



OPTICAL DENSITY AND DEPTH OF CURE IN VISIBLE LIGHT-CURED FILLED-RESIN DENTAL RESTORATIVE MATERIALS

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Introduction

The identification of the correct exposure (irradiance \times time, I.t) of a direct-placement, visible light-cured, filled-resin dental restorative material in order to achieve “complete” reaction is of continuing concern.¹ Essentially, in order to attain the intended set of mechanical properties, and thus (presumably) maximize the service life of the restoration, the degree of conversion of reactable vinyl groups must also be maximized. This involves, typically, a diketone-amine photosensitized free-radical polymerization system, irradiated by light of wavelengths in the region of 400 – 500 nm, and then in which a kinetically-complicated series of processes occur in a highly-viscous, non-isothermal medium, approaching the glassy state as reaction proceeds. Reaction does not come to a stop on cessation of irradiation but continues for some time afterwards. There is economic pressure on the dentist to minimize the time spent performing the irradiation, and thus a concomitant drive to increase the irradiance to achieve this, frequently on the erroneous assumptions that total energy is the criterion and that reciprocity holds.^{2,3}

Tests of the effects of exposure involve specimens of finite thickness and, given that absorption and scattering of light occur, varying exposure (sc. irradiance) with distance from the irradiated surface. Macroscopic mechanical tests therefore involve either a measurement of the net effect of variation over the depth of the specimen if exposure is specified, or the hope that the mechanical properties attained are uniform over that depth for what must be guessed as sufficient to attain completion at the greatest depth, given that reciprocity may not hold.⁴

The manufacturer’s concern is to characterize a product; the dentist’s is to receive unambiguous instructions, understand the consequences of failure to comply with these when material thickness is not readily controllable, irradiance is affected by problems of access (proximity of light source to material surface), and the above-mentioned economic pressure is present.

“Depth of cure” is commonly used to characterize a material, indicating the maximum thickness that may be treated for a given exposure. However, this is an ill-defined concept commonly represented, for example, by the depth at which an indentation hardness of 80% of the surface value is attained. There is no known justification for this approach other than convenience, accepting as it does less than full “cure”. Logically, “depth of cure” can only be the depth at which maximum conversion occurs for a given surface irradiance and duration, but difficulties can be envisaged for measuring this given that the values are of the order of a millimetre or two.

Nevertheless, some elementary physics appears to have been overlooked that offers some clear insight in the relevant processes and that may point the way to a rational and absolute characterization. It is the present purpose to set out this physics and test its applicability.

Theory

Lambert’s Law for the attenuation of light in a medium is:

$$I = I_0 e^{-\mu x} \quad (1)$$

with I the irradiance at depth x in the medium, I₀ the initial irradiance, i.e. at x = 0, and μ the linear attenuation coefficient:

$$\mu = \tau + \sigma \quad (2)$$

due to true absorption (τ) and scattering (σ). This may be tested by plotting:

$$\ln(I/I_0) = a - \mu x \quad (3)$$

where a subsumes experimental unknowns. Optical density (D) is defined as:

$$D = \mu x \cdot \log_{10}(e) \quad (4)$$

A proportion of light incident on the ‘front’ surface is reflected so that I on the ‘inside’ of the boundary, I₀’, is attenuated with respect to the outside:

$$I_0' = I_0 \cdot R_f \quad (5)$$

where R_f is the reflectance of that front surface. Similar reflection occurs at the ‘back’ surface of a finite-thickness body (R_b). The measured optical density D* of a disc of material is then

$$D^* = D + D_{Rf} + D_{Rb} \quad (6)$$

where

$$D_R = -\log_{10}(R) \quad (7)$$

D_{Rf} and D_{Rb} cannot be measured separately, but since the reflectance of an interface is symmetrical (apart from exceeding the critical angle),

$$R_f = R_b = R \quad (8)$$

assuming similar surface roughness and angular irradiation distribution. Thus, the effects can be cancelled:

$$D_1 = \frac{D_x^* - D_x}{x_2 - x_1} = \mu \cdot \log_{10}(e) \quad (9)$$

where D₁ is the true optical density of a unit thickness of material. The value of the reflectance is then accessible:

$$2D_R = D_x^* - x\mu \cdot \log_{10}(e) = D_x^* - xD_1 \quad (10)$$

For a medium of indefinite depth (that is, lacking the back-surface reflection):

$$D_x = D_R + xD_1 \quad (11)$$

which therefore provides a criterion for ascertaining the thickness corresponding to a chosen critical relative irradiance, allowing for D_R:

$$x_{\text{CRIT}} = D_{\text{CRIT}}/D_1 \quad (12)$$

Thus, from an optical density measurement on each of two thicknesses of the test material, the characteristic property of D₁ can be obtained, and providing a value for D_{CRIT} can be chosen (entirely arbitrarily), that is

$$D_{\text{CRIT}} = -\log_{10}(I_{\text{CRIT}}/I_0) \quad (13)$$

corresponding to the irradiance at which “complete” polymerization is only just obtained in a specified irradiation time, the effective “cure depth” is calculable. That is, a working “attenuation ratio” needs to be chosen. This is, of course, predicated on I₀' > I_{CRIT}, else “complete” polymerization will not occur anywhere. The irradiance of the top surface must be well in excess of that for “complete” polymerization if an appreciable thickness of material is to be treated in a specified time.

The reflectance of interfaces with the matrix strip normally used on the upper surface of a test specimen, that is, air-matrix and matrix-material, are part of the system, as is any sleeve or cover used on the curing light source tip for reasons of protection or hygiene. Since optical densities are additive, D_R (equation 11) can be taken as including all such decrements to the irradiance. In addition, it is implicit above that the specimen is of indefinite width such that the (imperfect) reflectance of containing walls does not interfere.

Two further aspects are relevant: spectrum and differential absorption. Filled-resin restorative materials are not neutral in colour, indeed, they come in a great variety of shades. The value of D₁ must therefore be wavelength-dependent (as it is by differential absorption that the shade is generated) and thus for a general illuminant it is affected by both the shade of the material and the spectrum of the illuminant. Effective polymerization depends on the concentration and absorption spectrum of the photosensitizer, and therefore on the spectrum of the illuminant (as is well-understood). This includes the effect of the changing spectrum of the light as it travels through the medium due to differential absorption, whether by the photosensitizer or the colouring materials used to create the shade. Curing depth is thus similarly affected and therefore can only be determined for a given material under specified illumination conditions. The value of D₁ is therefore not strictly constant for large values of x. However, for modest values of D₁, and for test thicknesses x₁, x₂ similar to the scale of normal working, the discrepancy may be negligible.

Experimental

There were two trials: to test that the Lambert Law applies to the transmission of the curing illuminant, and to determine D_1 directly. A wide variety of materials of various shades, from several manufacturers, were tested, about 150 products in all.

Proof of concept. A 10-mm diameter, ~3-mm thick disc of material, exposed beyond sufficiency, was successively ground plano-parallel in ~0.5 mm increments, recording in triplicate the transmitted irradiance indicated by a radiometer (Cure Rite, EFOS, New York NY, USA) with the disc resting on the sensitive window, which was 3.5 mm from the tip of the filtered quartz-tungsten-halogen (QTH) curing light (Optilux 400, Demetron Research, Danbury CT, USA). Blank readings were taken before and after each (~600 mW/cm²). Data were plotted as suggested by equation (3), and the value of μ calculated by linear regression. This was done for 65 materials.

Direct determination of D_1 . Two disks of each material were prepared, ~1 and ~2 mm in thickness, >~10 mm in diameter, by irradiating beyond sufficiency a blob of material between glass slides using spacers in a paralleling press. The cured discs could be separated cleanly from the glass. The optical density (Transmission Densitometer DT1405, RY Parry, Berks, UK) and thickness (micrometer screw gauge, Mitutoyo, Japan) of each were measured, and the value of D_1 calculated (equation 9). The densitometer (which used a QTH lamp) had been modified to include the blue-pass dichroic filter from a QTH curing lamp (Luxor, ICI, Macclesfield, Cheshire, UK), thus using for these measurements an illuminant similar to that in the above trial. This was done for the above 65 materials plus the remainder.

Results and Discussion

Proof of concept. Over 9 brands of material, from 3 manufacturers, and a total of 65 materials, the Lambert Law was found to hold for the curing lamp illuminant over 0.5 ~ 3 mm (Figure 1). There was no indication that differential absorption effects were significant for any brand or shade.

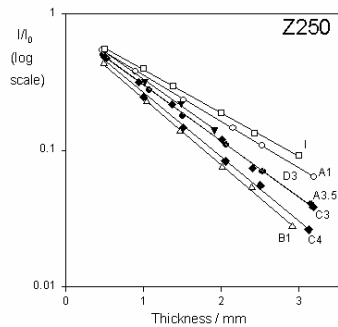


Figure 1. Example of plotted data from proof of concept trial for 3M Z250.

Direct determination of D_1 . For the same materials as used above, there was the clear expected relationship of the calculated μ values (allowing for the ln/log scale change) to the D_1 values (Figure 2); the intercept was indistinguishable from zero and the very highly significant slope (Table 1) did not differ significantly from unity ($p > 0.318$).

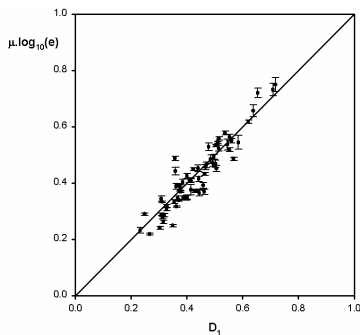


Figure 2. Relation of regression-fitted μ to D_1 . The solid line is drawn for reference at a slope of 1, through the origin. Error bars: ± 1 s.e.

Table 1. Regression analysis for μ vs. D_1

	value	s.e.	t-statistic	sig. prob.
int.	-0.0315	0.022	-1.407	>0.164
slope	1.050	0.050	21.088	$<1 \times 10^{-13}$
r^2	0.876			residual df: 63

It would therefore appear that a routine determination of D_1 will suffice as a direct measure of the curing light attenuation. It follows that, making due allowance for the attenuation arising from the reflections at the (usual) air-matrix strip and matrix-material interfaces (the latter being less important because of the closer refractive index match), it is clearly possible to determine a value for x_{CRIT} once an exposure to attain satisfactory or maximum degree of conversion can be identified. This will be dependent on product formulation (photosensitizer, amine, and their concentrations, as well as colourants), illuminant source and filtration, and dependent on reciprocity holding for general applicability (which is known not to be the case³). Purely to put the situation in perspective, and not to impute any statistical importance for the distribution, it can be seen from the values of x_{CRIT} determined for the arbitrary selection of products tested here, and allowing for attenuation to one-half of the initial (sub-surface) irradiance (Figure 3) that the range is ~0.4 – 1.3 mm, or a 3-fold variation between extremes.

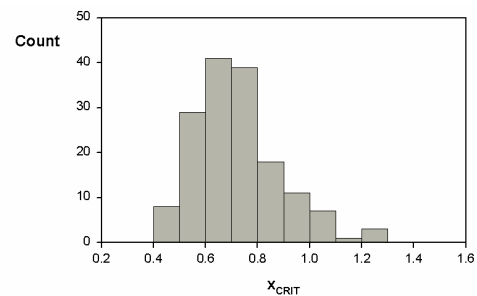


Figure 3. x_{CRIT} values for tested materials calculated on $I_{\text{CRIT}}/I_0' = 0.5$.

It is apparent that systematic investigation of the effects of variation in photosensitizer and its concentration, and other related factors such as choice of lamp, on the kinetics of polymerization in these systems may be put on a more rational footing, for relevant dental standards specifications to be written more logically, as well as it becoming feasible for manufacturers to provide more specific and useful instructions.

Conclusions

Providing a reference value of “sufficient” exposure can be identified, a critical depth may be explicitly determined for any material for a chosen exposure in excess of that reference value; the amount of excess (*i.e.* working attenuation ratio) needs to be chosen. Reciprocity failure may require explicit determination of that critical depth with respect to I.

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