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Determination of curing time in visible-light-cured composite resins of different thickness by electron paramagnetic resonance

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The irradiation time of a visible-light-activated composite necessary to achieve full polymerization throughout the material was studied. Curing-time dependence on the thickness of the material was also investigated. To monitor the visible light-activation effect, the free radical concentration was measured as a function of irradiation time. If the composite sample is less than 0.5 mm thick and exposed to light for a time interval recommended by the manufacturer, full radical concentration is indeed created uniformly. This is not the case in thicker samples. Electron paramagnetic resonance (EPR) was used to monitor the concentration of free radicals in the samples. The number of radicals was monitored as a function of irradiation time during which the radicals were generated in samples 0.5, 0.8, 2.0, 3.0 and 5.0 mm thick. An EPR X-band spectro-meter was used to detect the free radical spectra. The number of free radicals per unit mass as a function of irradiation time shows that 60% of the maximum concentration of radicals in a 1 mm sample is reached in 24 s curing time, while in thicker samples it takes hundreds of seconds. On the basis of the experiments, a depth and irradiation time-dependent radical concentration model was developed. This model shows that a 2.0 mm thick sample is cured at the bottom side if irradiated for 60 s. It is proposed that the measure of the degree of polymerization in composite materials should be the polymerization of the bottom layer of the sample which is modelled from the number of free radicals generated in the sample.

1. Introduction

For more than 20 years the visible-light-cured (VLC) dental composite resin has been universally accepted as a restorative material owing to its workability and good mechanical properties. In comparison with the chemically cured restorative resins, where chemically induced polymerization takes place uniformly throughout the bulk of the material and curing depth does not depend on the material thickness, the presence of filler particles and the light absorbency of the VLC resin itself limit the polymerization, which in this case varies with depth [1]. There have been many reports in the literature in which the dependence of resin curing on light intensity [2, 3], irradiation time [4], spectral absorbency of the resin material [5], mould material and cavity size [6], sample thickness [7], different matrices and light positions [8] and different light sources [9], are discussed.

Composite resin curing was evaluated by infrared spectroscopy [10–15], where the polymerization is determined by the proportion of the remaining concentration of the aliphatic C=C double bonds in a cured sample relative to the total number of C=C bonds in the uncured material. The double-bond concentration is monitored by an infrared absorption peak at 1636 cm^{-1}. The curing depth was also evaluated by mechanical methods, such as microhardness and scraping tests. The surface microhardness tests (Vickers and Knoop) are used to evaluate the hardness profile throughout the sample [16–18]. Scraping tests were found to be inadequate to determine the border line between cured and insufficiently cured material [19]. By comparing this technique with others, it was concluded that both the scraping test and the optical demarcation test tend to overestimate the curing depth [13, 19].

Recently, electron paramagnetic resonance (EPR) spectroscopy was applied to study the polymerization in VLC dental composites [20, 21]. The photo-initiator of light-activated composite resins breaks down due to visible-light (VL) irradiation into radicals which react with monomer molecules. In a chain reaction, the radicalized monomers combine to form progressively longer polymer chains which make up the polymer matrix. The radical is the well-known unpaired methacrylic electron localized on the carbon

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atom. This electron significantly overlaps with protons of the nearest CH_2 and CH_3 groups. Owing to the hyperfine interaction of this electron spin with the three methyl protons, its EPR spectrum is a quartet [20]. Each of the four lines is further split into a triplet, due to the weaker hyperfine interaction with the CH_2 protons. The g-factor is 2.003. The free radical concentration was monitored by the EPR absorption intensity, which is exactly proportional to their number. The number of radicals formed has been shown to increase with the irradiation time as with the saturation function, $N_o[1 - \exp(-t/\tau)]$, where τ is the characteristic time for completion of radical formation, and N_o is the maximum number of radicals (per unit weight) which can be generated. If curing time t is set equal to 3τ then $N_o(1 - \exp - 3) \sim 0.95\ N_o$. However, it is accepted that the material is cured when the free radical concentration reaches 60% of its maximum value throughout the sample, including its deepest layers. This occurs at $t = 0.91\ \tau$.

Whenever, in the deepest layer of the material, the radical concentration is lower than 60%, local setting of the composite is incomplete and this may lead to restoration failure and/or adversely affect the pulp tissue [22]. Consequently, we are proposing that curing-time definition be changed to "characteristic time at which 60% of all monomers are converted throughout the sample". Because there is no appreciable molecular diffusion in composite materials, this implies that 60% of monomers have to be converted also at the bottom layer of the sample. The difference between this proposal and the definition based on the average number of radicals is negligible in thin samples of less than 1 mm. If samples are 2 mm thick the difference is substantial and it becomes an order of magnitude if sample thickness is extended beyond clinical practice dimension (e.g. 5 mm). There 60% of all monomers are converted in ~ 120 s, see Fig. 2 below, while 60% of monomers are converted at the bottom of such a sample in ~ 1300 s, see Fig. 3 below.

2. Materials and methods

Electron paramagnetic resonance is a spectroscopic method which is used to determine the concentration of free radicals in studied samples. Free radicals are electrons with unpaired spins located on a molecule or a molecule fragment. Owing to the fact that composite polymerization is driven by free radicals, EPR was used to monitor the number of radicals as a function of irradiation time, during which the radicals were generated. From the shape of the EPR spectrum, the type of free radical was identified [19], and from its intensity (which is proportional to the area under the absorption curve) the radical concentration was calculated. Because EPR is a non-invasive method, it could be used to monitor continuously the free radical concentration during the composite resin setting. This is possible because the EPR observation is performed by irradiation with 9 GHz photons which carry only $\sim 40\ \mu$eV energy quanta, which is below any chemical bond-breaking threshold. For this reason, EPR is truly non-invasive. In order to detect free radical spectra, an EPR X-band Spectrometer (Bruker ESP-300, Germany), operating at 9 GHz, was employed.

The radicals were studied in a visible-light-cured (VLC) dental restorative composite material Herculite XRV, Kerr, Germany. This material is a bisphenol-A-glycidal methacrylate (BIS-GMA) resin-based hybrid composite, which contains approximately 59% by volume of inorganic filler consisting of 0.1–2.0 μm particles. We selected the least absorbent composite shade A2. The samples were cylindrical of 5 mm diameter, and 0.5, 0.8, 2.0, 3.0 and 5.0 mm thick. Each was mounted on a teflon stand and placed in the resonator of the EPR spectrometer (Fig. 1). Above the cylindrical sample was the end face of a light guide, connected to a standard commercial source of 0.4 W power (Translux Standard EC, Kulzer, Germany). The spacing between the end of the light guide and the upper surface of the sample was 3 mm. All measurements were taken at room temperature. After analysis of the polymerization curves of 0.5, 0.8, 2.0, 3.0 and 5.0 mm thick samples, which were irradiated for 300 s (Fig. 2),

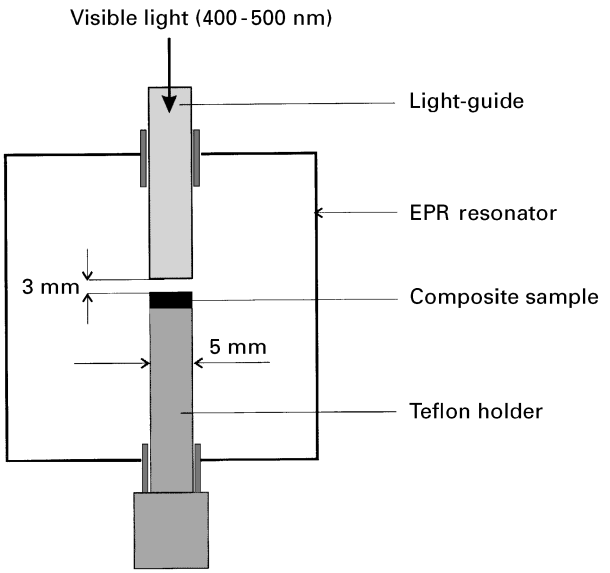

Figure 1 EPR resonator with teflon holder and sample. Note that the distance between the light guide and the top surface of the VLC composite cylinder is 3 mm.

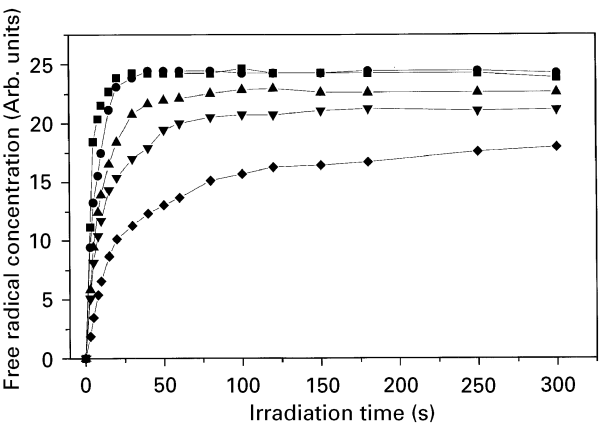

Figure 2 Free radical concentration curves of composite samples of different thicknesses, irradiated for 300 s by VL: (■) 0.5 mm, (●) 0.8 mm, (▲) 2.0 mm, (▼) 3.0 mm, (◆) 5.0 mm.

a further experiment was performed. Two groups of composite samples, 0.8 and 5.0 mm thick, were VL polymerized for 1200 s and the curing process was followed by EPR spectroscopy.

The concentration of free radicals was evaluated by integrating the EPR absorption spectra. The resulting intensities were normalized to unit weight. Each individual radical concentration measurement per unit weight is accurate to $\pm$ 1%; when different experimental runs are compared the accuracy is only $\pm$ 2%. The accuracy of EPR monitoring was optimized by having each sample in a fixed position during the entire setting of the composite (Fig 1). The number of radicals was detected after each burst of VL irradiation. The effects of irradiation bursts (of progressively longer duration) were assumed to be additive; e.g. the first burst of 2 s duration, followed by a 3 s long second burst of irradiation were assumed to create radicals equivalent to a single burst of 5 s duration. This assumption is good, because the characteristic radical recombination time at room temperature is on the order of 10^6 s. The VL irradiation times were from 2–1200 s. To ensure that EPR spectra of different samples were compatible, special care was taken with the placement of the sample holder within the EPR cavity.

3. Results and discussion

In Fig 2, the number of free radicals per unit mass as a function of VL irradiation time is shown for 0.5, 0.8, 2.0, 3.0 and 5.0 mm thick composite samples. It is well understood that VL, having wavelengths in the range 400–500 nm and with a light intensity beyond a minimum threshold of 500 W mm^{-2} for activation of polymerization, is capable of breaking bonds on polymerization initiator molecules thus forming radicals [23]. The unpaired electron of the broken bond is quickly transferred to the methacrylate monomer, thus forming the radical $R–CH_2CH_3C^{\bullet}COOCH_3$ which begins the polymerization process when joining with an intact monomer molecule. This process continues until, ideally, all the monomers become building blocks of polymer chains forming a polymer network. When polymerization takes place, these polymer chains bind the microscopic filler particles into a "cured" composite. For this to be achieved, the polymerization process must be completed throughout the composite material.

Unfortunately, the photons of visible light do not penetrate the composite material without losses. Not only are photons lost while breaking the bonds of the initiator molecules, most are lost by scattering off the filler particles [1]. The loss of photon flux, Φ, with penetration depth, x, could be described by an exponential law

$$\Phi(x) = \Phi_0 e^{-\alpha X^n} \quad (1)$$

where α is the extinction coefficient and Φ_0 is the flux on the top surface of the composite, which depends on the power of the VL source only. Consequently, the number of VL photons which reach the surface of the composite decays quickly with penetration depth and may, at some depth, be insufficient to generate sufficient radicals for the polymerization process to run its full cycle. As a result, only short polymer chains are formed and many monomers remain in the structure. Such a composite has insufficient mechanical properties and could fail when applied in restorative dentistry [24].

The question, therefore, is how long should one irradiate a composite sample to achieve full polymerization throughout? How does this sufficient irradiation time depend on the thickness of the sample? If the composite sample is very thin, e.g. 1 mm, it could be assumed that a full radical concentration is created uniformly. In such a case reaching the maximum number of radicals follows the saturation law:

$$N(t) = N_0[1 - e^{(-t/\tau_0)}] \quad (2)$$

where $N(t)$ is the number of radicals formed as a function of irradiation time, N_0 is the maximum number of radicals and τ_0 is the characteristic time. The value of τ_0 will depend in such a thin sample only on the power of the VL source. The manufacturers would have us believe that for a 0.4 W VL source, this can be achieved in 40 s, in any sample thinner than 2.5 mm. This is not true. It will be shown below, that in samples 3 mm thick, for example, it takes 165 s to polymerize sufficiently the matrix at the bottom layer of the samples.

Because in some clinical applications, samples as thick as 3 mm could be used, it is easy to believe that a reasonable extension of the irradiation time interval, perhaps by doubling it to 80 s, will be sufficient to cure even such thick composite material adequately. This is not the case either. The discussion of the clinical thickness limit begins by noting that the photon flux decreases exponentially with depth, Equation 1. Therefore, the characteristic radical saturation time (which is proportional to the flux of photons) should be

$$\tau_n(X) = \tau_0 e^{\alpha X} \quad (3)$$

for each layer (at depth x) of the material. These layers are from 0 to d deep and the saturation of free radicals in each has to be considered.

For a sample of thickness d, therefore

$$N(t) = \frac{N_0}{d} \int_0^d [1 - \exp(-t/\tau_0 e^{\alpha X})]\,dx \quad (4)$$

The parameters τ_0 and α were determined by fitting the radical concentration dependence on irradiation time in samples 0.8–5.0 mm thick (Fig. 3). In a very thin sample, e.g. 0.5 mm, the photon flux is nearly uniform throughout. Then $N(t)$ follows Equation 2, approximately. Next we modify $N(t)$ for sample thickness using Equation 4. By inspecting Fig. 3 it is striking how different is the thin (0.8 mm) sample curve and the curve for a 5.0 mm sample, where concentration increases with time almost linearly between 500 and 1000 s. This difference demonstrates the broad distribution of curing times in the thick sample. Fitting

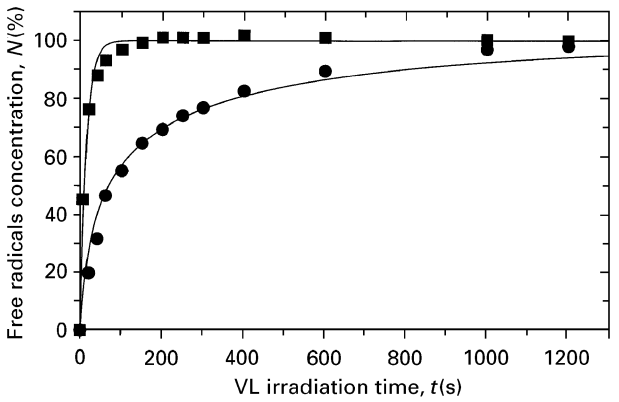

Figure 3 Typical experiments on (■) 0.8 and (●) 5.0 mm thick samples. The error of a single observation is $\pm$ 1%. The differences between samples of the same thickness fall in the range $\pm$ 3%. Note that the function, Equation 4, fits the data quite well. However, small deviations at the knee of the 0.8 mm sample curve and near the full radical concentration of the 5.0 mm curve, indicate that the model fits the experiment to within $\pm$ 4% only.

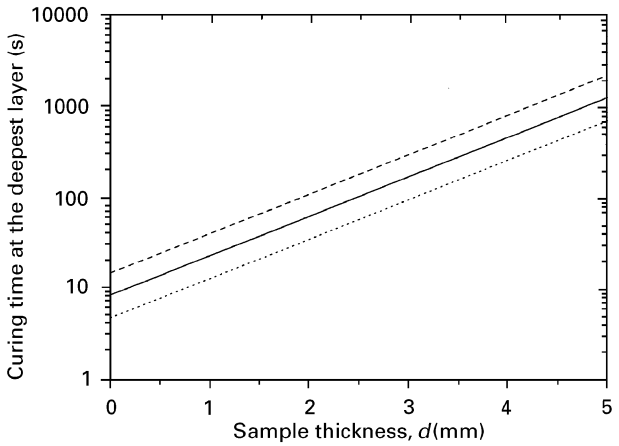

Figure 4 Curing time in which (- - -) 40%, (———) 60% and (– – –) 80% of all monomers are activated, at the bottom layer of the VLC composite sample of thickness, *d*. The VL source power was 0.4 W.

Equation 4 to these experiments, see Fig. 3, we obtain $\tau_0 = 9.0$ s and $\alpha = 1.0\,\text{mm}^{-1}$. This fit agrees with observations.

In this case, 3 mm below the surface of a thick composite sample the characteristic time for radical formation becomes τ at 3 mm = 9 exp 3 = 180 s. Because 60% of all radicals are activated at 0.91 τ it takes $0.91 \times 180 = 165$ s to create 60% of the maximum number of radicals at the bottom layer of the 3 mm thick sample (Fig. 4). This is sufficient for proper polymerization throughout the sample. The two constants in the above example which were obtained from the analysis of radical creation with time of irradiation in samples 0.8 and 5.0 mm thick, are also in good agreement with a larger set of observations, all employing the same 0.4 W VL source described in Section 2.

4. Conclusion

This analysis has enabled us to understand why, for example, a 3.0 mm thick sample requires an irradiation time longer than 0.91 τ_0, at which time the total number of radicals formed in a very thin sample reaches 60% of the maximum value. In the studied material this would be 8 s. By considering the extinction of visible light at 400–500 nm, we find that at 3.0 mm depth the curing time is 165 s. Only then, at that depth and obviously everywhere else, is a sufficient number of radicals generated. On the basis of our results, we conclude that insufficient radical concentration in the deepest layer of thicker composite material may result in a softer polymer matrix which is bound to fail in clinical applications.

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