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Polymerization of resin composite restorative materials: exposure reciprocity

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Abstract

Objective. To examine whether there is reciprocity between irradiation time and irradiance with regard to the mechanical properties of filled, resin composite restorative materials (RCs).

Methods. Four visible light-cured RCs, all of shade A3, were used: Heliomolar Radiopaque (HR) and Tetric Ceram (TC) (Ivoclar, Schaan, Liechtenstein), Filtek Z250 (FZ) (3M, St Paul, MN, USA) and Prodigy condensable (PR) (Kerr, Orange, CA, USA). Bar specimens ($1.0 \times 1.5 \times 16.0$ mm^3) were cured at irradiances (I) ranging from 25–1500 mW/cm^2 and irradiation times (t) of 1–3000 s. Six specimens at 250 combinations of t and I were prepared and stored in artificial saliva of pH 6, at 37 °C for 7 d before performing three-point bend tests for flexural strength (F), flexural modulus (E) and total energy to failure (W). Contour plots of property value vs. t and I on log scales were prepared.

Results. The contour plots showed three regions: unset at low $I \cdot t$, a plateau corresponding to more or less full property development, and connecting ramp. The boundary between the plateau and the ramp suggests the minimum acceptable exposure. No practical lower limit to irradiance was detected, but there may be no benefit from increasing I beyond about 1000 mW/cm^2. The slopes of the contours in the log–log plots provided a test of the hypothesis of reciprocity. These slopes were ~ -1.5 for HR, TC and PR; and ~ -1 for FZ, compared with the expected value of -1. The general hypothesis therefore fails. The existence of localized maxima in property values is further evidence of that failure, even for FZ.

Significance. Dentists may use any lamp, including LED sources, and attain satisfactory results providing irradiation time is long enough. Manufacturers ought to supply a graph indicating the minimum acceptable exposure for each product for specified curing lamps. Calculations based on total energy delivered to guide irradiation protocols are invalid and do not recognize product behavior.

Keywords: Filled resin composite restorative materials; Irradiance; Irradiation time; Exposure; Reciprocity; Strength; Modulus of elasticity

1. Introduction

The intensity of the incident radiation in the 'appropriate' wavelength range and the time of irradiation are crucial to the completeness of polymerization, and determine the development of the physical and mechanical properties of light-cured filled, resin composite restorative materials (RCs). Irradiance (I) expresses indirectly the rate of delivery of photons and thus that of the free radicals generated, while irradiation time (t), at a given I, determines the total number of free radicals generated, although not necessarily proportionally in either case. Although some recommendations have been made for the minimally acceptable I for a given t at a given incremental thickness, e.g. 280 mW/cm^2 for 60 s for 1 mm increments [1], 400 mW/cm^2 for 60 s for less than 2 mm increments [2] and 600 mW/cm^2 [3], there is still no consensus on an adequate exposure or 'energy density' ($I \cdot t$ in mJ/cm^2), i.e. to cause acceptable polymerization. This is not surprising given the variations in composition of RCs, emission spectra of light sources and responsivity of detectors. Indeed, it seems illogical to expect that one figure could be generally meaningful. Thus, dental practitioners are obliged to rely on information provided by the manufacturers. Unfortunately, this is often quite insufficient, only stating t and incremental thickness but not I. Besides, even the recommended irradiation times have been reported to be

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generally inadequate in ensuring 'complete' polymerization of RCs [4]. The use of dental curing lamps with 'inadequate' irradiance, as is reported to occur in dental practice [5–7], further raises the possibility of under-exposing these materials. Clearly, there is need for the values of I and t at a given incremental thickness necessary to cause 'sufficient' polymerization of a given RC to be specified. If this is done, then problems such as poor mechanical properties due to insufficient exposure ('under-cure') and over-heating due to over-exposure, that may have serious clinical implications, might be reduced or eliminated.

It has been suggested that light sources with less than 'optimal' output (although this is not clearly defined) can still yield satisfactory cure provided t is 'sufficiently' long [1,8,9]. Then, more recently, plasma arc (PA) lamps producing very high irradiances have been introduced along with the claim that very short irradiation times (e.g. ~ 3 s) can cause adequate polymerization of RCs. There is a great deal of confusion over such claims, but they seem to have been based on an assumed simple reciprocal relationship between I and t. Indeed, previous studies have claimed to show just such a relationship [10,11]. However, in the one case, only narrow ranges of moderate irradiances and irradiation times were examined: i.e. $I = 100$–$400\ \text{mW/cm}^2$, for $t = 30$–120 s [11]. The absolute irradiance values used in the other study [10] were not stated, but only modest light output can be assumed as a quartz-halogen (QH) lamp (New Light VLII, GC, Tokyo, Japan) was used, with the irradiance varied from 12.5 to 100% of the maximum with $t = 10$–80 s. Given the complexity of the kinetics of polymerization, a simple extrapolation of reciprocity between I and t, implied in the earlier-mentioned studies, to cover very high I (as obtainable from PA lamps) and extremely short t, cannot be assumed.

The object of this present study was therefore to re-examine reciprocity between I and t with regard to the mechanical properties of RCs over a wide range of I and t. It may be noted that the implication of reciprocity is that K in

$$K = I \cdot t \tag{1}$$

represents the minimum exposure (mJ/cm^2), i.e. total energy delivered, required for adequate polymerization; it is therefore implicitly a material constant. Were such a figure to be known, the appropriate irradiation time for any given irradiance could be calculated, i.e. allowing for variation between curing lamps and for their ageing.

2. Materials and methods

Four commercially-available visible light-cured, RCs were studied (Table 1): Heliomolar Radiopaque (HR), Tetric Ceram (TC), Filtek Z250 (FZ) and Prodigy Condensable (PR), all of shade A3. Specimens were fabricated using a knife-edged split aluminium mold [12]. Excess uncured resin was extruded directly into the mold, covered by a transparent strip (Hawe Transparent Strips, No. 697, HaweNeos Dental, Bioggio, Switzerland) backed by a glass microscope slide and placed under 10 N load in a leveling press (Leitz, Wetzlar, Germany) for 3 min. The light guide, made to order (C Technologies, Cedar Knolls, NJ, USA), had a circular collection port (10.0 mm diameter), but the optical fibers within the bundle were randomly re-arranged to form a rectangular exit window, $3.0 \times 25\ \text{mm}^2$. This was mounted such that the exit window could be placed in contact with the transparent strip, after the mold had been removed from the leveling press, centered on the rectangular slot ($1.5 \times 26\ \text{mm}^2$) of the mold, thus enabling even illumination of the working portion of the specimens ($1.5 \times 16\ \text{mm}^2$) as well as handling tabs in a single shot. Two types of lamp, a QH (250W, 24V: HLX 64653, Osram, Germany) and a PA lamp (Arc Light IIM, Air Techniques, Hicksville, NY, USA), were used in order to cover the intended range of the values of I; both were employed with a 400–500 nm bandpass filter, made up from a heat-reflecting mirror (HR-750-S, Corion Franklin, MA USA) and the 'blue' filter extracted from a commercial curing lamp (Luxor-4000, ICI, Macclesfield, UK). QH was used for polymerization of specimens at irradiances of 25–400 mW/cm^2, while PA was used for 500–1500 mW/cm^2. To use the latter with the special light guide and attain the maximum irradiance it was necessary to mount the light source outside the original casing, but this was limited to 500 mW/cm^2. Accordingly, for the higher values of I specimens were irradiated directly at a position that had been determined to be of sufficiently uniform ($\pm 5\%$) irradiance of the appropriate value. The QH lamp was driven from a stabilized power supply (6274B, Hewlett-Packard, Loveland, CO, USA). Irradiance was determined using a silicon detector (DET110, ThorLabs, Newton, NJ, USA) and neutral density filters (QD-x-F series, Corion, Franklin, MA, USA) as necessary, the scale being calibrated to align with that of a hand-held radiometer (Demetron 100, Demetron Research, Danberry, CT, USA) that is commonly used in dental clinics. The time to reach a relatively stable

Table 1
Products used and exposure recommendations

Product	Code	Batch no.	Manufacturer	Irradiation time (s)	Increment (mm)
Heliomolar Radiopaque	HR	A02633	Ivoclar, Schaan, Liechtenstein	40	2
Tetric Ceram	TC	A0741	Ivoclar, Schaan, Liechtenstein	40	2
Filtek Z250	FZ	OEN	3M Dental products, St Paul, MN, USA	20	2.5
Prodigy Condensable	PR	007686	Kerr, Orange, CA, USA	40	5

emission for the QH lamp was ~10 min, thus measurements and adjustments of irradiance were made 10 min after switching on. The lamp was then left switched on throughout a period of specimen preparation but checks and adjustments of irradiance were made every 90 min to control the decline to within 5% of the set point. Adjustments to the required irradiance value were made by moving the collection port nearer or away from the lamp. Irradiance was set at 25, 100 and 300 mW/cm^2 for all, and additionally at 50, 200, 250 and 400 mW/cm^2 for HR and TC during initial exploration of the response surface, using the QH lamp, and at 500, 1000 and 1500 mW/cm^2 with the PA lamp. Irradiation times at each tested value of I were 1, 2, 5, 10, 50, 100, 300, 500, 1000 and (for HR and TC at $I \leq 250$ mW/cm^2) 3000 s with six replicates at each combination, excluding those where sufficient setting for a testable specimen was not obtained, for a total of some 1500 trials at 250 exposures. All work was done in darkness, under photographic safelight, or with the curing light shielded by aluminium foil, as necessary. Irradiation was effected by removing and replacing the foil shield for QH. For the PA lamp, the control unit timer (max. 60 s) was employed; for longer time intervals the lamp was promptly (delay ~0.3 s) switched back on again the appropriate number of times. The decline in irradiance was less than 5% even at 3000 s. Specimens were placed promptly in artificial saliva [13] of pH 6, at 37 °C, and stored in light-tight containers for 7 d before testing.

Mechanical testing of the specimens in three-point bend (16 mm span) using a universal testing machine (1185, Instron, High Wycombe, UK) at 0.50 mm/min cross-head speed, was done in fresh artificial saliva at 37 °C to determine flexural strength, flexural elastic modulus and total energy to failure. A few specimens with evident flaws were discarded without replacement. Data acquisition was done in software (LabVIEW version 5.1, National Instruments, Austin, TX, USA) on a personal computer, as was the programmed calculation of ultimate flexural strength (F), using the corrected formula, and flexural elastic modulus (E) as:

$$F = \frac{3PL}{2bd^2}\left[1 + \frac{6D^2}{L^2} - \frac{4dD}{L^2}\right] \quad (2)$$

$$E = \left(\frac{\Delta P}{\Delta y}\right)\frac{L^3}{4bd^3} \quad (3)$$

where P is load to fracture, L the support span, D the maximum deflection of the beam, d and b specimen depth and breadth, and $\Delta P/\Delta y$ the gradient of the (steepest) linear portion of the deflection curve [14]. Total energy to failure (W) was calculated as the area under the load–displacement curve. The two portions of the beam were retrieved after failure of the specimen; d and b were measured at the fracture using a screw micrometer (No. 193-111, Mitutoyo, Tokyo, Japan). Load string stiffness was sufficiently high that crosshead displacement was an accurate enough proxy for beam deflection, simplifying the set-up; the maximum displacement error was calculated to be about +1% of D, but the effect on the calculated value of E was much less because of the definition of $\Delta P/\Delta y$. Data were processed and plotted in software (SigmaPlot v.7, SPSS, Chicago, IL, USA).

3. Results and analysis

The results of the tests are shown in the form of fitted contour maps for each material and each property (Figs. 1–4). In general, three regions can be identified in each plot: an unset (untestable) region in the lower left corner; a 'ramp' region of increasing property value as exposure ($I \cdot t$) increased; and a 'plateau' region where the property value had attained more or less the maximum or the rate of variation was markedly lower than in the ramp.

To enable comparisons, and to assist in making the judgment as to when reaction was 'complete enough', a line has been drawn, by eye, on the basis of the flexural strength data, for each material separately, to demarcate the apparent boundary between ramp and plateau; this line has then been copied to the elastic modulus and total energy plots for comparison (heavy diagonal line, Figs. 1–4). It can be seen that this criterion is not uniform across the three properties. For example, the plateau in E for FZ is attained at somewhat greater exposures (Fig. 3), while that for W in HR occurs at lower exposures (Fig. 1).

Two further lines have been added to those plots to enable comparisons with the recommendations made by the manufacturers: a horizontal line at $I = 300$ mW/cm^2, nominally representative of recommendations commonly made regarding minimum irradiance [15], and a vertical dashed line representing each manufacturer's recommended time for the suggested increment thickness (Table 1).

Noting that the contours in the ramp region are fairly evenly spaced and generally fairly straight, some regularity in the development of the properties was evident with a clear relationship to exposure. Hence, to test the hypothesis of reciprocity, the inclination (i.e. with respect to the x-axis) of the ramp region contour lines of the mechanical property vs. irradiation time plots on log–log scales was determined by visual inspection using graphical analysis software (TableCurve 3D v3, SPSS, Chicago, IL, USA). This approach was taken because the three-dimensional surface plots were of unknown form and a least squares analysis could not be applied. Thus, setting equal ranges and lengths of the x- and y-axis scales, and viewing the 3D plots parallel to the xy-plane, rotation of the plot about the z-direction (i.e. property value axis) permitted the identification of an orientation in which the data points in the relevant region exhibited least scatter. This was possible to within about ±1°. The tangent of this viewing angle (second quadrant) then represents the nominal slope of the contours

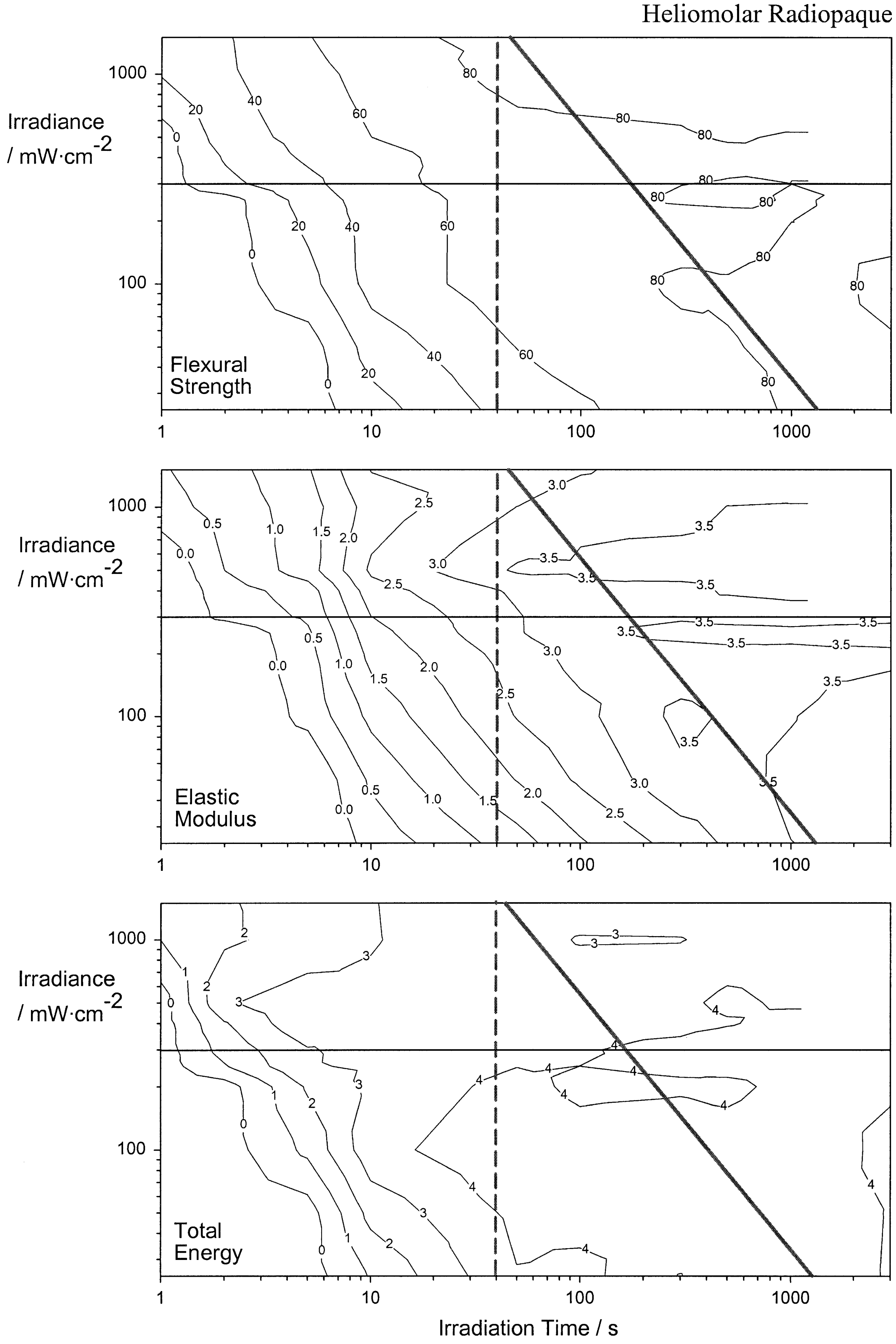

Fig. 1. Heliomolar Radiopaque (HR): contour plots on log–log scales for flexural strength (F) (top), modulus of elasticity (E) (center) and total energy to failure (W) (bottom) as a function of exposure. Diagonal line: estimated minimum acceptable exposure on the basis of F data; vertical broken line: manufacturer's recommended irradiation time (Table 1); horizontal line at $I = 300\ \mathrm{mW/cm^2}$: assumed nominal minimum recommended irradiance, for comparison.

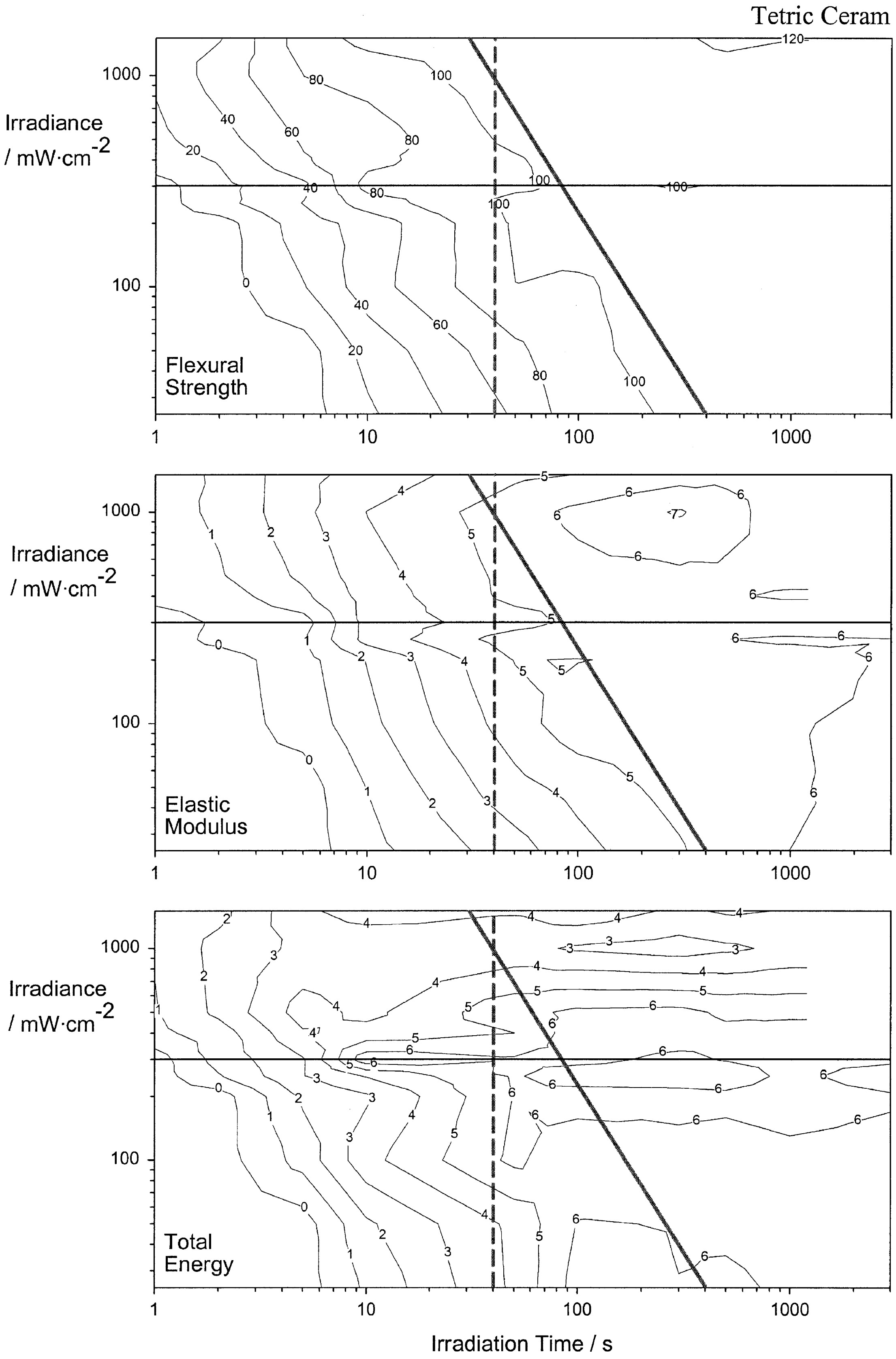

Fig. 2. Tetric Ceram (TC): contour plots on log–log scales for flexural strength (F) (top), modulus of elasticity (E) (center) and total energy to failure (W) (bottom) as a function of exposure. Diagonal line: estimated minimum acceptable exposure on the basis of F data; vertical broken line: manufacturer's recommended irradiation time (Table 1); horizontal line at $I = 300$ mW/cm^2: assumed nominal minimum recommended irradiance, for comparison.

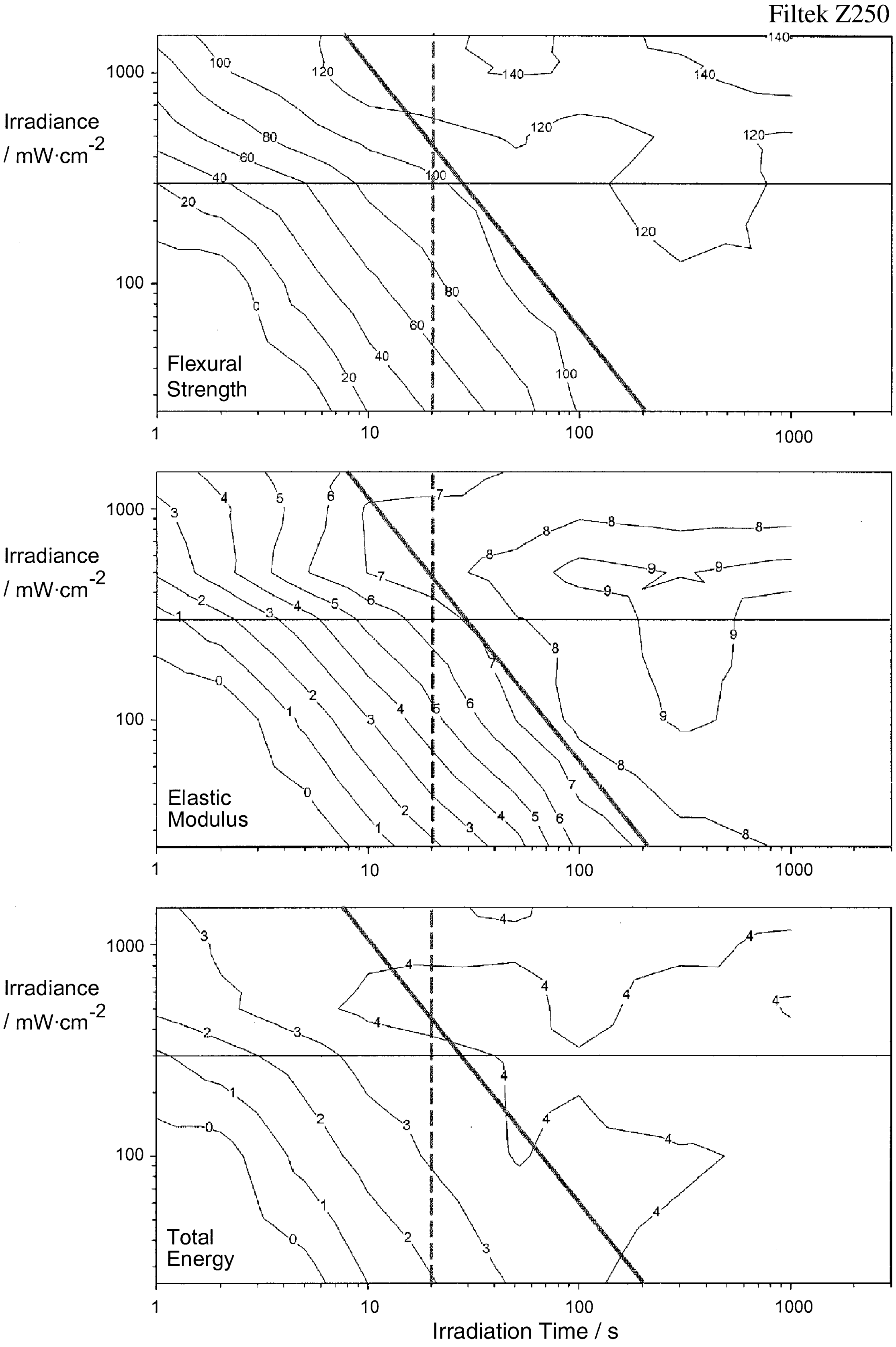

Fig. 3. Filtek Z250 (FZ): contour plots on log–log scales for flexural strength (F) (top), modulus of elasticity (E) (center) and total energy to failure (W) (bottom) as a function of exposure. Diagonal line: estimated minimum acceptable exposure on the basis of F data; vertical broken line: manufacturer's recommended irradiation time (Table 1); horizontal line at $I = 300$ mW/cm^2: assumed nominal minimum recommended irradiance, for comparison.

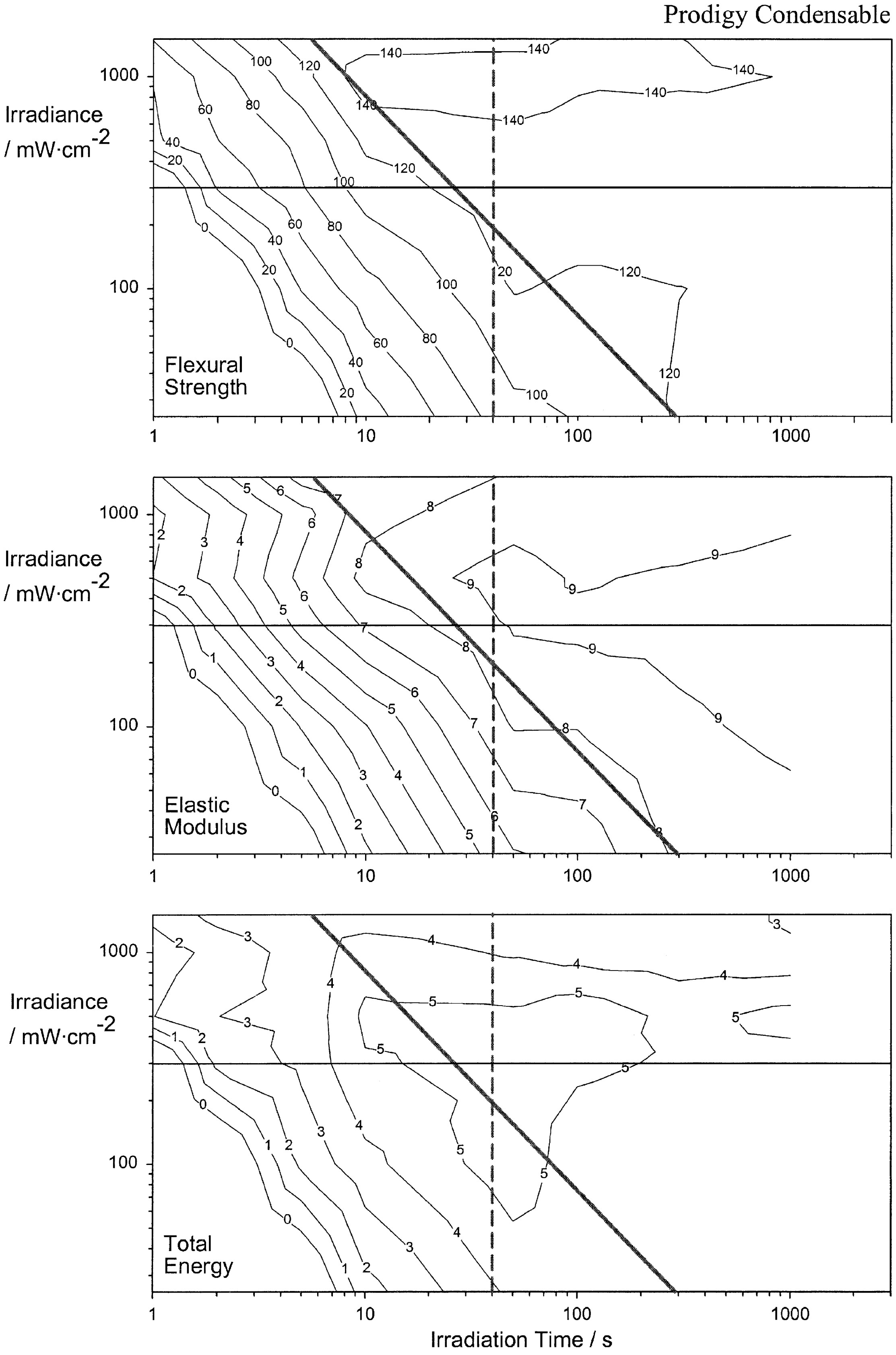

Fig. 4. Prodigy Condensable (PR): contour plots on log–log scales for flexural strength (F) (top), modulus of elasticity (E) (center) and total energy to failure (W) (bottom) as a function of exposure. Diagonal line: estimated minimum acceptable exposure on the basis of F data; vertical broken line: manufacturer's recommended irradiation time (Table 1); horizontal line at $I = 300\ \mathrm{mW/cm^2}$: assumed nominal minimum recommended irradiance, for comparison.

Table 2
Slopes of contours in ramp region of Figs. 1–4, corresponding to the reciprocity exponent (Eq. (4)) for irradiance vs. irradiation time. Uncertainties range from about ±0.03 at −0.90 to ±0.08 at −1.88

	Reciprocity exponent		
	Flexural strength, *F*	Flexural modulus, *E*	Total energy, *W*
Heliomolar Radiopaque	−1.54	−1.38	−1.88
Tetric Ceram	−1.33	−1.60	−1.66
Filtek Z250	−0.90	−1.04	−1.11
Prodigy Condensable	−1.43	−1.48	−1.80

in the log–log plots of Figs. 1–4, the results of which calculation are shown in Table 2.

4. Discussion

The unset region corresponds to those exposures for which insufficient polymerization and cross-linking had occurred to take the system into the so-called gel state where a continuous network had formed. The material remained semi-solid. The ramp region corresponds to the development of the network, presumably largely through increasing cross-linking. Although there are minor variations, the ostensible completion of the process is well-marked in most cases, consistent with the expected rapid reduction in the rate of reaction as the glass-transition is approached.

There is some variation evident in the position of the ‘zero’-contour, i.e. the threshold for the solid (as opposed to semi-solid), mechanically-testable condition to be attained. This may reflect variation in stabilizing inhibitors or their concentration [16], but must also be dependent on the rate of effective cross-linking, since mere polymerization can only increase viscosity, and thus the reactivity and diffusibility of the various monomers may be involved [17]. However, the identification of this threshold might be of practical relevance with respect to the concept of ‘soft-start’ polymerization, that is, to determine the ‘initial dose’ required to overcome the effect of inhibitors. It may also be related to ambient light sensitivity, i.e. the avoidance of premature setting. Nevertheless, some criterion more precise than ‘mechanically testable’ would have to be identified.

If reciprocity were to hold, i.e. the same outcome in terms of material properties regardless of irradiance so long as the minimum exposure *K* were provided, then the plateau region would be just that — flat to the right of the ‘acceptable’ line. That this is not so is plain from the results. Thus, for *E*, a clear maximum occurs around (100, 400) for PR, (300, 300) for FZ, (300, 1000) for TC, and (1000, 700) for HR (each in terms of *t*, *I* coordinates). Similarly, for *F*, although the plateau seems fairly uniform for HR and TC, there is a clear maximum for FZ at around (50, 1500), and for PR centered on (60, 1000). Moreover, there is some evidence for a decrease in *E* for TC and FZ, if irradiation time or irradiance are increased further, and PR shows a clear deterioration in *E* for too great an irradiance, and even a decrease in *F* for PR at 1500 mW/cm^2. The behavior of *W*, which may be taken as an approximation of toughness, is not unreasonable as regards the general maximum observed in the irradiance direction: increasing stiffness must first increase the area under the curve then decrease it unless there is an associated remarkable increase in strength. The corollary of stiffness is generally brittleness. Nevertheless, these data underline the need to be very clear about what criterion is to be used in assessing the quality of a product, for there is unlikely to be simultaneous optimization, as is shown here.

Two points may therefore be made at this juncture. Firstly, there is no apparent lower limit to the irradiance that may give effective polymerization, at least down to 25 mW/cm^2. This is in accord with theoretical expectations: there is no reason why a chain should not propagate even if only one is ‘alive’ at a time. Even at 25 mW/cm^2 good values of *F* and *E* were obtained, albeit at very long irradiation times. This means that the concept of a functional ‘minimum’ irradiance for this class of materials is faulty, even if operationally *t* may be inconvenient at low *I*. There is therefore no intrinsic reason for discarding an old but functioning lamp, providing *I* is known and appropriate compensation in *t* can be made. Of course, convenience is another matter that needs to be considered, and excessive *t* is possibly problematic. Secondly, it is possible for over-exposure to be detrimental, whether by extending the irradiation time or the choice of a high-irradiance lamp. While the time required for such effects to be manifest may seem unlikely to be a problem for a dentist, the implications for the kinetics of the reactions and diffusion of reactants may be worth exploration. However, the fact that a light can be too bright is more significant because it falsifies the implicit assumption behind the introduction of PA and similar sources that brighter is better. On the basis of the present results, there seems little point in exceeding 1000 mW/cm^2.

The clear failure of HR and TC to attain anywhere near satisfactory mechanical properties at very high *I* (i.e. ≥ 1000 mW/cm^2) and very short *t* (say < 5 s) suggests strongly that great care should be taken to use appropriately sensitive products with high-*I* curing lights. In fact, even for PR and FZ such attainment is dubious, noting that it is impossible for a dentist to determine that the polymerization process has been driven to near-completion. This is in agreement with reported work [18,19], while other studies have demonstrated that $t = 3$ s (as typically recommended for PA lights) is insufficient for the development of adequate mechanical properties in RCs [20–22]. It has also been demonstrated that leaching of monomers from RC specimens cured using a PA lamp for 3 s was four times higher than those cured with a halogen lamp for 40 s [23], again indicating insufficient polymerization.

It should also be noted that the creation of the excited state of the photosensitizer reduces the concentration of excitable molecules and therefore the efficiency of absorption declines exponentially in accordance with the usual Beer Law. But since decay or conversion and reaction of the excited state is kinetically limited [24], the photosensitizer system may rapidly become saturated as I is increased, when no further improvement in the rate of polymerization initiation is possible. There is therefore a practical limit to the value of I that may be used efficaciously with any given RC. This also means that sufficient time must be allowed for recycling photosensitizer from fluorescent decays (i.e. those that do not result in initiation) until sufficient reaction chains have been created, there being a quasi-steady state in the meantime [25]. Furthermore, at high rates of generation of initiating radicals, mutual annihilation [17] leads to reduced reaction chain length and thus poorer network formation and poorer mechanical properties. Evidence of this is already present in the E data for all materials tested here. Thus, the pursuit of high-I sources may be counterproductive without strong evidence of benefit, which has not so far been forthcoming.

As indicated by Eq. (1), if reciprocity were to hold, irradiance and irradiation time would be linked through a material constant K such that

$$I = K \cdot t^b \tag{4}$$

where the ‘reciprocity exponent’ b has the value -1. Reciprocity would be indicated in the log–log contour plots (Figs. 1–4) by the contours in the ramp region having a slope of -1, i.e. corresponding to $I \propto t^{-1}$.

Although the method for determining the value of b was informal, it was nevertheless straightforward to apply and the results unambiguous (Table 2). Thus, it is clear that for HR, TC and PR the slope is of the order of -1.5, while for FZ it is about -1.0. It would therefore appear that while FZ exhibits a good approach to reciprocity in the ramp region, HR, TC and PR do not. This is enough to invalidate the general assumption which appears to have been the basis of the recommendations regarding high power lamps that total energy delivered is the criterion.

Since the value of the reciprocity exponent depends on the particular chemistry of the product, specifically the kinetics of the process of initiation and polymerization, then the similarity of the result for TC and HR is not surprising given that they are from the same manufacturer. The marked distinction between these and FZ suggests that this may be a sensitive way of determining some details of the polymerization process, although further refinement of the method may be necessary for improved accuracy and discrimination. For example, there is a suggestion in the case of FZ that at high I, low t the slope for F may be lower (less negative) than -1, while the form for E is more complicated.

Comparison of the present findings with the manufacturer’s recommendations regarding curing time is instructive. It is noteworthy that the diagonal line for ‘adequate’ polymerization crosses the 300 mW/cm^2-line at rather higher values of t than those recommendations in the case of HR, TC and FZ, the minimum difference being about a factor of two. Given that those recommendations were for increment thicknesses of 2 or 2.5 mm (Table 1), the effective difference is even greater. While the same comparison for PR appears at first to be on the safe side, the recommendation was in fact for a 5 mm increment. It is doubted that satisfactory curing could occur at the bottom of such an increment, if the criterion is flexural strength. These observations may be compared with the conclusion that ~100 s might be a more appropriate value of t [26,27]. As mentioned earlier, manufacturers’ instructions are inadequate, because I is usually not stated (certainly, not for the products tested now), a concern which has been raised before [28,29].

However, a single value for I is unlikely to be sufficient. Given now that reciprocity does not, in general, hold, calculations based on a value of the putative ‘material property’ K can be seen to be inadequate. Even so, it must be noted that energy is not, in fact the issue: it is very simply the photon count that matters in terms of the integrated quantum yield over the wavelength range within which excitation of the photosensitizer is possible. It requires no more than one photon to achieve excitation, but the efficiency of absorption clearly varies with wavelength and is never 100%, and the efficiency of the creation of free radicals will also be less than 100%, as indicated earlier. Coupling these issues with variation in choice of photosensitizer (and hence the absorption spectrum), light source (emission spectrum), filtration (transmission spectrum), incidental losses (product shade, i.e. absorption spectrum), and differential absorption (due to increment thickness the irradiation spectrum at each level varies) it should be clear that a single figure will be meaningless and attempts to define one pointless, even for a single RC. The complexity is great and a rational approach is required.

Thus, the practical problem remains of determining the appropriate exposure for a given product, assuming that the irradiance of the curing light at the working tip has been measured. As was mentioned above, the criterion for adequate exposure needs to be decided, but assuming that the criterion is flexural strength (F) (although a case might well be made for elastic modulus), and that attaining the plateau is the goal, the diagonal lines drawn on those graphs in Figs. 1–4 might form the basis. These lines are copied to Fig. 5, where a direct comparison may be made between products. The differences are striking. Were the manufacturer to provide such a graph in the product instructions, the user would have immediate guidance on the time required, and especially if the lamp output changed with age or supply

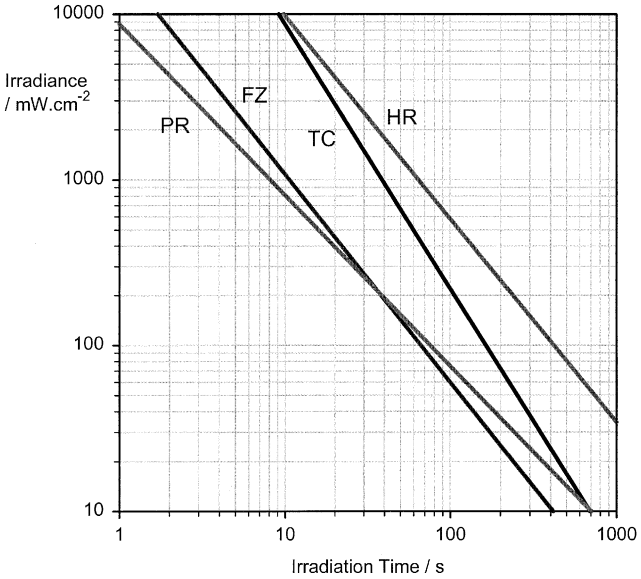

Fig. 5. Suggested form of manufacturer's 'minimum recommended exposure' graph, flexural strength criterion. Lines copied from Figs. 1–4 for comparison.

voltage. It follows from the argument above that substantial differences in the position of that recommendation line might occur for various commercial curing lights: several lines might be, in fact probably would be necessary. Important differences might also occur between shades, and these too could be indicated. Of course, it would require a substantial amount of work to produce such a graph for a product (and the lines may not necessarily be straight), but this would seem to represent the minimum information necessary for the dentist to make the necessary decisions, on the assumption that the highest possible quality outcome is the goal, however that quality is to be measured.

The observations made here suggest that it might be possible to engage in product design and development more productively than hitherto since it is obvious that the common one-dimensional approach of considering only irradiation time can provide only limited insight into reaction kinetics, network development, choice of lamp and so on. Optimum conditions for exposure in terms of mechanical properties clearly must vary between products according to chemistry, even down to the investigation of novel monomers. The true effects of ramp, pulse and other irradiation protocols might also be investigated more usefully using the present approach, instead of being dominated by the now obviously irrelevant total energy considerations [30,31].

Proposals have been made to use blue light-emitting diodes (LEDs) in dentistry [32–34], but with the emphasis on replacing existing lamp systems. However, the observation now that very low irradiance can give effective polymerization not only suggests that their use is feasible but also leads to a proposal for a means of employing them to avoid appreciable heating and possibly permitting the flow necessary to minimize the effects of polymerization shrinkage, as embodied in soft start and similar exposure protocols. Very simply, an intra-oral device, a 'curing appliance', could be designed utilizing LEDs to provide extended low-level exposure. It is envisaged that this would resemble a mouth guard or bite-block, run off an intrinsically-safe power supply, and allow the patient simply to sit while the curing proceeded and the dentist dealt with another task. The pressures on the dentist to complete treatment rapidly (but riskily), using high cost equipment, would be removed. This approach would also circumvent the dubious attempts to use multiple LEDs to attain the assumed minimum irradiance. It is envisaged that the threshold exposure might be necessary in the conventional manner to attain the gel state, and an 'insurance' post-cure irradiation would not be precluded. An additional advantage might be that designs could incorporate means of applying some pressure to the restoration, possibly through a bite-block and transparent silicone elastomer pressure pad, to ensure that polymerization shrinkage occurred in the direction away from the free surface.

5. Conclusions

Exposure reciprocity is not a general feature of the curing of RCs, so calculations based on this energy density concept are invalid. High-I curing lights can give satisfactory results, but the irradiation time required may be far in excess of recommendations for some products. The identification of an exposure threshold might be worth investigating to guide soft-start curing protocols.

The absence of a lower absolute cut-off for irradiance suggests that greater flexibility is available to the dentist, at lower cost, since even at very low intensities adequate polymerization is attainable at 'sufficiently long' irradiation times. In order to be able to ascertain what time is necessary, manufacturers ought to supply, as a matter of course, an exposure graph for recommended curing lights and for each shade, where this makes a difference.

The effectiveness of low-I curing suggests a novel approach for RC restorations: the LED curing appliance.

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