2.303b), encompasses all absorbed and scattered radiation. The magnitude of $a$, then, depends not only on the concentration of photoinitiator, but also on the amount and size distribution of filler, the refractive indexes of the filler and resin, and pigmentation. The above equations describe the
amount of light penetrating to a given depth within the RBC. The intensity actually absorbed by the photoinitiator ($I_a$ in equation (1)) at the corresponding depth can be expressed by the following:

$$I_a = 2.303\varepsilon_a S_l \times 10^{-\alpha l}$$

(7)

where $\varepsilon_a$ is the molar absorptivity of the photoinitiator with a concentration of S.

All the above equations describe an exponential decay of light through the composite. The significance of this is readily appreciated by considering that, for a typical microfill RBC, light intensity can be reduced twenty times upon doubling the thickness from 2 to 4 millimeters (3M Silux Plus, Universal shade). For a small particle hybrid composite, the corresponding reduction is around ten times lower (3M Z100, A3.5). Increasing photoinitiator concentration or its absorptivity will tend to limit the depth of cure further. A related complication arises from the need to balance reactivity with operator light stability—enhancing the former, either by modifying initiator formulation or increasing resin reactivity, unavoidably shortens the latter. Further, increasing translucency, while a seemingly simple solution to improve cure depth, is not without esthetic concerns.

In the expressions for transmittance given above, it is assumed that reflectance is negligible and the sum of the transmittance and absorptance ($\alpha = (I_o - I)/I_o$) is unity. Consequently, as the thickness of the sample approaches zero, the transmittance will approach a value of one (Lambert law, equation (5)). Experimentally, with RBC materials, the intercept at zero thickness is typically much less than one and signifies appreciable reflection. While attenuation is dominated by the exponential relationship with depth, reflectance, from a source normal to a planar surface, has been measured to be between 25 and 38 percent for various RBC materials. The reflected loss is expected to be greater in-vivo where irregular surfaces are irradiated with non-normal light sources. Additional loss of intensity occurs clinically due to the distance separating the light guide and the composite. This loss is especially significant in posterior restorations where the distance between the bottom of the preparation and light guide can easily measure 7-8 mm. This effect is explored in greater depth in Appendix 1.
1. A distinction between "true" and "apparent" transmittance (and absorbance) has been discussed in the literature to ensure conformity to the Beer-Lambert law [37].
Light source and photoinitiating system

As a simplification, kinetics of photoinitiated systems is typically described in terms of monochromatic radiation. In reality, typical dental lamps exhibit non-uniform polychromatic emission. Complexity arises since the probability of photon absorption by the photoinitiator, designated by the absorption coefficient ($\varepsilon_\lambda$) in equation (7), is, similarly, wavelength dependent. Characterizing photoinitiator absorbance is readily accomplished spectroscopically. The most common initiating system in dentistry involves camphorquinone and amine. Camphorquinone absorbs very strongly in the ultraviolet region between 200 and 300 nm ($\varepsilon_{\text{max}}$ circa 10,000) and much less strongly in the visible range between 400 and 500 nm ($\varepsilon_{\text{max}}$ circa 40) [38]. Thus, from $\varepsilon_{\text{max}}$ values, the probability that a quantum will be absorbed at visible wavelengths is around four orders of magnitude less than in the ultraviolet range. The relatively low absorbance in the visible range is of little consequence since increasing CPQQ concentration can compensate. The absorbance between 400 and 500 nm appears relatively bell-shaped with a maximum around 468 nm. Absorption of a photon of wavelength within this range promotes a ground state electron to an excited, singlet state, which may then transition to a triplet state via intersystem crossing. Provided an amine is in the vicinity within the lifetime of the triplet state, an excited state complex (exciplex) may form through charge transfer from the lone electron pair on nitrogen to the carbonyl of CPQ. Following proton abstraction from the amine, two radicals are formed, of which, only that from the amine is sufficiently reactive to initiate polymerization. Non-CPQ initiators are also known to dentistry—benzoyl phosphine oxides form very reactive phosphonyl radicals through a Norrish type I cleavage [39]. Compared to CPQ, the maximum absorbance of these initiators generally occurs at shorter wavelengths (circa 380 nm for bisacylphosphine oxide). This shift must be considered when assessing the compatibility with the light source as described below.

Taking into account the wavelength dependence on both incident intensity and the absorption coefficient, the total intensity absorbed by the photoinitiator per unit volume at depth, $I$, (7) becomes [28, 40]:

$$ I_\lambda = 2.303 S \int I_0(\lambda) \varepsilon_\lambda(\lambda) 10^{-a(\lambda)\ell} d\lambda $$

(8)

For a particulate filled system, the wavelength dependence on $a$, arises
from differential scattering related to particle size combined with wavelength dependent absorption of any components including the photoinitiator. It is instructive to express equation (8) in terms of the number of quanta absorbed by the photoinitiator over an exposure duration (t) considering the energy per quantum equals $hc/\lambda$, where $h$ is the Planck constant and $c$ is speed of light:

$$Q_a = \left(\frac{2.303}{hc}\right)\delta t \int I_{\lambda(\lambda)}(\Phi_n)\lambda 10^{-a(\lambda)\delta} d\lambda$$

(9)

The number of primary radicals generated per unit volume at depth, $\lambda$, will be the product of the number of initiator molecules excited ($Q_a$) and the quantum yield for radical initiation ($\Phi$). The efficiency of a light source can be characterized from the variables on the right-hand side of the integrand. Optimum radical yield is associated with, 1) maximum overlap of the spectral range of absorbance and lamp emission, and 2) lamp intensity. The former becomes a concern when lamps with narrow spectral emission optimized to CPQ $\epsilon_{\text{max}}$ are used with non-CPQ initiated resins. Radical yield is also directly related to the value of the wavelength as noted in equation (9). Since the energy per quantum is proportional to the reciprocal wavelength, for an equivalent energy exposure, greater quanta are produced at longer wavelength. Under these conditions, radical yield will then depend upon $\epsilon(\lambda)$. For CPQ, in the case where the relative probability of absorption is 50% (around 490nm and 432nm), an approximate 13% greater radical yield is predicted at the longer wavelength (490nm) with an equivalent exposure. Limited practical significance is expected from this difference since transmittance properties, as explained above, are expected to be dominant with respect to depth of cure. Thus, equation (9), in its entirety or in simplified form, provides a means of predicting efficiencies for various curing lamps.

**Extent of Cure: Clinical Relevance**

Many of the cure dependent properties that are expected to affect clinical performance of RBC materials have been studied in the laboratory —eg., hardness [35, 41, 42], solubility [42,43] wear resistance [44], fracture toughness [45]. Yet, despite years of study involving these factors, the extent of cure required for a long lasting restoration has not been determined. The lack of data on this topic is not surprising considering the ethical sensitivities that would be associated with such studies. However, it is not unreasonable to expect, considering the prevalence of
under-performing curing lamps in private practice [46-48], that insufficient polymerization may be a contributing factor in restoration failure. This association, perhaps, partly explains the observation that failure rate of posterior RBC restorations is greater in cross-sectional studies in comparison to controlled, longitudinal studies [2]. Lack of clinical data notwithstanding, the performance of restorations polymerized by light sources operating at the lowest levels of output found in surveys is questionable. At intermediate levels of polymerization, the impact on performance is less clear—the ambiguity arising from material property requirements and the benefit of reduced polymerization contraction. Linear contraction measurements have shown, for both unfilled and filled resins, that a reduction in conversion was accompanied by a proportional reduction in contraction [49,50]. In a bonded restoration, reduced contraction will be related, in some manner, to reduced stress at the composite-preparation interface. Any resulting benefit in enhanced interfacial integrity must be weighed against reduced physical properties of the composite and potential biocompatibility issues resulting from increased monomer leaching. At the occlusal surface, maximum cure can be obtained with relatively modest exposures [51] and insufficient conversion is not expected to be a significant problem. However, measurable differences in abrasive wear have been observed from relatively small reductions from maximal conversion in an in vivo denture model [44].

Due to the absence of clear, clinically defined targets for extent of cure, recommendations have been suggested from laboratory studies. Hardness measurements have yielded considerable information on the cure profile throughout photopolymerized RBC [35,51-54]. Typical measurements depict a gradual declining hardness followed by a more severe reduction. Because the nature and amount of filler in an RBC influences the hardness value, absolute hardness is of little value when comparing materials. For this reason, hardness values for comparative purposes are generally expressed relative to the maximum measured hardness, which usually occurs at or near the surface [55]. Depth of cure associated with 80 percent maximum Knoop microhardness was described as a relative parameter for comparing the curing potential of different curing lamps and RBC materials [52]. This was an arbitrary definition and, as such, was not meant as criteria for sufficient clinical cure. Inspection of Knoop hardness profiles generally reveals the 80% value occurs at a depth just past the plateau and into the portion of the curve where the declination is
rapidly increasing. A more rigorous, yet still arbitrary, definition of 90% maximum Knoop microhardness was suggested as a clinical specification for depth of cure [56]. This point generally occurs before the rapid decline in microhardness. Clinical simulated fatigue testing has suggested that 73% maximum Knoop (or 80% maximum conversion) is sufficient at the gingival margins of a class II restoration [57]. A specification of 90% maximum Barcol hardness has been suggested from a mathematical model describing hardness maturation of RBC polymerized in 2.5mm thick molds [55]. In comparison to Knoop microhardness, the depth of cure associated with 90% Barcol hardness was observed to be around 40 percent greater than the same specification for Knoop (90%) [53]. While providing a relatively simple and inexpensive method for assessing the hardness of materials, the aforementioned highlights the relative insensitivity of Barcol hardness in comparison to microhardness for characterizing depth of cure of RBC materials. Past and current ISO specifications for depth of cure have relied upon the "scrape-back" method whereby a cylinder of RBC is cured and the unpolymерized material scraped-off. The original specification identified depth of cure by the full length of the cylinder measured after removing the uncured material [58]. This depth has been shown to correlate to microhardness values near zero [53] and obviously is associated with very low conversion. With the current ISO specification, the length of the scrape-back sample is divided by two [59]. At this depth, the sample has yet to show appreciable solubility. Just beyond this depth, the increase in solubility is more pronounced [53]. This definition for depth of cure is the most conservative of the various specifications described above, yielding values that were on average around 20 percent less than the depth correlating to 90% maximum Knoop [53,60].

Investigators have used the above specifications to identify associated exposure conditions for various RBC materials. The parameters typically explored are lamp intensity, exposure time and light attenuating material properties such as filler type and shade. The objective of many such studies is to define a minimal acceptable output of the curing lamp and minimum cure times. Acceptable cure has been associated with minimum lamp outputs of between 185 and 400 mWcm⁻² with increments ranging from one to two millimeters and curing times up to 60 seconds [51,61,62]. The variation in acceptable cure specifications and the broad range in light transmittance across and within different brands of RBC
materials make such recommendations potentially confusing for the clinician. Compounding the uncertainty is the observation that commercial radiometers marketed to the dental profession have been shown to differ in their measurement by as much as 19% [63].

**Aim and outline of investigation**

Assuming the extent of cure is dependent purely on the exposure energy, the conversion of RBC can be related by the product of intensity and exposure time. Deriving such an energy-conversion relationship provides a means of predicting conversion under, theoretically, an infinite set of exposure conditions. The energy-conversion relationship, together with the attenuating properties of the RBC, defines a means of predicting conversion throughout photoinitiated RBC. Extending the analysis to include the spectral characteristics of the photoinitiator ($\epsilon_{\lambda}$) and lamp emission ($I_0^{\lambda}$) permits a unifying process for the prediction of conversion throughout RBC with any light source.

An accurate analysis of methacrylate conversion should consider potential limitations of the instrumental method. **Chapter 2** explores the impact methacrylate-functional silane may have on the measured matrix conversion when using infrared spectroscopy. The effect of filler loading on conversion is also explored.

**Chapter 3** develops the energy-conversion relationship (ECR) for various commercial RBC materials from thin film FTIR analysis. Using the thin-film method, reciprocity between lamp irradiance and exposure time was explored for two of the materials.

The experiments described in **Chapter 4** were to develop the energy-conversion relationship (ECR) from bulk cured RBC from the incident energy and RBC transmission properties and confirm the reciprocal relationship between lamp irradiance and exposure time. The energy-conversion relationship was then used to predict the cure through RBC under various exposure conditions. It was also the intent to define a critical scrape-back energy and use this value to predict scrape-back lengths at various exposure energies and RBC opacities.

**Chapter 5** defines a universal energy-conversion relationship (ECR_u) predictive of conversion throughout RBC polymerized by any light
source. The ECR was used to predict conversion and scrape-back lengths for a tungsten-halogen and LED lamp at various exposure energies.
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