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## Review

## A brief history of LED photopolymerization

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## ABSTRACT

**Objectives.** The majority of modern resin-based oral restorative biomaterials are cured via photopolymerization processes. A variety of light sources are available for this light curing of dental materials, such as composites or fissure sealants. Quartz-tungsten-halogen (QTH) light curing units (LCUs) have dominated light curing of dental materials for decades and are now almost entirely replaced by modern light emitting diode light curing units (LED LCUs). Exactly 50 years ago, visible LEDs were invented. Nevertheless, it was not before the 1990s that LEDs were seriously considered by scientists or manufactures of commercial LCUs as light sources to photopolymerize dental composites and other dental materials. The objective of this review paper is to give an overview of the scientific development and state-of-the-art of LED photopolymerization of oral biomaterials.

**Methods.** The materials science of LED LCU devices and dental materials photopolymerized with LED LCU, as well as advantages and limits of LED photopolymerization of oral biomaterials, are discussed. This is mainly based on a review of the most frequently cited scientific papers in international peer reviewed journals. The developments of commercial LED LCUs as well as aspects of their clinical use are considered in this review.

**Results.** The development of LED LCUs has progressed in steps and was made possible by (i) the invention of visible light emitting diodes 50 years ago; (ii) the introduction of high brightness blue light emitting GaN LEDs in 1994; and (iii) the creation of the first blue LED LCUs for the photopolymerization of oral biomaterials. The proof of concept of LED LCUs had to be demonstrated by the satisfactory performance of resin based restorative dental materials photopolymerized by these devices, before LED photopolymerization was generally accepted. Hallmarks of LED LCUs include a unique light emission spectrum, high curing efficiency, long life, low energy consumption and compact device form factor.

**Significance.** By understanding the physical principles of LEDs, the development of LED LCUs, their strengths and limitations and the specific benefits of LED photopolymerization will be better appreciated.

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*“All truth passes through three stages. First, it is ridiculed. Second, it is violently opposed. Third, it is accepted as being self-evident.”*

Arthur Schopenhauer

## 1. Introduction

The introduction of resin-based dental materials near the middle of the last century was a revolution in restorative dentistry. Dental composites are esthetically pleasing since they possess a tooth-like appearance, are stable within the oral environment, are relatively easy to handle and set on command via self curing or light curing.

Today, almost all commercial dental composites utilize photopolymerization reactions initiated by blue visible light. Light curing units (LCUs) based on different physical principles, such as quartz-tungsten-halogen (QTH) bulbs, laser, plasma arc lights, and light emitting diodes (LEDs) are available. Nevertheless, LED LCUs are currently the standard devices in most modern dental practices.

In many cases, clinicians using LED LCUs on a daily basis are unaware of the physics and/or history of their development. This knowledge, however, is essential so that LED LCUs can be used to their full potential and are applied appropriately in any particular clinical situation.

In addition, there is currently no scientific review paper focusing on the LED photopolymerization of available dental materials. This review, therefore, addresses this need and is based mainly on peer-reviewed and frequently cited research articles in international journals available through the Web of Science. This current paper reviews the history of LED photopolymerization in the area of oral biomaterials/dental materials. Within this framework, the basic principles of LEDs, the history and evolution of commercial LED LCUs, the materials science of dental materials photopolymerized with LED LCUs, aspects of commercial LED LCUs as well as their clinical applications are discussed.

## 2. Basic physics and technology of LEDs

LEDs are a part of our daily lives. LED technology is applied in modern light sources for room lighting, car headlights and dashboards, traffic lights, state-of-the-art television flat screens or as LASER LEDs in CD or blue-ray DVD data/video storage equipment [1]. Compared to conventional light sources, LEDs are small and energy efficient. Hence, dental

light curing units (LCUs) based on LEDs are relatively small and can be battery powered, using high performance nickel-metal hydride (NiMH) or lithium-ion (Li-ion) batteries [2].

Users of dental LCUs are often not fully aware of the physics of these devices. Because light emission of LED LCUs differs greatly from that of other, more traditional types of LCUs, it is worth having a closer look at the physical principles of LEDs. This knowledge may not only help to better understand how LEDs work, but it may also contribute to the appropriate use of LED LCUs in clinical practice and to recognize the strengths and limitations of these devices in daily use.

LEDs are semiconductor-based photonic devices in which the elementary particles of light (photons) play the key role. LEDs convert electrical energy into optical radiation [3]. It has been known for more than one hundred years that light can be generated if an electric current passes through a material under bias [3]. This phenomenon is called electroluminescence and was discovered in 1907 in the natural semiconductor silicon carbide [4].

LEDs emit light under forward biased conditions. To understand this, one has to consider the energy states of electrons in the semiconductor. Through the quantum mechanical interaction of large numbers of atoms ( $\cong 10^{25}$ ) and electrons in the solid state, the electronic states may spilt into very closely spaced electron states called electron energy bands [5]. The valence energy band is associated with the highest energy, occupied with electrons at 0 K. The band with the next higher electron energy is called the conduction band and also contains no electrons at 0 K. The valence and conduction bands are separated by a band gap in which the Schrödinger equation has no solution, i.e., no electrons are allowed in this band gap under normal circumstances. For semiconductors, the typical band gap energies are generally less than 2 eV [5]. Fig. 1 shows the band structure of an intrinsic semiconductor.

In intrinsic semiconductors, the electrical behavior is based on the electronic structure inherent in the pure material, such as silicon [5]. If impurity atoms are introduced to dictate the electrical behavior of the semiconductor, it is called an extrinsic (doped) semiconductor. LEDs use both, n-type and p-type doped extrinsic semiconductors, indicating the majority charge carriers are electrons or holes, respectively. Doping a semiconductor with atoms of the group VA of the periodic table creates n-type extrinsic semiconductors, whereas doping with atoms from the group IIIA of the periodic table creates p-type extrinsic semiconductors [5]. The former leads to new, so-called electron donor states in the band gap just below the conduction band, whereas the latter leads to acceptor states in the band gap just above the valence band.

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