What Happens When I Irradiate a BFC?

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A basic question is: *What is light?* Over the past three centuries, *particle* and *wave* models have competed for dominance. However, thanks to quantum theory, a truce has been declared. Paradoxically, both models are now considered to be "true." Light behaves as a stream of particles (*photons*), but collectively—or even single photons—exhibit wavelike character, including interference and diffraction. The photon (particle) concept is essential to explain the photoelectric effect, the mechanism behind the operation of digital cameras and solar roof panels.

In terms of waves, a light beam has a *wavelength* (λ): the distance between successive peaks or troughs. This can be re-expressed as a *frequency* (ν), reciprocally related via a simple equation involving the *velocity* (c) of light.

$$c = \nu \cdot \lambda \tag{4.1}$$

A beam of visible (white) light consists of a range (or *spectrum*) of wavelengths (or frequencies). As Isaac Newton showed, white light can be split via a glass prism into its constituent wavelength ranges, *from red to violet*, often denoted by the capital letters: ROYGBIV. As, James Clark Maxwell showed, theoretically, and Heinrich Hertz showed experimentally, visible light is merely a central part of the whole electromagnetic spectrum (Fig. 4.1) with *ultra-violet* (UV) extending beyond the violet and *infra-red* (IR) and radio waves extending beyond the red [1, 2].

According to the quantum theory, each photon of light has an energy (E) given by the product of its frequency (ν) and Max Planck's constant (h).

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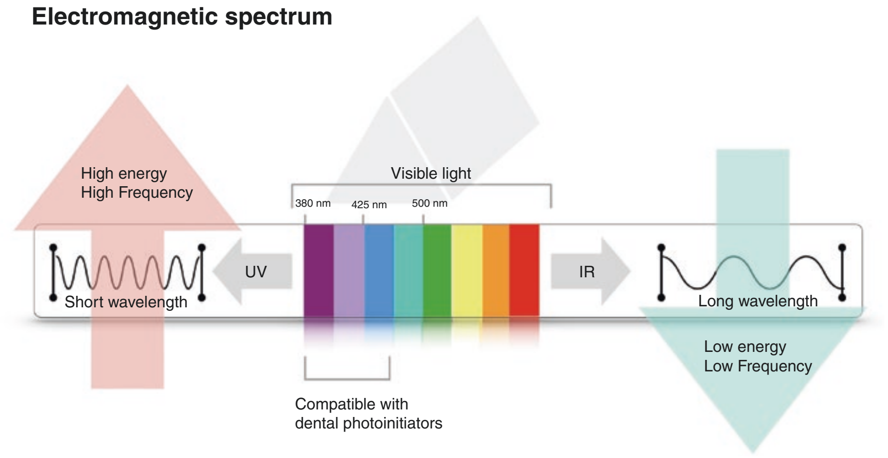

Fig. 4.1 Light of wavelengths visible to human eyes is a central part of the electromagnetic spectrum

$$E = h \cdot \nu = h \cdot c / \lambda \tag{4.2}$$

Planck's constant is almost unimaginably small ($6.62607004 \times 10^{-34}$ m^2 kg/s). Therefore, contrary to popular parlance, a *quantum leap* is the *smallest* possible change in energy! This also means that a solitary blue photon has only a small quantity of energy.

When using a light-curing unit (LCU), based around a light-emitting diode (LED) chip, the *Radiant Exitance* (mW/cm^2) is a measure of output ***power*** (Watts) *per unit area*. Power (W) is ***energy*** (Joules) *per unit time*. When we consider the light energy falling on a target surface, we use the term *Irradiance* (*I*), with the same units as radiant exitance. Thus, assuming irradiance remains constant, over time (*t*), the **radiant exposure** or energy (*E*) delivered is:

$$\text{Energy}\left(\text{J} / \text{cm}^2\right) = \text{Irradiance}\left(\text{W} / \text{cm}^2\right) \times \text{Time}\left(\text{s}\right)$$

or

$$E = I \cdot t \tag{4.3}$$

The above three equations are the main ones for understanding this subject. But understanding involves thinking about their physical meaning, magnitudes, and units, plus how they connect together.

When you use a torch or a light-curing unit, it is conceptually helpful to think of this as pumping out (irradiating) a continuous stream of photons. Even LCUs that deliver a relatively modest irradiance, are pumping out some *billion billion* (10^{18}) photons every second. However, these photons are not all necessarily "suitable". The criteria for suitability depends upon their frequency or spectral wavelength. Most LED-LCUs output visible blue light of wavelength circa 470 nm. But violet light chips may also be used, emitting at shorter wavelengths, circa 410 nm.

We must next consider *what happens to these photons?* There are two main questions:

1. How deeply do these photons penetrate into bulk fill RBCs?
2. What happens when a suitable photon meets a photo-sensitive molecule within the resin part of the resin-composite.

Before addressing these questions, let us briefly review the composition of RBCs that also applies to bulk fill formulations.

4.1 Formulation of RBCs

All RBCs are formulated with monomer (resin) mixtures that can be chemically *polymerized* to form a solid organic resin matrix. The near-universal types of monomer in current formulations are predominantly *dimethacrylates* that incorporate pairs of carbon–carbon double bonds (C=C) at either end of each monomer molecule. There are different types of organic structures between that vary in stiffness/flexibility and length (or size). It is the C=C bonds that undergo polymerization to create single C-C bonds in their place, linking the original monomers into linear or branched polymer networks, like beads on a necklace.

Pre-dispersed within the monomers are high volume-fractions of inorganic filler particles [3, 4]. These (mainly inert) particles are normally coated with a silane coupling agent that can co-polymerize with the resin matrix [5, 6]. These components are designed to create strong, stiff restorative materials that bear some comparison, both structurally and in properties, with the major tissues (enamel and particularly dentine) that the RBC is intended to repair. This outcome depends upon successful photopolymerization of the resin-phase. To achieve this goal, photo-initiator (PI) system molecules are also pre-dispersed within the resin-phase at a concentration of circa 1%.

4.1.1 Q1. Photon Penetration into RBCs

Firstly, before the stream of photons from the LCU optic tip reach the surface of the target composite, some may be lost if the optic tip is any distance from the target. This is due to the divergence angle of the light beam, whereby the irradiance generally decreases with distance from the tip [7–11]. That is why the distinction between *radiant emittance* and *irradiance* is important. These quantities are only numerically equal when the tip is in immediate proximity to the target. However, clinically, this is not always possible; for example, in a Class I or Class II cavity, the remaining cusps may create a “standoff” for the optic tip, above the occlusal surface of the restoration (Fig. 4.2).

Secondly, when light is incident on the RBC-paste surface a significant fraction may be *reflected* back, as expressed by the quantity **r** in Eq. (4.4).

Thirdly, the light that penetrates into the top surface of the composite may be subject to *attenuation* via two main processes: (1) absorption and (2) scattering. The

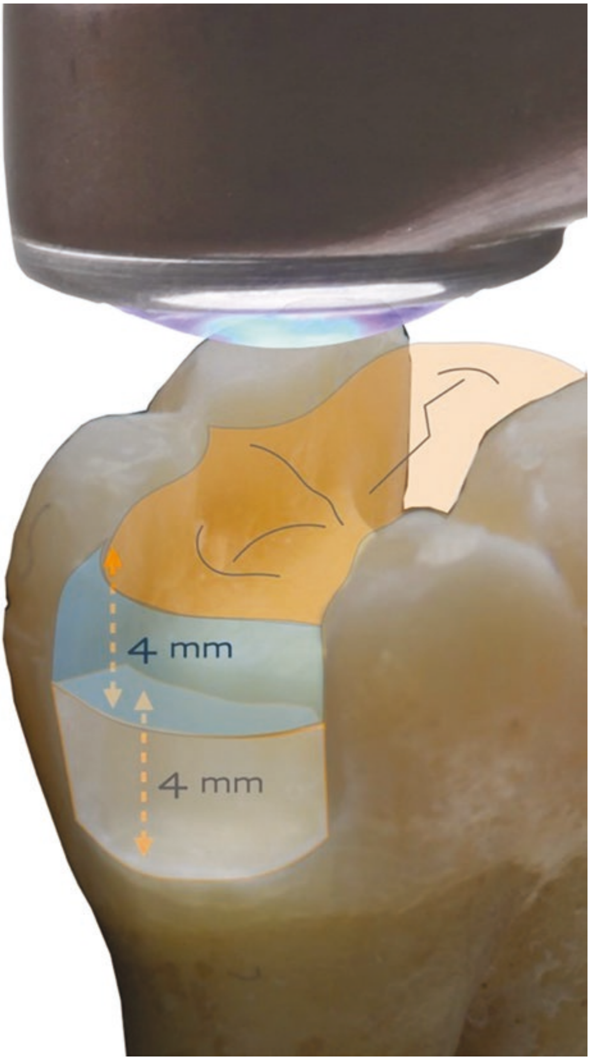

Fig. 4.2 Even with direct contact of the light guide tip and the occlusal surface, there can be a finite distance to the proximal box

combined effect of these processes is characterized by the Beer–Lambert law [12] that expresses an exponential *decrease* of irradiance (***I***) with depth (**d**), with an *attenuation coefficient* (μ).

$$I = I_0\left(1 - r\right) \cdot e^{-\mu \cdot d} \tag{4.4}$$

where ***I₀*** is the irradiance incident upon the top surface and **r** is the fraction of light undergoing specular reflection from the surface.

$$\mu = \mu_a + \mu_s \tag{4.5}$$

The attenuation coefficient is the sum of the coefficients for absorption and scattering, as per Eq. (4.5), Scattering of light is commonplace at internal interfaces, especially where there is a change of *refractive index* (*n*) between two phases, such as resin and filler particles [13]. Some bulk fill RBCs incorporated quantities of short fibres. These are normally arranged in random orientations: their spatial distribution being *isotropic* (equal in all directions). Consequently, they exhibit no special optical phenomena. Scattering increases appreciably with shorter wavelengths, so blue light penetrates more than violet light [14, 15]. Filler-particle size (or fibre diameter) has a major effect [13, 16, 17]. Often particle or fibre diameters are *greater* than the wavelength of light (ca. 470 nm or 0.47 μm), so the light beam "sees" the particles and is refracted as it passes through, i.e. scattered from its original direction of travel [16, 17]. By contrast, nanoparticles (ca. 100 nm) are not "seen" by the light beam and so do not scatter light. The art and science of RBC formulation takes these physical factors into account to mitigate undesired effects. This has been particularly critical in designing bulk fill materials with optimized light transmission and using high efficiency photo-initiator mixtures.

Absorption of light occurs as photons encounter: (a) pigment molecules or similar species and (b) photo-initiator molecules. We will now consider PI systems in more detail.

4.1.2 Q2. Photons Encounter PI Molecules

Photo-sensitive compounds occur rather widely in the natural world. The best known is *chlorophyll* in plants and cyanobacteria; its green colour is due to the fact that it mainly absorbs blue and red wavelengths from sunlight.

Within dental RBCs, *suitable* photo-initiator systems respond to (absorb) visible blue and/or violet light (Fig. 4.3). This starts a photochemical process that initiates *free-radical addition polymerization* reactions. PI systems may be classified into two types: Norrish Type I and Norrish Type II. Camphorquinone/amine was the first

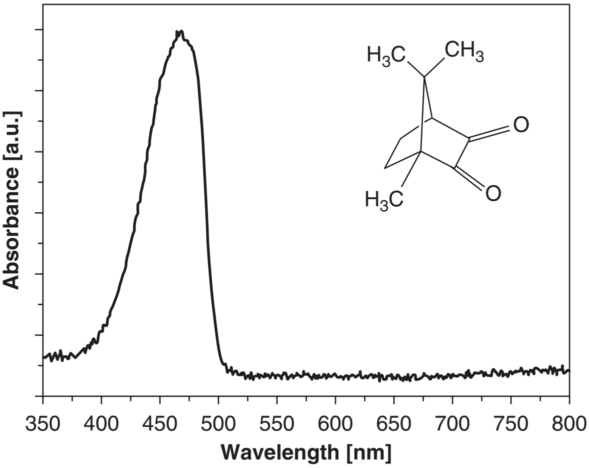

Fig. 4.3 The photo-initiator camphoroquinone absorbs light in the blue region of the visible spectrum

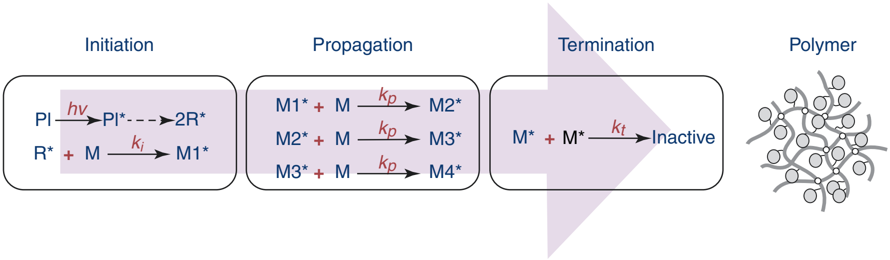

Fig. 4.4 Free-radical polymerization involves successive steps. *Initiation* creates monomer molecules with unpaired electrons. During *propagation* these radicals combine with further monomers forming growing polymer chains. Eventually the growth process stops due to one or more *termination* reactions

system to be developed for dental RBCs and this is Type II. More recently, Type I systems have also been used that involve a simpler bond-cleavage mechanism. Both types result in the formation of free radicals; i.e. highly reactive molecules with an unpaired electron. The propagation of the polymerization reaction involves radical-ended chains reacting with successive monomer molecules (Fig. 4.4).

Suitability, of a PI system, means that it corresponds to or matches the output wavelengths of the light-curing unit, by having an absorption band within the output wavelength range [18, 19]. Comparison might be made with a successful postal delivery. It is not sufficient to take a letter or parcel to a destination; there must be a letter box large enough to receive the letter (unless the door is opened)! Therefore, the critical light energy "*delivered*" is that which actually reaches its intended destination *and is absorbed* [20–22].

The types of monomer used to form dental resin matrices are mainly dimethacrylates, such as bis-GMA and TEGDMA. Each monomer has two methacrylate groups; one at either end. These are commonly represented by their principal feature: C=C. That is, a carbon–carbon *double* bond. In consequence, polymerization results in extensive cross-linking which creates a 3D network structure, rather than either linear or branched polymer chains [23]. Formation of this network structure causes a rapid increase in *elastic modulus* (i.e., stiffness, per unit cross-section) and an increase in local molecular density [23, 24], that corresponds to bulk polymerization shrinkage [25, 26].

It should be clearly understood that the irradiation, or photon dose "delivery", functions as a "trigger" such that the reaction continues long after the light has been switched OFF. However, the reaction continues only in regions of the material initially reached by photons and thus where free radicals have been generated. The initial phase of the reaction kinetics is marked by an auto-acceleration until a point is quickly reached when auto-deceleration sets in and further progress occurs increasingly slowly [27]. By this point the material is transitioning into the glassy state and internal movement of residual free radicals is slow [23, 24].

Once the composite has reached a hard glassy consistency, slow continued polymerization of the resin-phase is manifest by an increase in surface and bulk properties. Thus, surface hardness is known to gradually increase over periods of 1 month, or longer. However, intra-orally, water sorption may serve to soften surface layers [28].

4.2 Degree of Conversion

The kinetics (speed) of the polymerization process can be followed in a science lab by several complementary techniques. These include infra-red spectroscopy and monitoring shrinkage changes of the RBC that generally keep in step with the underlying polymerization reactions.

The most widely referenced quantity for expressing the immediate molecular "success" of photopolymerization is the Degree of Conversion (**DC**). **DC** of a composite surface or thin film is the percentage of C=C *double* bonds within the monomer molecules that have "disappeared" or rather converted to C-C single-bonds by polymerization. **DC** is measurable by infra-red spectroscopy [29, 30]. For a well-polymerized dimethacrylate composite **DC** is typically in the range 60–70%, not at all close to 100% (Fig. 4.5).

The reason for **DC**% values much less than 100% is that polymerization of these cross-linking molecules is a self-limiting process. As the monomer begins to polymerize, viscosity rises rapidly and within seconds the material has vitrified (entered the glassy state of matter), so the network becomes topologically entangled and the mobility that is requisite for further reaction is either greatly reduced or becomes impossible.

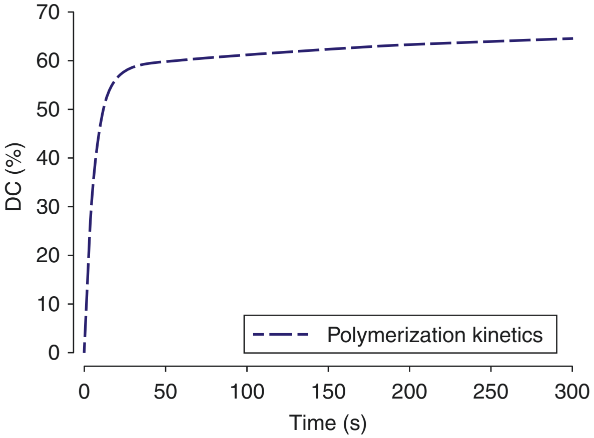

Fig. 4.5 During dimethacrylate photopolymerization, as shown over a linear timescale, the *degree of conversion* normal increases rapidly and then—more slowly—approaches a maximum value: ca. 60%. Complete 100% conversion is not reached at oral temperatures because formation of the cross-linked network is increasingly a self-limiting process as the material converts from a mobile paste to a hard solid

DC is the main parameter used to express the state of the polymer network in RBCs. However, even starting with the same monomers *different network structures* may be generated that nevertheless have the *same* **DC**. This will be the case if the different structures exhibit variations in their cross-link densities. Such an outcome can arise by using ultra-rapid curing versus slower photo-curing. Solvent swelling measurements can give an indication of such differences. More exact characterization involves X-ray diffraction experiments using synchrotron light sources.

4.3 "Bleaching" of Photo-Initiators and Colour Stability of BF-RBCs

Widely used Type II photo-initiators, such as camphorquinone (CQ), are yellowish compounds precisely because they absorb blue wavelengths from white light. When CQ molecules react photochemically they are "destroyed" and so lose their yellow appearance. This is termed "bleaching" of the PI. Ideally the amount of CQ formulated is just sufficient for the photochemical reaction, leaving no residual CQ. Otherwise the RBC may have an undesired yellow appearance. Additionally, CQ is used with an amine molecule (co-initiator). Again, residual amines can change chemically and develop a yellow appearance over time, thereby affecting the colour stability of the RBC. Managing this situation by the clinician is mainly down to: (a) being aware of the potential problem and (b) selecting RBC products that are known to be less susceptible to this problem.

4.4 The Reciprocity Hypothesis

As noted in Eq. (4.3), above, the light energy applied to the material is, by definition, the product of **irradiance** (***I***) and irradiation **time** (***t***). The first photo-cured dental resin-composites were considered to require irradiation for $\boldsymbol{t} = 60$ s. Subsequent developments have enabled irradiation times to be reduced from 60 > 40 > 20 > 10 s, or—with specially formulated RBCs—even shorter times: >5 > 3 s.

To some extent, there has been an implicit assumption of a *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" [31–36]. An assumption is thereby made that the *if the irradiance is increased sufficiently* the irradiation period may be *reduced proportionately* without incurring inadequate consequences. As a general rule, this reciprocity assumption is over-optimistic and could be seriously misleading. Resin-composites are not all created equal. Some have been specially formulated with advanced photo-initiator systems to permit ultra-rapid cure within 5 or even 3 s [34, 37]. In other cases, it has been proposed that there is theoretical and experimental support for reciprocity to apply to monomer systems incorporating Type I photo-initiators [32] or to composites possessing a certain range of viscosity [35]. But in other cases, there may be anomalies [33] or reciprocity only to a limited extent [36].

On this point some conclusions may be drawn:

- For some specially formulated RBCs and with matched LCUs, ultra-rapid cure may be safe and feasible.
- With the majority of composites on the market, it is best not to assume exact reciprocity but to apply a safety factor of at least 2, especially with darker composite shades. That means irradiating for *at least double* the time corresponding to exact reciprocity. And even then, a means of checking the radiant emittance of the LCU is essential.

4.5 Shrinkage Phenomena

During polymerization of dimethacrylate monomers, the conversion of C=C bonds involves an *intrinsic densification* or shrinkage as the original *inter*-molecular spacings between individual monomer molecules are replaced by shorter C-C bonds creating the polymeric chains. As the proportion of the resin-monomer phase is reduced by addition of filler particles so the overall shrinkage is reduced. Nevertheless, even the most optimal RBC formulations exhibit some shrinkage. Shrinkage by itself is not the problem, but shrinkage stress—that arises when the RBC is photo-cured in the confined space of a cavity. When non-bulk fill composites are placed in a deep cavity, the traditional means of mitigating stress is to place the material incrementally. Bulk fill composites are intended to obviate the necessity for incremental placement. The good news is that, with many recent formulations, shrinkage phenomena are moderate [38]. Manufacturers have striven to design and formulate against excessive shrinkage. Since RBC placement is both an art and a science the practitioner can resolve to learn more about optimal placement with different cavity shapes, sizes and designs.

4.6 Photo-Curing of Highly Filled Systems Following Pre-Heating or Sonication

There are several highly filled composite systems available that require either preheating [39] or sonication before bulk placement. The effect of these pre-treatments is to enhance flowability and thus reduce the viscosity to ensure good cavity adaptation. Once placed in the cavity these materials revert to a stiff and carveable consistency. When the desired occlusal anatomy has been achieved it is vital to proceed to apply the recommended photo-cure procedures. Without that essential step, clinical failure is certain!

4.7 Depth of Cure

Finally, since we are considering bulk fill composites, we consider *Depth of Cure* (**DoC**).

Bulk fill composites are, by definition, those having a **DoC** of 4 mm or greater. The practitioner should note specific manufacturer claims for each product. These should include the precise irradiation regime that should be followed. Further details of how Depth of Cure can be verified and validated are presented in the following Chap. 5.

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