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Curing-light attenuation in filled-resin restorative materials

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ABSTRACT

Objective. To characterize the attenuation of the curing light in filled resin restorative materials (FRRMs) to aid understanding of curing depth.

Materials and methods. One hundred and eighty materials of various shades from several manufacturers were tested in various ways. One set (66 materials) was used to determine the applicability of Lambert's Law using a quartz-tungsten-halogen curing light (Optilux 400, Demetron Research) by measuring the transmitted light with a dental radiometer (Cure Rite, EFOS) for successive thicknesses of ground 10 mm diameter specimens from 3 to 0.5 mm in 0.5 mm steps. A second set (17 materials) were similarly tested with separate specimens from 1 to 5 mm in thickness using a transmission densitometer (DT1405, RY Parry) fitted with a curing-light dichroic filter. For a third (overlapping) set (165 materials), the 1 mm pure (reflectance-free) optical density (D_1 value) was determined from two specimens, ~1 and ~2 mm thick using the densitometer as above. From D_1 the critical thickness (x_{CRIT}), identified as depth of cure (DoC) for an excess surface exposure factor of 2, was calculated.

Results. Lambert's Law was found to hold with no evidence of appreciable differential absorption effects. Attenuation coefficient and D_1 were significantly correlated ($P < 1 \times 10^{-13}$). D_1 varied between about 0.23 and 0.72, for corresponding x_{CRIT} values of 1.3 and 0.4 mm. There was no correlation between D_1 and reflectance ($P > 0.09$), and no systematic effect due to shade letter, but a highly significant ($P < 7.5 \times 10^{-8}$), but weak (−0.066 mm/unit), correlation between shade number and D_1.

Significance. Depth of cure can be calculated directly from the D_1 value determined via simple optical density measurements on two specimens providing that (a) an irradiation time can be determined for the surface of a specimen to be "sufficiently" cured (i.e. for DoC = 0 precisely), and (b) an excess internal surface exposure ratio can be chosen such that the corresponding DoC is attained in a practicable irradiation time.

1. Introduction

One of the problems associated with the use of direct-placement, visible light-cured, filled-resin dental restorative materials is the decrease in curing-light intensity with depth in the material. The intensity of light (strictly, the irradiance), at a given depth and for a given irradiation period, is a critical factor in determining the extent of reaction of monomer into

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polymer, typically referred to as "degree of conversion" [1–3], which is significantly associated with the values of mechanical properties [4], biocompatibility [5], colour stability [6], and as such would be expected to be associated with the clinical success of the restoration. It is therefore important to achieve sufficient irradiance at the bottom surface of each of the incremental layers used in building up the restoration. The concept of the point of sufficiency in this respect is called "depth of cure" (DoC).

Absorption and scatter within the material are the major factors associated with light attenuation [7], other than reflection from the restoration surface [8], for this is dependent on the formulation of the material, particularly the filler size, type and content [9,10], and the shade of the material [11–13]. There are marked variations in formulation between products so that similar variation in the rate of light attenuation may reasonably be expected. Previous studies have clearly shown significant variations in depth of cure between products [14–16], which has primarily been attributed to scattering of the activating radiation, thus indirectly demonstrating differences in light attenuation between materials. However, despite these clear differences, a 2 mm incremental thickness at a minimum irradiance of 280 mW/cm^2 has been recommended [17], apparently for all filled-resin composites. Increments of up to 5 mm have also been recommended for some materials, e.g. for the product "SureFil" [18].

It thus emerges that the identification of the correct exposure, E (irradiance $\times$ time ($I \times t$)) that will achieve "complete" reaction is of continuing concern. Essentially, in order to attain the intended set of mechanical properties (which ordinarily might be understood as meaning highest strength and stiffness), and thus (presumably) to maximize the service life of the restoration, the degree of conversion of reactable vinyl groups must also be maximized. This reaction involves, typically, a diketone-amine photosensitized free-radical polymerization system, irradiated by light of wavelengths in the region of 400–500 nm. A kinetically complicated, diffusion-limited series of processes then occur in what is even initially a highly viscous medium, but one which is increasingly so. The glassy state, in which reaction rates may fall by several orders of magnitude, is approached as reaction proceeds because of the typically high degree of cross-linking arising from the bifunctional reactants. The system is also non-isothermal as a result of thermalized absorbed radiation as well as generated heat of reaction, both of which are non-uniform. The nature of free-radical polymerization is such that reaction does not come to a stop on cessation of irradiation but continues for some time afterwards, so care in defining the point at which property values are determined is required.

Those are chemical and physical issues, but there is also (self-generated) economic pressure on the dentist to minimize the time spent performing the irradiation, and thus there is an associated drive to increase the irradiance to achieve this, frequently on the erroneous [19] assumptions that total energy is the criterion [20,21], that reciprocity holds [3,22], and that the mechanical outcome is the same no matter how the exposure was obtained (i.e. I and t combinations). However, an important reaction involves the mutual annihilation of free radicals, the rate of which, therefore, depends on the square of their concentration. Thus, to assume implicitly that the rate of mutual annihilation of radicals (as opposed to being involved in chain growth) could be independent of their concentration is simply wrong, thus the network characteristics must be functions of I and t, not just E ($I \times t$). Even so, it is not within the power of the dentist to determine whether a correct exposure has actually been used.

In filled resins, the transmission of radiation is affected by a number of factors. Primarily, absorption by solutes of a purely chemistry-dependent kind, affected by species concentration, controls the transmission spectrum and is therefore dependent on the incident radiation spectrum. There is also absorption by opaque substances (pigments). These differential absorption effects also mean that the transmitted spectrum changes continuously with depth and that deviations in behaviour will occur for both concentrated absorbents and long paths. Secondly, partial reflection at all interfaces where there is a change of refractive index means that for a particulate dispersion there will be a great deal of scattering [8] and thus increased path lengths, and therefore both escape from the specimen other than at the measurement site and greater true absorption. In addition, refractive index changes with polymerization (increase) and temperature (decrease), and both change continuously through the irradiation process [23]. The molar extinction coefficients of components in pure (unfilled) resin cannot be applied to calculations without this effect being accommodated; mean path length is likely to be hard to obtain, even if worthwhile. This applies not only to the filler but also to bubbles inevitably present at manufacture as well as those introduced during handling. Other scattering mechanisms exist for very small particles [9]. Thus, it is more appropriate to refer to curing-light attenuation rather than absorption since it is not possible to disentangle the two and it is the combined effects that are relevant to the context. That is, the attenuation must be determined for the actual material and a specific irradiating spectrum. Thus, separate determinations should be made for each type of curing lamp that might be used.

The determination of the mechanical outcome of the effects of exposure necessarily involve specimens of finite thickness. Hence, since absorption and scattering of light occur, irradiance varies with distance from the irradiated surface, even if it is assumed that the common practice of overlapping spots [24–26] can be avoided [27,28] and that the still less-understood variation in irradiance from place to place within the illuminated area can be ignored. 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.

Ultimately, the manufacturer's and the standards compliance testing laboratory's concern is to characterize a product. On the other hand, the dentist's concerns are simply to receive unambiguous instructions that will lead to a predictably satisfactory outcome, and to understand the consequences of failure to comply with these—given that 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 these materials, supposedly 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 [29–31]. There is no known justification for this approach other than convenience, accepting as it does less than full cure. Logically, it would seem that depth of cure can only be the depth at which maximum conversion occurs for a given surface irradiance and duration. Experimentally, difficulties can be envisaged in measuring this given that the values are of the order of only a millimetre or two. It might be argued that for a condition that is necessarily approached asymptotically, both in space and time, it is not meaningful to be so definite, yet even a criterion such as 95 or 98% conversion would be similarly problematic. Note that this kind of criterion is not equivalent to the 'percentage of maximum hardness' idea above; it has not been shown that there is a general equivalence relationship, nor would one be expected. These points arise from the fact that indentation hardness depends on the monomers involved, type and density of cross-linking, filler size, shape and proportion, boundary layer behaviour as well as degree of conversion. But even within one system, at one temperature, a linear relationship could not be predicted, bearing in mind that degree of conversion itself says nothing about the state of network development.

Overall, it is apparent that little reference has previously been made to the physics of light attenuation in these systems. Despite it generally having been overlooked, this physics seems likely to offer some clear insight into 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 by reference to a number of commercial products, ultimately with a view to identifying means to ensure that irradiation would be sufficient to expect sufficient polymerization at a specified incremental thickness.

2. Theory

Under usual circumstances, the attenuation of light in a medium follows Lambert's Law, expressed in differential form as:

$$-\frac{dI}{dx} = \mu I \tag{1}$$

where I is the irradiance at depth x in the medium, and μ is the linear attenuation coefficient (dimension L^{-1}). In a composite material, with its various refractive indices and interfaces (including the effect of any manufacturing process bubbles), the latter parameter has two components:

$$\mu = \tau + \sigma \tag{2}$$

i.e. due to true absorption (τ) and scattering (σ). However, this does not affect the behaviour as the integration to give the familiar exponential form still simply yields:

$$I = I_0\, e^{-\mu x} \tag{3}$$

where I_0 is to be read as the initial irradiance, i.e. at $x = 0$. This is commonly rearranged to show the transmittance (T) of the medium:

$$T = \frac{I}{I_0} = e^{-\mu x} \tag{4}$$

which for convenience is often expressed as the optical density D:

$$D = -\log_{10}(T) = \log_{10}(e^{-\mu x}), \quad \text{i.e. } D = \mu x \log_{10}(e) \tag{5}$$

whereby it is seen that optical density is a simple linear function of the depth of the material (assuming uniformity). In fact, from Eq. (4) we have directly:

$$\ln(T) = a - \mu x \tag{6}$$

where a allows for some possibility of experimental unknowns.

However, as the refractive index of the (composite) medium in the present case is substantially different from that of air, a proportion of light incident on the 'front' surface will be reflected [8] so that I on the 'inside' of the boundary, I_0', will be attenuated with respect to the outside:

$$I_0' = I_0 R_f \tag{7}$$

where R_f is the reflectance of that front surface. Note that this is a purely surface phenomenon and the effect of scatter from deeper in the medium back out of the body is already accounted for by σ at Eq. (2). A similar reflection occurs at the 'back' surface of a finite-thickness body (R_b). In effect, the overall optical density D^* of a disc of material, as measured from the emergent light, will be represented by:

$$D^* = D + D_{Rf} + D_{Rb} \tag{8}$$

where

$$D_R = -\log_{10}(R) \tag{9}$$

since optical density is simply additive; the components are independent and the reflectances are therefore fixed, unaffected by the intervening thickness. It will be apparent that measurements of D_{Rf} and D_{Rb} cannot be made separately, but since the reflectance of an interface is symmetrical, i.e. unaffected by the sense of the direction of travel (apart from exceeding the critical angle), we may write

$$R_f = R_b = R \tag{10}$$

assuming similar surface roughness and angular irradiation distribution. Thus, for measurements made on two finite thicknesses of the medium, the effects can be cancelled:

$$D_1 = \frac{D^*_{x_2} - D^*_{x_1}}{x_2 - x_1} = \mu \log_{10}(e) \tag{11}$$

where D_1 is the true optical density of a unit thickness of material (obviously, if desired, the value of μ can be calculated from

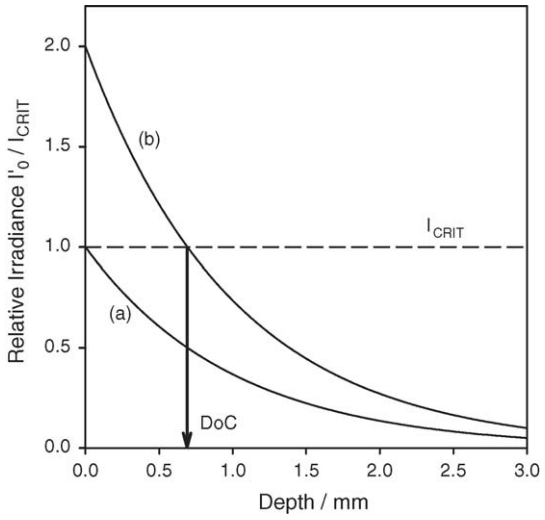

Fig. 1 – The concept of critical irradiance. Curves drawn for $\mu = 1$ (i.e. $D_1 = 0.43$) for a fixed irradiation time: (a) relative irradiance curve inside a material when "sufficient" irradiation I_{CRIT} is attained just inside the adit surface; DoC = 0; (b) relative irradiance curve when excess internal exposure ratio, $\alpha = 2$; DoC = x_{CRIT} = 0.69 mm.

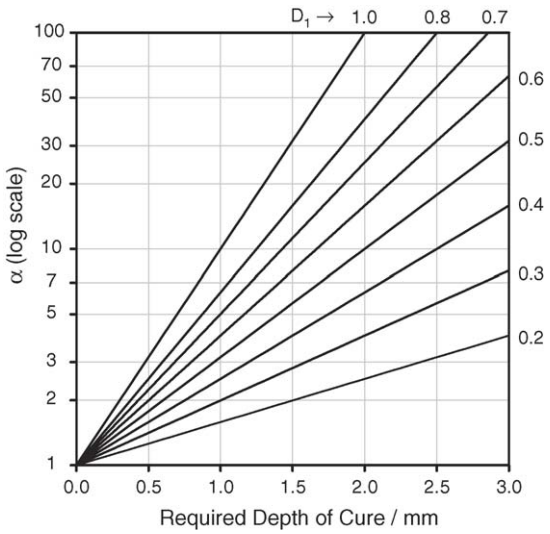

Fig. 2 – Relationship of value of α necessary to attain required depth of cure for various values of D_1.

D_1, although in the present context it has no particular separate utility). The value of the optical density of the disc due to reflectance alone is then accessible:

$$2D_R = D_x^* - xu\log_{10}(e) = D_x^* - xD_1 \tag{12}$$

In other words, for a medium of indefinite depth (that is, lacking the back-surface reflection, as would apply for a second increment which wetted the first)

$$D_x = D_R + xD_1 \tag{13}$$

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

$$D_{CRIT} = x_{CRIT}D_1, \quad \text{i.e. } x_{CRIT} = \frac{D_{CRIT}}{D_1} \tag{14}$$

It is, therefore, apparent that from an optical density measurement on each of two thicknesses of the test material, the characteristic properties of D_1 and D_R can be obtained, and that providing a value for D_{CRIT} can be specified, that is

$$D_{CRIT} = -\log_{10}\left(\frac{I_{CRIT}}{I_0'}\right) \tag{15}$$

corresponding to the irradiance at which sufficiently complete polymerization is only just obtained in a specified irradiation time, the effective "depth of cure" is calculable (Fig. 1). This, therefore, requires that a working attenuation ratio needs to be chosen. This is, of course, predicated on $I_0' > I_{CRIT}$, else "sufficiently complete polymerization" will not occur anywhere. In other words, the presumption has to be that the irradiance of the top surface is well in excess of that required for complete or even merely "adequate" polymerization if any appreciable thickness of material is to be treated at a time. An alternative view can be taken which is perhaps more easily interpretable in practice. Since x_{CRIT} is by definition the depth of cure (DoC), we have:

$$\text{DoC} = \frac{\log_{10}\alpha}{D_1}, \quad \text{where } \alpha = \frac{I_0'}{I_{CRIT}} \tag{16}$$

and α can be termed the "excess internal surface exposure ratio", that is, after allowing for the surface reflection, by how much the irradiance just inside the front surface (I_0') exceeds that required for maximum conversion (say), I_{CRIT}. The implications of this interpretation are illustrated in Fig. 2. It can be seen that if a target value for DoC is selected, say 2 mm, a considerable range of values for α might be necessary, depending on the D_1 value. Likewise, and perhaps more to the point, for a given value of α, say 5, the corresponding DoC can vary markedly.

It should be borne in mind that 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 simply additive, D_R in Eq. (13) must therefore be taken as including all such decrements to the illuminant. In addition, it is implicit above that the specimen is of indefinite width such that the (imperfect) reflectance of containing walls does not interfere.

It is now necessary to consider two further aspects of the system that were briefly alluded to above: spectrum and differential absorption. Given that filled resin restorative materials are not neutral in colour, indeed, they come in a great variety of shades, the value of D_1 must 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 (or photoinitiator), 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 the differential absorption, whether of the photoinitiator system or the colouring materials used to create the 'shade'. Curing depth is thus necessarily similarly affected and therefore can only be determined for a given material under specified illumination conditions. The value of D_1, therefore, cannot be strictly constant for large values of thickness x. However, for modest values of D_1, and test thicknesses x_1, x_2 similar to the scale of normal working, the discrepancy can be taken as negligible.

3. Materials and methods

There were three trials conducted. The first and second to determine whether Lambert's Law applies to the present system in two configurations, and the second to determine the value of D_1, x_{CRIT}, and so on, for a larger number of materials.

3.1. *Trial 1: proof of concept: dental radiometer*

Eleven representative brands of direct-filling, light-cured, filled-resin restorative materials (FRRMs) from a variety of manufacturers were used (Table 1), with as wide a range of shades as possible. One fissure sealant (conseal f) was included for comparison. Cylindrical specimens (10 mm diameter and ~3.0 mm thick) were fabricated in acrylic moulds, with a very thin smear of a release agent (petroleum jelly, K-Mart, Troy, MI, USA), placed on matrix strip (Henry Schein, Port Washington, NY, USA) backed by a glass microscope slide. The uncured resin was extruded directly into the mould from the supply syringe, taking care to avoid bubbles and seams, covered by a second matrix strip, again backed by a glass slide, and placed under ~5 N load in a levelling press (Leitz, Wetzlar, Germany) for ~60 s. The load and glass slide were then removed and the specimen cured using a quartz-halogen light (Optilux 400, Demetron Research, Danbury CT, USA) by placing the tip of the light guide (12 mm diameter) in direct contact with the transparent strip, and irradiating the specimen for 120 s at 765 mW/cm^2 as measured with a digital radiometer (Cure Rite, EFOS, New York NY, USA), containing a 400–500 nm filter. The specimen was turned over and irradiated from the bottom surface for another 120 s. The specimen was then pressed out of the mold. Specimen thickness was determined using a vernier caliper gauge (Mitutoyo, Japan).

Curing-light attenuation by the set FRRM was then determined as follows. The tip of the irradiating light guide was clamped directly above and perpendicular to the sensitive window (diameter 6.5 mm) of the radiometer, at a distance of ~3.5 mm; all readings were taken at 20 s after the lamp was switched on. The fiducial radiometer reading under these conditions (i.e. no specimen) is referred to as the irradiance at zero thickness (I_0). In the absence of a specimen, the radiometer reading varied from ~620 mW/cm^2 at switch-on to ~575 mW/cm^2 after ~240 s due to heating effects. Hence, for measurements, the light was switched on and slight position adjustments made such that at 20 s the reading was within (595 ± 5) mW/cm^2. The lamp was switched off after 60 s to allow it to cool for about 120 s before being switched back on. The sequence was repeated with the test disc inserted in the gap between the light tip and radiometer to completely cover the sensitive window. The reading was then taken 20 s after the lamp was switched back on. Thus the lamp cycle was 60 s on, 120 s off, with the fiducial adjustment made in the first, and the sample reading made in the second of each pair of cycles. In this way, three pairs of readings, at ~180 s intervals, were taken for each specimen thickness, controlling I_0 to within (595 ± 5) mW/cm^2 each time. The ~3.0 mm-thick specimen was then successively ground down to ~2.5, ~2.0, ~1.5, ~1.0 and ~0.5 mm thickness, preserving plano-parallel surfaces, using 400 grit, followed by 600 grit abrasive paper, under streaming water; the corresponding transmission was measured as above. A lapse of at least 10 min occurred before taking transmission measurements for successive specimen thicknesses. A commercial dental radiometer was used for this purpose as this is the usual means of determining and expressing curing irradiance, and therefore would be capable both of being interpreted in a relevant context and reproducible widely. The initial reading, I_0 ($x = 0$) and the transmission, I, was recorded in triplicate for each specimen. The transmittance, T, was then calculated as the ratio of the means of the three sets of readings:

$$T = \frac{\bar{I}}{\bar{I}_0} \tag{17}$$

Then, given Eq. (6), with x in millimeters, the data were plotted as $\log_{10} T$ versus x. The slope of the regression line, multiplied by $\ln(10) = 2.302\ldots$, is then an estimate of the attenuation coefficient; $\log_{10} T$ was used in the plot for ease of visual interpretation and comparison with the results of the next section. That slope and its standard error were calculated.

3.2. *Trial 2: proof of concept: densitometer*

A selected group of materials were examined to ascertain whether Lambert's Law applied in a second experimental set-up, by way of verifying that equivalent results would be obtained. A series of discs of each material, from ~1.0 to ~5.0 mm thick, in 0.5 mm steps, and >10 mm diameter, were prepared by first extruding sufficient material directly onto a glass microscope slide (again avoiding bubbles and seams), supplying appropriate spacers either side. Then, with a second microscope slide on top, the material was formed by placing the assembly in a levelling press (Leitz), applying pressure for about 30 s. The discs were cured by irradiating with an LED lamp (Radii, SDI, Melbourne, Australia) (ramp over 5 s to 1400 mW/cm^2, 440–480 nm; SDI) for at least 50% longer than the manufacturer's recommended time (typically 60–120 s), in two periods, one either side, with the assembly resting on bright aluminium foil to increase irradiance by reflection. Generally, polymerization shrinkage caused separation of the material from the glass (often with an audible click), or this could be achieved by slight flexing of the slide, hence no grease was used and smooth surfaces were obtained.

The optical density of each disc was then determined directly (Transmission Densitometer DT1405, RY Parry, Berks,

Table 1 – Products tested and values of scaled attenuation coefficient, D_1 D_R and x_{CRIT} as determined from Trials 1–3 (T1–T3)

Brand	Manufacturer	Shade	Lot no.	T1	T2	T3	$\mu \log_{10}(e) \pm$ S.D.	D_1	D_R	x_{CRIT}	t	x
A110	3M	A1E	20020118	#		#	0.372 ± 0.005	0.429	0.05	0.702	20	2
		A3D	20011219	#		#	0.533 ± 0.004	0.503	0.06	0.599	40	2
		A3E	20020122	#		#	0.468 ± 0.013	0.502	0.03	0.599	20	2
		B1	20020106	#			0.486 ± 0.006			0.62	20	2
			2001-09			#		0.567	0.09	0.53	40	2
		B2E	20020120	#		#	0.453 ± 0.012	0.44	0.06	0.684	20	2
		B3D	20020108	#		#	0.550 ± 0.007	0.56	0.08	0.538	40	2
		C2D	20020123	#		#	0.578 ± 0.007	0.537	0.07	0.561	40	2
		C2E	20020104	#		#	0.543 ± 0.003	0.511	0.07	0.589	20	2
		C3E	20020208	#		#	0.562 ± 0.011	0.553	0.04	0.544	20	2
		C4D	20020109	#		#	0.656 ± 0.021	0.638	0.08	0.472	40	2
		D3D	20020101	#		#	0.523 ± 0.010	0.514	0.04	0.586	40	2
		D3E	20011219			#		0.48	0.04	0.627	20	2
		DYD	20020110	#		#	0.720 ± 0.017	0.654	0.08	0.46	40	1.5
		DDYD	20020102	#		#	0.731 ± 0.022	0.709	0.07	0.425	40	1.5
		I	20020110			#		0.395	0.05	0.761	20	2
		YBD	20020112	#		#	0.750 ± 0.024	0.717	0.1	0.42	40	1.5
Freedom	SDI	A1	10839	#			0.313 ± 0.011			0.96	20	2
		A2	11105			#		0.363	0.08	0.83	20	2
		A3	10809			#		0.377	0.06	0.798	20	2
		A3.5	10666	#		#	0.411 ± 0.008	0.413	0.09	0.728	20	2
		A4	70936			#		0.424	0.09	0.709	20	2
		B4	101829			#		0.41	0.08	0.734	20	2
		C4	905	#		#	0.457 ± 0.010	0.467	0.08	0.645	20	2
		D3	11035	#		#	0.347 ± 0.006	0.386	0.08	0.779	20	2
Glacier	SDI	A1	11070	#		#	0.286 ± 0.006	0.318	0.06	0.945	20	NS
		A2	11216			#		0.35	0.07	0.859	20	NS
		A3	11223	#		#	0.348 ± 0.010	0.399	0.05	0.755	20	NS
		A3.5	11231	#		#	0.426 ± 0.008	0.4	0.105	0.753	20	NS
		A4	613	#		#	0.442 ± 0.013	0.359	0.134	0.839	20	NS
		B	614			#		0.379	0.07	0.794	20	NS
		B1	10933	#		#	0.289 ± 0.004	0.309	0.08	0.973	20	NS
		B2	11211			#		0.384	0.06	0.784	20	NS
		B3	11043			#		0.424	0.07	0.71	20	NS
		B4	723			#		0.426	0.07	0.706	20	NS
		C1	958			#		0.348	0.07	0.865	20	NS
		C2	10924	#		#	0.384 ± 0.013	0.376	0.09	0.802	20	NS
		C3	1033			#		0.391	0.08	0.769	20	NS
		C4	10906	#		#	0.449 ± 0.005	0.423	0.1	0.711	20	NS
		D3	10806	#		#	0.344 ± 0.009	0.308	0.128	0.977	20	NS
		I	608	#		#	0.218 ± 0.003	0.266	0.08	1.13	20	NS
		OA3	1926			#		0.402	0.09	0.748	20	NS
		OA3.5	10531	#		#	0.464 ± 0.010	0.47	0.09	0.641	20	NS
		OB3	10705			#		0.439	0.1	0.686	20	NS
		OB4	818	#		#	0.493 ± 0.008	0.497	0.08	0.606	20	NS
		OC2	628			#		0.434	0.1	0.694	20	NS
		OC4	11017	#		#	0.536 ± 0.019	0.545	0.08	0.552	20	NS
		OD3	748			#		0.472	0.04	0.638	20	NS
Herculite	Kerr	A1		#			0.284 ± 0.004			1.06	40	2
		A3	108359	#		#	0.391 ± 0.005	0.37	0.103	0.814	40	2
		B1	105815	#		#	0.277 ± 0.004	0.313	0.07	0.963	40	2
		C4	107758	#		#	0.544 ± 0.025	0.585	0.07	0.515	40	2
P60	3M	A3	20020104	#		#	0.364 ± 0.011	0.444	0.02	0.677	20	2.5
		B2	20020116	#			0.346 ± 0.007			0.87	20	2.5
		B2	4NM		#	#	0.355 ± 0.003	0.367	0.08	0.82	20	2.5
		C2	20011227	#		#	0.432 ± 0.005	0.464	0.05	0.649	20	2.5
Prodigy condensable	Kerr	A1	108646	#		#	0.289 ± 0.004	0.248	0.161	1.214	40	2
		A3	7686	#		#	0.388 ± 0.010	0.361	0.126	0.833	40	2
		B1	109A85	#		#	0.333 ± 0.003	0.311	0.127	0.968	40	2
Revolution	Kerr	A1	111441	#		#	0.392 ± 0.010	0.458	0.05	0.657	40	2
		A3	201486	#		#	0.451 ± 0.011	0.505	0.05	0.596	40	2
		B1	202221	#		#	0.373 ± 0.005	0.436	0.06	0.69	40	2

Table 1 (*Continued*)

Brand	Manufacturer	Shade	Lot no.	T1	T2	T3	$\mu \log_{10}(e) \pm$ S.D.	D_1	D_R	x_{CRIT}	t	x
		C4	111709	#		#	0.617 ± 0.006	0.621	0.08	0.485	40	2
Wave	SDI	A1	10839	#			0.224 ± 0.006			1.34	20	2
		A2	11238	#		#	0.231 ± 0.010	0.232	0.108	1.296	20	2
		A3.5	11232	#			0.356 ± 0.015			0.85	20	2
		B2	10652	#		#	0.241 ± 0.006	0.303	0.05	0.993	20	2
		B3	1067	#		#	0.376 ± 0.019	0.414	0.03	0.726	20	2
		C2	10404			#		0.347	0.06	0.866	20	2
		C3	10753	#		#	0.334 ± 0.007	0.355	0.06	0.849	20	2
		D3	10120	#			0.287 ± 0.016			1.05	20	2
		G	10127			#		0.386	0.07	0.78	20	2
		I	10112			#		0.237	0.05	1.27	20	2
		OA2	10310			#		0.301	0.09	1.001	20	2
Z100	3M	A1	20020201	#			0.306 ± 0.005			0.98	40	2.5
			4GN		#	#	0.309 ± 0.004	0.327	0.08	0.92	40	2.5
		A2	?			#		0.379	0.08	0.795	40	2.5
		A3	20011212	#			0.369 ± 0.004			0.82	40	2.5
			4JA		#	#	0.345 ± 0.006	0.377	0.07	0.798	40	2.5
		A3.5	?			#		0.403	0.08	0.746	40	2.5
		A4	?			#		0.447	0.08	0.673	40	2
		B2	20011220	#			0.316 ± 0.003			0.95	40	2.5
			4HM			#		0.338	0.07	0.89	40	2.5
			?			#		0.362	0.07	0.831	40	2.5
		B3	20011121	#		#	0.369 ± 0.009	0.462	0.03	0.651	40	2.5
		C2	?			#		0.428	0.08	0.703	40	2.5
		C4	20011130	#			0.410 ± 0.009			0.73	40	2.5
			2CK		#	#	0.383 ± 0.006	0.409	0.05	0.735	40	2
		CY	20011101	#		#	0.485 ± 0.015	0.486	0.09	0.619	40	2
		D3	20011106	#		#	0.349 ± 0.007	0.401	0.05	0.751	40	2.5
		I	20011130	#		#	0.262 ± 0.006	0.316	0.05	0.954	40	2.5
		P	20011130			#		0.339	0.06	0.888	40	2.5
		UD	20011121	#		#	0.558 ± 0.006	0.515	0.09	0.585	40	2
Filtek Z250	3M	A1E	20020104	#		#	0.339 ± 0.003	0.371	0.06	0.812	20	2.5
		A3	OFY		#	#	0.359 ± 0.004	0.405	0.06	0.744	20	2.5
		A3.5	20020111	#			0.408 ± 0.006			0.74	20	2.5
			4XR		#	#	0.394 ± 0.004	0.414	0.08	0.726	20	2.5
		B0.5	20020104	#		#	0.529 ± 0.013	0.478	0.08	0.629	30	2
		B1	20020109	#			0.487 ± 0.008			0.62	20	2.5
			4LG		#	#	0.340 ± 0.004	0.357	0.09	0.843	20	2.5
		C3	20011226	#		#	0.414 ± 0.009	0.442	0.07	0.68	20	2.5
		C4	20011218	#		#	0.471 ± 0.012	0.493	0.05	0.611	30	2
		D3	20011206	#		#	0.404 ± 0.011	0.385	0.08	0.782	20	2.5
		I	20011308	#		#	0.318 ± 0.005	0.328	0.07	0.918	20	2.5
		UD	20001121	#			0.519 ± 0.007			0.58	30	2
			3PH		#	#	0.514 ± 0.006	0.552	0.08	0.545	20	2.5
Amelogen Microfill	Ultradent	B-2	?		#	#	0.439 ± 0.006	0.475	0.06	0.634		
Amelogen U	Ultradent	B-2	?		#	#	0.433 ± 0.003	0.44	0.07	0.685		
Durafill	Kulzer	B	MR286/138			#		0.564	0.07	0.533	20	
		BO	MR286/154			#		0.585	0.07	0.514	40	
		G	MR286/152			#		0.475	0.05	0.634	20	
		GO	MR286/144			#		0.472	0.06	0.638	40	
		L	MR286/134			#		0.444	0.06	0.679	20	
		LO	MR286/116			#		0.408	0.06	0.738	40	
		S	MR286/133			#		0.463	0.04	0.651	20	
		U	MR286/148			#		0.481	0.06	0.625	20	
		UO	MR286/145			#		0.567	0.06	0.531	40	
		YO	MR286/138			#		0.555	0.06	0.542	40	
Durafill VS	Kulzer	A10	31.12.96 030			#		0.396	0.103	0.76	40	
		A20	31.12.92 029			#		0.46	0.06	0.654	40	
		A30	31.12.92 025			#		0.481	0.06	0.626	20	
		A35	30.06.96 033			#		0.581	0.07	0.518	60	
			30.06.93 027			#		0.542	0.06	0.556	20	
		B10	30.06.94 028			#		0.421	0.07	0.716	20	

Table 1 (*Continued*)

Brand	Manufacturer	Shade	Lot no.	T1	T2	T3	$\mu \log_{10}(e) \pm$ S.D.	D_1	D_R	x_{CRIT}	t	x
		B20	31.12.95 033			#		0.458	0.07	0.658	20	
		B30	31.12.95 023			#		0.503	0.06	0.598	20	
		C20	31.12.93 027			#		0.466	0.04	0.646	20	
		C20	30.06.96 030			#		0.463	0.05	0.651	40	
Estilux hybrid VS	Kulzer	A20	?			#		0.438	0.06	0.688	20	
		A30	?			#		0.471	0.08	0.639	20	
		A35	?			#		0.525	0.08	0.574	20	
		B10	?			#		0.345	0.07	0.872	20	
		B20	?			#		0.393	0.08	0.766	20	
		B30	?			#		0.449	0.08	0.67	20	
		C20	?			#		0.444	0.08	0.678	20	
		C40	?			#		0.552	0.06	0.545	40	
		I	?			#		0.278	0.06	1.084	20	
Estilux posterior CVS	Kulzer	A20	?			#		0.437	0.07	0.689	20	
		A35	?			#		0.526	0.07	0.572	20	
		B30	?			#		0.449	0.08	0.671	20	
		XR1	?			#		0.389	0.05	0.774	40	
Fulfil	Caulk	UB62	409874		#	#	0.268 ± 0.002	0.294	0.09	1.022		
Heliomolar RO	Vivadent	A3	B38982		#	#	0.516 ± 0.007	0.576	0.08	0.523		
K-0112	Dentsply	U	UK26-171-1			#		0.241	0.05	1.248		
Opalux	Coe	YO	LN190040187		#	#	0.638 ± 0.011	0.608	0.1	0.495		
Pekafill	Bayer	Y	?		#	#	0.415 ± 0.008	0.451	0.06	0.668		
Prisma APH	Caulk	DG	411892			#		0.453	0.08	0.664		
		DY	221902			#		0.633	0.06	0.476		
		GB	319905			#		0.539	0.101	0.559		
		I	92890			#		0.292	0.05	1.029		
		L	22790			#		0.283	0.09	1.064		
		LG	1201893			#		0.357	0.08	0.843		
		LGO	103928			#		0.423	0.09	0.712		
		LO	62990			#		0.387	0.08	0.778		
		LYO	103926			#		0.512	0.08	0.588		
		U	?			#		0.43	0.09	0.699		
		UO	9202111			#		0.496	0.08	0.607		
		XDG	9203236		#	#	0.546 ± 0.008	0.546	0.08	0.551		
				#			0.666 ± 0.018			0.45		
		XDY	809913			#		0.639	0.07	0.471		
		XL	920618			#		0.299	0.08	1.008		
Prisma TPH	Caulk	B1/L	930614		#	#	0.278 ± 0.002	0.292	0.08	1.032		
		B3	?			#		0.401	0.08	0.751		
		C2 op/UO	9405021			#		0.52	0.09	0.579		
		C40	30.06.89 021			#		0.547	0.05	0.55	40	
		I	31.12.94 027			#		0.319	0.01	0.943	20	
Spectrum TPH	Caulk	A2	1285			#		0.366	0.08	0.823		
		A3.5	848			#		0.438	0.07	0.687		
		A4	1224			#		0.467	0.07	0.645		
		B1	543			#		0.345	0.08	0.872		
		B1 incisal	169			#		0.302	0.06	0.997		
		B2	683			#		0.405	0.08	0.743		
		B3	1574			#		0.443	0.07	0.68		
		C2	422			#		0.42	0.08	0.717		
		C3	1141			#		0.44	0.07	0.684		
		C4	1535			#		0.44	0.08	0.684		
		D3	544			#		0.39	0.08	0.773		
Tetric ceram	Vivadent	A3	C17994		#	#	0.360 ± 0.004	0.386	0.07	0.78	40	2
Conseal f	SDI	White	11127	#		#	0.248 ± 0.004	0.35	0.1	0.861	20	NS

Also shown are the manufacturer's values for maximum increment and required irradiation time where known (NS: not stated in supplied instructions). Literature for older materials not traced. Where a material was tested only in Trial 1, the value for x_{CRIT} is shown to two decimal places to reflect the different conditions and possible lack of comparability with Trial 3 values. Where a material was tested in Trial 2 (and hence not in Trial 1), the value for scaled attenuation coefficient, $\mu \log_{10}(e)$, shown was calculated from these data.

Table 2 – Analysis of regression of scaled attenuation coefficient, $\mu \log_{10}(e)$ (Trial 1) against D1 (Trial 3)

	Value	S.E.	t-Statistic	Significance probability
Intercept	−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	

UK) as well as the thickness (micrometer screw gauge, Mitutoyo, Japan). The densitometer had been modified by the insertion in the illuminating light path the blue-pass dichroic filter from a quartz-halogen curing lamp (Luxor, ICI, Macclesfield, Cheshire, UK) such that the illuminant for the measurement was similar to that used for curing generally, and to that used in the above trial. Optical density was then plotted against thickness, and the fitted regression lines examined.

3.3. *Trial 3: determination of D_1*

The materials used in the first part (Table 1) and a wide variety of other products, of various ages, were examined to determine the value of D_1, and thus x_{CRIT}, for each. A simpler (and more economical) procedure could be adopted, as indicated by Eq. (11), in which just two discs of each material, ~1.0 and ~2.0 mm thick and >10 mm diameter, were used. The procedure was identical to that of 3.2, above, except that D_1 was then calculated according to Eq. (11).

Plotting and statistical analysis were done in software (SigmaPlot v9; SigmaStat v 2.03, SPSS, Chicago, IL, USA).

4. Results

Some results for nine brands of the first trial are illustrated in Fig. 3. Inspection showed that Lambert's Law was obeyed closely for the range of thicknesses tested. There was no indication that differential absorption effects were significant for any brand or shade over the thickness range tested. The failure of all lines to extrapolate to the point (0, 1) was evident.

The results for some of the materials of the second trial are illustrated in Fig. 4. Again, there was no indication that Lambert's Law did not apply, any differential absorption effects being undetectable. However, the intercept of the ordinate is marked and highly significant in each case (all $P < 0.002$).

The values of the scaled attenuation coefficient, $\mu \log_{10}(e)$, obtained in the first trial were then plotted against the values of D_1 determined for the same 65 materials (Fig. 5). It can be seen that the relationship is very clear and strong, and that the intercept was indistinguishable from zero (Table 2). The slope itself did not differ significantly from unity (t-test, $P > 0.318$).

The values determined for $\mu \log_{10}(e)$ and D_1 are included in Table 1.

5. Discussion

It was, of course, not possible to do the transmission measurements on fresh resin without effecting curing of the materials. Theoretically, curing is expected to reduce the absorption by consumption of photosensitizer. However, it is not considered likely that this change would be significant in the present context, bearing in mind that during normal curing there will be a progressive change in the available amount of photosensitizer over the time of irradiation to a low value more representative of the end rather than the beginning of irradiation. In addition, any side reactions which produce other chromophoric groups must tend to increase absorption, but with a different spectrum. There is a further effect: polymerization changes the refractive index of the matrix, and thus the reflectivity at the filler–matrix interface [23]. These effects would be very difficult to disentangle, but it might be worth investigating whether there is a chromaticity shift during normal irradiation, or indeed whether continued irradiation causes this. However, the differences are expected to be proportionately very small, partly because the absorption efficiency of photoinitiators is typically rather low, but also because their concentration must also be low, certainly to avoid the strong yellow colouration that would otherwise result. Whether the effect would be detectable and alter appreciably the values obtained would require a more elaborate investigation. Even so, it is unlikely to affect the relative values, that is, between materials and shades. In any case, what is sought is a measure and criterion of efficacy; safety margins can always be added.

The regression lines of Fig. 3 are not fitted including the origin, as might be expected, because the reflection losses at the top and bottom interfaces of the specimen with the air are appreciable, as indicated at Eq. (8). This is re-emphasized by the results of Trial 2 with respect to the intercept (Fig. 4). Thus, it is essential to allow for the effects of reflection when considering material optical density. While the reflection at the upper (adit) interface is clinically significant inasmuch as it affects the irradiance just inside the material, i.e. effectively for $x = 0$, reflection at the exit interface – back into the material – means that irradiance there is actually somewhat higher than the measured transmission would otherwise imply. However, allowance for these factors cannot be made explicitly for a single measurement, and it is better to rely on the effect of changing the material thickness between these interfaces, as here. Nevertheless, it should be realized that there is a loss at each such interface, and the use of a matrix strip, while replacing the material–air interface with the better matched material–strip interface, adds one between the strip and air. For very thin specimens, such that the exit surface reflection results in an appreciable increment to the illuminance at the adit surface, further complication might be anticipated; it is not the present purpose to explore this.

It is also relevant in this context to notice that the specimen width to thickness ratio was deliberately large, effectively eliminating wall effects. This is necessary as the path taken by light in the medium of the material is not a straight line from source to detector as might occur in single phase media. Consider the cylinder of the material defined by projection of the radiometer sensitive window diameter. Some light which entered that cylinder from its top surface will be scattered across that boundary and, with attenuation, be scattered back. Likewise, light entering the material from outside the boundary of its end circle will be scattered inward. Thus the irradiance measured at the exit circle depends in part on light crossing that cylindrical surface in either direction. Were the boundary to be replaced by an absorbing interface such as

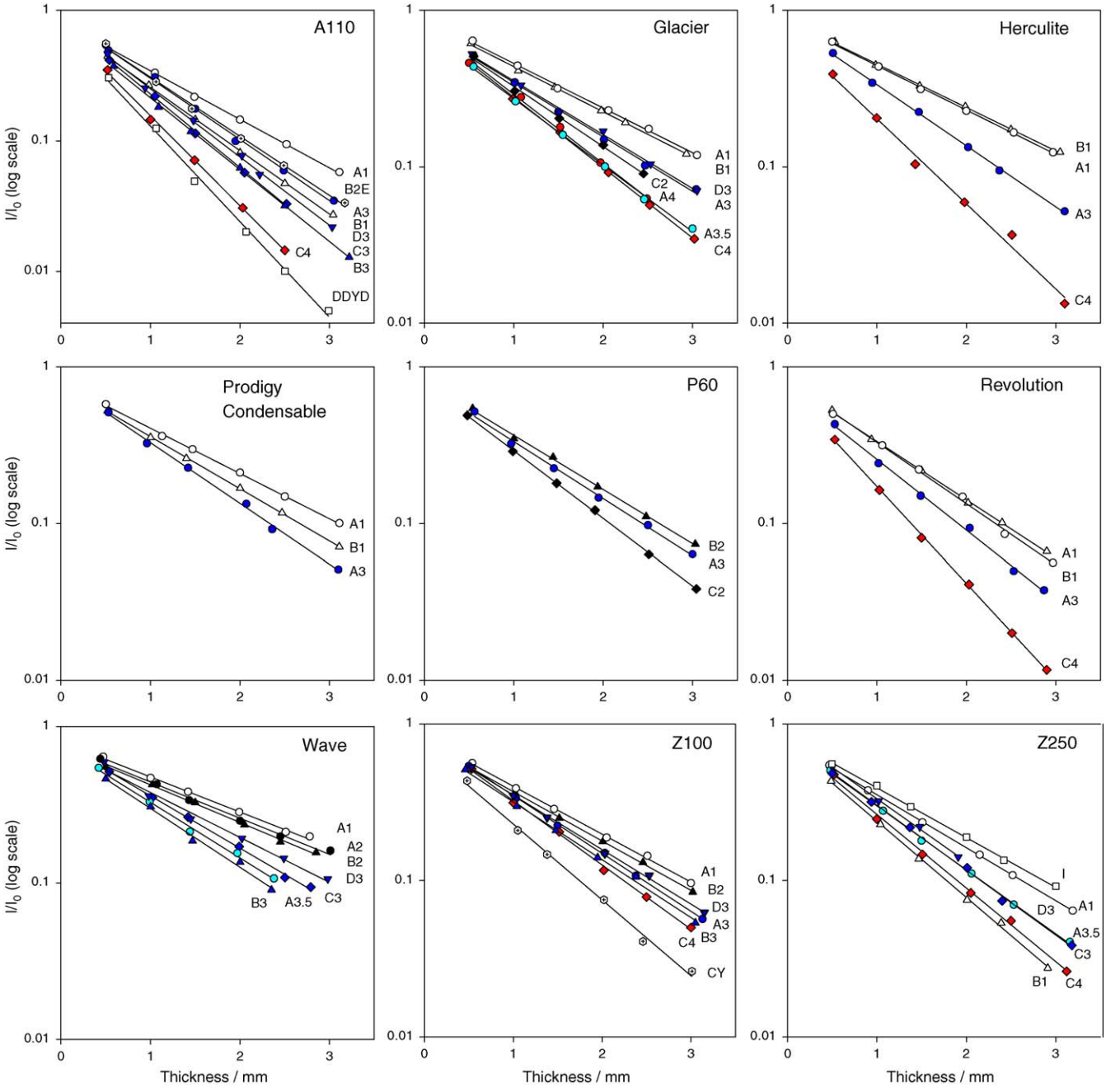

Fig. 3 – Representative Trial 1 results: log(relative irradiance) using dental radiometer vs. specimen thickness. Shade designation is indicated for each line. Lambert's Law appears to apply for a curing light and dental radiometer combination.

with a black nylon mould, a white diffusely-reflective surface such as polytetrafluoroethylene, or a metallic reflection from, say, stainless steel, one would expect results to vary. Thus, attempts to measure depth of cure (however defined) with this aspect uncontrolled cannot be expected to be consistent in outcome. Similar issues apply for varying diameter, and variation in degree of conversion across the diameter would also seem inevitable if equivalence were not obtained. Whilst it is true that these materials are typically used in contact with enamel, and that that would be the appropriate kind of interface to reproduce, width is uncontrolled. It is considered that the 'semi-infinite' approximation is better, where the diameter of the specimen is larger than both the fibre-optic exit window and the radiometer sensitive window (or densitometer detector), such that this excess is large in proportion to the thickness.

A certain degree of conversion (DC) in resin-based materials must be achieved for the material to develop 'adequate' physical and mechanical properties so as to withstand masticatory forces and also attain adequate biocompatibility (i.e. with respect to leachable substances). The reaction chain leading to the formation of initiating radicals involves several steps, and a complex kinetic equilibrium is established between formation and consumption (whether con-

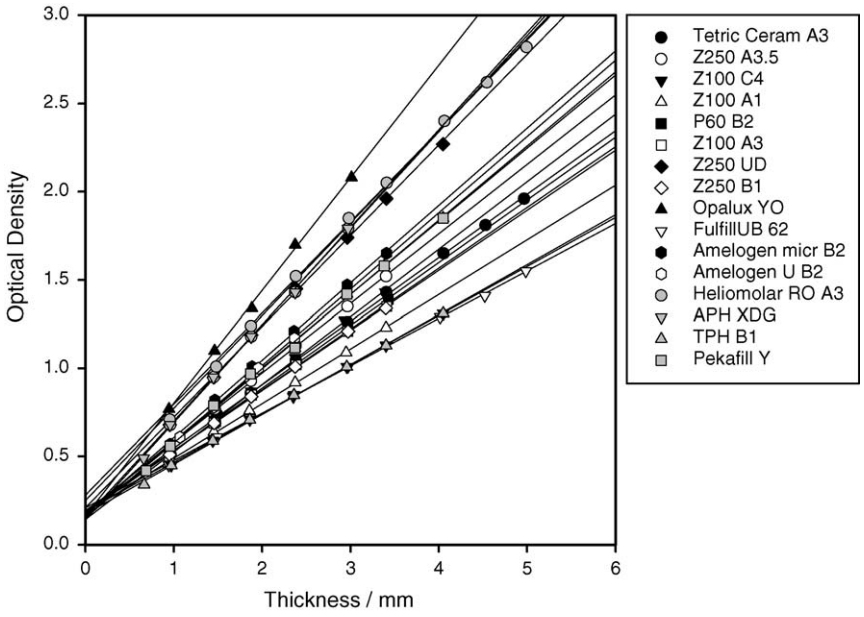

Fig. 4 – Trial 2 results: direct measurement of optical density vs. thickness. Lambert's Law appears to apply for a densitometer using a curing-light filter for the illuminant.

structively through initiation or destructively through annihilation). Annihilation rates depend on usable free radical concentration (squared), and potential polymerization chain length inversely so. Hence, simply increasing their concentration (and thus, by implication, irradiance) is not necessarily going to result in increased DC. Indeed, there must be a maximum point in the plot of DC versus I (at given t). This arises because the rate of reaction of free radicals with double bonds depends on the their concentrations to power one. Hence, no matter the rate constants, at some point the annihilation rate must overtake propagation. If the initiating radical species

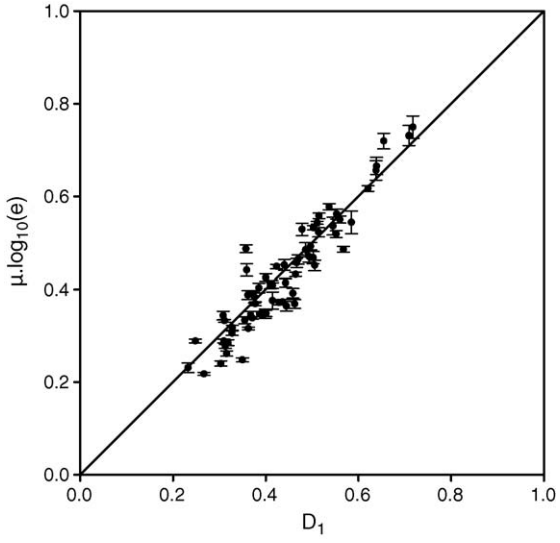

Fig. 5 – Trial 3 results: comparison of scaled linear attenuation coefficient, $\mu \log_{10}(e)$ and D_1 from two-point measurement using the densitometer with curing-light filter. Error bars: ±1 S.E. of fitted slope from Trial 1. Solid line: slope of unity, zero intercept, for comparison.

concentration is high enough, these will mutually annihilate, and thus will not even begin a polymer chain. Small chains will also be involved in like fashion and not contribute to the network. Thus surface hardness, for example, may decline, even if DoC continues to increase because attenuation with depth ensures that the "optimum" will occur somewhere. A further complicating factor is the presence of inhibitors, required for stable storage: a minimum exposure (not irradiance) is required to consume these before irradiation actually becomes effective for curing [19].

The dramatic attenuation in irradiance with increasing specimen thickness observed in the present study (Fig. 3), is in accord with previous reports [21,32], even though little consideration seems to have been given to the essential physics then. Although this attenuation is expected to be in part dependent on filler volume fraction, particle size distribution, particle shape (roughness) and refractive index difference (compared with the matrix), it is difficult to make direct comparisons because of the lack of adequate data on the fillers (and no theoretical or experimental treatment of these issues is known). Variations in resin chemistry are also relevant, in addition to intended absorptions (shade) and incidental absorption (photosensitizer). However, while comparisons might be made, generalization is not particularly helpful, partly because shades are not uniformly labelled across brands but also because too many factors are involved. Thus, A110, a microfill material (Table 3), tends to have the highest attenuation for any given shade, despite having probably the lowest filler content (40 vol.%), while Wave (average particle size 1.5 μm), with a relatively low filler content (50 vol.%), has some rather low values. In contrast, Revolution (average particle size 1 μm), with a comparatively lower filler content (43 vol.%) has high attenuation, comparable with A110. Clearly, a direct measurement of the overall effect of all factors is far preferable to theoretical musings in this sense.

Table 3 – Filler characteristics for some materials tested

Classification	Brand	Filler content (vol.%)	Average particle size (range) (μm)
Microfill	A110	40	0.04 (0.01–0.09)
Small hybrid	Herculite	59	0.6
	Z100	66	0.6 (0.01–3.5)
	Z250	60	0.6 (0.01–3.5)
	Prodigy	60	0.6 (0.6–1.0)
	Glacier		0.7 (0.04–10)
Midsized hybrid	Freedom	62	1 (0.04–10)
	Wave	50	1.5 (0.04–10)
	P60	61	(0.01–3.5)
Flowable	Revolution	43	1

It might be anticipated that the light reflected at the adit and exit surfaces would be subject to the same or similar set of influences. However, there is no significant correlation between the vales of D_R and D_1 ($P > 0.09$) (Fig. 6). The mean reflection (one surface) is of the order of 15% (mean $D_R \sim 0.072$), although the range is quite large.

As indicated above, shade might be expected to have an effect on critical depth. The relationship of x_{CRIT} to shade letter is shown in Fig. 7. The shade designations used by the various manufacturers are not uniform, so only those with a simple letter–number code (A–D, 0.5–4; plus *I*, incisal) were checked. It is apparent that apart from the expected greater value for the "incisal" material, there is no pattern for the letter codes A–D. However, there is a significant association (linear regression, $P < 7.5 \times 10^{-8}$) between x_{CRIT} and shade number for the same letter range pooled (Fig. 8). It is noted, nevertheless, that the distinction between shades on average is rather small (indicated by slope: −0.066 mm/unit), and apart from one or two anomalies this appears to be the case within brands (thin lines). The contrast between brands is more marked. Whether this curing-light variation reflects the white-light colour (normal appearance) variation would need to be checked, but it suggests that standardization is not that strong and that knowledge of one brand is not necessarily informative about another, even if the designations are similar.

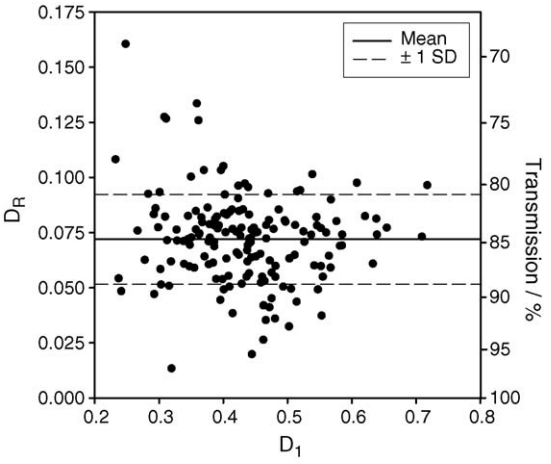

Fig. 6 – Trial 3 data: single surface reflection optical density (D_R) vs. "pure" unit optical density (D_1). No association is evident.

It can be seen from Table 1 that the values for D_1 range from about 0.23 to 0.72 (Wave A2, A110 YBD), and the corresponding values of x_{CRIT} for $\alpha = 2$ are ~1.3–0.4 mm; that is, a factor of about 3 between extremes. The majority lie in the region of 0.5–1.0 mm, and although this is not a statistically meaningful sample, the sense of a typical range is clear enough. However, given the sensitivity indicated by Fig. 2, the question arises of the effect of error in the increment thickness on required irradiation time. It seems to be asking rather a lot to control the distribution of a portion of material such that the recommended maximum is not exceeded—judging an increment to ±0.25 mm is unlikely to be reliably attained, for example, especially given the economic pressure to avoid unnecessary steps in the procedure. Lambert's Law allows the effect of thickness errors on the required exposure time to be calculated:

$$\frac{t_2}{t_1} = e^{\ln(10) D_1 (x_2 - x_1)} \tag{18}$$

where t_1, t_2 are the irradiation times for the intended thickness (x_1) and the actual thickness (x_2). This function is plotted in Fig. 9 for a few values of D_1 and $x_1 = 2$ mm. The effect can be

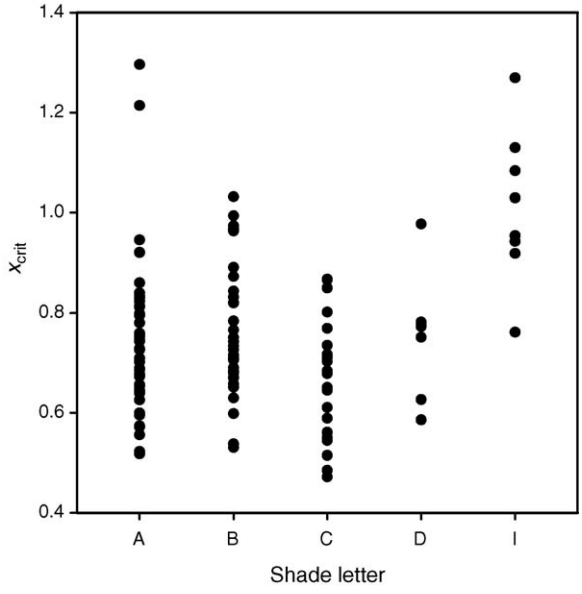

Fig. 7 – Variation of critical depth, x_{CRIT}, by shade letter for $\alpha = 2$; selected materials. No systematic effect is discernible.

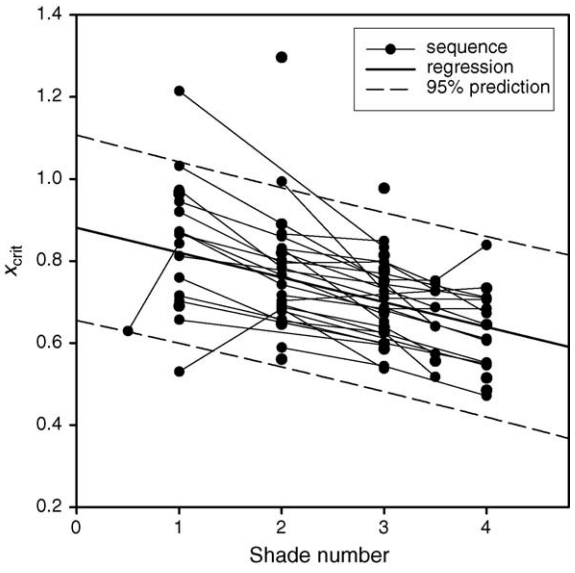

Fig. 8 – Variation of critical depth, x_{CRIT}, by shade number for $\alpha = 2$; selected materials. Prediction limits indicate general expectation for new products on this pattern; "sequence" lines indicate brand and type groups to show commonality of trend and departures from it.

dramatic: even at $D_1 = 0.6$, an error of +0.5 mm requires a doubling of the irradiation time; a 1 mm excess doubles it again. Even at $D_1 = 0.2$ an extra 25% is required for +0.5 mm, which in a 40 s exposure is not negligible. What is not known is how much leeway is built into manufacturers' recommendations to allow for this and other errors and discrepancies, although other evidence suggests that there may be none [19].

The standardized test for depth of cure [33] considers achieving a hardness equivalent to 80% of surface hardness acceptable (assuming that the maximum possible hardness has been attained on the top surface) but does not provide sufficient scientific justification. Typically, well-cured FRRMs have

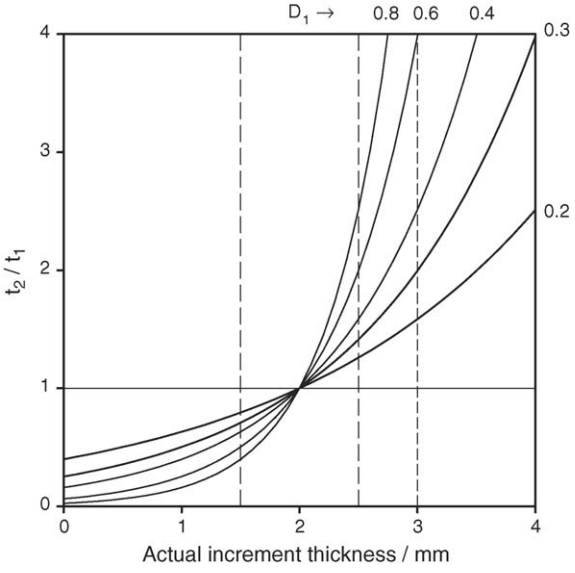

Fig. 9 – Effect of error in increment thickness for a reference thickness of 2 mm. Dashed lines shown at ±0.5 and +1 mm.

a DC of ~65% (the other 35% consisting of network pendant groups, unreacted acrylic functional ends of silane coupling agents as well as residual monomers). DC at the depth which hardness corresponds to 80% of surface hardness must be much less than 65% and it is unclear whether such a material would have adequate biocompatibility let alone mechanical properties, yet the test is widely accepted and used in the evaluation of the curing performance of both halogen [16,34,35] and light emitting diodes (LEDs) [36,37]. The definition of depth of cure (DoC) used here is rather different as the implicit expectation is that the reaction will have been driven as far as is practicable at that point (we ignore oxygen inhibition for simplicity).

The dependence of DoC on shade and illuminant effectively means that no one figure is meaningful for a given brand of FRRM. Worse, the value for a shade within a brand can strictly speaking only be for a specified curing lamp, i.e. not simply the type of illuminant source (filament lamp, LED, plasma arc) but including all filtration applied internally. To that extent, the values in Table 1 are illustrative rather than definitive, and factors such as the match of illuminant with the critical absorber's spectrum still need to be taken into account. Indeed, there is likely to be an effect due to the spectral sensitivity of the densitometer detector, although this we believe to be relatively small. Nevertheless, with the identification of the independent values of D_1 and D_R, it is now possible to investigate separately the true effects of factors such as filler loading, shade, photoinitiator system, photoinitiator concentration, type of illuminant, lamp voltage, and so on in a physically meaningful way.

As has been pointed out previously, exposure reciprocity cannot be relied on to determine equivalent exposures [19]. However, it should be apparent that the then-suggested exposure guide only needs adjusting to take into account the effects described here now, providing a reference value of "sufficient" exposure can be identified experimentally. A critical depth – DoC – may then be explicitly determined for any material for a chosen exposure in excess of that reference value, under specified conditions of illuminant; the amount of that excess in terms of irradiance, α, needs to be chosen. If reciprocity failure is appreciable, explicit determination of that critical depth with respect to irradiance may be necessary in order to keep the irradiation time sensible. In the end, what is chiefly required is the specification of two figures that the clinician can rely on to ensure that at the bottom of an increment of material the minimum acceptable properties will be attained: the value of x_{CRIT} and a duration, for a given value of I_0, the primary irradiance – the brightness, if you will – of the source.

6. Conclusion

Lambert's Law can be used to characterize FRRMs with respect to depth of cure, providing allowance is made for reflectance, "sufficient" exposure can be determined, and a suitable excess exposure ratio can be chosen. In practical terms, a cautious approach in this respect would be to (a) ensure that the specific product shade instructions were checked, (b) that thinner rather than thicker increments were used, (c) that longer rather shorter irradiation times were used, and (d) that any-

thing affecting actual irradiance (lamp, distance, angulation) was compensated for generously.

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