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Characterizing surface viscoelastic integrity of ultra-fast photo-polymerized composites: methods development.

Short title: Surface integrity of composites.

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Abstract

Objective: Resin-Composites are now available designed for polymerization using 3 s of intense light irradiation. The aim was to develop an experimental method to probe their surface viscoelastic integrity immediately following such rapid photo-cure via macroscopic surface indentation under constant stress as a function of time.

Methods: Two bulk-fill composites (Ivoclar AG) were studied: Tetric PowerFill (PFill) and PowerFlow (PFlow). Split molds were used to fabricate cylindrical {4 mm (dia) x 4 mm} paste specimens, irradiated at 23 °C at 0 mm from the top surface with a Bluephase *PowerCure* LED-LCU, with 3 s or 5 s modes, emitting 3 and 2 W/cm², respectively. Post-irradiation specimens were immediately transferred to an apparatus equipped with a flat-ended indenter of 1.5 mm diameter. 14 MPa compressive stress at the indenter tip was applied centrally in < 2 min and maintained constant for 2 h. Indentation (I) magnitudes were recorded in real-time (t), with I(t) data re-expressed as % indentation relative to the 4 mm specimen height. After 2 h, the indenter was unloaded and indentation recovery was monitored for a further 2 h. Parallel sets of measurements were made where indentation was delayed for 24 h. Further measurements were made with more conventional composites: EvoCeram Bulk Fill (ECeram) and Tetric EvoFlow Bulk Fill (EFlow). These were irradiated for 20 s at 1.2 W/cm². Kinetic data were curve-fitted to exponential growth functions and key parameters analyzed by ANOVA and *post-hoc* tests ($\alpha=0.05$).

Results: I(t) plots looked initially similar to bulk creep/recovery: rapid deformation plus viscoelastic response; then, upon unloading: rapid (elastic) recovery followed by partial viscoelastic recovery. However, unlike multiply irradiated and stored bulk-creep specimens, the present specimens were exposed to only 3 or 5 s “occlusal” irradiation; generating “hard” surfaces. Subsequently, during the 2 h indentation, the polymer matrix network continued to harden and consolidate. Upon initial loading, I(t) reached 2 – 3 % indentation, depending upon the formulation. Upon unloading at 2 h, elastic recovery was only *ca.* 1 %. Delayed loading for 24 h, generated I(t) plots of significantly reduced magnitude. Most importantly, however, the I(t) plots for ECeram and EFlow, after 20 s irradiation, showed I(t) magnitudes quite comparable to the PFill and PFlow rapid-cure composites.

Significance:

Macroscopic indentation creep has been shown to be a workable procedure that can be applied to rapid-cure materials to assess their immediate surface integrity and developing viscoelastic characteristics. The applied stress of 14 MPa was relatively severe and the indentation/recovery profiles of PowerFill materials with only 3 or 5 s irradiation demonstrated comparability with their established 20 s cure siblings, evidencing the suitability of the *PowerCure* system for clinical application.

Keywords: photopolymerization; dimethacrylate; AFCT; RAFT; resin-composite; indentation-creep; stretched-exponential; viscoelasticity; post-cure.

Introduction

There are several current trends in the incremental development of dental resin-composites by academic researchers and particularly by the R&D departments of dental manufacturing companies [1]. Many developments are driven by (a) competition between manufacturers and (b) requested innovations by clinical dentists. One of the items on the ‘wish list’ of many restorative dentists is *more rapid* photo curing (photo polymerization) that maintains the *reliability* of the cure process, assuming that the clinician follows the manufacturers’ instructions precisely.

Visible Light Curing (VLC) by means of *Light Curing Units* (LCUs) has changed in many respects since the 1970s when it was first introduced [2, 3]. The major changes were: (i) the early transition from UV to *visible* blue light curing (wavelengths ca. 470 nm) and (ii) the change from filtered multi-wavelength *Quartz Tungsten halogen* (QTH) LCUs to *Light Emitting Diode* (LED-LCUs), with either a single LED chip (output at 470 nm) or two types of chip (blue: 470 nm and violet: 410 nm) [4]. The latter are effectively wide-spectrum LCUs.

Photo curing requires the active material to incorporate a photo-initiator (PI) with an *absorption* spectrum that corresponds to the *output* spectrum of the LCU. Sufficient light **irradiance** (I_{λ}) is also necessary (corresponding to the LED emission rate: photons/s). Each photon carries a certain energy given by $h\nu$ where h = Planck’s constant and ν is the frequency of the light. The further major variable is the **time period** of irradiation (t).

The first photo-cured dental resin-composites were considered to require irradiation for $t = 60$ s. Subsequent developments have enabled irradiation times to be reduced from $60 > 40 > 20 > 10$ s.

Commercial composites exist for which the required time is claimed to be as low as 5 s. And there is now a product – or product system - available for which $t = 3$ s (Ivoclar-Vivadent AG) [5].

These developments have been facilitated by (i) refinements of the photo-initiator system and (ii) boosting the irradiance (or Radiant Emittance; mW/cm^2) of the LCUs. The Ivoclar *PowerCure* system comprises an advanced Bluephase *PowerCure* LED-LCU able to deliver $3 W/cm^2$ for 3 s irradiation and two specially formulated composites: *PowerFill* and *PowerFlow*.

Photo-polymerization of resin-composites rapidly transforms fluid or ‘plastic’ paste formulations into hard solids *within* the irradiation period. However, further post-curing is known to occur that increases both surface and bulk mechanical properties over timescales ranging up to a month post-irradiation [3, 6]. The 3 s *PowerCure* irradiation mode should therefore be capable of producing sufficient material properties *within 3 seconds* that are *demonstrably comparable* to properties attained by generally equivalent composites after the more conventional 20 s irradiation.

The experimental challenge is to devise a method to probe mechanical material properties *immediately following* 3 s *PowerCure* irradiation. This requirement rules out time-consuming specimen preparation to fabricate flexural bar specimens, for example. It also rules out bulk compressive creep measurements that typically require 6 x 4 mm solid cylindrical specimen *that have been well irradiated from multiple directions* [7-11]. Nano-indentation might at first sight appear to be a possibility [12-14]. However, this requires polished specimen surfaces and only

probes a shallow surface layer and a very small indentation area. Hence, with composite materials, anomalies are possible by nano-indentation of particle phases, rather than the organic matrix [15].

In this investigation, we propose a method that is novel in the context of photo-polymerized resin-composites. This involves immediate time-dependent indentation-creep measurements, with a *rigid loaded axisymmetric cylindrical flat-ended* punch, into a plane photo-polymerized composite surface. Indentation-recovery measurements are also to be made subsequently on the unloaded specimens.

The null hypotheses to be tested are that:

No significant differences exist between indentation /time profiles, during the loading and recovery periods, for 3 & 5 s *PowerCure* composites and conventionally photo-cured comparator composites.

Theoretical Background

Two distinct levels of theoretical analysis are relevant to this topic: (i) continuum mechanics of indentation into materials exhibiting plastic, elastic and/or viscoelastic behavior; (ii) molecular theory of photo-polymerization.

Continuum mechanics of surface indentation.

The problem of a rod or pillar loading a “foundation” material is an ancient one, dating back to the temples built in classical Greece, especially when the supporting material was non-rigid soil, with important implications for the safety of foundations. Within the terms of the classical theory of elasticity, the distribution of stress in a solid when deformed by a rigid punch was first considered in 1885 by Boussinesq [16]. Subsequently several alternative solutions were derived, as summarized by Galin [17], particularly by Harding and Sneddon [18] and Sneddon [19, 20].

A central distinction in contact mechanics is between stresses acting perpendicular to the contacting bodies' surfaces (the normal direction) and frictional stresses acting tangentially between the surfaces.

Figure 1: Indentation of a plane surface by a flat-ended cylindrical punch of diameter $2R$ to a depth d under an applied axial load, F .

For a cylindrical flat-ended punch indentation the contact geometry is relatively simple because there is no pile-up at the contact edge. The radius of the contact remains fixed and equal to the radius, R , of the punch (Figure 1). When it is pressed into the free surface of an *elastic* solid, the relationship between the indentation depth (d) and the normal compressive force (F) is given by the *linear* relationship, [21] (p.117):

$$F = 2R.E^*.d \quad \text{Equation 1}$$

where the reduced (or combined) modulus, E^* is given by

$$\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \quad \text{Equation 2}$$

E_1 and E_2 are the elastic moduli of the test material and rod, and ν_1 and ν_2 are their Poisson's ratios.

If these 4 parameters remain constant, together with force F , then indentation depth (d) will also be constant and time invariant. However, if the modulus (E_1) of an *elastic* test material were to *increase* (e.g) due to progressive curing, then indentations into *successive* specimens would exhibit a progressive *reduction* in elastic indentation depth, under constant load.

The present investigation is concerned with a specific strain history, wherein the *creep* (progressive deformation) is measured in response to an applied *step function* of stress, (or loading force). That is, the materials are subjected to an approximately *instantaneous* loading – and subsequent unloading. The applied stress σ at time $t = 0$ is:

$$\sigma_0 = F/A = F/\pi.R^2 \quad \text{Equation 3}$$

The strain $\epsilon(t)$ in a *viscoelastic* material will increase with time. The creep compliance, $J(t)$, is defined as the ratio:

$$J(t) = \epsilon(t)/\sigma_0 \quad \text{Equation 4}$$

The *relaxation magnitude*, in the compliance formulation, from “start” (0) to “finish” (∞) over the experimental time range is ($J_\infty - J_0$).

In *linear* viscoelastic materials, the creep compliance is independent of stress level. Under those circumstances, constitutive equations may be developed using the *Boltzmann superposition principle*, which is a statement of *linearity*: that the effect of a compound cause is the sum of the effects of individual causes. However, particularly in the case of indentation creep, the assumption of linearity may not hold making the scope for exact analysis severely circumscribed, [21, 22].

Nevertheless, a range of models have been devised to account for viscoelastic behavior. These commonly incorporate various serial or parallel combinations of elastic and viscous ‘elements’, rather like the spring and damper systems of a motorcar. The springs are assumed to be perfectly

elastic. The dashpot element may be envisaged as a piston-cylinder assembly in which motion of the piston causes a viscous fluid to move through an aperture. However, real materials are not generally describable by models containing a small number of springs and dashpots.

The simplest pair of models, due to Voigt and Maxwell respectively, consist of a spring and dashpot - arranged *either* in parallel *or* in series. Somewhat more realistic behavior can be modeled by the *standard linear solid*, which contains three elements (Figure 2):

Figure 2: Mechanical model systems consisting of series and/or parallel combinations of elastic and viscous elements.

For the Voigt (or Kelvin) model (Figure 2), both the spring and the dashpot experience the *same deformation*, or strain, and the total stress is the sum of the stresses in each element. From this, it can be shown [22] (p. 55f) that the creep response is:

$$J(t) = \frac{1}{E}(1 - e^{-t/\tau_c}) \quad \text{Equation 5}$$

In which $\tau_c = \eta/E$ is referred to as the retardation time.

A single exponential relaxation or retardation function undergoes most of its change over about one decade (a factor of 10) in time scale. However, real materials creep or relax over many decades of time.

There is a more general and rather ubiquitous expression for a normalized *relaxation* processes: the stretched exponential or **KWW** (after Kohlrausch, Williams, Watts) form [23, 24] with a fractional exponent: $0 < \beta \leq 1$.

$$\phi(t) = e^{-(t/\tau)^\beta} \quad \text{Equation 6}$$

τ is the relaxation (or characteristic) time.

A corresponding normalized stretched-exponential *growth* process is represented by:

$$1 - \phi(t) = \{1 - e^{-(t/\tau)^\beta}\} \quad \text{Equation 7}$$

Dynamic or frequency domain behavior, corresponding to this relaxation function, can be obtained analytically for $\beta = 0.5$ [24]. For general values of β numerical methods are available [25].

Complex materials with strongly interacting constituents often exhibit **KWW** behavior [26 – 29]. Crosslinked dental resin-composites incorporate strongly interacting constituents and so this functional form is likely to be applicable to the indentation creep behavior. Indentation data can be presented either as absolute depth values (mm or μm) or as percentages of the specimen thickness. In the present work, we will use the latter option for the time-dependent growth of $I(t)$.

$$I(t)_{\%} = A \cdot \{1 - e^{-(t/\tau)^\beta}\} \quad \text{Equation 8}$$

or

$$I(t)_{\%} = A \cdot \{1 - e^{-(t/\tau)^\beta}\} = A \cdot \{1 - e^{-(t^\beta/T)}\} \quad \text{Equation 9}$$

where A corresponds to what would be the magnitude of $I(t)_{\%}$ as $t \rightarrow \infty$.

Again, the parameter τ is the characteristic time. $T = \tau^\beta$ is an alternative representation. The fractional exponent β mathematically *stretches* the viscoelastic process over time (Figure 3), away from a simple exponential change, known as Debye behavior, for which $\beta = 1$.

Figure 3: Stretched exponential *relaxation* functions (cf. Equation 6). Arbitrary units of (eg) modulus and ($\log_{10}$) time. As β reduces, the relaxation process is increasingly stretched over the time scale.

For this **KWW** approach, an expression for the *rate of indentation* (%/s) can be obtained by differentiation of equation 7:

$$\frac{dI}{dt} = (\beta/\tau) \cdot (t/\tau)^{\beta-1} \cdot e^{-(t/\tau)^\beta} \quad \text{Equation 10}$$

Molecular theory of photopolymerization

The molecular theory of free-radical photopolymerization has been widely discussed in both the polymer and dental literature, focusing especially upon the characteristics of multi-methacrylate monomers and the resulting cross-linked networks that form the matrix of resin-composites [6, 30]. Particular attention has been given to photoinitiator systems and the effects of varying light-irradiation protocols [5, 31-33]. A more recent development has been the possibility of incorporating chain-transfer agents, particularly of the reversible *addition fragmentation* (AF) type, variously denoted by the acronyms RAFT or AFCT [34]. One such agent is β -allyl sulfone (Figure 4). This becomes incorporated in the growing network and can modulate the inherently uncontrolled radical chain-reaction so that it proceeds more like a step-growth polymerization and results in a more homogenous network structure [35].

Figure 4. β -allyl sulfone AF chain transfer reagent.

Materials and Methods

The experimental design concerned four materials (Table 1). The independent variables were material, curing mode and post-irradiation time. The measurement times began either “immediately” or 24 h post-irradiation. A total of 48 specimens ($n = 4$ /group) were required.

Table 1: Materials Investigated: manufactured by Ivoclar-Vivadent AG, Liechtenstein

Material Codes	Product Name	Lot Number	Resin Matrix*	Filler Load § % (wt); (vol)
PFill	Tetric PowerFill	W92823	Bis-GMA, Bis-EMA, UDMA, Aromatic Dimethacrylate, DCP	79; NA
PFlow	Tetric PowerFlow	WM1175		71; NA
ECeram	Tetric EvoCeram Bulk Fill	U53769	Bis-GMA, Bis-EMA and UDMA	80; 61
EFlow	Tetric EvoFlow Bulk Fill	U42390	Bis-GMA, Bis-EMA, TCDD	68.2; 46.4
*Matrix Monomers: Bis-GMA: bisphenol-A-diglycidyl dimethacrylate; Bis-EMA: bisphenol-A-polyethylene-glycol-diether dimethacrylate; UDMA: urethane dimethacrylate,				
§ Filler percentages as reported by the manufacturer. Typical contents: Ba/Al-silicate glass, Isofiller, YbF ₃ , spherical mixed oxide.				

Specimen Preparation:

Stainless steel (SS) split molds were used to fabricate cylindrical-shaped composite paste specimens - each 4 mm diameter and 4 mm thick. For each specimen, the resin composite material was placed in the mold, covered with Mylar strip then pressed by a glass slab to ensure a smooth surface and to eliminate any voids. The glass slab was then removed to facilitate close proximity of the light-curing tip above the composite paste surface (covered by Mylar strip).

The specimen was then irradiated directly from the top “occlusal” surface in accordance with a selected *Irradiation Protocol* (Table 2). The power density of each LCU was verified for each set of specimens using a radiometer (MARCTM Light Collector, Blue-light Analytics Inc., Halifax, NS, Canada).

Table 2: Irradiation Protocols with two Light-Curing Units (LCUs):

P-Cure = Bluephase *PowerCure* (Ivoclar Vivadent AG); S10 = *Elipar* S10 (3M).

LCU Code	Irradiance (W/cm ²)	Irradiation Time (s)	Material Codes
P-Cure	3	3	PFill, PFlow
P-Cure	2	5	PFill, PFlow
S10	1.2	20	ECeram, EFlow

Following irradiation, each specimen was transferred within its SS mold for indentation loading either “immediately” (within 2 min) or at 24 h post-irradiation. The “24 h” specimens were stored dry at 37°C in the dark.

Indentation Measurement

The indentation equipment was designed to measure the viscoelastic properties and recovery of resin composites under a static indentation stress. This was achieved by modification of an apparatus for measurement of bulk compressive creep and recovery, as described previously [8, 9, 11].

All specimens were measured within their SS molds at $23 \pm 1^\circ\text{C}$. A mold containing a specimen was placed on a raised metal platform. A vertical loading rod, terminating in a 1.5 mm diameter cylindrical indenter punch (Figure 5 a), was axially aligned and centralized over the specimen surface (Figure 5 b). This rod also carried a platform that contacted a calibrated LVDT transducer to detect and record strain changes in the specimens (Figure 5 c). A cantilever arm could be rapidly raised or lowered onto the top of the loading rod to transfer load to generate compressive stress. The cantilever load was selected to generate, via the indenter punch, a stress of 14 MPa.

Figure 5: Configuration of the indentation-creep instrument: (a) the indenter punch; (b) the indenter in contact with the surface of a specimen contained within its stainless-steel split mold; (c) the assembly mounted on a fixed platform with the transducer tip registering axial movement of the load rod and indenter punch.

Once the specimen was placed in position a static force was applied, via the axial rod and the cantilever loading system (not shown), for a period of 2 h. After 2 h, the load was removed and changes in the indentation depth were monitored for a further 2 h.

The LVDT mV signals were amplified and sent to an analogue-to-digital converter and computer/software (PicoLog 6, Pico Technology, Hardwick, Cambridge, UK). These signals were converted firstly into μm displacement (Δ_t), via a calibration coefficient, and then secondly into percentage indentation depth (relative to specimen height: 4,000 μm).

$$I(t)\% = [\Delta_t / L_o] \times 100 \quad \text{Equation 11}$$

L_o is the specimen height and Δ_t is the indentation (μm).

Statistical and Graphical Analysis

Sample size calculations were made with G*power software (V. 3.1.3; Heinrich Heine University, Germany) based on a pilot study. A sample size: $n = 4$ was sufficient to give a power of 80%.

Each of the ($n=4$) datasets per material, irradiation and loading condition were averaged and plotted. Dynamic curve fitting to the indentation /time plots was achieved using SigmaPlot software (ver. 14).

SPSS 22.0 software (IBM, New York) was used for statistical analysis of key parameters. Normality of distribution was confirmed by the Shapiro-Wilk test. Two-way ANOVA was used for maximum and residual indentation (%) at both post-irradiation times showing a significant interaction ($p < 0.05$). Therefore, one-way ANOVA and Tukey *post-hoc* tests were applied. Irradiation protocols were compared via independent sample t-tests ($\alpha = 0.05$).

Results

The indentation *versus* time plots during the 2 h loading period were curve fitted, with the **KWW** stretched exponential function (equation 8) generating close fits for *immediate* indentation. By contrast, a simpler exponential growth function (equation 12) was more appropriate for modeling the 24 h *delayed* loading data. The associated parameters are shown in Tables 3 and 4 and the specific plots and equations for the critical case of PFill, after 3 s irradiation, are presented in Figure 6.

$$I(t)_{\%} = y_0 + a \cdot \left\{ 1 - e^{-b \cdot t} \right\} \quad \text{Equation 12}$$

Figure 6: **KWW** stretched exponential analysis of *immediate* indentation creep response of PFill, irradiated for 3 s, (upper curve) and simpler exponential analysis of response after 24 h delayed indentation (lower curve).

Table 3: **KWW** stretched-exponential parameters for *immediate* indentation-creep response.

Material	A	Time constant: τ	Stretching exponent: β	R
PFill 3s	3.09	0.0201	0.1756	0.9981
PFill 5s	2.91	0.0122	0.2187	0.9976
PFlow 3s	3.92	0.0103	0.2303	0.9969
PFlow 5s	2.56	0.0132	0.2235	0.9987
ECeram 20s	2.70	0.0080	0.1731	0.9972
EFlow 20s	3.52	0.0081	0.1596	0.9953

Table 4: Exponential growth parameters for 24 h *delayed* indentation-creep response.

Material	y_0	a	b	R
PFill 3s	1.29	0.23	2.0272	0.9332
PFill 5s	1.50	0.26	2.0772	0.9336
PFlow 3s	1.53	0.29	2.1434	0.9339
PFlow 5s	2.39	0.95	4.3164	0.9451
ECeram 20s	1.21	0.18	2.4531	0.9123
EFlow 20s	1.35	0.28	2.1579	0.9413

Indentation (%) *versus* time (h) for each material, irradiation time and measurement time are plotted in Figures 7 (a)-(f).

Figure 7 (a)

Figure 7 (b)

Figure 7 (c)

Figure 7 (d)

Figure 7 (e)

Figure 7 (a) – (f): Indentation as a function of time under 14 MPa stress for 2 h and unloaded recovery for 2 h for materials loaded both immediately (within 2 min – solid curves) and 24 h after irradiation (dashed curves). Each dataset plotted was the average of 4 specimens.

Figure 7 shows the indentation and recovery data for each group of materials for both immediate and 24 h initial loading. The maximum of the indentation (Y-scale) range was set at 4 %. This corresponds to 160 μm penetration into the surface. Immediately following light irradiation, the maximum indentations ranged between 2.5% to 3.8 %, and reduced to 1.41 % to 1.83 % following the 24 h delay. The residual indentation results seem to follow the trends for maximum indentation, ranging between 1.8 % to 2.8 % at immediate evaluation, which then reduced to 0.57 % - 0.98 % when measurements were made after 24 h. In general, all materials behaved *qualitatively* similarly but the measurement time differences (immediate vs. 24 h) gave statistically significant differences ($p < 0.05$).

Indentation curves for the two flowable (low viscosity) formulations were greater in magnitude than for the two non-flowable (regular viscosity) composites. When loaded “immediately” the maximum indentations were notably greater than when loading was deferred for 24 h.

Furthermore, at the time of load-removal, a period of 2 h had elapsed since initiation of loading. Thus, especially with “immediately” loaded specimens, further matrix polymerization occurred during this interval so that the recovery portions of the curves were reduced in magnitude compared to the response upon initial loading. The maximum and residual indentation data are summarized for each composite group in Figures 8 and 9 and in Table 5.

Figure 8: **Maximum indentations** (%) within 2 min (immediately) and 24 h after irradiation for each group.

Figure 9: **Residual indentations** (%) within 2 min (immediately) and 24 h after irradiation for each group.

Table 5. Mean Indentation Creep parameters for 4 materials subjected to 3 irradiation (light cure) protocols (cf. Table 2) following both immediate and delayed indentation. The parameters are (i) the maximum indentation (*I*) after 2 h loading and (ii) the residual indentation after 2 h unloading. (Standard deviations: in parentheses).

Measurement:		<i>Immediate</i> Indentation (< 2 min)		<i>Delayed</i> Indentation (24 h)	
Material	Irradiation	<i>I</i> max (%)	<i>I</i> residual (%)	<i>I</i> max (%)	<i>I</i> residual (%)
PFill	3 s	2.76 (0.24) ^{bcA}	1.95 (0.25) ^{abA}	1.54 (0.06) ^{aB}	0.58 (0.03) ^{bB}
	5 s	2.77 (0.08) ^{bcA}	1.95 (0.03) ^{abA}	1.77 (0.34) ^{aB}	0.98 (0.29) ^{bB}
PFlow	3 s	3.80 (0.21) ^{dA}	2.77 (0.23) ^{cA}	1.83 (0.11) ^{aB}	0.75 (0.06) ^{bB}
	5 s	3.41 (0.54) ^{cdA}	2.39 (0.43) ^{bcA}	1.68 (0.20) ^{aB}	0.74 (0.14) ^{bB}
ECeram	20 s	2.50 (0.30) ^{abA}	1.79 (0.23) ^{aA}	1.41 (0.03) ^{aB}	0.57 (0.02) ^{bB}
EFlow	20 s	3.21 (0.20) ^{cdA}	2.37 (0.21) ^{bcA}	1.65 (0.41) ^{aB}	0.69 (0.24) ^{bB}
Significant differences (p<0.05) are shown <i>between materials</i> , via different superscript lower-case letters and <i>between measurement times</i> via different superscript capital letters.					

The experiments showed, from both maximum and residual indentations, that PFill (with either 3 s or 5 s modes) and also ECeram (20 s) had generally *reduced indentations – and thus superior outcomes* - compared to EFlow and PFlow (with either 3 s or 5 s modes). The immediate performance of PFill and PFlow composites cured for 3 s were statistically equivalent to their comparators, ECeram and EFlow cured for 20 s (p>0.05). However, 24 h post-irradiation showed no statistically significant differences among the materials in either maximum or residual indentations (p>0.05).

Further analysis utilizing independent sample t-tests confirmed a significant difference considering viscosity, with PFlow and EFlow having significantly greater maximum and residual indentations compared to non-flowable PFill and ECeram (p<0.05).

Furthermore, there was no significant difference in the outcome using the 3 s or the 5 s modes (p>0.05) of the PowerCure LCU-LED.

Discussion

The main goal of the present work was to establish a new methodology for addressing critical questions about ultra-rapid photo-polymerized composite materials. Following clinical placement, key requirements for dental restorations include sufficient mechanical integrity during functional occlusal loading. Such clinical “challenges” are normally intermittent in character. However, from a materials science and bioengineering perspective – especially with viscoelastic substances, measuring a “time domain” response to step-function loading /unloading can give representative insights that otherwise would require multiple fatigue loading (on/off) cycles [7, 10, 21].

To achieve this, we have adapted established bulk compressive creep/recovery methodologies [7-11] by developing an indentation-creep approach based upon a flat-ended cylindrical punch. Because the 1.5 mm diameter punch is impressed into the center of a 4 mm diameter composite surface, the specimen can be retained within its rigid stainless-steel split mold. This facilitates rapid transfer of the mold plus irradiated specimen to the loading platform in less than 2 min after 3 s irradiation. In most cases, the transfer could be completed within 30 s.

In the present work, comparator materials to the *PowerCure* composites (PFill; PFlow) were chosen from the same manufacturer (ECeram; EFlow). We have also conducted studies with the same methodology on a range of dental composites from other manufacturers. These findings, which exhibit comparable trends to the present study, will be published separately [36]. Moreover, we have made parallel investigations into the kinetics of C=C bond conversion by FTIR-ATR methods that will also be reported separately [37].

The irradiation regimes (Table 2) selected were based upon manufacturer’s instructions. The delivered energy dose through the 5s and 3s modes were 10 and 9 J/cm², respectively. To some extent, there was an implicit assumption of the *general reciprocity hypothesis* that: “the same photo-cure outcomes will result from applying essentially constant energy densities despite reciprocal variations in the irradiance and time-period” [33]. However, with our use of the Elipar S10 LCU, the total energy delivery of 24 J/cm² was approximately twice that from the Bluephase *PowerCure* LCU. This was deliberately chosen to provide a severe comparative test of the PowerFill materials. A minimum energy dose of 14 J/cm² was suggested [38] to cure bulk-fill resin-composites. However, the outcome depends not only on the energy dose, but on the responsiveness of the photoinitiator system, such as its quantum yield, and other factors.

Surface indentation creep has been applied previously to materials such as solid polymers where – unlike the present experiments - the surface-properties were not subject to underlying chemical change. A number of experimental and theoretical analyses have been published [38-42]. Surface measurements have possible limitations, as far as evaluating bulk-fill dental composites are concerned, although it could be possible to invert the steel molds and measure indentations on the specimen surface remote from the irradiated surface. Nevertheless, the magnitudes of the surface indentations or “impressions” [39] are strongly dependent upon the state-of-cure of the underlying bulk material. This contrasts somewhat with the nature of surface microhardness indentations into resin-composites and particularly with nanoindentation [44]. Moreover, Degree of Conversion (DC) measurements of the Powerfill materials at 1 mm and 4 mm depths did not exhibit significant differences between the two depths [37].

We may critically review some of the measurement conditions of this experiment. *Firstly*, as with most conventionally photo-cured dental composites, there is a vast change in elastic modulus during the first 10 s of irradiation [45]. Therefore, with these ultra-fast materials, it was appropriate to probe the surface integrity as rapidly as possible; hence the “immediate” measurement condition. *Secondly*, a regime of load application for 2 h, followed by a further 2 h of unloaded recovery, was established by Ruyter [7] for bulk compressive creep and adopted by Watts *et al.* in many subsequent studies [8-11]. *Thirdly*, the applied stress was set at 14 MPa, which is a comparatively severe condition but here applied equally to each experimental group. *Fourthly*, the measurement temperature was the constant ambient laboratory temperature of 23°C. This contrasts with the 37°C conditions usually implemented in our bulk compressive creep experiments. To have attempted immediate indentation-creep measurements for ultra-fast photo-cured composites held at 37°C would have introduced complexities, logistical difficulties and potential errors. Moreover, even for bulk creep of composites, the effect of temperature over this small interval was not a major factor [46]. Of course, the polymerization process itself releases exothermic heat, to which the heating effect of the LED-LCU is added. However, the surrounding stainless-steel mold constitutes a heat sink. Furthermore, the moderate thermal diffusivities of dental composites and ultra-short exposures of 3 or 5 s with the PowerCure LCU must reduce the overall impact of any thermal impulse.

Upon initial loading, 2 – 3 % indentation was measured, depending upon the formulation. Upon unloading at 2 h, elastic recovery was only *ca.* 1 %. The reduction in elastic recovery could be at least partly caused by an increase in elastic modulus in accordance with Equation 1. The maximum indentation-creep under 14 MPa, observed with immediate measurements after 3 s (at 3 W/cm²) irradiation, was less than 150 µm, even for the flowable formulations. By contrast, delayed indentation by 24 h gave a maximum “impression” of only *ca.* 60 µm. These “worst-case” figures under a severe indentation stress might be compared with loss-of-surface-height during finishing and polishing and/or loss of anatomical form due to occlusal wear. However, the salient feature is that the *PowerCure* materials exhibited good viscoelastic stability, performing comparably to ECeram and EFlow, but with only half the total energy delivery. This supports their suitability for clinical application.

The post-irradiation time of 24 h was enough to elicit a significant improvement (reduced indentation) in the surface properties, which agrees with previous studies evaluating surface properties and post-curing [47-50]. Higher indentation-creep was seen in the flowable bulk-fill materials compared to PFill and ECeram. However, this variation was greatly reduced after 24 h, so the null hypotheses were accepted. The higher filler content incorporated in PFill and ECeram (79, 80 %wt, respectively) possibly explains the *ca.* 25 % lower indentations compared to the flowable PFlow and PFill under *immediate* loading.

In this report, the *PowerCure* composites (PFill and PFlow) were compared to the well-established composites (ECeram and EFlow) as the monomer composition and filler content are broadly similar (Table 1). These materials incorporated a photoinitiator based on benzoyl germanium, commercially known as Ivocerin, besides CQ. Main modifications to the PFill and PFlow materials [5] including (i) the elimination of TPO photoinitiator used in ECeram and EFlow, relying on CQ as the main photoinitiator and Ivocerin as a booster (ii) addition-fragmentation chain transfer (AFCT) reagent incorporation with the aim of inducing a more homogenous

network [5, 34, 35] (iii) tricyclodocane dimethanol dimethacrylate (DCP) and propoxylated Bisphenol A dimethacrylate as added monomers.

The two mathematical functions, illustrated in Figure 6 for PFill, are able to provide close fits, respectively, to either indentation-creep data for *immediate* loading (equation 8; Table 3) or for *delayed* loading (Equation 12; Table 4). **KWW** or stretched-exponential behavior is characteristic of complex materials in which hierarchical structures exist [26, 27]. The fractional exponents (β) were low and in the range 0.16 to 0.23.

Fancey [29] considered a complex and generalized Voigt model with Voigt elements connected in series (cf. Figure 2) with the aim of applicability to broad timescales. However, he noted that in these models, viscoelastic deformations are considered to vary *smoothly* i.e continuously with time. He considered an alternative approach in which viscoelastic changes are suggested to occur through discrete incremental jumps, via activated mechanical latches. On a molecular level, the phenomenon could be envisaged as segments of molecules jumping between positions of relative stability. This is certainly the concept accepted within the advanced science of polymers and networks. A link that has been proposed [51] between the **KWW** function and the potential energy barrier relationship as developed by Eyring et al. [52], since the latter relates the motion of matter to molecular jumps. The **KWW** function is shown to be an approximation to the potential energy barrier model [51]. Thus, during any photo-cure process, network links are formed - and some may also be broken under applied stress, particularly in a RAFT or AFCT system. Nevertheless, sufficient matrix-network connectivity is clearly established in the final polymerized materials.

Conclusions

The extent of immediate surface rigidity and developing viscoelastic characteristics of ultra-rapid photo-polymerized dental composites can be measured by a macroscopic indentation-creep method, following 3 s or 5 s exposures to irradiances, respectively, of 3 or 2 W/cm². The new methodology is described in detail. For rapid-irradiated *PowerCure* composites under 14 MPa *immediate* stress, the indentation-creep exhibited stretched-exponential kinetics with magnitudes after 2 h less than 150 μ m. When the stress application was delayed for 24 h, the indentation magnitudes were *ca.* 60 μ m. Completely comparable indentation /time profiles were exhibited by well-established composite formulations following 1.2 W/cm² irradiation for 20 s. As judged by the experimental indentation-creep methodology, the *PowerCure* system and materials demonstrated an acceptable level of polymerization/property performance, despite the ultra-short irradiation times, evidencing their suitability for clinical application.

Author Contributions

DCW conceived and commissioned the instrumental design, methods and theoretical analysis, guided the experiments and wrote the final manuscript to which both authors gave approval. HA performed the experiments, collated the data, performed statistics, contributed to the interpretation of results and to manuscript writing.

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Highlights

- The rapidly developing surface integrity of ultra-fast (3 s) photo-cure composites can be probed “immediately” by a new macroscopic indentation-creep methodology.
- *PowerCure* system and materials demonstrated an acceptable level of polymerization/property performance, despite the ultra-short irradiation times, as judged by this experimental criterion.

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