The Efficacy of LED Light Polymerization Units in Private Dental Offices in Toronto, Canada

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Faculty of Dentistry
University of Toronto

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Abstract

Light-emitting-diode (LED) light-polymerization units (LPUs) are currently routinely used for resin-based composites (RBC) photopolymerization. This study aimed to determine the effectiveness of LED-LPUs used in participating private dental practices in Toronto, Canada. One-hundred dental practices were recruited, and 113 LED-LPUs were examined. Part 1 evaluated radiant exposure (RE) of participants’ LED-LPUs. Majority of LPUs (n=87, 77%) passed the study-required criterion (delivering equivalent to 16 J/cm² in 20s). A strong, negative correlation between LPUs’ age, light-probe damage, and RE was found. Part 2 evaluated operator's technique to deliver 8 J/cm² of RE in 10s to simulated restorations before and post-instructional. Before instructions, 73.6% of participants delivered required-energy to anterior restoration, and 32.2% of participants delivered required-energy to posterior restoration. Following instructions, 94.3% of participants delivered required-energy
to anterior restoration, and 73.6% of participants delivered required-energy to posterior restoration. Part 3 examined relative-hardness (RH) of two RBCs polymerized at 1mm and 4mm, tip-to-target distance. Both RBCs polymerized at 1mm had average RH (ratio of mean lower/upper surface hardness) greater than 0.80, but not at 4mm tip-to-target distance. Part 4 evaluated the diametral tensile strength (DTS) of two RBCs polymerized with participating LED-LPUs. No significant difference between mean DTS values of two RBCs was observed. Mean DTS values were highly correlated among the LED-LPUs tested. In conclusion, 23% of LED-LPUs tested were deemed as incompetent for sufficient RBC polymerization. A high percentage of dental practitioners failed to deliver 8 J/cm² in 10s exposure cycle, even after receiving specific instructions (5.7% to anterior restoration and 26.4% to posterior restoration). The outcome was due to a combination of LPUs performance and operator's technique. This finding is alarming as it relates well to early failure of Class-2 RBC restorations due to insufficient polymerization.
Dedication

This thesis is dedicated to my beloved Father and Mother, who are the source of love, inspiration, and wholehearted support since the beginning of my life journey, and without whom, none of this would be possible.

Also, this thesis is devoted to my sons, Petar and Lazar for their endeavor of bringing so much love into my life, unshakable faith in the righteousness of my life’s decisions and for making my whole existence relevant.

Finally, this thesis is devoted to my sister and my brother-in-law who have supported and encouraged me in this venture since the early beginning.
Acknowledgements

First and foremost, my genuine gratitude goes to my supervisor, Dr. Omar El-Mowafy, who has supported me throughout my academic journey with his patience and knowledge, while permitting me to work in my way. His expertise, understanding, time and helpfulness, added considerably to my extraordinary pleasant graduate experience. I attribute the level of my doctorate degree to his encouragement and effort, especially with his support of my international exposures at the IADR conferences.

Special thanks to my co-supervisor, Dr. Wafa El-Badrawy, for her expertise, understanding, patience, professionalism, and mentorship during my educational venture at the Faculty. Her insight and guidance contributed significantly to this project.

Also, I wish to thank my other thesis advisory committee members, Dr. Richard Price and Dr. Gildo Santos for the time they provided throughout this project. Dr. Price's valuable and thorough comments, expertise, incredible support and suggestions helped significantly in improving the quality of this project. Dr. Santo's ideas and dedication have been invaluable for the completion of this project, for which I am incredibly grateful.

Additionally, I would like to thank my sons: Petar and Lazar for their support and great patience at all times. My parents and my sister's family have provided me their help unconditionally, as always, for which my mere appearance of thanks furthermore does not satisfy. Without their love, encouragement, on-going support and sacrifices throughout this process, I would not be able to complete this graduate program.
Furthermore, I am very grateful to my research assistants: Ms. Ana Burilo and Ms. Ivana Orlovic whose contribution to this project was significant for the duration of this project. I would like to express my sincere gratitude to Heather Sanguins from the Health Sciences Writing Centre University of Toronto for her enormous patience and the tremendous help with my thesis writing.

In conclusion, I realize that this research would not have been possible without the generous research material donations from Shashikant Singhal (Ivoclar-Vivadent, Amherst NY) and Sridhar Janyavula (Dentsply, York PA), as well as technical support and CheckMARC loan from Colin Deacon (BlueLight Analytics, Halifax NS). Their support is duly acknowledged. Furthermore, I am very appreciative to the University of Toronto for the financial assistance during the entire course of my graduate training and the funding of this project.
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Chapter 1

Introduction and Literature Review

Introduction

Direct esthetic restorative materials have experienced significant changes since the 1980s. Up to this time, amalgam was the material of choice for direct posterior restorations. However, over the past decade, extensive research into, and implementation of, innovative technologies have significantly improved the dependability and predictability of amalgam-alternative dental materials, especially direct resin-based composite (RBC) materials. At the same time, restorative dentistry has experienced a dynamic shift to adhesive dentistry. During the past decade, the use of RBC for direct restorations has increased exponentially, due to the high esthetic demands and increasing public awareness of mercury in dental amalgam, in addition to environmental concerns about the industrial use of mercury\(^1,2\). In 2013, the Minamata Convention on Mercury committed to the reduction and ultimate dismissal of the production and use of mercury-containing products globally. The use of RBC continues to increase worldwide. In some countries, however, RBCs have entirely replaced amalgam, such as Norway where amalgam elimination started in 2008\(^3\). According to the United States insurance data claims for the 2010 year, RBC has become the first-choice restorative material accounting for more than 65% of all private practice placements\(^4\). The RBC has three
distinct components, each with its role in influencing material properties: the organic resin matrix, the inorganic fillers, and the filler-resin interface (coupling agent). The resin matrix phase is composed of polymerizable monomers that convert to the highly crosslinked polymers upon photopolymerization, which catalyzes the development of active centers, which induce polymerization. The filler phase has several roles, including improving the mechanical properties, reducing thermal expansion, and decreasing polymerization shrinkage by reducing the resin content. Finally, silane at the filler-resin interface creates a bond between the filler particles and the resin interface that is important for their bonding capabilities.

Polymerization of RBC materials is initiated by the appropriate spectra and sufficient quantities of light in the blue region of spectrum from the LPU that activates photoinitiators with subsequent release of free radicals that initiate the polymerization reaction. During this process, the terminal aliphatic C=C bonds are severed and converted to the primary C-C covalent bonds. During the polymerization reaction, the monomer is converted into a polymer, nonetheless, full conversion is never achieved. Although the majority of monomers are transformed, however, a certain number of monomers remains unreacted or trapped in the polymeric matrix, and is the cause of the free monomer elution. The percentage of unconverted aliphatic C=C bonds in the polymeric matrix represents the degree of conversion (DC), the most important feature that affects the clinical performance of RBC materials.

The literature shows that the development mechanism of free radicals in the monomer differs according to the photoinitiator system used. Therefore, for adequate RBC photopolymerization, light-activated resins must not only receive sufficient radiant exposure
(J/cm²) but also must be given this energy within the appropriate wavelength range to match the spectral range of the photoinitiator system of the resin \(^{10}\).

The first law of photochemistry, the Grotthuss-Draper law, states that photon has to be absorbed by a chemical material for a photochemical reaction to take place. Therefore, the presence of light alone is not enough to trigger a photochemical reaction; the light must exhibit the correct wavelength match to be absorbed by the reactant used \(^{11}\). The second law of photochemistry, the Stark-Einstein law, states that for each photon of light absorbed by a chemical system, only one molecule can be activated for the photochemical reaction to occur. However, this fundamental principle applies to the photoinitiators with a low free radical production efficiency, such as the camphorquinone system (CQ) \(^{11}\). The ability to accurately determine the number of photons, leading to a reaction, enables the efficiency or quantum yield of the photochemical reaction \(^{11}\). Thus, the use of LED-LPUs that can generate adequate radiant power (mW) and spectral irradiance (mW/cm²/nm), which produces sufficient polymerization, is a crucial factor for the clinical success of RBC direct restorative materials \(^{12}\).

The factors affecting the photopolymerization efficiency of RBCs are intrinsic, related to the RBC composition, and extrinsic, related to the LPUs. The intrinsic factors are co-monomer composition and filler-content ratio, photoinitiator type, and concentration. While the extrinsic factors are the light spectrum, irradiation protocols, temperature, and light guide tip positioning. It is imperative for clinicians to comprehend and optimize the RBC photopolymerization process to maximize material properties. According to the results of a recent study (Kopperud et al., 2017) the majority of Norwegian dental practitioners did not demonstrate sufficient knowledge of this matter \(^{13}\). Furthermore, the majority of the study
participants (78.3%) were unaware of the irradiance value of their LPUs. It was reported that 78.3% of dentists failed to perform the regular maintenance of their LPUs. The research findings provide the foundation for many clinical practice guidelines developed to improve dental care procedures. Although contemporary dental practice exhibits a substantial increase in RBC restoration placements, the literature demonstrated that the longevity of RBCs has fallen short in comparison to that of amalgams. Consequently, the practitioners' selection of LPUs and RBC materials, as well as the latest guidelines to be followed, are important detrimental factors. The literature demonstrated a substantial effect of LPUs performance and clinician's polymerizations technique on the longevity of RBC restorations, and this project attempted to characterize and quantify findings from a group of private dental practices in the Greater Toronto Area and how these results correlate with published studies.

1.2 History of Resin-Based Composites (RBC)

The introduction of silicate cement as a direct restorative material in 1871 was the beginning of esthetic restorative dentistry. Silicates were noted for their anti-cariogenic effects and remained the material of choice for restoring anterior teeth until the early 1950s. However, silicates had some undesirable physical properties, especially color instability and quite a high rate of dissolution in saliva, which led to their discontinuation in the early 1960s. Acrylic resin (unfilled resin), another type of direct restorative material, was
developed in 1936, but was not used as a direct esthetic material until the late 1940s\textsuperscript{17}. It was composed of Poly methyl methacrylate (PMMA) and has also been used in dentistry in another form as a denture base material replacing vulcanite. Although unfilled resins offered benefits over silicates, bonding was not as yet discovered\textsuperscript{18}. In the mid-1950s, Buonocore was the first to introduce an orthophosphoric acid etching technique, which enabled the formation of a stable bond between enamel and acrylic resin\textsuperscript{18}. Knock and Glenn patented the first particulate-filled composite in 1951\textsuperscript{20}. However, their product lacked bonding between the resin matrix and the filler particles.

Composite dental materials were developed in responses to the shortcomings of silicate cement and unfilled resins. The breakthrough came in 1962 when Rafael Bowen patented a new resin, Bisphenol glycidyl di-methacrylate (Bis-GMA). This material resembled an epoxy resin except the epoxy groups were replaced by methacrylate groups\textsuperscript{21}. Bis-GMA formulations could polymerize rapidly under oral conditions, and they had less polymerization shrinkage than methyl methacrylate. Although Dr. Buonocore continued his acid etching research with various resins, however, he achieved the best bonding results at that time using the Bis-GMA resin\textsuperscript{22,23}. In addition to Buonocore findings, Regenos\textsuperscript{24} and others further developed the acid-etching concept using Bis-GMA resin to repair fractured incisors without drilling the dentin\textsuperscript{25,26}. The birth of adhesive dentistry was recognised as a consequence of Bowen's 1963 publication. Bowen successfully demonstrated that chemical treatment of silica particles' surfaces with vinyl silane, within the Bis–GMA resin matrix could produce a new direct restorative material with consistent mechanical properties and clinical effectiveness. Bis–GMA has become the basis for all RBC materials used in dentistry. Bowen worked at the U.S. National Bureau of Standards. Thus, he was in a
position to conduct testing in the areas of polymerization setting times, shrinkage, solubility, degradation, water sorption, color stability, mechanical testing, and toxicity.\textsuperscript{27, 28, 29, 30, 31}

The early two-paste chemically-polymerized RBCs required manual mixing. The mixing process was a technique-sensitive one. During the mixing, the mixture usually trapped air bubbles that had unfavorable effects on mechanical properties after RBC’s polymerization. Furthermore, these materials demonstrated excessive shrinkage, leading to sensitivity, and recurrent decay. Due to their relatively large size filler particles, RBCs from that era exhibited high wear rates. Over the course of 4 decades, the Bis-GMA chemistry has improved considerably, yielding clinically acceptable RBCs. The particle size of the fillers has been considerably reduced, and the resin chemistry further developed, allowing RBCs to exhibit superior physical and mechanical properties, which extended their clinical longevity.

As time progressed, photopolymerized RBC materials replaced the early two-paste self-polymerized ones in the 1970s. This development was regarded as a revolutionary step in dentistry which allowed quick chairside polymerization.

The photopolymerization technology was adapted from the chemical industry and modified for use in dentistry.\textsuperscript{33, 34, 35} The first LPUs were designed to emit ultraviolet light (UV).\textsuperscript{36} A 40s polymerization exposure was advocated, but 60s exposure provided enhanced results.\textsuperscript{37} The common issues associated with UV polymerization of RBCs were: a limited light penetration throughout the material (limited depth) and health hazards related to UV light exposure on the operators’ eyes.\textsuperscript{38, 39, 40} However, the rise of UV photopolymerization was short lived when in 1976 Bassojuny, at the University of Manchester, School of Dentistry, placed the first visible light-polymerized RBC restoration. Again, the technology
was adopted from the Imperial Chemical Industries of England and modified for dental use 41, 42, 43.

The new visible light polymerization technology initially used a photoinitiation system based on camphorquinone with a tertiary amine co-initiator, a system that was enhanced over the years and became a template for new RBCs 44, 45. The light source used to photopolymerize the newly developed RBCs was quartz–tungsten–halogen (QTH), developed by the Johnson and Johnson Company. The new venture launched the FotoFil restorative system and QTH light source unit 46. This technology enabled photopolymerization of a 2 mm thick increment of RBC 47, 48. Since that time, efforts have been directed to modify the filler particles of RBC to improve their mechanical properties. The macrofill RBC had filler particles of about 10 µm that exhibited excessive wear 49. In the 1980s, microfilled RBCs were developed for the first time 50. Due to microscopic filler particles (0.02 µm to 0.04 µm), microfilled RBCs demonstrated excellent polishing characteristics. Furthermore, they were translucent, however, due to their inferior mechanical properties, bulk fractures were common 51.

The concept of combining high strength and esthetic properties was accomplished with the launch of the first hybrid RBCs in the late 1980s 49, 52. These materials had improved strength and better wear resistance, however, the esthetic properties were inferior to those of the microfilled RBCs 53. The next development in the search for an ideal direct restorative material led to the creation of microhybrid RBCs in the mid-1990s. These materials had filler particles that were smaller than those of hybrid formulation, with better multi-modal distribution 54. The properties of these RBCs exhibited the strength of the hybrid RBCs with significantly improved esthetic attributes 54, 55. Further improvements in the filler technology
have allowed nanofillers to formulate nanohybrid RBCs, which became available in the early 2000s. Nanohybrid RBCs contain nanometer-sized filler particles (0.005–0.01µm), along with conventional fillers. They became the first genuinely universal RBCs with the handling and esthetic properties of micro filled RBCs and the strength and wear resistance of traditional hybrid RBCs.

The first generation of flowable composites, introduced in 1996, belonged to the hybrid category of RBCs. A notable reduction in the percentage of fillers and a particular modification of the resin matrix resulted in the low viscosity of the flowable RBCs. Flowable RBCs were used as luting materials for indirect restorations for a long time. However, they were reintroduced for direct restorative RBC materials in the late 2010s.

Following the success of nanotechnology and the incorporation of pre-polymerized resin fillers, a new epoch for nanofilled RBCs began. These materials have been produced with nanofiller and formulated with a nanomer® (Nanocor, Arlington Heights, IL) and nanocluster filler particles. Nanomers® are discrete nano-agglomerated particles with a size of 20 to 75 nm, while the nanoclusters represent loosely bound agglomerates of nano-sized particles. The combination of nanomer® and nanocluster formations reduces the interstitial spacing of the filler particles, which creates the ability to increase filler load with excellent polishing capability.

Since the mid-2000s, there has been considerable research for an alternative resin with less polymerization shrinkage and a higher degree of conversion. A newly discovered resin based on dimer chemistry, which exhibited higher than 70% conversion, was launched in the late 2000s.
Following the Dimer based RBCs’ commercialization, a novel organically modified ceramic (ORMOCER) was launched. Materials based on ORMOCER technology are inorganic-organic hybrid polymers that form a siloxane network selectively modified through the incorporation of organic groups. A distinctive feature of these RBCs is a blend of polysiloxane groups with photo-polymerizable methacrylate groups covalently bonded to silica. Because of its structural relation to silicate ceramic or glass, such materials are also known as organo-ceramics. These materials have exhibited up to 50% reduction in polymerization shrinkage when compared to traditional RBCs. The DC was reported to be in a range from 95% to 99%, which is virtually identical to that of indirect restorative RBCs. The new material exhibited a higher level of resistance to stain and hydrolysis. Thus, it was able to maintain a high degree of luster for a considerable long time. The latest innovation that has happened with ORMOCER materials was the fusion of nanohybrid and ORMOCER technology, which exhibited further improvements regarding initial shrinkage, shrinkage stress, esthetics, and biocompatibility of the nano ORMOCER materials.

However, in the late 2000s, a different resin synthesized from oxiranes and siloxane molecules, which became known as a Silorane RBC material, was developed. This new RBC material was introduced as an alternative to conventional RBC because of its hydrophobicity and lower polymerization shrinkage. When compared to methacrylate-based resins, the cyclo-aliphatic oxirane functional groups exhibit less shrinkage. Oxiranes are cyclic ethers that polymerize via a cationic ring-opening mechanism, while methacrylate polymerization is achieved via a free-radical polymerization process. The distinctive feature of Silorane RBCs arises from the ability of the
cyclosiloxane backbone to impart hydrophobicity, while the cyclo-aliphatic oxirane sites have high reactivity and less shrinkage than methacrylate RBCs. Silorane RBCs demonstrated improvements with delayed gel and vitrification points and reduced shrinkage strain. However, these materials tend to produce more heat during the cationic ring-opening polymerization. Furthermore, Silorane RBCs exhibit the high initial flexural modulus, which may explain its high polymerization stress values, despite the low volumetric shrinkage (both post-gel and total).

Recently, a new class of RBC materials has been introduced to the dental profession under the name of bulk-fill restorative materials, with the aim of simplifying and expediting the restoration process. It was available due to the use of new proprietary resins, individual modulators, and different filler particles. To reduce some of the disadvantages of incremental layering techniques and to save some chairside time, the innovative bulk-fill RBCs can be placed in a 4 mm single increment. The manufacturers’ claim that these materials can be adequately photopolymerized in bulk has been confirmed by in vitro infrared spectroscopy studies. More recently, flowable bulk-fill composites have been developed. They have been used along with conventional RBCs in a two-layer arrangement for esthetic considerations in posterior teeth. It was proven their use could lower the polymerization stress, enhance the flow and handling, and improve adaptation to the cavity walls, which resulted in substantial stress reduction at the cavity walls. The bulk-fill flowable RBCs can be used to restore posterior teeth using 4 mm maximum increments because this procedure does not reduce the mechanical resistance of the restored teeth while rendering the entire procedure less technique sensitive and more efficient.
The most recent development in contemporary dentistry was the introduction of flowable RBCs containing adhesive monomers. This new technology is based on enhanced traditional methacrylate resin that incorporates acidic-monomer chemistry from bonding agents, making them capable of interacting mechanically and chemically with tooth surfaces in an adhesive manner. Despite their limited use for direct restorations, they are considered to be futuristic materials in the continued search for universal, self-adhesive RBC direct restorative materials.

1.3 Classification of RBC

RBCs emerged during the past 50 years and with different formulations that have been successfully used as restorative material luting agents, sealants, provisional materials, and much more. The RBC material consists of three components: resin matrix (organic content), fillers (mineral content), and a coupling agent. The features of the filler particle and filler particle loading, are the most critical factors that influence the mechanical properties of restorative RBCs. The classification introduced by Lutz and Philips in 1983 divided the RBCs into macrofills; microfills; and hybrids, which are mostly a blend of ground glass and the microfill particles.

- **Type I: Macrofilled RBCs**

Type I, macrofilled RBCs, which were also known as conventional or traditional RBCs, provide some historical perspective. The fillers were composed of amorphous silica or quartz with relatively large particles from 1 μm to 50 μm. Due to the relatively large filler particles, however, they exhibited inferior wear resistance as a consequence of differential
wear, which led to rapid loss of resin compared with the filler. In addition, plucking of the large filler particles from the restoration surface resulted in surface roughness and was more receptive to stain and plaque accumulation. Because of these limitations, the use of these materials by dental practitioners has rapidly declined.

- **Type II: Microfilled RBCs**

For type II, microfilled RBCs, traditional microfillers were made from fumed silica prepared by a pyrogenic process, with an average particle size of 40 nm. The filler load in these materials was low, however, it was increased by adding highly filled, pre-polymerized resin fillers (PPRF)\(^9\). Due to the increased surface area of these relatively smaller filler particles, overall fillers percentage was 35 to 67 by weight\(^9\). The microfilled RBCs exhibited superior esthetic properties and for that reason, they were recommended for restoring the anterior teeth and cervical abfraction lesions. However, they were contraindicated in heavy-stress-bearing restorations because of an elevated risk of bulk-fractures and marginal chippings\(^9\). These materials were truly nanocomposites, with an average particle size of 40 nm. Although nanotechnology was not revealed in the 1980s, earliest microfilled RBCs would be recognized as nanofilled RBCs today.

- **Type III: Hybrid RBCs**

Hybrid RBCs were developed to retain the advantages of both traditional macrofilled and microfilled RBCs by combining the fillers of different particle sizes and multi-modal particle distributions. Thus, the hybrid RBCs were typically filled with a blend of 40 nm and 1\(\mu\)m to 5 \(\mu\)m particles. These materials exhibited much better wear resistance compared to
traditional macro filled RBCs, but surface properties remained less than ideal because of the 
natural wear pattern due to the presence of larger filler particles. In current terms, nearly all 
RBCs are hybrids, with particle distribution of two or more size ranges. In addition, the 
presence of amorphous silica has been used to improve handling properties of RBC 
restorative materials.

A classification introduced by Willems and Lambrechts in 1992, which is 
based on a filler volume fraction and filler size, categorized RBCs as: densified, microfine, 
miscellaneous, traditional, and fiber-reinforced. Based on Young's modulus value for 
dentin, a computed value of 60% filler load was established that further classified density 
filled RBCs as either midway-filled (<60 volume percentage) and compact-filled (>60 
volume percentage). Furthermore, each category has been further divided into ultrafine (<3 
μm) and fine (>3 μm) RBCs, based on the mean filler particle size. The average particle size 
of hybrids, microhybrids, and nanohybrids, is typically less than one μm, but more than 0.2 
μm. The larger particle sizes can extend to well over one μm. The nanohybrids have some 
particles in the nanofiller size range less than 100 nm, but they also contain particles in the 
range (0.2 to 1 μm). When the surface of the RBCs is subjected to wear, the resin between 
and around the particles is lost, leading to the creation of bumps and craters with subsequent 
loss of polish at the surface of restorations. Innovations in the sintering process 
enabled manufacturers to produce loosely agglomerated nanoparticles, i.e., nanoclusters. The 
nanoclusters exhibited a significant structural difference in comparison with densified 
particles. However, nanoclusters behaved similarly to the densified particles found in other 
RBCs that enable a high filler loading. The new nanohybrid RBCs were formulated using 
both engineered nanoparticle and nanocluster fillers. The nanocluster filler particles consist
of loosely bound aggregates of engineered nanofiller particles. The addition of engineered nanoparticles to formulations containing nanoclusters, the reduction of the filler particles interstitial space, results in higher filler loadings. The filled matrix (resin plus engineered nanoparticles) is harder and more wear resistant than the resin alone. The increased filler loading resulted in better mechanical properties and wear resistance. Therefore, nanohybrids are considered to be the first genuinely universal RBC materials, with the handling properties and polishability of microfilled RBC materials and the strength and wear resistance of traditional hybrid RBCs.

Since their introduction, flowable RBCs have been universally accepted among the clinicians, due to their remarkable versatility in a wide variety of clinical applications. From a materials science standpoint, the flowable RBCs represent a subclass of microfilled RBCs. The filler loading was reduced to 30% to 55% by volume, compared to 57% to 72% by volume as in traditional RBCs. The amount of fluidity or flowability varied considerably among the brands. Because of their physical properties, these materials are used in low-stress areas, such as the small Class I occlusal restorations, Class V restorations, and for pit and fissure sealants or conservative restorations. The rationale for their application in the Class V carious lesions and abrasion/abfraction lesions is because these materials exhibit a low modulus of elasticity and low viscosity. The use of flowables for an initial increment in the proximal box portion of a Class II restoration is somewhat controversial. Despite the many controversies associated with the use of flowables, these materials are often used as liners under hybrid materials for an initial increment in the proximal boxes of the Class II restorations.
For many years, an incremental layering technique was followed when placing posterior composite restorations. This procedure was deemed to offer the optimum polymerization of the restorations. In the late 1990s, the packable RBCs were developed to enhance incremental material placement. These products had high viscosity and contained a much higher filler content. Manufacturers claimed that their handling is amalgam-like and that their stiffness aided in forming good proximal contacts. However, the high viscosity of these materials made the cavity adaptation quite challenging. Furthermore, these materials exhibited a lower degree of monomer conversion and reduced polymerization depth. Even if the polymerization was acceptable, the clinical outcomes of high shrinkage and polymerization stress became more prominent with thicker layers of RBCs. These materials did not have high clinical success, and currently, they are no longer considered to be the mainstream of the RBCs.

The concept of bulk-fill materials gained momentum as a result of further RBC development. Through the use of innovative proprietary resins, alternative photoinitiator systems, different fillers, bulk-fill materials were designed to photopolymerize up to 5 mm thick increments. They exhibited low volumetric polymerization shrinkage and low-stress build-up upon polymerization, when compared with incrementally placed conventional RBCs. Adequate polymerization was achieved by efficiently adding novel photoinitiators, with higher quantum yield and polymerization modulators, which were responsible for decreased shrinkage stress. Furthermore, increased translucency and the incorporation of mixed oxide fillers with a refractive index matching that of the resin matrix or glass fibers enhanced the light penetration, which resulted in improved photopolymerization.
A further development in bulk-fill flowables has occurred by combining an enhanced material formulation with a sonic delivery system. The sonic energy generated by a particular handpiece causes a temporary reduction in RBCs viscosity, thus considerably improving the ability of the material to adapt to the internal surfaces of the cavity. By ending the sonic energy from the handpiece, the RBC gradually returns to its original viscosity before it is photopolymerized and finished using traditional techniques. According to the manufacturers’ claims, the material exhibits polymerization shrinkage of approximately 1.6% and can be adequately photo-polymerized to a depth of 6 mm in a single increment.

The critical breakthrough in the field of restorative materials occurred with the launch of advanced giomer restoratives. This class of restorative materials has the distinguishing feature of a stable glass ionomer core in a protective resin matrix. The different filler, Surface Pre-Reacted Glass (S-PRG), gives the material a composite-like feature in addition to a significant release of fluoride ions. Studies have shown that these materials, in both low and high viscosity consistencies, were able to achieve adequate polymerization, had excellent mechanical properties and demonstrated low polymerization shrinkage when compared with conventional RBCs.

Recently, increased use of bioactive restorative materials has been noticed as these products promise untapped benefits for long-lasting restorations. The idea of bioactivity of dental materials was proposed by Hench in the late 1960s, with the following definition: “A bioactive material is one that elicits a specific biological response at the interface of the material which results in the formation of a bond between the tissues and the material.” The concept of bioactive restorative dental material with the capacity of adhesion to tooth
structure and the fluoride-releasing ability has been widely used in dentistry for decades. However, the current concept of bioactivity is defined as the ability of the restorative material to develop a surface deposition of mineral apatite in the proximity of the restoration margin in the presence of an inorganic ions solution\textsuperscript{119}. In 2014, the Activa\textsuperscript{TM} Bioactive (Pulpdent, Watertown, MA) was launched, and that event changed a paradigm in the arena of bioactive types of cement and restoratives. Activa represents the first bioactive dental material with an ionic resin matrix (Embrace resin), a shock-absorbing resin component, and bioactive fillers that mimic the physical and chemical properties of natural teeth\textsuperscript{120}. The ionic resin contains phosphate acid groups. Through an ionization process that is dependent upon water, hydrogen ions break off from these groups and are replaced by calcium in tooth structure\textsuperscript{120}. This ionic interaction binds the resin to the minerals in the tooth, forming a robust resin-hydroxyapatite complex and a positive seal against microleakage, hence, the need for a separate bonding system is eliminated\textsuperscript{120}. The Activa exhibits higher resistance to fracture and chipping than any other dental restorative material due to a patented rubberized-resin component\textsuperscript{120,121}. In the oral environment, this product responds to pH cycles and plays an active role in release and recharge of substantial amounts of calcium, phosphate, and fluoride\textsuperscript{120}. The presence of these beneficial ions that supersaturate dental pellicle and saliva, enables hydroxyapatite or fluorapatite precipitation at favorable pH, mimicking the natural tooth behavior\textsuperscript{120}. Due to its patented resin formulation, Activa contains no Bisphenol A (BPA), Bis-GMA, or BPA derivatives\textsuperscript{120}. At the present moment, this class of bioactive materials is poised to offer substantial benefits to high-caries-risk patients and those with proven allergies to BPA derivatives in conventional RBC products, at a reasonable cost. Although results of in vitro and short-term clinical studies presented favorable results, there
is an urgent need for quality long-term clinical studies to confirm the advantages of bioactive restoratives over currently used restorative materials.

1.4 Classification of Bonding Agents

Since Dr. Michael Bounocore's work has revolutionized the world of adhesive dentistry, significant developments have taken place, which has contributed to an improved understanding of factors affecting the durability of adhesive resin restorations. The complexity of dentin-resin interfaces demands in-depth knowledge of all mechanical, physical, and biochemical aspects that collectively play a pivotal role in the adhesion of RBCs to the tooth structures. The ionic and hydrophilic nature of modern dental adhesives yields porous, unstable hybrid layers that are susceptible to water sorption, hydrolytic and bacterial degradation, and the resin by-products leakage. The hydrolytic activity of host-derived proteases also contributes to the degradation of resin-dentin bonds. Preservation of the collagen matrix is critical for the improvement of resin-dentin bond durability. Based on experimental results and clinical verification, enamel bonding is very predictable and reliable. However, dentin-bonding procedures are not that predictable. This situation is not surprising since dentin contains 17% collagen by volume encapsulated into the hydroxyapatite structure. Thus, the micromechanical retention can be achieved by utilizing the pores of dentinal tubules. These tubules contain fluid, which may prevent adequate bonding. Numerous factors influence the bonding mechanism: the number and direction of
tubules, the presence of cementum, the age of the tooth, the type of dentin, and the pulp approximation \(^{127}\).

Nakabyashi proposed the removal of the mineral phase of the surface layers of dentin by acid etching, which exposes the dentinal collagen matrix as a bonding substrate \(^{128}\). The subsequent penetration and interaction of the hydrophilic monomer within the porous tissue substrate creates a dentin-resin hybrid layer that represents a significant milestone in dentin–adhesive bonding \(^{129}\). The hydrophilic nature of this matrix prompted early researchers to use monomers with both hydrophilic and hydrophobic groups for improved adhesion. The rationale was that hydrophilic functionality would help promote penetration of the monomer into the collagen matrix, leading to the formation of a collagen-resin hybrid layer, whereas the hydrophobic groups would enhance bonding to the hydrophobic resin matrix of the RBC restoration \(^{129}\).

The presence of a smear layer was another hurdle in the dentin bonding process. The smear layer represents debris that is left untouched on the dentin surface after cavity preparation. Etching the dentin surface removes the smear layer and provides a predictable substrate for bonding \(^{130}\). The enamel conditioning by the acid enhances the removal of the smear layer and facilitates the creation of a honeycomb structure receptive to bonding \(^{131}\).

The flow of adhesive into this porous substructure improves the creation of the resin tags at the enamel-restoration interface for improved micromechanical bonding. In contrast, the etchant on the dentin surface removes the mineral phase and smear layer, which exposes the collagen fibril network \(^{132}\). This network appears to be a very complicated structure, wherein the naturally wet condition keeps it from collapsing, thereby allowing adhesive permeation into the substrate for adequate bonding. Research findings indicated that a
slightly moist environment at the collagen fibril network enhances the dentin bonding, which was referred to as wet bonding \textsuperscript{131,132,133}.

Bonding systems have evolved through several generations with improvements in their chemistry, reduction in the number of steps, simplified application techniques, and enhanced clinical effectiveness. New bonding agents were developed to combine one or more steps of etching, priming, and bonding, to reduce standard errors in an already technique-sensitive process. Thus, current bonding agents represent three categories:

- Three-step systems, whereby the etching (and rinsing), priming and bonding steps are carried out separately, are also known as total-etch systems.

- Two-step systems that include two different steps:
  - A. Etching and rinsing step followed by application of a self-bonding primer.
  - B. Application of a self-etching primer followed by a bonding step.

- Single-step systems, which are composed of self-priming, self-bonding adhesives where the etching, priming, and bonding are merged into a single step.

In the late 1980s, a new generation of bonding systems was introduced, with the premise of mildly acid etching of the dentin to partially remove and modify the smear layer \textsuperscript{129}. These systems utilized a phosphate primer to modify and to soften the smear layer. Due to limited penetration of the primer, bonding to smear layer did not reach a clinically accepted level \textsuperscript{130}.

In the early 1990s, complete removal of the smear layer was accomplished with a new generation of bonding agents. These systems use the total-etch technique, which
involved the simultaneous etching of enamel and dentin with phosphoric acid. The system facilitated the establishment of resin tags into tubules and adhesive lateral branches for an enhanced bonding process, while the resin tags sealed the tubule orifices firmly. The total-etch systems exhibited excellent bonding results, which have become a gold-standard for dental bonding.

The next generation of bonding agents was introduced in the mid-1990s. The bonding systems from this generation met demands of the profession to simplify the clinical procedures and to prevent the collapse of the collagen after the acid-etching of the dentin surface. It consisted of two distinct types of adhesive systems. A single bottle system combined the primer and adhesive into one solution to be applied after etching the enamel and dentin. This system exhibited high bond strength to enamel and dentin by micromechanical interlocking with the formation of the hybrid layer, resin tags and adhesive lateral branches. The next generation of bonding employed another type of bonding agent, known as a self-etching primer, which was the combination of etching and priming steps in one solution (phenyl-P and HEMA). However, in comparison to the one-bottle system from the same generation of bonding agents, the bond strength of this method seemed to be less predictable. Moreover, the self-etching primer system resulted in clinically-relevant higher microleakage than what is performed with the one-bottle system. The bonding agents of the next two generations eliminated the need for etching with phosphoric acid by incorporating an acidic primer.

In the mid-1990s, two ingredients: an acidic primer and wetting agent and an unfilled bonding agent were combined. Self-etch adhesives, which comprised an aqueous mixture of acidic functional monomers that were phosphoric acid esters, did not require a separate acid-
etch step and subsequent rinsing. This generation of bonding agents had two unique types of specific two-bottle systems. Type I consisted of self-etching primer and adhesive. This system required the application of self-etching primer first, which is followed by an adhesive. Type II consisted of two bottles or unit doses containing acidic primer and adhesive. In this case, a drop of each liquid was mixed and applied to the tooth. Since the etching and bonding procedures were almost instantaneous, there was minimal potential for postoperative sensitivity. However, these bonding systems showed lower enamel bond strength, which prompted some manufacturers to advocate separate enamel acid conditioning before the application of self-etching adhesive \(^{136}\).

The next generation of bonding systems was introduced in the mid-2000s. This generation of bonding agents, simplified bonding procedures, increased bond strength, and significantly reduced microleakage. Using a single-step technique lessens the clinical application time, but also notably reduces technique sensitivity. Adhesion is consequently obtained micro-mechanically through shallow hybridization and by the supplementary chemical interaction of particular carboxyl/phosphate groups of functional monomers with remaining hydroxyapatite \(^{137}\).

The latest advances in dental bonding systems were launched in 2012 in the form of universal bonding systems. These single-bottle, multi-mode bonding systems are designed to bond to tooth structures in either the etch-and-rinse or the self-etch mode, depending on the clinician's preference. According to the adhesion-decalcification concept proposed for self-etching adhesives, aggressive demineralization of hard tissues by strong acids will result in the dissolution of apatite crystallites. Demineralization reduces the opportunity to establish a chemical bond between functional adhesive resin monomers and hydroxyapatite and also
reduces the potential for creating nano-layers of calcium precipitates with phosphate resin monomers with extended spacer groups\textsuperscript{138,139}. Research has shown that universal adhesives with the acidic resin monomer 10-MDP (10-Methacryloyloxydecyl dihydrogen phosphate), which has been acknowledged as a gold-standard functional monomer, responsible for chemical bonding to hydroxyapatite, demonstrated improved bond strength, increased resistance to hydrolytic degradation, and reduced nano leakage\textsuperscript{140,141}.

The ideal bonding system should be biocompatible, have an excellent bond strength to dentin, be resistant to degradation and be simple to use. Unfortunately, even though extensive research has been achieved in the past 50 years of adhesive dentistry, the ideal bonding system has not been realized as yet. However, it is crucial to understand the nature of bonding to see the clinical implications of bond failure, which ultimately lead to failure of RBC restorations. In a typical case with weak bonding to dentin, the low bond strength is not sufficient to resist the forces of RBC polymerization shrinkage (about 24 MPa in Class I cavities). Thus, one or more of the bonded walls could exhibit some level of separation and gap formation, which can create bacterial leakage through the permeable dentin, resulting in the pulp irritation\textsuperscript{142}.

1.5 Evaluation of Photopolymerization Efficiency

Light-polymerization units (LPU), introduced into dental practice in the 1970s, paved the way to simplified restoration procedure. A large number of studies has been conducted on several types of light sources, including quartz–tungsten–halogen (QTH) and
light-emitting-diodes (LED) \(^{305-317}\). In today's contemporary dental office, LED LPUs are the primary source of photopolymerization. In the majority of LED LPU light-spectrum ranges from 400 nm to 515 nm, with a high peak around 468 nm, referred to as monowave LED LPU, the light spectrum which is the most efficiently absorbed by a combination of camphorquinone (CQ) and a tertiary amine (Type II system) \(^{97,143}\). On the other hand, LED LPUs that are capable of generating more than one peak, are referred as multiwave (Polywave\(^{®}\)) LED LPUs, capable of activating the alternative photoinitiators, in addition to the CQ systems. The Polywave\(^{®}\) technology is registered trademark of Ivoclar-Vivadent. The light spectrum of multiwave LED LPUs has a high peak around 470 nm and secondary peak around 400 nm depending on the manufacturer's specification for the coverage of alternative photoinitiators (Type I systems) \(^{97,143}\). For example, phosphine oxide derivatives diphenyl (2, 4, 6-trimethylbenzoyl) phosphine oxide (TPO) and phenylbis (2, 4, 6-trimethylbenzoyl) phosphine oxide (BAPO), like any other Type II photoinitiator system, do not require a tertiary amine for generating free radicals \(^{143}\). The TPO high peak absorption is around 400 nm and features much higher absorption efficiency and quantum yield \(^{143,144}\). It has been reported that TPO is very efficient visible light photo-sensitizer, comparable to CQ for the initiation of RBC photopolymerization \(^{145}\). However, there are other commercially available photoinitiators such as phenylpropanedione (PPD) and Ivocerin\(^{®}\), incorporated into various formulations of commercially available RBC materials. The physical properties of polymerized RBCs are affected by the generation of primary radicals during the initial stage of polymerization \(^{143}\). Thus, free radicals created in this process, attack the carbon double bonds of the monomers, and rapidly convert the resin to a cross-linked three-dimensional polymer network \(^{143}\). Ideally, during the polymerization process, all monomers should be
converted into polymers. However, in clinical settings as well as under laboratory conditions, not all monomers are polymerized. Also, the monomer molecules exhibit loosely bonded configuration by weak Van der Waals force. Following the polymerization, the monomers are tightly linked by covalent bonds into a polymer with a smaller distance between the molecules, which is the principal factor for polymerization shrinkage 97. Inadequately photo-polymerized RBCs exhibit inferior mechanical and physical properties, which ultimately lead to compromised longevity of the restoration. Research has shown that degree of conversion (DC) is a co-determinant of mechanical properties of restorative RBC materials 146. Furthermore, the literature has also shown a significant correlation between DC and hardness, modulus of elasticity and flexural strength of RBCs 147. A large number of factors can influence the effects of photopolymerization. The filler particle size, geometry, and filler load, polymeric matrix, refractive indices, radiant exposure, and a distance from the light probe to the RBC surface. In addition, the polymerization protocol can also influence the DC of RBCs and thereby their mechanical properties 148, 149. The recent photopolymerization studies support the assumption that LPUs irradiance and exposure time independently affect the mechanical and physical properties of RBCs 150, 152, 153. Adequate polymerization of RBCs is needed for desired physical and mechanical properties, biocompatibility, and longevity 154, 155.

1.5.1 Degree of conversion

During the RBC photopolymerization reaction, the radiant exposure (RE) and irradiance are principal factors that influence the degree of conversion (DC) and ultimate clinical success of the restorations 156-160. The exitant irradiance (mW/cm²) represents the
flux incident over the total surface area of the light probe, while RE (J/cm²) is the product of the exposure time and the incidence irradiance at the RBC surface. During the free-radicals photopolymerization, double bonds in the resin of the RBCs are converted into single covalent bonds, enabling converting monomers into the linear or cross-linked polymers. Thus, the DC represents the ratio of converted single bonds to a total number of remaining double bonds. Aforementioned is an important determining factor for polymerization kinetics, which is highly correlated to mechanical, physical, and chemical properties of RBCs. Fourier transform infrared (FTIR) and Raman spectroscopy are broadly used for characterizing the DC of polymerizable RBC materials. Both quite similar techniques produce molecular changes in vibrational energy state by subjecting them to excitation radiation in selected spectral regions. However, FTIR and Raman spectroscopy differ in the means by which photon energy is transported to the molecules. Thus, FTIR is an absorption technique, while Raman spectroscopy represents a scattering method. Since the bands in FTIR spectra are due to polar functional groups while the bands in Raman spectra are due to nonpolar functional groups, FTIR and Raman spectroscopy are complementary techniques. The process of measuring DC (methacrylate-based RBCs) is mainly based on comparing the frequency band (1634 cm⁻¹), which corresponds to C=C vinyl group stretching vibration and those of an internal standard frequency band (1608 cm⁻¹). That frequency band corresponding to very stable aromatic rings during the polymerization process, to those frequencies of an unpolymerized RBC material. Even though FTIR and Raman spectra are parent techniques, some studies are more efficiently conducted in FTIR than in Raman spectroscopy, depending on the chemical formulation of tested materials.
The literature showed that differential thermal analysis (DTA) using a split fiber-optic light source was a convenient and a valuable method for investigating polymerization performance of light-activated RBCs. However, this approach introduced by McCabe showed some drawbacks with different composition of commercial RBCs, empowered with nano-technology. The literature revealed that the most meaningful evaluation of DC of dental resin materials is obtained by utilizing FTIR and Raman spectroscopy. However, the relative microhardness (bottom/top ratio) can provide reasonably accurate estimates.

Rueggeberg and Craig reported that microhardness values exhibit more sensitivity in identifying minuscule changes in the DC after the network is cross-linked, in comparison to FTIR. The literature has shown that radiant exposure (J/cm²) and irradiance (mW/cm²) of the LPUs are highly correlated to DC of RBC materials. However, the study conducted by Selig showed that high irradiance values had a significantly high effect on DC, compared to time increase of RE. The high irradiance could enable a more substantial number of free-radicals due to a higher rise in exothermic heat. The subsequent temporal viscosity of a polymeric matrix decreases, allowing the polymer chains increase mobility, consequently resulting in a much higher DC. Thus, the concept of exposure reciprocity law, which proposes the reciprocity between the incident irradiance and exposure time, suggests that observed DC values will be similar if the same amount of radiant exposure is delivered to the RBC surface, however, it is not applicable to the majority of contemporary RBCs.
1.5.2 Degree of crosslinking

Dimethacrylate monomers produce a highly crosslinked network after induced photopolymerization. Glass transition temperature can indirectly measure the degree of crosslinking, while the frequently used softening test can also determine the degree of crosslinking in a relatively simple way. The degree of crosslinking, which is closely related to the function of the DC, is an influential determinant of photopolymerization efficiency, which has clinically significant implications for the mechanical properties and ultimately the longevity of RBC restorations. During the photopolymerization reaction, the conversion of C=C double bonds into primary covalent C-C bonds, which allow high mobility and free rotation of polymer chains results in a highly crosslinked structure. However, the double bonds conversion is never complete and always contains considerable quantities of unreacted double bonds. Therefore, these residual double bonds can influence the degree of crosslinking, by reacting with propagating radicals to form a crosslinked, primary, or secondary cycle. The primary cycle is created when a radical reacts with an unreacted double bond on its kinetic chain, while the reaction of the free radical on a different kinetic chain, which becomes crosslinked, is called a secondary cycle. The primary cycles create microgels and lead to heterogeneity in the polymer network, with co-existence of loosely crosslinked and more highly crosslinked microgel regions. The formation of the cycles enhances a higher local conversion rate, with almost no influence on the chain mobility.

The literature reports a strong correlation between the degree of crosslinking and fracture toughness, elastic modulus, solvent resistance, and glass transition temperature of RBCs. Studies have shown that polymerization modes had an essential influence on
the DC and mechanical properties of RBCs. Thus, at the same time, polymerization modes have an impact on a degree of crosslinking which subsequently lead to the formation of more linear polymer networks \(^{168-171}\). The pulse delay or slow start mode has often been correlated with the creation of a polymer structure with a lower degree of crosslinking, which is more affected by an organic solvent attack during the softening tests \(^{172}\). Furthermore, a slow start polymerization technique generates a few cycles per area, which creates a more linear polymer structure with relatively few crosslinks. In contrast, a rapid start continuous polymerization technique creates a multitude of growth cycles per area, resulting in a polymer with a higher degree of crosslinking \(^{172,173}\).

These results supported the sentiment, previously seen in DC that incident irradiance and not radiant exposure has a tremendous influence on the degree of crosslinking \(^{154,155}\). The increased concentration of crosslinks has been correlated with improved physical properties and stability of polymers \(^{168}\). It has been established that DC does not provide a complete characterization of polymer structures, due to polymers with similar DC may exhibit a different degree of crosslinking \(^{168,171}\). The assessment of the degree of crosslinking can be performed by measuring a resin glass transition temperature, using the Arrhenius plot \(^{175}\). Within the dimethacrylate monomers, a degree of crosslinking influences the reduction of molecular mobility, which increases the transition temperature \(^{175}\).

The characterization of the crosslinked network structure presents a challenge due to the structural heterogeneity that develops in the polymer during photopolymerization. Although some studies have used the ethanol solution softening test, a hardness measurement is taken before and after ethanol immersion, as an alternative method of evaluation of the degree of crosslinking. Furthermore, some researchers advocate acetone solutions for
softening test. It has been recognized that crosslinked methacrylate networks swell when exposed to organic solvents. Apparently, the covalent bonds forces between the polymer chains are exceeded by the forces of attraction between solvent molecules and components of the chains. Thus, a higher degree of crosslinking is fundamental for better mechanical properties and enhanced resistant to solvents.

1.5.3 Mechanical properties of RBC materials

The relationship between mechanical properties of RBCs and their intraoral performance has been a subject of numerous studies. For instance, Ferracane showed that mechanical properties such as Fracture Toughness (FT) and Flexural Strength (FS) of RBCs are strongly correlated to the clinical performance of RBC restorations. Likewise, a strong inverse correlation exists, between wear and FT, and wear and FS, and a weaker inverse correlation between wear and hardness. Moreover, for the quicker and meaningful characterization of mechanical properties, the identification of one parameter can lead to the discovery of other properties, based on these correlations. For example, by obtaining hardness data and retrieving the correlation between hardness and elastic modulus (EM), it could be possible to estimate the EM of any RBC material. However, comparing results of different studies and the variability among them makes it difficult to make a meaningful conclusion, due to the differences in their experimental methodology. For example, the FS values are usually enhanced when a higher cross-head speed of the universal testing machine is applied.
The effect of filler (load, composition, size, etc.) on mechanical properties of RBCs has been widely demonstrated. It has been observed that as a result of increased filler content, the modulus of elasticity and surface hardness increase accordingly, while volumetric shrinkage decreases\textsuperscript{183,184}. Some researchers are considering the more biomimetic approach, formulating RBCs with the closest possible mechanical properties of dentin, in which Young's modulus (20–25 GPa) and ultimate tensile strength (UTS) values in the range of 52–105 MPa\textsuperscript{185}. According to ISO 4049 international standards requirements, FS and EM are to be measured by a three-point bending test on 25mm×2mm×2mm sample\textsuperscript{186}. However, these standardized dimensions are not clinically realistic, considering the teeth diameter and length average. Due to the overlapping irradiation required to polymerize the entire portion of the specimen, may render the reliability of this testing procedure somewhat questionable\textsuperscript{187}. The FT is an important mechanical property, which characterizes the relative resistance to crack propagation from the surface or inherent flaws in the RBC material\textsuperscript{188}. Innovative technologies currently employed, such as fiber or whisker reinforcements have produced very significant enhancements in FT of RBCs, however, not to the level of high toughness ceramics or casting alloys, and this may be what is required to render the materials substantially fracture resistant in the clinical settings\textsuperscript{189}.

The testing procedure of FT and FS are similar, with the exception that FT specimens have a notch, and the same overlapping irradiation protocol is applied with this testing method. Diametral tensile strength test (DTS) has been designed to test brittle materials by utilizing a cylinder-type specimen that is subject to compressive load across its diameter. It has been observed that materials which exhibit plastic deformation would produce false DTS values\textsuperscript{16}. Although DTS test is not a part of the ISO 4049:2009 standards, it was recognized
as technically reliable and a straightforward test for the assessment of RBC mechanical properties. However, DTS test can provide useful information about the effectiveness of RBC polymerization and in conjunction with other measuring methods can provide meaningful data on the mechanical properties of given materials. Vickers and Knoop microhardness tests are routinely employed for testing of RBCs' mechanical properties.

Hardness (H), represents an important parameter in the characterization of the surface properties of the material on a microscopic scale, which is established as the ratio of the applied load (P), to the contact area (A), which caused subsequent indentation impression:

\[ H = \frac{P}{A} = \beta \frac{P}{d^2} \]  

(1)

Where \( d \) represents the size of indentation, and \( \beta \) represents a constant related to the geometry of a given indenter. Vickers and Knoop are the most frequently employed microhardness tests for characterization of RBC materials by utilizing a pyramid-based indenter. The Vickers hardness number (VHN) is determined by using the contact area of the indentation impression and the parameter \( d \) in Eq. (1), which is described as an average of the two diagonals of the resultant square-shaped impression. Thus, the \( \beta \) constant for VHN calculation is 1.8544. The Knoop microhardness test uses a pyramid-based indenter with the length to width ratio of 7:1 and with corresponding face angles of 172.5 degrees for the long edge and 130 degrees for the short edge. The Knoop hardness number (KHN) is calculated as applied load (measured in kilograms-force) divided by the square length of the long diagonal of the indentation in mm, and the constant of indenter associating the projected area of the indentation to the square of the length of the long diagonal, equal to 0.07028.
Although the measurement of a residual surface plastic impression is the basis for the hardness measurement, however, this surface property test represents an elastic-plastic surface deformation process. Thus, the relative importance of reversible (elastic) and irreversible (plastic) components of surface deformation induced by the hardness indenter could be evident in the elastic recovery during unloading of the indenter. Therefore, this elastic depth recovery following the maximum indentation should be taken into microhardness calculation. The literature has shown, especially concerning RBC materials, the inequality between the plastic zone beneath the indentation and the surrounding elastic matrix exists. The elastic recovery is highly related to the surface geometry of an indenter, which differentiates the elastic recovery of Vickers indentation in comparison to Knoop indentation. The elastic recovery attributed to Vickers indentation usually develops along the depth of the indentation, while the diagonal length of the surface impression remains unchanged, in contrast to the Knoop indentation, where the elastic recovery appears as a result of a minor diagonal contraction of the indenter. The Knoop microhardness computation takes the length of the longer diagonal only into the calculation of KHN, thus making this method preferred for its reliability over other methods. A linear correlation exists between Knoop microhardness and the mechanical properties of the RBC; and Knoop microhardness and the irradiance of LPUs.
1.5.4 Shrinkage and shrinkage stress

Despite significant developments in the field of adhesive dentistry, the occurrence of RBCs’ polymerization shrinkage and shrinkage stress remains a clinically relevant issue. During the polymerization reaction, the distance between monomer molecules becomes reduced by the transitional changes from loosely bounded Van der Waals forces, into tightly linked covalent bonds of the polymer network, which produces the shrinkage stress. Cavity-restoration interface exhibits the maximum shrinkage stress force, with degradation of that interface resulting in subsequent microleakage and gap formation. The consequences of gap formation may increase the possibility of tooth hypersensitivity and an adverse pulpal reaction, with a high probability of detrimental effects on restoration longevity.

Stress represents a complex interaction among the following: the resin viscosity, the volume shrinkage, the polymerization rate, the DC, modulus development, and network structural evolution. However, each of these properties cannot be individually manipulated and studied without having a significant impact on the others. Thus, polymerization shrinkage stress is multifactorial, being related to cavity configuration and RBCs properties.

The cavity configuration properties are defined by the geometry and size of the preparation and its C-factor. The C-factor, or cavity configuration factor, represents the ratio of bonded to non-bonded preparation wall areas, which have also been a subject of intense debate in the literature. Empirically, the higher C-factor, the higher the stress level generated. According to the literature, when a rigid (non-compliant) testing system is utilized, a direct relationship between the contraction stress and C-factor value was reported, while results of the studies using a less rigid, more compliant set-up, showed an inverse
relationship\textsuperscript{194,195}. However, from a clinical standpoint, the C-factor seemed to be a valid parameter for the comparison of restorations with identical shapes and volumes, as reported in experimental settings\textsuperscript{196}.

The material properties associated with RBCs’ polymerization shrinkage stress include filler content, resin-matrix composition volumetric shrinkage, and elastic modulus and viscous flow\textsuperscript{197}. The literature has shown that RBCs with a high filler content exhibit low volumetric shrinkage and high stiffness\textsuperscript{195-197}. Furthermore, strain capacity is inversely correlated to the filler content of RBCs\textsuperscript{198}. For instance, microfilled RBCs usually experience lower elastic modulus, a higher strain capacity and similar volumetric shrinkage properties in comparison with hybrids, due to their relatively lower filler volume percentage, which is in a range from 35\% to 50\%\textsuperscript{199}.

Viscoelastic properties define another essential factor in contraction stress development of RBCs during photopolymerization, the flow capacity at initial stages of the polymerization, and the elastic modulus generated during the polymerization reaction\textsuperscript{200}. Composite flow is influenced by the structure of individual molecules, crosslinking, the filler/matrix interfacial characteristics, reaction kinetics, and the C-factor. Flow can happen quickly when the RBC is allowed to shrink, which means that flow can be increased when the preparation C-factor is low\textsuperscript{201}. Polymerization shrinkage is positively correlated to the DC. Thus, an increase in the DC leads to higher polymerization strains because more covalent bonds and more highly cross-linked networks are formed\textsuperscript{202}. The higher DC values of RBCs correlate with improved mechanical and chemical properties, color stability and biocompatibility. Therefore, the stress reduction cannot be accomplished at the expense of adequate DC.
Various methods are aimed to measure polymerization shrinkage stress. Shrinkage strain-rate and stress are measured during the polymerization reaction with a tensiometer, based on the cantilever beam deflection theory \(^{203}\). Various devices and methods have been used for the measurement of polymerization shrinkage regarding volumetric and linear shrinkage and the cuspal displacements. The reasonably straightforward, indirect techniques to measure shrinkage include the microleakage assessment test and finite element analysis, which utilize a three-dimensional micro-CT data \(^{203}\). For maximum accuracy and clinical relevance, the instrument compliance should be as close as possible to the features of a natural tooth \(^{203}\). Clinical performance of Bis-GMA based RBCs could be enhanced by maximizing the DC and elastic modulus, decreasing volumetric shrinkage (maximizing viscous flow), and by minimizing the polymerization stress \(^{203}\). Another stress reduction mechanism readily available is to increase the compliance of the preparation walls by applying an intermediate, low-modulus layer, using a low-shrinkage flowable RBC material \(^{203}\).

1.5.5 Depth of polymerization

Achieving sufficient photopolymerization of RBC materials is a critical parameter to maximize mechanical properties of the restoration and to obtain a desirable clinical outcome. The depth of polymerization (DP) of light-activated RBCs depends on the filler composition and resin formulation, resin shade and translucency, photoinitiators content, the intensity and spectral distribution of the LPU, and finally on the irradiation protocol. There are two DP assessment techniques: direct and indirect. The indirect method for DP assessment includes scraping tests \(^{204}\), the dye uptake tests \(^{205}\), and the surface microhardness tests \(^{206}\). The direct
method measures the polymerization efficacy by utilizing spectroscopy, as a part of the DC assessment, which has not been routinely used due to the cost associated with this complicated methodology.

The simple scrape test has been modified and became a part of ISO 4049 standardized testing procedures. The test utilizes a 4 mm diameter stainless steel mold, filled with the RBC, and polymerized with the LPU from a single side only. At the non-irradiated side of the specimen, a plastic spatula is used to scrape any material that is soft (inadequately polymerized), leaving remaining hard and apparently polymerized material. The measured remaining thickness of the RBC specimen is divided by 2 and is referred to as the DP scrap test value, expressed in mm. This technique, while simple, it has several disadvantages. The method does not provide an accurate estimate of the polymerization quality in any region of a given material, especially in the deeper layers adjacent to the soft, slightly polymerized resin which has been removed. The results of some studies found that scraping methods severely over-estimated DP as compared to relative hardness testing or DC analysis. The results verified that DC appeared to be the most sensitive test for DP. A good correlation exists between the Knoop microhardness testing and infra-red spectroscopy. Microhardness testing is the most popular method for investigating factors that influence DP, because of its relative simplicity and accuracy.
1.5.6 Biocompatibility

Although RBC products are known to be highly stable structures, they are susceptible to degradation, because of insufficient polymerization. Several components could be released from RBC restorations into the oral environment. Thus, biocompatibility is not a direct way to assess the photopolymerization efficiency. However, it is an essential prerequisite of all materials that are placed into a biological system to be bio-friendly to the environment. RBCs can affect the oral cavity in at least two ways: through the elution of bioactive substances and by a quick and sharp temperature increase during polymerization. Sufficient polymerization renders superior mechanical, physical, and chemical properties of RBCs, which prevents and limits leaching of potentially harmful components from the materials.

The cytotoxicity of RBCs has been attributed to the leaching of unpolymerized monomers, such as products of an incomplete polymerization and consequently the by-products of the resin matrix degradation processes in the oral cavity. The most commonly used monomers in RBC compositions include Bis-GMA, TEGDMA, and UDMA, all of which have been identified as cytotoxic molecules. Further, literature has shown particular concern with TEGDMA, which seems to be a mutagenic compound in mammalian cell assays. It appears that these cytotoxic molecules induce gene mutations, by covalent binding to the host DNA. Several factors influence the release of unbound substances from polymerized RBC materials. The literature shows that DC values are highly correlated with the amount of leachable components from any given RBC material. The solvent composition, which is applied for the extraction, affects kinetics and mechanism of the elution process. The chemical characteristics, as well as the size of leachable...
substances, moderate diffusion through the polymer network. The current concept presumes that smaller molecules have enhanced mobility and exhibit a faster elution rate \(^{213}\).

Chemical degradation of RBCs can be attributed to hydrolysis and attack of salivary enzymes in the oral cavity \(^{213}\). Studies showed that percolated monomers enhance bacterial growth and are responsible for glutathione depletion, which is a critical factor in pulp or gingival cell apoptosis and production of reactive oxygen species (ROS) \(^{214}\). Additionally, leached substances are associated with a variety of allergic reactions \(^{214}\). Therefore, the toxicology results from the cell cultures have revealed that monomers released from the RBCs generate ROS and, therefore, affect the redox balance in the oral tissues cells \(^{208-212}\).

The occurrence of diffusion of small molecule monomers throughout the polymer network is more easily accomplished, due to their small and flexible structures, polar ends, and flexible and smaller suspended groups \(^{215}\). TEGDMA is considered the most frequently eluted monomer among RBC materials, because of its monomer molecular structure and higher solubility \(^{213,214,215}\). Compared with TEGDMA, however, Bis-GMA monomer is reported to be much less soluble because of its hydrophobic nature and reduced diffusion in liquid environment \(^{216}\). Furthermore, the hydrophilic monomers such as HEMA, which is very abundant in bonding agents and TEGDMA, predominantly found in RBCs, are the monomers capable of diffusion through the dentin, endangering the pulp vitality \(^{213,215}\).

The magnitude of monomer diffusion is displayed in a millimolar/Liter (mmol/L) range, which is the clinically significant concentration that could cause detrimental effects on pulpal homeostasis \(^{217}\). The literature showed that diffusion rate increases when the remaining dentinal pulpal coverage thickness is less than 1mm, and the cavity has been conditioned with acid before the bonding procedures \(^{218}\). In addition, experimental research
showed that HEMA pulpal concentrations could be in the range of 1.5–8 mmol/L, whereas TEGDMA concentrations could be in the range of 4 mmol/L, respectively \(^{219,220}\). These concentrations have been found to cause significant cytotoxicity through mechanisms associated with oxidative stress, ROS production, and depletion of intracellular glutathione with the consequences of cell death, mainly via apoptosis. Long-term exposures to nontoxic concentrations of HEMA (0.05–0.5 mmol/L) and TEGDMA (0.05–0.25 mmol/L) significantly delay physiological migration, odontogenic differentiation, and mineralization process of human deciduous teeth pulp stem/progenitor cells in a concentration-dependent manner \(^{221}\). Furthermore, just a single exposure to higher HEMA concentrations of at least of 2 mmol/L and TEGDMA at least of 1 mmol/L have caused inhibition of the formation of reparative dentin entirely \(^{220,221}\).

The methodology used to evaluate eluted compounds from RBC materials into biological fluids is based on chromatography, which is an analytical procedure that isolates molecules related to differences in their structure and composition \(^{221}\). High-performance liquid chromatography (HPLC) is now one of the most influential tools in analytical chemistry, capable of separating, identifying, and quantifying the compounds that are present in any sample, dissolved in a solvent \(^{221}\). However, reversed-phase liquid chromatography appears to be the most preferred method in a dental materials analysis \(^{222}\). Improvements in the properties of RBCs to reduce and prevent some leachable compounds are continually being studied. Thus, improvements in the photopolymerization quality could minimize all detrimental consequences to the pulp health.
1.6 Evolution of Light Polymerization Units (LPUs)

The LPUs have become the essential instruments in the contemporary dental practice because a large number of dental procedures requires some photopolymerization. These units emit a beam of light having a specific spectral output that activates photoinitiators in a wide range of photopolymerizable materials. Since their introduction into the dental profession in the 1970's, the evolution of LPUs started from UV polymerization and developed to visible light polymerization. During this time, LPUs became smaller, battery-powered, and capable of delivering a high amount of energy in a brief time.

From the historical perspective, polymerization technology was adapted from the chemical industry and modified for the use in dentistry. The first LPUs were designed to emit ultraviolet light. The typical polymerization time was the 40s, but a 60s exposure provided enhanced results. Initially, the technology was far from perfect, but it was revolutionary for that era. The limitations associated with UV polymerization included limited light penetration through the RBC material (limited depth) and health hazards related to UV lights exposure on the eyes. However, UV polymerization was short lived when Dr. Bassojuny at the University of Manchester School of Dentistry, in 1976, placed the first visible light polymerized RBC restoration. The Imperial Chemical Industries of England developed the novel technology and modified for dental use. The new visible light photoinitiation system was based on the photoinitiator camphorquinone along with a tertiary amine co-initiator. This system underwent through several modifications over the years. However, it is still in use with today's modern RBC materials.

The initial light sources used to photopolymerize the new RBC were based on quartz–tungsten–halogen (QTH) lamps developed with the Johnson and Johnson partnership. The
new venture launched the FotoFil restoration system and QTH dental light source. Although this new technology had the capability to adequately photopolymerize a 2 mm thick increment of RBC material, the QTH technology could not eliminate the hazard for ocular damage without an appropriate eye protection. The QTH LPU used an incandescent quartz light bulb consisting of a tungsten filament surrounded by a halogen gas, which emitted a beam of filtered white light which provided a broad spectrum between 400 and 500 nm. Although these light sources were manufactured with relatively low-cost technology, the short lifespan of the QTH light bulb with a gradual degradation of the filter, compromised their light output consistency. The QTH LPU exhibited a low energy performance because the filter system wasted a considerable amount of radiation, which transferred the majority of the unwanted radiation into heat. Therefore, a cooling mechanism was needed with these light sources. The QTH became the mainstream LPUs, for many years. Even after the introduction of LED LPUs in the 1990s, the QTH LPUs underwent a series of modifications and improvements, in such a way that the bulb power increased from 35W up to 100W. The QTH LPUs have been typically used for the 40s to 60s polymerization exposure, for a 2 mm thick increment of the RBC. The inconvenience for the cooling timeout was a disadvantage. Furthermore, the excessive heat produced by these LPUs reduced their clinical effectiveness and impacted their lifespan significantly.

In the late 1990s, the next generation of LPUs was developed, with the most promising technology at the time: the argon laser units and plasma-arc (PAC). The principal reason for their introduction to dental practice was to enhance the effectiveness, and to increase the magnitude of the light output and to shorten the exposure time.
The argon laser (Light Amplification by Stimulated Emission of Radiation), with an active medium of argon gas, unlike QTH LPUs, does not employ filters. It produces a collimated (focused, non-divergent) beam of coherent energy, when applied to a particular target, resulting in a more consistent radiant exitance over the tip-to-target distance. Unfortunately, the major output wavelengths were out of the absorption range of CQ, and thus, this type of laser was nowhere near as effective as it could have been, if the output had been a slightly shorter wavelengths. Although this novel technology showed some exceptional improvements (coherent beam of light energy), it experienced some drawbacks. For instance, the light beam should not be allowed to be directed to the eyes, as the eye exposure would result in an immediate retinal damage. Although the size, weight, and portability of newer argon laser LPUs have been improved dramatically in recent years, they often take considerably more space than QTH LPUs. Laser LPU generate a substantial amount of heat, the cooling fan tends to be noisy, and these LPUs were very expensive. Thus, these LPUs never gained popularity. However, laser polymerization demonstrated an immediate higher DC than that obtained with the QTH LPU. The laser LPUs enhanced RBCs polymerization, which resulted in improved physical properties and bond strengths.

The Plasma arc (PAC) LPUs, use technology that uses plasma for the light source. The PAC, initially designed in France, consisted of two tungsten electrodes separated by a small distance, embedded in a high-pressure xenon gas chamber. When electric current passes through the plasma, it generated the emission of the UV light with a broad spectral range. The PAC LPUs uses sophisticated bandpass filters to curb UV and IR radiation, while the light is delivered by utilizing a three-foot-long liquid light guide. Early PAC LPUs produced spectral output wavelengths between 370 to 450 nm (low spectrum units) or
between 430 to 500 nm (high spectrum units), and a typical radiant exitance was around 2,000 mW/cm$^2$. The early PAC light (the Apollo) produced broad, banded, white light. The different tip ends had filters that only passed light of shorter or longer wavelengths to pass either wavelengths more near violet or more near blue. The clear tip passed all wavelengths, emitting white light that was used to enhance tooth bleaching.

The PAC LPUs were designed to produce a 3s exposure, while an upgraded version of these LPUs was launched with four adjustable polymerization modes with exposure up to 10s $^{229}$.

Although PAC LPUs exhibited an adequate RBCs' polymerization, faster than other LPUs, they were frequently associated with a higher risk of pulpal damage $^{229}$, as result of their increased heat production compared to the QTH LPUs. Furthermore, due to a relatively high cost, this technology had limited utilization in dental practices.

The LED LPUs are the most popular and the most current source of photopolymerization in dental practices. The light-emitting diode technology uses two semiconductor crystals, type "n" and type "p" with different electron density $^{230}$. When electrical current passes through these crystals, light is generated at the "np" junction, with the wavelength determined by composition difference between the semiconductor substitutes.

The LED LPUs produce high efficiency and medium-intensity light, which does not require filters nor fans. Unlike QTH light sources, LED LPUs generate light within a narrow spectral range. For instance, gallium nitride diodes produce light with wavelengths between 450 and 490 nm with a peak at 460 nm. LED light sources often require less power to operate, which gave them the ability to be smaller in size, portable, and battery operated. The LED LPUs have shown another advantage: extended service life compared to any other light types. For instance, the halogen bulbs' life expectancy, under best condition, can last a hundred hours,
whereas the LEDs can last thousands of hours $^{230}$, which could be a reason behind the enormous LED LPUs popularity among dental practitioners. The spectral output of the first developed LED LPUs was not tailored to match the maximal absorption of CQ photoinitiator. However, it happened to be a close match. The evolution of LED LPUs can be observed as a function of the power increase, the ability to polymerize alternative photoinitiators, and the LPUs beam profile homogeneity $^{243}$. The first generation of LED LPUs started in the early 2000s, with the launch of the Lux $^9$Max (Akeda Dental A/S, Lystrup, Denmark), a product based on prototype patented in the US $^{231}$. It was a first ever, large, pen-like, NiCad battery- powered LPU, having seven discrete LEDs. The concept of the first generation of LED LPU design was to use multiple single-emitting LEDs, with each LED being able to produce 30 to 60mW of radiant power, embedded into an axial array to provide sufficient spectral power output to start activation and subsequent photopolymerization $^{232}$. Other manufacturers followed the lead and launched their versions of LED LPUs.

Performance of the first LED LPUs was not in line with the high expectation, as they were relatively low-powered, compared to the traditional QTH LCUs at that time. The early results of LED LPUs performance, in comparison with QTH LCUs, as well as issues with NiCad batteries, led to some unanticipated, negative predictions for LED LPUs future $^{233}$. However, a high success achieved in the blue LED semi-conductor research boosted the efficiency of the first generation commercially available LED LPUs. Therefore, in late 2001, a launch of the Elipar$^{\text{TM}}$ FreeLight (3M/ESPE, St. Paul, MN) dramatically changed the outlook of LED LPUs market, by increasing the efficiency and the performance of LED light sources $^{234}$. The new Elipar$^{\text{TM}}$ FreeLight had an innovative design, with a 10 mm light probe,
incorporating 19 discrete LEDs in an array and was capable of generating a radiant exitance of 400 mW/cm². The success achieved by the incident irradiance level increase was partly contributed to the use of a tapered, fused glass fiber light guide. According to the manufacturer's claim, the radiant exitance level produced by new LED LPUs was equivalent to the 800 mW/cm² value generated by the conventional QTH LPUs.

The second generation of LED LPUs started in the early 2000s, due to advances in the LED chip industry and incorporation of the new 1-W chips into the LED arrays, which enabled the production of more powerful, single LED devices. In addition, the chip manufacturers started fabricating chips specifically within the wavelength required for the polymerization of RBC materials. Examples of these single more powerful LED emitters were the Luxeon LXHL-BRD1 in 2004, which produced 140 mW (1 W chip) or 600 mW (5 W chip) of blue light. Moreover, the more recent LED Engin Inc., LZ4-00B200 in 2012, which produced 4,200 mW or 5,600 mW of radiant power depending on the chip. The launch of the 2nd generation LED LPUs officially started with Elipar™ FreeLight 2(3M/ESPE, St. Paul, MN), an improved version of Elipar™ FreeLight. The new LED LPUs successfully increased 2.5 times radiant exitance, by utilizing the tapered waveguide (the so-called “turbo-tip”) to boost emitted irradiance. Nickel metal hydride batteries were the power source that enabled the breakthrough. Other manufacturers started launching different designs: a first in this group, L.E. Demetron II® (Kerr Dental, Orange, CA) began in 2005. This unit had a conventional pistol grip design, with a built-in cooling fan, which was a compromise to heat sink design. However, like other manufacturers, the light guide exhibited a tapered turbo-tip to boost the incident irradiance. Later, manufacturers started to experiment with light probe design, which led to the launch of the SmartLite PS® (Dentsply,
Milford DE), an ergonomic-pen-style light, which was small (24cm long), lightweight (100g), and silent (no fan) \(^{239}\). The manufacturer claimed that device could generate a radiant exitance up to 950 mW/cm\(^2\). The advantage of this design allowed LPUs to produce a more unidirectional light, with a substantial reduction in light loss, without a light guide between the light source and the material to be polymerized. In addition to an increased irradiance level, this innovation led to lower power consumption, longer battery life, and most importantly, the significant reduction in heat production. This innovative technology helped the industry to resolve the disadvantage associated with tapered light guides: more divergent light beam and a smaller light tip.

In late 2010, this problem seemed to be resolved with the innovative design of Elipar\textsuperscript{TM} S10 (3M ESPE. St. Paul MN). This light featured a 10 mm diameter, and a parallel glass fiber light guide \(^{240}\). The manufacturer claimed that the LPU could generate the radiant exitance up to 1,200 mW/cm\(^2\). The second generation of LED LPUs, have experienced tremendous improvements, a substantial radiant power increase, which enabled sufficient photopolymerization in shorter exposure time. All previously mentioned LED LPUs were designed to produce a single peak of spectral irradiance to match the maximum absorption spectra of CQ photoinitiator system, they are referred as single-peak, or monowave LED LPUs \(^{243}\).

The third generation of LED LPUs provided an extended light spectrum in the violet range, to match the range of alternative photoinitiators, as well as the CQ photoinitiator spectra. Thus, the third generation of LED LPUs have the blue-light chips with a spectrum from 420 nm to 510 nm and the violet-light chips with a spectrum from 380 to 420 nm. The new LED generation was marked by significant improvements in power conversion, which
drastically reduced the internal but not external heat generation. Also, the LPUs showed a substantial power increase, ability to control their exposure time, radiant exitance values and the polymerization protocol. This new LED technology referred to as "multiwave," was produced by some manufacturers, although Ultradent initially applied for the patent, Ivoclar-Vivadent was allowed to patent this broad-spectrum technology as Polywave® (Dual-peak) LED LPU. The majority of the manufacturers continued development of the second generation of LED LPUs. The first multi-peak (multiwave) LED LPU became available in 2003 when the Ultralume 5® (Ultradent Products, South Jordan, UT) came to the market. (Figure 1.6.1).

Figure 1.6.1 Ultralume 5® (Ultradent Products, South Jordan, UT) source:

This unit was a corded, pen-shaped LPU, powered with a 5W blue LED central chip surrounded by 4, low power violet LEDs, capable of producing a broad spectrum, with high peaks around 403 nm and 453 nm and the manufacturer claimed a radiant exitance of 1,200 mW/cm². The LPU featured no fiber optic light guide. The results from a study evaluating polymerization performance of 4 LPUs, by conducting a microhardness test, showed that the
Ulbralume 5 achieved the highest KHN of all RBC materials tested, outperforming all of the
2nd generation LEDs and QTH LPUs. In 2004, the first product of the Bluephase® family
(Ivoclar-Vivadent, Amherst, NY), with a radiant exitance of 1,100 mW/cm² came to the
market.

An improved product, the Bluephase 20i, exhibited a more traditional gun-shape with
a pistol grip, and standard fused-glass fiber light guide. The new multiwave LPUs from the
Bluephase family could generate radiant exitance up to 2,200 mW/cm², which brought back
the more advanced cooling features to their design. Furthermore, these LPUs featured highly
sophisticated, programmable polymerization modes for the variety of clinical applications, an
extended spectrum with two spectral peaks at approximately 410 nm and 470 nm.

The Valo® (Ultradent Products, South Jordan, UT), represented the hallmark of the
multiwave light sources approach. A wand-shape design of the Valo featured two blue
emitters (around 460 nm), and one violet (about 445 nm), capable of producing a spectral
output from 395 nm to 480 nm. The Valo is made from a solid bar of tempered, high-
grade aerospace aluminum, which provides this light source with unsurpassed durability and
superior heat dissipation. The ergonomic and streamlined design enables this unit to easily
access intraoral locations to provide optimal light for polymerization, without sacrificing
patient comfort. The unit featured an optimally collimated, almost homogenous beam profile,
which had not been seen by any LPU before. The LPU exhibited programmable
polymerization options: Standard Power (1,000 mW/cm²), High Power (1,400 mW/cm²), and
Xtra Power (3,200 mW/cm²).

The launch of a multiwave LPU, the ScanWave® (Acteon, Mettmann, Germany),
which has not gained much popularity in North America, showed an entirely innovative and
sophisticated product. The LPU used 4 different wavelength LED emitters (405nm / 440nm / 460nm and 480nm), capable of producing spectral output coverage from 390 nm to 505 nm. The ScanWave® incorporated a laser aiming system using a wavelength of 655nm, which allowed a precise light delivery for the light probe. According to the manufacturer's claim, the LPU is capable of generating a radiant exitance of 2,200 mW/cm$^2$ over a 5.5mm light probe diameter. The unit featured very sophisticated programming options, where the manufacturer claims that LED LPU can optimize polymerization while minimizing the heat generation within the target. The ScanWave® is equipped with a system for the detection of possible unit operation anomalies. Thus, the third generation LED LPUs represented the examples of state-of-the-art light sources, able to generate low or high power in a variety of clinical scenarios that had never been seen before.

While the LED LPUs have become the gold standard for the polymerization in the contemporary dental practice, they have some inherent drawbacks, particularly concerning the non-homogeneity of their irradiance beam profiles. This drawback is because irradiance does not represent a single value, but rather the mean of all irradiated light intensities. Thus, with a non-uniform beam profile of LED LPUs, the irradiance value can range from 300 mW/cm$^2$ to 3,000 mW/cm$^2$, which can make a significant difference in polymerization efficiency and the RBC's surface hardness profiles. Spectral non-homogeneity of multiwave LPUs beam profiles relates to different wavelengths of embedded LEDs within the LPUs light beam profile. Newly developed LED LPUs with much more uniform beam profile have been designed to overcome the shortcomings of the previous generation of light sources could be identified as the fourth generation of the LED LPUs. The examples are
Bluephase Style (Ivoclar-Vivadent, Amherst, NY) and DeepCure-S (3M ESPE, St. Paul, MN).

1.7 Intrinsic Factors Affecting Photopolymerization Efficiency

RBC restorative materials represent one of many success stories in advanced biomaterials research, as evidenced by their use increasing exponentially in the last decade. However, simplifying numerous factors that affect their polymerization efficiency is not an easy task because commercial RBCs represent a variety of chemical formulations that are not readily revealed, due to the trade secrets. The following factors were researched extensively: the photoinitiator systems, alternative monomer chemistry, and a novel formulation of fillers and their coupling agents. The fundamental understanding of photochemical reactions is critical to establish correlations among the RBCs, to modulate desired photopolymerization outcome.

The photochemistry represents the analysis of chemical reactions and physical behavior that occur under the influence of visible and ultraviolet light. Two fundamental principles are the foundation for understanding photochemical transformations. The first law of photochemistry, the Grotthuss-Draper law, states that a photon has to be absorbed by a chemical material for a photochemical reaction to take place \(^{11}\). Therefore, the presence of light alone is not enough to trigger a photochemical reaction; the light must exhibit the correct wavelength match to be absorbed by the reactant species \(^ {11}\). The second law of photochemistry, the Stark-Einstein law, states that, for each photon of light absorbed by a chemical system, only one molecule can be activated for the photochemical reaction to occur.
Light must be present, and it must then be absorbed. In other words, there is a one-to-one correspondence between the number of absorbed photons and the number of excited species. However, not all absorbed photons can produce the same number of reactive species. The ability to accurately determine the number of photons leading to a reaction enables the efficiency or quantum yield of the photochemical reaction. The practical implication of photochemistry is of immense importance, as it is the basis of photopolymerization of RBC restorative materials. LED LPUs deliver light energy to the surface of RBC material. The capacity of LPUs to deliver a sufficient quantity of photons within the appropriate spectra is the critical step in a photochemical process. In regard to the previously mentioned, the photoinitiator system is elevated to a state of higher energy, which represents the photoexcitation state, a fundamental requirement for photopolymerization. For instance, if a system does not absorb the light of a particular wavelength, no photochemistry will occur, regardless of the duration of the light exposure. Thus, the prime objective of successful photopolymerization would be an adequate quantity of light to be delivered to the surface of any given RBC material, and the closest match between the spectra of incoming light and a corresponding RBC photoinitiator system.

1.7.1 Photoinitiator systems

The dimethacrylate-based RBC material is the most frequently employed chemistry formulation among the commercially available RBCs, and it has been a focus of extensive studies since its introduction into general practice. Due to the RBCs’ exponential clinical
acceptance, clinicians focused their expectation for fast polymerization, superior mechanical properties, and greater longevity of the restorations on the photopolymerization concept.

A photopolymerization reaction is a complicated process induced by the LPU’s irradiated light over the RBC surface, which in essence the photo-reactive systems absorb light irradiation, and the monomers in the molecular structure become excited resulting in the formation of a polymer structure. The free radicals that trigger the polymerization process are formed by exposing a photo-unstable compound, the photoinitiator, to the appropriate light source's quantities and wavelengths, causing the photolysis. The radicals have unstable (reactive) groups of atoms with at least one unpaired electron in their methacrylate-based radical groups.

The classification of photoinitiators is based on the wavelength range of light used for activation or according to the mechanism employed for the photolysis. The light sources used in dentistry for the photopolymerization produce a spectral emission in a range from 380 nm to 515 nm. This spectrum is apportioned into the violet light range, from 380 nm to 420 nm, and the blue light, from 420 nm to 515 nm. Because the photon energy is inversely proportional to its wavelength, the photons in the violet light spectrum exhibit more energy than those in the blue light spectrum. Radicals that initiate a polymerization reaction are either formed by using the bond fusion or by contacting the hydrogen atom (H transfer) to a second compound, the so-called “co-initiator”. Regardless of the mechanism used, it is of the greatest importance that the photoinitiator reaches an excited state. Many photoinitiators contain carbonyl groups as light-absorbing species. The majority of RBCs contain methacrylic acid esters, which are used as radically polymerizable monomers. Depending on their number of polymerizable methacrylate groups, they are classified into monofunctional...
(n = 1; e.g. methyl methacrylate), difunctional (n = 2) and multifunctional (n > 2) methacrylates. During the radical photopolymerization of monofunctional monomers, linear polymers are developed. The rate of the radical formation is dependent on irradiance of the LPU, the photoinitiator quantum efficiency, the extinction coefficient of the photoinitiator and its concentration, and the thickness of the layer through which light passes through. Useful photoinitiators are defined by high quantum efficiency and a high extinction coefficient, i.e., the capacity to show a rapid absorption of the light in the wavelength range applied.

There are two types of photoinitiator systems currently employed among commercial RBC materials: Norrish Type I and Norrish Type II systems. Camphorquinone (CQ), a Norrish Type II system developed by Dart and Nemcekin in 1972, became the most common photoinitiator system for dental applications. CQ has a visible light absorption range from 360 to 510 nm, with a maximum absorption peak at 468 nm. This Type II system of photoinitiator reacts by bimolecular hydrogen abstraction from suitable co-initiators, preferentially aromatic amines, such as ethyl-4-dimethylaminobenzoate (EDMAB), aliphatic amines, such as 2-(dimethylamino) ethyl methacrylate (DMAEMA), or a common piperidines derivate, such as 1,2,2,6,6-Pentamethylpiperidine. The first step in this photopolymerization reaction is high-speed electron transfer radical. During a much slower proton transfer process, two radicals are created, of which only an amine-based radical initiates a photopolymerization reaction. The photochemical radical formation is a diffusion-controlled process. In the case of high viscosity formulations, the efficiency of type II photoinitiator is considerably decreased. Several attempts have been made to combine a photoinitiator with the co-initiator in one molecule, either in a low molecular dimer or a
copolymer. The study results which utilized a low molecular dimer showed an increase of up to a factor of 2 in the rate of a photopolymerization reaction. However, on the contrary, in the study where the copolymer has been used, a decrease in reactivity was observed. The free radicals generated in this process attack the C=C bonds of monomers, resulting in the formation of new radicals with a much longer chain. This process propagates through a cascade of chain reactions, which includes an auto-acceleration and, auto-deceleration, coupled with high polymerization rates, along with diffusion-controlled termination, followed by the free radical entrapment. The Type I photoinitiators exhibit greater absorption efficiency and quantum yield compared with Type II photoinitiators.

Although CQ systems exhibit a very high acceptance among the RBCs manufacturers, there are some drawbacks associated with their usage. Small amounts (ppm) of yellow-colored CQ have a profound influence on color properties of RBC materials. It has frequently been observed, that, under the effect of LPU’s irradiation leachable by-products could be generated, with the capacity to produce visible discoloration under restorations. Also, the α-diketone group, derived from CQ, has a peak absorption in a visible range, which could initiate RBCs’ polymerization under ambient light, significantly reducing a working time of the materials. Furthermore, some concerns regarding the biocompatibility and toxicity of used amine compounds have been proposed. As a possible solution for previously mentioned concerns, adding a small amount of specific polymeric or macromolecular photoinitiator aromatic tertiary amine, with a bisphenol-A skeleton to CQ chemistry, has been proposed. In addition, the initiator CQ can be substituted by polymeric radical photoinitiators bearing the photo-sensitive CQ groups in the side chain.
The Type I photoinitiator system, is based on the photochemical cleavage of aldehydes and ketones into two free radical intermediates, which initiate polymerization without the need for an additional amine \(^{248}\). Type I photoinitiators exhibit much faster photopolymerization kinetics under short irradiation times, improved functional group conversion, reduced monomer elution, and improved mechanical properties \(^{180}\). The second law of photochemistry, the Stark-Einstein law, states that for each photon of light absorbed by a chemical system, only one molecule can be activated for the photochemical reaction to occur \(^{11}\). However, this fundamental principle applies to photoinitiators with a low free radical production efficiency, as seen with camphorquinone (CQ) \(^{11}\). For instance, as much as four reactive radicals could be produced from one molecule of Irgacure 819, compared to only one obtained from CQ \(^{253, 255}\). Thus, photon absorption efficiency (PAE) is a very useful parameter to determine the most efficient photoinitiator with corresponding LPU’s spectral irradiance \(^{254}\). Therefore, photoinitiators absorption spectra should be highly correlated with the spectral emission profiles of LPUs. The type I systems, currently used with commercially available RBC include:

- Phenylpropanedione (PPD) (1-phenyl-1, 2-propanedione), with a maximum absorption spectrum in the range of 398 nm \(^{249}\).
- Lucirin TPO Diphenyl (2, 4, 6-trimethylbenzoyl) phosphine oxide, with a maximum absorption spectrum in the range of 381 nm \(^{254}\).
- Irgacure 819 (bis-(2, 4, 6-trimethylbenzoyl) phenyl phosphine oxide), whose maximum absorption spectrum is in the range of 370 nm \(^{255}\).
• Ivocerin ® represents a blend of germanium-based compounds such as benzoyl trimethyl germane (Ge-1) or dibenzoyl diethyl germane (Ge-2), whose maximum absorption spectra are 411 nm and 418 nm respectively. The bis-(4-methoxybenzoyl) diethyl germane Ge-3, with the broad absorption bandwidth to 460 nm, which exhibits a maximum absorption spectrum at 408 nm.

The literature reports a quantum efficiency of the light-induced cleavage for Ge-2 is 0.85, while that for Irgacure 819 is 0.59. In addition to the photoinitiator concentration and the irradiation protocol, specific characteristics related to the chemistry of the molecule itself can also affect polymerization initiation. The photoinitiator molecule must have a high molar extinction coefficient, which is defined as the absorption per unit length divided by the molar photoinitiator concentration of the solution.

Efficiently absorbed energy has enormous influence on a photoinitiation process. Therefore, absorbed irradiance should be reported as well, to make a meaningful comparison among the photoinitiators. Type I photoinitiator systems exhibit a higher molar extinction coefficient when compared with Type II systems. The probability for CQ to absorb photons at its maximum absorption peak is significantly lower than for any Type I system, excluding Ivocerin, which has a much higher order of magnitude than any other Type I photoinitiator system. The Type I systems do not need an amine co-initiator. Furthermore, they also exhibit exceptional color stability, and they are employed in many commercially available RBCs' bleach shades. Several studies report good results with mixtures of CQ and other photoinitiators, resulting in more dependable polymerization.

Besides other factors, viscosity alone may significantly affect the polymerization efficiency of a given photoinitiator during the evaluation process. The result of a well-
controlled study validated the assumption that the initiation system exhibited the significant influence on the conversion and a degree of network crosslinking of highly-filled RBCs\textsuperscript{258-260}. Those studies highlighted the advantages of using MAPO photoinitiator systems (Type I) in a highly-filled dimethacrylate-RBCs with the assumption that a sufficient Bis-GMA content (>40 mol %) and an adequate light spectrum were applied\textsuperscript{259}. Moreover, the radiant exposure values for the proper polymerization of tested systems ranged from 3 J/cm\textsuperscript{2} for MAPO systems, having values around 20 J/cm\textsuperscript{2} were commonly reported for CQ systems\textsuperscript{259}. The MAPO photoinitiator systems, with Bis-GMA fractions of 40 mol\% or more, have experienced an increased trapped radical concentration, a reduced monomer elution, and superior mechanical properties, in comparison to the CQ photoinitiator systems\textsuperscript{259}.

1.7.2 Viscosity, monomers, and fillers

Abundant evidence exists to support the assumption that initial RBC viscosity plays a significant role in the reaction kinetics and final DC by affecting the mobility of each monomer, and its ability to react\textsuperscript{197}. It is universally recognized that the initial viscosity of RBC and its composition, pre-determine the extent of polymerization, through mobility restrictions, with the onset of auto-acceleration and the beginning of diffusion-controlled termination being changed to earlier stages of the conversion\textsuperscript{197, 261}.

The local viscosity is primarily influenced by the monomer composition and a filler load. The polymerization efficiency is profoundly affected by the monomer molecular structure. The viscosity exponentially increases as the percentage of a filler volume increases but decreases significantly with a temperature increase\textsuperscript{288}. Although the majority of
commercial RBCs are very sophisticated in their chemical formulation, they are primarily composed Bis-GMA (2, 2-bis-[4-(methacryloxy-2-hydroxy-propoxy)-phenyl]-propane), or its derivates blended with TEGDMA (Triethylene glycol dimethacrylate) as a diluent. The function of inorganic fillers is to improve mechanical properties and to reduce polymerization shrinkage and to minimize the thermal expansion coefficient 197-200.

The viscosity of RBCs depends on the composition and ratio of the resin matrix, the content and shape, size distribution and silane treatment of the inorganic filler, interlocking between the filler particles, and interfacial interaction between the filler particles and the matrix resin 171. Bis-GMA is the main monomer that is frequently used for the production of commercial RBCs. Bis-GMA shows a relatively low polymerization shrinkage (around 6%), rapid hardening by free-radical polymerization, low volatility, and acceptable mechanical properties after the polymerization 260. Bis-GMA has a very high viscosity at ambient temperature, which requires its dilution with a low viscosity monomer, to obtain an organic matrix that can be mixed with an adequate amount of inorganic fillers 260. However, dilution with low viscosity monomers (mostly TEGMDA) leads to a significant deficiency. Because viscosity is correlated with the molecular weight of monomers, and because low molecular weight monomers have higher polymerization shrinkage, it can be assumed those different formulations of Bis-GMA/TEGMA could have a significant influence on polymerization efficiency 199.

Although RBCs that have been analyzed exhibited the same total inorganic filler weight content, their rheological behavior is very different from one to another 199. For instance, 60 wt% of macrofillers alone do not have a considerable influence on the viscoelastic properties of the material, except that they increase the viscosity of the material
in the way, which a slight shear-thinning behavior appears. However, by increasing the microfiller content, a more complex viscosity increases. For instance, adding 60% of macro-filler to a 50/50 Bis-GMA/TEGDMA mixture changes the viscosity from 0.2 Pa s to 1.4 Pa s at 1 rad/s. Regardless of RBCs formulation, RBCs will experience deformation when applied to the cavity walls, and that phenomenon is called thixotropy. Thixotropy is always anticipated from shear-thinning mechanism. Thixotropy occurrence is always observed because of the finite time required for flow-induced changes in the microstructure, and the process is entirely reversible. Therefore, in clinical situations, RBCs are photopolymerized in a state which is very far from their rheological state of rest. It could further indicate that RBCs should ideally be polymerized after the restructuring phase. From that point of view, and considering the present results, it has been recognized that the time needed for the RBCs to reach equilibrium after their deformation is exceptionally long. It has been shown that RBCs need approximately 3,600 s to reach 80% of their initial viscosity, and from 7,200s to 14,400s to return to their state of equilibrium. However, that would be impossible to implement in clinical practice. Fillers have a significant impact on polymerization efficiency, by increasing a filler volume fraction, the maximized DC has been acknowledged.

The RBCs viscosity change is related to an increase in filler volume percentage, filler size and, morphology. The viscosity of RBCs is substantially influenced by a resin matrix chemistry, the shape, and size, as well as the content of a filler particle. Furthermore, the viscosity is dependent on interlocking between the filler particles and the interfacial interactions between the filler and a resin matrix. It has been shown that the resin matrix exhibits major influence on polymerization shrinkage stress than the filler content. Therefore,
further research has been conducted with the aim of reducing stress by modifying the resin chemistry, without the reduction of a filler content \(^{263}\).

The incorporation of a novel class of mono vinyl (meth) acrylate monomers that contain secondary and tertiary functionalities such as urethanes, carbonates, cyclic acetyl, morpholine, cyclic carbonates, hydroxy/carboxy, oxazolidones, and aromatic rings, significantly enhance the polymerization kinetics and significantly improve mechanical properties of conventional RBCs \(^{263}\). The incorporation of reactive organic nano gel-polymer into the standard dimethacrylate matrices have been reported to delay vitrification and elastic modulus development \(^{264}\). Nanogels provide a stable, transparent solution of swollen, dispersed or overlapped particles. During the polymerization reaction, nano gels enhance a physical entanglement and potential chemical crosslinking between nano gel structures and the resin network, which consequently reinforce mechanical properties of the final network structure \(^{264}\).

Temperature has a significant, inverse correlation to viscoelasticity changes of RBCs, in the way that temperature increase will lead to an exponential decrease of RBCs viscosity \(^{265}\). This phenomenon was explained by the Arrhenius equation, which represents the relationship between the temperature and the viscosity of the fluid \(^{265}\). The research showed that a relatively weak molecular bond exists in a high-concentration suspension of the filler particles in a resin matrix. For example, if a shear force is generated, the resultant shear flow can induce the rolling of the fillers, which can increase the interstitial distance between the filler particles, or between the filler and a resin matrix, which results in individual bonds between molecules to become broken. Further increase of shear rate, an array of particles becomes directional, which leads to diminished interactions between particles. As a result,
viscosity decreases with the shear rate increase. This phenomenon represents ‘shear thinning,' which can further explain why a rapid, slight tapping after the RBC placement, can enhance RBC flow and better adaptation to the preparation walls.

Although mechanical properties of RBCs, which exhibit viscoelastic behavior, have often been characterized using static tests, these tests were primarily focused on the elastic component of RBCs, without the valuable information about the viscous domain of the material tested. Therefore, static tests are considered appropriate for characterization of the ultimate strength of RBCs. Additionally, the results of commonly used tests with static loading, including the creep test, stress relaxation test, and steady shear test, are in essence with a low level of clinical relevance, because masticatory loading conditions are dynamic. There are two test methodologies for RBCs viscoelastic properties characterization exist: irreversible (destructive) and reversible (non-destructive). Although static and dynamic destructive tests such as tensile and dynamic mechanical analysis (DMA) were extensively conducted to measure viscoelastic properties of RBC materials, due to their irreversible nature and problems associated with specimens' standardization, have been replaced with non-destructive tests. A non-destructive methodology has the ability for a quick and accurate estimate of RBC’s viscoelastic properties, without any specimens' damage. Therefore, the majority of DMA tests that are accepted for characterization of RBC's viscoelastic properties employ this methodology. For example, a dynamic oscillatory shear test is the most often used test to characterize the linear viscoelastic properties of RBC restorative materials. The analysis employs the resonant vibration, which primarily generates specimens’ mechanical vibration in any of selected modes: torsional, transverse, or longitudinal, over a specific range of frequencies.
1.7.3 Optical properties

The optical properties of RBCs and their photopolymerization reaction are interdependent, in the way that material constituents affect light transmission, which further influences the polymerization depth. Light penetration of RBC materials is defined by the use of the Beer–Lambert's law. According to this law, if a beam of monochromatic radiation passes through a medium, its power attenuates based on the following equation:

\[ P = P_0 (1 - R_F) \exp(-\alpha d) \]  

(1)

Where \( P_0 \) is initial optical power, \( R_F \) is the total Fresnel reflectance coefficient, \( \alpha \) is the attenuation coefficient, and \( d \) is the thickness of the sample. However, in a function of the RBC sample, the attenuation of LPUs' irradiance in the RBC sample follows Lambert's Law, expressed in differential formats:

\[ - \frac{dl}{dx} = \mu I \]  

(2)

Where \( I \) represents the irradiance at depth ‘\( x \)’ in the RBC specimen, and ‘\( \mu \)’ is the linear attenuation coefficient (dimension L\(^{-1}\)). Furthermore, the RBC material exhibits various refractive indices and interfaces, including trapped air bubbles, and thus \( \mu \) needs to be further divided into two components, due to a true absorption ‘\( \mathcal{T} \)’ and scattering ‘\( \delta \)’. It was discovered that the scattering coefficient is relatively consistent among the tested volume fractions. Based on Eq. (2) the further rearrangements to show the transmittance (T) of the RBC specimen, is often expressed as the optical density D of the RBC specimen:
\[ D = \mu x \log_{10}(e) \]  

(3)

It can be recognized, based on Eq. (3) that optical density is a mere linear function of the depth of the RBC sample (assuming uniformity). However, taking into the consideration that most frequently used LED LPUs, do not generate a monochromatic light spectrum, some further adjustments should be made, however, the basic principle of the law is very relevant to RBCs polymerization. Thus, the law describes the loss in optical power due to reflections, absorption and scattering upon LPUs light transmission through the RBC materials.  

As previously mentioned, LPUs do not produce a monochromatic light beam, as their spectral irradiance depending on the type of LPUs, which can vary from 380 nm to 515 nm. The portion of that LPUs spectrum referred to as a violet spectrum, usually interacts with a particular type of RBC materials by producing Rayleigh scattering. The Rayleigh scattering law states that the percentage of the light that will be scattered is inversely equivalent to the fourth power of the wavelength. Small particles will scatter in a much higher percentage of short wavelength (violet spectrum) than long (blue light) wavelength. Because the mathematical association comprises the fourth power of the wavelength, even a small wavelength difference can mean a substantial difference in scattering coefficients.  

The following contributing factors are correlated with RBCs light attenuation: the surface gloss, the resin matrix composition (resin volume fraction), filler composition (filler volume fraction), the content of pigments, the presence of some chromatic by-products, and refractive indices of monomers, silane, and the filler particles. The surface light reflection has two functional components, the diffuse component, which results from a light penetrating
surface, following the multiple reflections and refractions and also re-emerging at the surface. The spectral element is a surface phenomenon, which can be represented as a function of the incidence angle and the refractive index (RI) of the material, the surface roughness, and a geometrical shadowing function. The color coordinates of RBCs (value, chroma, and hue) are related to the scattering and absorption characteristics, light reflectivity, and translucency of the material. Translucency is one of several factors that determine the optical features of the material and refers to the partial passage of light through a particular structure. Therefore, the presence of different degrees of translucency in any RBC material is a determining factor in the quality of esthetic restoration.

The RI of RBCs plays a significant role in their optical properties. Therefore, studies have confirmed that transparency, opacity, and surface gloss values were profoundly correlated with the RI value. Furthermore, a decreased transparency value will be correlated to increased value for the opacity and surface gloss, while at the same time, the RI value will be increased. Concerning polymerization depth, several factors can interfere with the light transmission throughout the RBC material. The pigments and photoinitiators can absorb the light photons. The light interference with pigments and a variety of shade additives has been documented. The darker shades would experience a lower DC at the same irradiance, in comparison to lighter shades. The inverted relationship between the photoinitiator’s molar absorptivity of the incident light and polymerization depth has been established. Thus, the higher molar absorptivity will present the lower polymerization. The most of RBCs are formulated with camphorquinone (CQ) as a profoundly yellow photoinitiator, which has a profound influence on the color of RBC materials. During the photopolymerization process, depending on quantity and spectral emission of the LPU, the
color transformation of CQ changes to the transparent under favorable polymerization conditions. However, a certain degree of yellow remains within the material insufficiently polymerized. Thus, the further conversion of CQ continues under the influence of ambient light. Therefore, the “bleaching” represents the conversion of CQ from yellow color to almost transparent as a result of “adequate” polymerization.

The relationship of filler particle size and attenuation of light has been a subject of extensive research. The following features of filler particles such as filler size, geometry, density, and silane treatment, have an enormous effect on reduction of light intensity. Therefore, an increase in filler content will accelerate light absorbance. Furthermore, light scattering will be increased, with a significant difference in refractive indices of the matrix and the filler particles. The RBCs light intensity reduction has been explained by the Rayleigh equation, which demonstrates relationships between the following factors: the thickness of a specimen, filler volume content, particle radius, refractive indices of the particles, refractive indices of the matrix, and wavelength of incidental light. The following relationships can be observed:

- In the case when the refractive index of the matrix is smaller than the particle's refractive index, light transmittance reduction will occur with the increase of a filler particle radius and filler volume fraction, while an increase in transmittance will happen with an increase of incidental light wavelength;

- In the case where the matrix refractive index is higher than the particle's refractive index, an increase in transmittance will occur with an increase of a filler particle radius and filler volume fraction, and a reduction in transmittance will happen with an increase of wavelength of incidental light;
Furthermore, the effect of each of the factors is differentiated, because a filler particle radius is elevated to the third power, the wavelength of an incidental light to the fourth power and a multiplier factor of 3 is attained to the filler volume fraction\textsuperscript{272,273}. However, this complex theoretical model has some meaningful, practical explanation. For instance, Rayleigh scattering is contributed to the higher attenuation of LPUs' incident light in a particularly short wavelength spectrum (under 420 nm), in comparison to the longer wavelengths spectrum (above 420 nm). Furthermore, an incident light wavelength hitting the equal or a smaller filler particle size, produces scattering of a higher magnitude. A considerable extent of scattering would be expected when a filler particle size approaches to the half of LPUs' wavelength, resulting in that the extent of light scattering is inversely proportional to the fourth power of an incidental light wavelength\textsuperscript{273}. Based on these findings, the LPUs with a violet spectrum should not be used for the bulk-fill composite polymerization, because the violet spectrum has induced a substantial scattering effect and reduced polymerization efficiency. Furthermore, the thickness of a specimen plays a significant role in light attenuation.

1.8 Extrinsic Factors Affecting Photopolymerization Efficiency

RBCs' polymerization quality is determined by a variety of factors, which could be classified into the two groups: intrinsic and extrinsic factors. The intrinsic factors are frequently associated with RBCs properties. However, extrinsic factors are related to features of LPUs: the radiant power and irradiance, the spectral emission, light beam profile, distance from the light probe, the exposure time, and irradiation modes.
1.8.1 Light polymerization units (LPUs) and emission spectrum

LED LPUs are the most common photopolymerization light sources in a contemporary dental practice because a large number of dental procedures require photopolymerization. The LED LPUs offer several advantages over other light sources: a relatively high radiant exitance, enhanced mobility, a low operational cost, and an affordable price structure. The two main designs are a gun-looking shape with a traditional light probe or a turbo-probe, and a wand-type style, which has an LED source at its distal end sealed with a fixed lens. However, the Bluephase Style is a wand-style unit having its emitting chips still within the body of the wand, and not at the tip end. The advantage of the wand type LPUs is easy to access to posterior teeth, especially in pediatric patients or in patients with limited mouth opening. Furthermore, these types of LPU’s have a well-collimated light guide, contrary to a turbo light guide that provides a significant irradiance decrease as a result of an increased distance between the light tip and the RBCs.

The first and foremost property of LED LPUs is their ability to deliver adequate quantities of energy to the RBCs, to achieve maximum polymerization. Thus, LPUs need to have an appropriate radiant power output (mW) as well as spectral irradiance (mW/cm²/nm), with as close as a possible match to the maximum absorption spectrum of the photoinitiators present in the RBCs. It is well-recognized that monowave LED LPUs can deliver irradiance spectra in the range to the maximum absorption spectrum of CQ (468 nm), while multiwave LPUs deliver a broad range, with usually two peaks of spectral irradiance, suitable for the activation of CQ and the alternative photoinitiators. However, a reduced polymerization
depth has been observed with bulk-fill RBCs, polymerized with multiwave LED LPUs, proposedly attributed to the significant Rayleigh scattering effect between a filler particle size and shortwave visible light\textsuperscript{273, 274}.

Despite conflicting views in the literature, some manufacturers have been working on Norrish Type I photoinitiators, particularly with the PPD, Lucirin-TPO and the latest one, Ivocerin\textsuperscript{®} a germanium-based photoinitiator. Absorption spectra of those photoinitiators are predominantly in the violet spectrum range: between 380 to 420 nm. Furthermore, due to their absorption quantum yield and superior polymerization kinetics, these photoinitiators have been attributed to the significant DC improvements and increased the degree of crosslinking, resulting in much better mechanical properties of RBCs\textsuperscript{273, 275}. The combination of Type I and Type II photoinitiators in commercial RBC formulations is associated with significantly better mechanical properties that of CQ when used by itself\textsuperscript{276}. The results were further validated by successful use of various blends of the CQ with of Lucirin-TPO and Ivocerin\textsuperscript{®} in Ivoclar-Vivadent commercially available RBCs\textsuperscript{276, 277, 278}.

The uniformity of the LPUs beam profile has been a subject of much research lately. The spectral analysis of the LPUs irradiance beam profile showed enormous differences in their light distribution across the light tips. Those LPUs without a uniform irradiance distribution are associated with the production of hot spots (high irradiance) and cold spots (low irradiance) on the RBCs surface\textsuperscript{279}. As a result, materials polymerized with these LPUs exhibit areas with adequate and inadequate polymerization. Furthermore, a strong positive correlation has been found between microhardness and elastic modulus values and beam profile irradiance values\textsuperscript{279}. This issue could potentially have more detrimental clinical
results with the use of multiwave LPUs when using a non-uniform spectral irradiance beam profile of the violet and blue light spectra.

1.8.2 Radiant exposure, irradiance, and irradiation time

There is much of a debate about the accuracy of reported values for LPUs’ output in the literature, as different studies report their findings using their terminology, which has created a controversy. Because LPUs used for photopolymerization of RBCs produce electromagnetic radiation of a specific wavelength range, primarily from 360 nm to 515 nm, sufficient radiometric quantities should always be stated.

The radiant power is the correct term to describe the output from the LPU and is expressed in units of mW. The next important feature of the LPU is the radiant exitance, which characterizes the radiant power output from an LPU emitted thought out the area of the light probe tip, expressed in mW/cm². However, the most critical term regarding the light source, which is often incorrectly used in the literature, is the incident irradiance. This parameter represents a radiant power incident on a surface of the RBC material, expressed in mW/cm². The incident irradiance can be used to characterize the radiant exitance at 0 mm target distance. The radiant exposure is the product of the irradiance and the exposure duration: expressed in J/cm². Due to a nonhomogeneous beam profile, the incident irradiance represents a mean of all values irradiated throughout the tip surface, which is substantially affected by the change of a tip diameter size. The tip diameter has been a center of a controversy. There is a substantial difference, between an optical tip diameter and an
effective tip diameter, which the former represents the actual, light-emitting area of the light probe end.

A data set founded on the erroneous measurement of an optical instead of an active tip diameter would potentially compromise the results of any study. In addition, a correct tip diameter measurement should be comprehended to any LPU's operator. The clinically relevant issue occurs with the Class II restorations, whether the LPUs' diameter of the light probe irradiating the surface of Class II proximal box portion has enough of the beam diameter coverage to irradiate the restoration. In this situation, an optical diameter of the LPU tip should be at least 2 mm greater than the assumed surface of the restoration so that the polymerization could be achieved in a single exposure.

The International Organization for Standardization (ISO) has also adopted a set of standards, mainly for testing LPUs performances, known as 10650-1 (ISO 2004) and 10650-2 (ISO 2007, updated September 2015) standards. The ISO 10650 standard for measuring the LPUs' output, uses a laboratory grade power meter to measure the radiant power output, however, that device is not readily available to dentists. The most common of all available devices to measure the light emission from LPUs, frequently employed in dental offices, are hand-held dental radiometers. However, it has been published that dental radiometers were not reliable sources for the accurate measurements of LPUs' performances. The irradiance measurements from hand-held dental radiometers are affected by a correct tip diameter, the light beam profile and the LPUs emission spectrum. Furthermore, these devices are calibrated for a particular brand and a model of LPU. Thus, measurements of other brands of LPUs with it may not render accurate results, which would cause a significant discrepancy.
The radiant exposure, a product of incident irradiance and an exposure time is a critical factor that controls mechanical properties of polymerized RBCs. The radiant exposure required for any given RBC depends on two factors: a material’s formulations and the LPU’s properties. Thus, these variations could be in a range from 6 J/cm$^2$ to 48 J/cm$^2$ as reported in the literature$^{284}$. 

Another issue that caused considerable debate over the last decade was the reciprocity law. In photography, reciprocity has the inverse relationship between the intensity and duration of light that determines the reaction of a light-sensitive material$^{285}$. Thus, the exposure reciprocity law (adopted from photography) has been proposed based on the concept that a given quality is directly subordinate on its exposure dose, but independent of the individual values of the irradiation and exposure time$^{151, 152}$. In the wake of some advanced LPUs that can generate more than 4,000 mW/cm$^2$, ultra-fast polymerization becomes an attractive feature for a significant clinician’s chairside reduction, while researchers are trying to answer a question of the validity of the exposure reciprocity law in dentistry.

Recent studies demonstrated that the majority of RBCs should not be expected to follow the reciprocity law$^{152}$. As per increased irradiation, mostly above 1,500 mW/cm$^2$, the overall dose required to achieve an adequate conversion is also increased, and this polymerization behavior is resultant from the dominant bimolecular termination mechanism for the free radical polymerization. It has been confirmed that final conversion of RBCs, as well as their ultimate shrinkage stress values, were not dependent upon a dose of light energy delivered, but instead were dependent on the irradiance and a corresponding polymerization rate$^{151, 285}$. 

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1.8.3 Light exposure

Contemporary LPUs are usually equipped with programmable polymerization modes that can deliver radiant energy in different forms: continuous, pulse-delay, or stepped mode. The continuous mode delivers the same amount of exitant irradiance from the start to the end of the polymerization cycle. The pulse-delay mode initiates light emission by a short flash of emitted light, followed by a programmable time delay before the final exposure is performed. In a step-polymerization mode, an initial cycle starts with a low exitant irradiance, for a precise period, then is promptly followed by a much higher exitant irradiance. The ramp-mode starts with zero amount of exitant irradiance, and then the amount of exitant irradiance reaches the maximum almost immediately, continuing the same level for the rest of the cycle. Polymerization with a pulse delay and a stepped mode are ordinarily regarded as "soft-start" modalities. Soft start exposures typically do not start at zero, but instead initiate at a very low level and apply that low level for a specified time period (step), or they gradually increase output over time, until full output is generated (ramp). The soft-start polymerization modes have been associated with a significant reduction in gap formation, due to a lower level of a polymerization stress formation at the cavity margins because of the contraction stress. Research has shown, however, that this polymerization type has been associated with a reduction of DC, in addition to a significantly lower degree of crosslinking, which caused substantial mechanical properties decrease. Literature reports that a 40s radiant exposure has not produced any statistically significant differences among the polymerization
modes used, however, by using a ramped soft-start polymerization mode, a substantial reduction in a contraction strain and a corresponding polymerization temperature has been recognized. Consequently, with the latest RBCs’ developments, in particular, with the introduction of low-shrinkage materials and the alternative photoinitiator systems, the relevance of this issue will probably become less important.

1.8.4 The effect of temperature on photopolymerization

Temperature has a significant effect on RBCs polymerization. It has been reported that for each one °C temperature increase, the corresponding polymerization reaction increases by 1.9%. However, an initial RBCs' temperature increase from 25 °C to 35 °C, duplicates the corresponding rate of the DC, which also correlates to an elevated and swift polymerization stress build-up, compared to the RBCs at ambient temperature.

Photopolymerization generates an elevated temperature due to a chemical exothermal reaction and the incidental radiant energy from the LPUs source. The extent of generated heat depends on the incident irradiance values, the thickness of the RBC sample, and the corresponding polymerization rate. The LED LPUs with an extraordinary high radiant power can generate a sudden temperature spike, which can cause a sharp temperature increase near the pulp, as much as 5.5 °C, the value that is considered harmful for the pulp. Further, a recent in-vivo study revealed, a high, positive correlation ($r^2 = 0.92$) between the radiant exposure and the pulpal temperature increase. This correlation was observed, especially in the cases where the radiant exposure reached 80 J/cm$^2$ which increased a 5.5 °C pulpal
temperature. Depending on the tooth and patient age, the level of 5.5°C pulpal temperature increase can lead to irreversible pulpal damage. It is interesting to note that some RBCs, due to their much higher monomer content, exhibit an elevated exothermal polymerization reaction, as seen in flowable RBCs. Thus, clinicians should avoid using LPUs with high radiant power output, particularly with flowable RBC, due to a possible pulpal damage.

Preheating RBC just before its placement into the preparation has recently gained popularity among dental practitioners. This procedure results in viscosity reduction with the following potential clinical outcomes: enhanced marginal adaptation, improved handling, an increase in polymerization rate, an increase in the DC values, and improved mechanical and physical properties. However, the exact relationship depends on the chemical formulation and the intrinsic properties of RBCs. It would be recommended for the refrigerator-stored RBCs to be preheated to at least to 45°C, before the placement into the oral cavities.

### 1.8.5 Light guide tip positioning

Adequate LPU’s light probe positioning has a crucial influence on the quantities of light energy received by the restoration during the radiant exposure. All types of LPUs, but the laser, deliver a non-coherent light beam profile. Furthermore, there is loss of incident irradiance, with an increased tip-to-object distance. Manufacturers always report the irradiance of their LPUs at 0 mm distance, without any consideration to a clinically relevant distance in the molar region, which can be more than 7 mm.
The Class II restorations, regarding location accessibility, exhibit challenging locations for proper light energy delivery. The challenges associated with photopolymerization in the posterior region are attributed to the rather small inter-occlusal distance, resulting in a significant degree of a light probe positioning difficulty, in addition to lack of visualization, rendering inadequately polymerized RBCs. An increased distance, between the tip of the LPU light guide and the surface of the RBC restoration from 0 to 10 mm has caused a 23% reduction in incident irradiance, which was associated with a substantial decrease in the DC at the bottom of a 2 mm thick RBC specimen. Good clinical practice fosters the closest possible positioning of the LPU light probe tip to the material being polymerized. Practitioners should always pay full attention and make sure that the LPU’s tip is positioned at the right angle to the material surface. The light probe should be stabilized to prevent any movements during the entire polymerization cycle. In addition, practitioners need to have a clear view of the light probe to correct any misalignment of the light probe. The constant monitoring of the polymerization process involves a two-hand polymerization technique. The one-hand polymerization technique usually results in poor stabilization of the light probe tip or its misalignment, which subsequently renders an unsatisfactory clinical outcome.

It is well-known that LED LPUs produce electromagnetic radiation in a range from violet to blue light wavelengths. LPUs exhibit the enormous potential for ocular damage in the range from 435 nm to 440 nm, because these blue light wavelengths are efficiently transmitted to the retina, where they can express local harmful effects. Thus, clinicians should be encouraged to use appropriate orange blue-blocker eye protection, which renders an adequate level of safety for watching for the appropriate light probe position during the
entire photopolymerization cycle. Furthermore, dental practitioners are required to protect their patients and employees from ocular hazards associated with LPUs.

1.9 Review of studies on RBCs Longevity and Effectiveness of LPUs

Although RBC placement is a technique-sensitive procedure that requires clinicians’ full attention, polymerization by LPUs may not receive the same consideration as it should. Many factors are affecting the longevity of RBCs. The main factors are the RBCs' property and the clinical skills of the operators, as well as LPUs' performances. Those factors are elaborated in selected studies on the RBCs’ longevity and LPUs’ effectiveness.

1.9.1 Longevity of RBCs direct restorative materials

Due to an increased demand for esthetics, as well as environmental concerns regarding mercury in amalgam restorations, an exponential use of RBCs, has been observed, as either a primary RBC placement or as amalgam replacement. Although amalgam has been a direct restorative material in continuous service for more than 150 years, presently it is not considered a material of choice for posterior restorations, due to an exponential increase in RBC placements that was reported in many industrialized countries. However, in developing countries, amalgam remains the restorative material of choice, at least for posterior restorations, perhaps because of economic issues.
The abundance of published studies on the clinical performance of RBC restorations exists, however, a direct longevity comparison of different types of restorations among different studies is almost impossible for numerous reasons. The following studies published in the last 13 years are about to present more knowledge on performances and longevity of posterior RBC restorations.

The first comprehensive study, (Manhart et al., 2004), which has evaluated longevity and annual failure rates of Class I/II restorations, restored with amalgam, direct RBC, compomers, glass ionomers and derivative products, composite and ceramic inlays, and cast gold, since the 1990s to 2003. The analysis has shown that an average annual failure rate (AFR) for posterior restorations were: 3.0% for amalgam restorations, 2.2% for direct RBCs, 3.6% for direct RBC with inserts, 1.1% for compomers, 7.2% for regular glass ionomer (GI) restorations, 7.1% (for tunnel GIs, 6.0% for ART GIs), 2.9% for composite inlays, 1.9% for ceramic restorations, 1.7% for CAD/CAM ceramic restorations, and 1.4% for cast gold inlays/onlays. The factors that were associated with amalgam restorations failure included secondary caries, a high incidence of bulk and tooth fractures, in addition to cervical overhangings and marginal discrepancies. The principal mode of RBC restoration failure included secondary caries, bulk fractures, marginal deterioration, and wear. This study showed that amalgam and RBC restorations exhibited similar annual failure rate.

An international study that evaluated retrospective longitudinal data for posterior RBC restorations, which covered a period from 1996 to 2011, with a minimum observation period of five years included a total of 34 Class I/II studies (Demarco et al., 2012). The results revealed AFR for vital teeth ranged from 1% to 3%, while at the same time AFR of non-vital teeth 2% to 12.4%. Interestingly, the study was the first to indicate that differences
in RBCs’ filler characteristic may have some influence on restoration longevity. The principal factors accredited to failure were secondary caries and restoration/tooth fracture, however, patient caries-risk factor, the clinical setting of the study, and the socioeconomic characteristics of the study population expressed the effect to a certain degree.

A Systematic Review and Meta-analysis (Opdam et al., 2014) investigated nine prospective and three retrospective studies on direct Class II or Classes I and II RBC posterior restorations in the permanent dentition. The analysis consisted of a total of 2,816 restorations (2,585 Class II and 231 Class I). It was concluded that the overall RBCs annual failure rate at five years and ten years was 1.8% and 2.4%, respectively. It was reported that secondary caries and bulk fractures were frequently associated with the restoration failure. The authors observed that a yearly failure rate was significantly higher in high-caries-risk patients (4.6%) compared to low-caries-risk patients (1.6%). The findings revealed that a patient caries-risk status has a substantial influence on long-term survival of posterior RBC restorations.

A 10-year retrospective study investigated longevity of 2-surface/3-surface Class II restorations (molar/premolar), using 4 microhybrid RBCs (Lempel et al., 2014). A total of 225 adult patients (86 males, 139 females) with 701 RBC restorations were evaluated by two operators using the modified USPHS criteria. The average AFR of RBCs tested was 0.52%, with the range from 0.08% to 0.71%. According to the study authors, a 10-year survival rate of 97.86% could be associated to a well-motivated patient group (university clinical practice affiliation), which exhibited high socio-economic standards and were subjected to periodical examinations, oral hygiene, and instructions regarding dietary habits. Similarly, the main
reasons for the failures in this study were secondary caries, fracture, and endodontic failure. Furthermore, similar survival rates were observed between molar and premolar restorations.

Results of a randomized controlled 27-year follow-up study (Pallesen et al., 2015) of three RBCs in the Class II restorations, showed acceptable longevity over the 27-year evaluation period. Thirty participants, 25 females and five males (mean age 38.2 years, range 25–63), received at least three Class II restorations of moderate size. The evaluation was carried out with modified USPHS criteria at baseline, 2, 3, 10 and 27 years. The 27-year overall success rate was 56.5%, with an annual failure rate of 1.6%. The failed RBC restorations were analyzed for the restoration failure cause. It was discovered that secondary caries (54.1%), occlusal wear (21.6%), and bulk fracture (18.9%) were reasons for RBCs failure. In addition, extended longevity was recognized with the 3-surface restorations, in comparison to 2-surface restorations, however, the difference was not statistically significant.

A 2014 Cochrane systematic review of longevity of direct RBC restorations versus amalgam restorations in permanent posterior teeth, presented a different picture. The authors included seven clinical trials, separated into two groups (a two and a five split-mouth trials group) in the systematic review. The analysis of a two-trial group included 1,645 RBC restorations and 1,365 amalgam restorations (921 in children), while the five split-mouth trials analysis included 1,620 RBC restorations and 570 amalgam restorations (unspecified number of children). The results demonstrated that in the 5-7 years’ follow-up of RBCs exhibited a significantly higher risk of failure, compared to amalgams, with a risk ratio (RR) 1.89, and an increased risk of secondary caries RR 2.14. However, without any substantial evidence of restoration fracture risk, which was recorded to be RR 0.87. Nevertheless, the authors reported some problems associated with the analysis: all seven trials were
experiencing a high-risk of bias, and there were problems with data recording in the five split-mouth trials. Moreover, analyzed data were perceived as "low-quality evidence." The authors concluded that posterior RBC restorations exhibited a decreased longevity and a higher incidence of secondary caries than the amalgam restorations. However, the frequency of bulk fractures is similar for both materials, during the observed period of 5 to 7 years. It was concluded that RBC restorations have a shorter lifespan in comparison to amalgams, however, long-term, and superior quality randomized clinical trials should be conducted to elucidate the current state of the RBC restorations longevity.

An Austrian study (Beck et al., 2017) \(^{302}\), analyzed RBC longevity of the Class I/II prospective studies and clinical trials that occurred from 1996 to 2015, which included a total of 88 studies. Studies were classified based on the observation period (all studies vs. short-term vs. long-term studies). The average AFR was 1.46% for short-term studies, and 1.97% for long-term studies. The difference in failure rates between materials tested was not significant. Further analysis showed the influence of operators, isolation techniques and bonding systems on the overall failure rate to be not significant, while the filler-size effect was statistically significant. The results of short-term observation studies (>5 years), the most common reasons for failure were fractured restorations, followed by marginal defects and secondary caries. In more prolonged study periods (<5 years) secondary caries and tooth-fracture were the predominant reasons for failure.

A recent international study (Borgia et al., 2017) \(^{303}\), examined clinical performance of RBC restorations placed in Class I/II molars/premolars over the course of 5 to 20-year observation period. The study analyzed 105 restorations, from which 101 RBCs were placed on vital teeth, and only 4 restorations were placed in endodontically treated teeth, restored
without a post. The subjects consisted of 40 women and 21 men. The evaluation used modified Ryge criteria (marginal adaptation and discoloration, and surface morphology, with a 3–level assessment criteria). The observed mean survival time of restorations that remained functional was 11 years and seven months. At the time of the examination, 103 (98%) RBCs were still in function: 62 premolars and 41 molars. Two (2%) RBCs had failed. It was observed that 98 RBC restorations (95.1%) were rated as clinically successful. It was noted that there was a significant difference between RBC clinical performances of premolars and molars (60.2% vs. 39.8%), and corresponding restoration size and location. Clinical performances among hybrids, microhybrids, nanohybrids, and microfilled or midfilled RBCs were evaluated. The analysis revealed no statistically significant difference among all RBCs used. However, Heliomolar (Ivoclar-Vivadent), an inhomogeneous microfilled RBC, exhibited the longest mean survival time.

A Finish study (Palotie et al., 2017), analyzed the longevity of 2-surface and 3-surface posterior restorations according to the tooth type, restorations’ size, and the restorative material used in Public Dental Services in Helsinki City. A total of 5,542 restorations were placed in 40% premolars and 60% molars at the baseline. These 2-surface and 3-surface posterior RBC and amalgam restorations were followed indirectly from 2002 to 2015. Out of a total number of restorations, 93% were RBC, and 7% were amalgam. Sixty-one percent of the restorations were placed in female patients, and 39% were placed in male patients, and recorded patient age was between 25-30 years. AFRs of restorations were calculated separately by tooth type, restoration size, and the material used. The most extended median survival time and the smallest failure rates were found for teeth in the maxilla, for premolars, and for 2-surface restorations. The median survival time of all
restorations was 9.9 years. It was noted that restoration replacements happened less often in
the maxilla (AFR 4.0%) than in the mandible (AFR 4.7%). The median survival time of
RBCs was greater for 2-surface than for 3-surface restorations. The overall AFR across 13
years was 4.3%, as observed to be smallest for 2-surface RBC restorations in premolars and
largest for 3-surface RBC restorations in molars. Furthermore, the mean AFR in 13 years
showed that the values of 2-surface amalgams and 2-surface RBCs in molar teeth were
similar (4.7 vs. 5.0). However, the mean 13-year AFR for 3-surface amalgams was
statistically significant in comparison with 3-surface RBCs in molar teeth (5.2 vs. 7.1). The
authors concluded that longevity of posterior RBC multi-surface restorations is comparable
to the longevity of amalgam restorations.

1.9.2 Effectiveness of LPUs in dental practices

Although there was a plethora of laboratory studies on LPUs' performance, however,
a small number of studies that evaluated LPUs in dental practices have been published. The
first ever published study that characterized LPUs' performance in Britain's dental practices
was (Dunne et al., 1996) 305, a survey of QTH LPUs effectiveness and a comparative
evaluation of light testing devices. The authors characterized the light output from 49 LPUs
in clinical use. Also, they measured the effect on depth of polymerization (DOP) of RBCs
caused by a range of light outputs, and they assessed the relationship between radiometer
meter readings and DOP of RBC in a human tooth model and a Heliotest. The evaluation of
LPUs was carried out by an analog “Lamp Checker” radiometer. Although the manufacturer
of the radiometer considered optimal light output to provide a meter reading to be within the
range 5.0 to 7.0, the mean meter reading produced by the 49 LPUs using a lamp Checker
radiometer was 4.4 (+/-2.4 SD), range 0.3 to 10.0. The cumulative study results (DOP and Lamp Checker) revealed that more than 50% of tested LPUs have been underperforming.

Following the previous study findings, another study (Burke et al., 1997) brought new light about the QTH LPUs effectiveness in dental practices in Great Britain. These findings were based on a survey that tested LPUs effectiveness used in general dental practices by conducting the Heliotest (Ivoclar-Vivident) and Z100 RBC (3M ESPE). Heliotest is, in essence, a modification of a simple scrape test. The test utilizes a 3 mm diameter split plastic mold, which is filled with the RBC, and polymerized with the LPU from the top side only. At the bottom side of the specimen, any soft material is removed. The height of the remaining hard, polymerized material is measured top-to-bottom and expressed in mm, which represents the Heliotest result. The LPUs characterization was in a function of DOP assessment (Heliotest and Z100). The mean incremental depth stated as being used by the respondents was 2.6 mm. It was found that 43.5% of the participants’ LPUs (n = 63) produced DOP below that value. Although reported results could exhibit inaccuracies to a certain degree, the findings were in line with the previous study.

An Australian study, (Martin et al., 1998) assessed the adequacy of QTH LPUs output, their pattern of usage and the maintenance, based on the survey conducted by 3M Health Care representatives who paid visits to approximately 4% of dental practices in Australia. All 3M representatives were trained so that data collection could be standardized. The incident irradiance of LPUs was tested using an analog radiometer (Demetron Research, Danbury, CT, USA). The irradiance recordings were assigned into three categories: 400 mW/cm² and above (sufficient intensity), 201-399 mW/cm² (marginal intensity; where additional exposure time would be required), and 200 mW/cm² and less (low intensity). A
total number of units assessed was 214. Based on the minimum irradiance passing criterion of 400 mW/cm² that was established for this study, it was found that 47.7% of LPUs tested showed substandard performances. Moreover, the age of LPUs tested, ranging from 6 months to 19 years. The participating dental practitioners exhibited a general lack of awareness of the need for maintenance of their LPUs.

Another international study (Pilo et al., 1999) published results from the Middle East with similar findings. The incident irradiance of 130 LPUs from 107 dental offices was assessed with analog (P/N 10503) and heat (P/N 10517) radiometers (Demetron Research Corporation, Danbury, CT, USA) according to manufacturer's instructions. Also, Knoop hardness values of 50 randomly selected LPUs were taken to calculate relative hardness (bottom/top ratio). The irradiance of tested LPUs ranged from 25–825 mW cm². The study design followed manufacturer’s recommendation that incident irradiance value of 300 mW/cm² was recognized as a passing standard. The results of this study revealed that 55% of LPUs tested were underperforming. However, data obtained by the heat radiometer showed that only 24% of tested LPUs were underperforming. When hardness data applied, 46% of LPUs tested were found to be inadequate, which was in line with previous findings.

A South African study (Solomon et al., 1999) conducted assessment of QTH LPUs used in private dental practices, and in state and, trade union dental clinics. The irradiance of each LPU was measured using an analog radiometer Cure Rite (Efos, Mississauga, ON). The mean reported values ranged from 22 to 448 mW/cm². The authors reported that 45.7% of LPUs tested functioned below the proposed standard (300 mW/cm²).

The following studies conducted in Canada and Brazil exhibited similar results, regardless of the study design. The Toronto study (El-Mowafy et al., 2005), which
subsequently was succeeded by the Brazilian study (Santos et al., 2005) \(^{311}\), evaluated a large sample size that measured incident irradiance of QTH LPUs, using a dental radiometer in conjunction with a Knoop microhardness test. The Toronto study evaluated incident irradiance values of 214 QTH LPUs with an analog radiometer. The number of the participating private dental offices was 100. In this study, an irradiance level of 400 mW/cm\(^2\) and above was deemed sufficient. It has been shown that 65 LPUs had irradiance values below 400 mW/cm\(^2\), and 14 LPUs had irradiance values lower than 233 mW/cm\(^2\). Therefore, a total of 30.3% of LPUs tested generated less than the sufficient irradiance values, which was a significant improvement in comparison with the 1999 study net results, regardless the difference in methodologies employed in those studies. The Brazilian researchers \(^{311}\) visited 100 private dental offices in El-Salvador, Brazil and evaluated 120 QTH LPUs, using an analog radiometer (Optilux 100, Kerr). The recorded exitant irradiance values ranged from 10 to 1,000 mW/cm\(^2\), with an average mean value of 255.8 mW/cm\(^2\). Based on a passing criterion that was set at 300 mW/cm\(^2\), 56% of LPUs tested were considered underperforming. The age of LPUs tested varied significantly, with a range from 1 to 21 years.

Other international studies evaluated several QTH and LED LPUs, with interesting findings. First, an Indian study (Hedge, 2009) \(^{312}\) investigated a pool of 200 LPUs, consisted of 81 LED and 119 QTH LPUs. An L.E.D Radiometer (Kerr, Orange CA) was used. They set up 400 mW/cm\(^2\) as a passing irradiance criterion. The results showed that only 10% of LED LPUs and 2% of QTH LPUs were able to meet this criterion. These results were very discouraging and alarming, since most of LPUs tested could not sufficiently polymerize RBCs.
Studies conducted in Saudi Arabia (Al-Shaafi et al., 2012) followed by Jordanian study (Maghaireh et al., 2013) shed some new light on LPUs' effectiveness in private dental practices in the Middle East. It is critical to note that the Saudi study had a mixed pool of 140 LPUs (67 LED LPUs and 73 QTH LPUs), which was examined by a laboratory-grade spectroradiometer, in selected urban and rural areas of Saudi Arabia. The passing criteria were 300 mW/cm² for QTH, and 600 mW/cm² for LED LPUs. The results showed that urban areas had a significantly higher number of LPUs that performed according to the passing criteria. The passing scores reported in rural versus urban areas were 32% and 49%, respectively, for QTH LPUs, and 66.7% and 70.5%, respectively, for LED LPUs. The results showed that LED LPUs outperformed QTH LPUs by a large margin.

The Jordanian study examined a total of 295 LPUs (154 LED and 141 QTH) using the L.E.D Radiometer (Kerr, Orange CA) in 295 dental clinics. The researchers found that 79.2% of LED LPUs and 26.2% of QTH LPUs could generate incident irradiance at least of 300 mW/cm². Again, these results showed that QTH LPUs exhibited severe performance issues and that they should be replaced with LED LPUs.

Furthermore, the results from a Swiss study (Sadiku et al., 2010), that used an integrating sphere to evaluate a total of 220 LPUs, which more than 65% were LED LPUs, showed that the total amount of insufficient and damaged LPUs was as high as 40%.

A Kenyan study (Kassim et al., 2013) examined (irradiance, depth of polymerization (DOP) and Vickers hardness) of 83 LPUs in private and public dental health facilities in Nairobi, Kenya. The irradiance assessment was conducted using a Cure Rite radiometer (Efos, Mississauga ON). LPUs tested included a total of 43 (51.8%) LED LPUs, 39 (47.0%) QTH LPUs, and only one (1.2%) Plasma Arc Curing (PAC) LPU. Thirty-five
(42.17%) LPU generated the irradiance levels in the range from 0 to 300 mW/cm$^2$, while forty-three (51.8%) of LPU tested produced the irradiance between 300 and 1,200 mW/cm$^2$. The authors did not differentiate the irradiance value differences among LED, QTH, and PAC LPUs. However, they concluded that generally, any irradiance level above 600 mW/cm$^2$ yielded acceptable surface microhardness but only intensities above 900 mW/cm$^2$ resulted in adequate DOP (2 mm or more).

The latest published international study (Hao et al., 2015) investigated the incidence irradiance values, and LPUs` service information used in private dental offices in Changchun City, China. The irradiance recordings were grouped into two categories: 300 mW/cm$^2$ and higher (adequate), and 299 mW/cm$^2$ and less (inadequate). A digital Cure Rite radiometer (Dentsply Caulk, Milford, DE,) with a range of 0–2,000 mW/cm$^2$ was used to characterize the irradiance of LPUs tested. A total of 196 LPUs from 156 private dental offices in Changchun City were tested. These units included 132 QTH LPUs and 64 LED LPUs. Survey samples covered 31 brands of LPUs, 14 of which were foreign brands, and 17, domestic. The mean irradiance of the 196 light units was 453.1 mW/cm$^2$, and the distribution of the irradiances varied widely from 0 (2 units) to 1,730 mW/cm$^2$. The average irradiance value of the QTH LPUs was 340.5 mW/cm$^2$, while the LED LPUs had an average irradiance of 682.5 mW/cm$^2$. The results showed that 31.6% of all tested LPUs were performing below the 300 mW/cm$^2$ passing criterion. Also, 76 (57.6%) of QTH LPUs and 58 (90.6%) of LED LPUs exhibited irradiance of 300 mW/cm$^2$ or more. The study researchers concluded that LED LPUs have a more extended clinical life in comparison to QTH LPUs.

A Norwegian study (Kopperud et al., 2017), which examined light polymerization procedures: LPUs` performance, clinicians’ knowledge, and safety awareness among
participants in Norwegian Public Dental Service in 2015, presented some interesting findings. The survey investigated dentists’ knowledge on practical use and technical features of their light sources as well as their safety awareness. The authors invited a total of 1,313 dentists to participate in the study. However, only 748 dentists responded and agreed to participate. In addition, 35 dentists from those who responded, stated they were not proficient in restorative procedures and were excluded from statistical analyses. It is important to notice that out of 713 participants in the study, 69.6% were females and 30.4% males. The results showed that participants on a daily basis used the average of 57.5% of their time for RBC placements, which ranged from 1 to 30 (mean 7.7, SD 3.6). The average radiant exposure per a single increment of RBC was 27s. The longest individual mean polymerization cycle per day was about 100 cycles longer than the shortest one. Furthermore, the majority of participants (78.3%) were unaware of the irradiance value of their LPUs, while a significantly higher percentage of dentists in this group had not performed regular maintenance of their LPUs compared with all participants (17.1% vs. 3.3%). Moreover, almost one-third of participants used inadequate eye protection during the light polymerization. The findings revealed considerable variation among Norwegian dentists in the Public Dental Service concerning participants’ knowledge about light polymerization, the LPU common clinical daily usage, the maintenance protocol implemented in their practices, and safety protection during the polymerization. Although two-thirds of participants showed adequate knowledge and practice in regard to photopolymerization, the number of dentists that have not presented sufficient awareness about personal protection during the polymerization, or lack of knowledge about their LPUs, is still very high. Furthermore, the majority of the study participants (78.3%) were unaware of the irradiance value of their
LPUs, thus rendering the radiant exposures uncertain. Based on these findings, the authors concluded that a substantial number of practitioners in Norwegian Public Dental Service had exhibited inadequate knowledge and technical skills for sufficient RBC polymerization. The findings are somehow alarming because in Scandinavian countries amalgam placement is almost eliminated and has been replaced with RBCs.

Although all of these studies reported that LPUs employed in dental practices include a relatively large number that produce inadequate irradiance levels, it was evident that LED LPUs have shown much better results than QTH LPUs. Although, geographic variations, different methodologies, and differences in study designs, present challenges in making meaningful comparisons, needless to mention that effectiveness of LED LPUs require further investigation because the percentage of inefficient LED LPUs remains relatively high.

All the previously mentioned studies concluded that there was a persisting problem associated with LPUs used in dental practices. In addition, the effectiveness of LPUs used in dental practice depends on the LPUs performance as well as the operator's ability to deliver light energy to the restoration. Therefore, there was a need to conduct a new study to determine the combined effects of both, LPU efficiency and the adequacy of operator's light-application technique, collectively.

To the authors’ best knowledge, this would be an essential and pertinent study, which would shed some light on those two factors, closely related to the proper polymerization of RBC restorations. For that reason, we focused our research on the LED LPUs used in Toronto private dental practices, to characterize crucial factors that have been shown to have profound effects on light polymerization of RBCs. Furthermore, the data obtained in this
study will be compared with the QTH LPU survey conducted in Toronto, Canada, ten years prior.

Chapter 2

Objective and Aims
The literature review made it clear that adequate RBC polymerization is highly dependent on the capacity of LPUs to generate sufficient quantities of energy at appropriate wavelengths and the ability of dental practitioners to deliver the right amount of energy during the polymerization.

With state-of-the-art equipment, the goal of this project was to measure the effectiveness of and characterize LED LPUs in collaboration with 100 dental practices in the Greater Toronto Area.

The aims of this study were:

1. Quantify exitant irradiance and the 10s radiant exposure of LED LPUs in the participating dental practices using the CheckMARC® system,
2. Assess LPU operators' technique and consistency of a10s radiant exposure with LED LPUs using the MARC® Patient Simulator, and
3. Evaluate the mechanical properties of RBC samples polymerized with previously tested LED LPU in the participating dental practices by conducting the Biaxial Tensile Strength (BTS) test and Knoop b/t ratio hardness (RH) test.
Chapter 3

Manuscript 1

Assessment of LED Light-Polymerization Units Used in

Toronto’s Dental Private Practices
Assessment of LED Light-Polymerization Units Used in Toronto’s Dental Private Practices

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Abstract

Objectives: To characterize the radiant exposure of LED light-polymerization units (LPUs) in 100 private dental practices in Toronto and evaluate the effect of age on their performance. Materials and Methods: 100 dental practices from the Greater Toronto Area were recruited. Each LPU was assessed for age and light-guide condition, and its 10s radiant exposure (RE) measured by the CheckMARC® (BlueLight Analytics, Halifax NS). A Bluephase Style (Ivoclar-Vivadent, Amherst, NY, USA) unit served as a reference LPU. A 10s RE was multiplied by 2 to represent a 20s RE and compared to an arbitrary passing criterion of 16 J/cm². Data were statistically analyzed using Pearson correlation and independent-samples t-tests at the 95% Confidence level. Results: 113 LPUs were tested. LPUs age ranged from 1 to 5.5 years, and damage levels to light-guide were between 0 and 4 (scale 0/8). RE ranged from 3.8 to 59.6 J/cm² (M=21.7, SD=8.6). A considerable number of LPUs (26 LPUs) did not pass the 16 J/cm² criterion. The independent-samples t-tests showed that LED LPUs that did not produce the minimum energy level, were older, t (113) =5.16, p<0.001, and their light-guide had damage, t (113) =7.17, p<.001. Conclusions: A wide range of RE (3.8-59.6 J/cm²) was recorded among 113 LPUs tested. Seventy-seven percent of LPUs were able to generate 16 J/cm² RE. LPUs with accumulative damage above 2.5(0/8), and at least 3.5 years in service could not produce a study-required RE. A strong, (r=-0.67, p<0.001) negative correlation between LPUs' age and light-guide damage and LPUs' incident irradiance was found. Clinical significance: 23% of LPUs tested failed to meet an arbitrary RE value of 16 J/cm², while 47.8% of LPUs tested performed below the reference LPU RE value of 21 J/cm².
Keywords: Light Polymerization Unit (LPU); Irradiance; Radiant exposure; CheckMARC® device.
Introduction

Due to an increased demand for natural-looking restorations, as well as health and environmental concerns regarding the mercury in amalgam restorations\(^1\), a rapid increase in use of resin-based composite (RBC) materials have been observed, as either a primary RBC placement or amalgam restoration replacement\(^2, 3\). However, the literature has shown that longevity of RBCs has been significantly shorter than that of amalgams\(^4\). The most commonly reported consequences associated with RBC failure are secondary caries and bulk fractures\(^5, 6\). The failure of RBC materials could be attributed to insufficient polymerization, in particular in the Class II proximal boxes\(^7\). Although RBC placement is a technique-sensitive procedure that requires clinicians’ full attention, however, polymerization by Light Polymerization Units (LPU) may not receive the attention it merits\(^7\). Adequate RBC polymerization is much more than a simple point-and-click procedure\(^8\).

In contemporary dental offices, light-emitting diode (LED) LPUs have become the standard units for RBC materials polymerization\(^9\). The LED LPUs have not been exclusively used for the polymerization of RBC materials, rather their use has been extended to a wide range of clinical procedures, from fissure sealants to veneer cements. The LED light sources offer several advantages over other light sources, such as a relatively high radiant exitance, enhanced mobility, and affordable price structure\(^10\). Currently, two main types of LED LPUs are available. Single peak LED LPUs, which deliver their spectral irradiance in the closest range to the maximum absorption spectrum of camphorquinone (CQ) photo-initiator \(\lambda_{\text{max}}=468 \text{ nm}\), referred to as monowave LPUs\(^11\). Multiwave LED LPUs (also known as Polywave\(^\circ\), a trade name of the Ivoclar-Vivadent company), which are suitable for activation
of CQ and the alternative photoinitiators (primarily PPD, Lucirin TPO, and Ivocerin), usually deliver two peaks of spectral irradiance 11.

Because LPUs produce electromagnetic radiation of specific wavelengths, mainly from 360 nm to 515 nm, radiometric nomenclature should be used 12. The output from LPUs, which is accurately termed the radiant power, is expressed in mW. Another essential feature of any LPU is the radiant exitance, which characterizes the LPU’s radiant power output emitted throughout the area of the light probe tip, expressed in units of mW/cm². The most important feature of LPUs, often incorrectly reported, represents the incident irradiance, which is the radiant light power delivered to the RBC material surface, expressed in mW/cm². The term irradiance can also be used to characterize the radiant exitance at 0 mm light source distance 13. The radiant exposure is the product of irradiance applied to the RBC surface and exposure time, and its value is expressed in J/cm². Due to a non-uniform irradiance beam profile 13, the value represents a mean of all values irradiated throughout the tip of the light probe surface, which is considerably affected by a change to the diameter size at the tip of the light probe 14.

Dental radiometers usually are used for measurement of the LED LPUs’ irradiance in most dental practices. However, some studies have warned about erroneous readings associated with dental radiometers 15,16. However, they can be used to rank LPUs on a relative basis.

Adequate polymerization of RBCs is critical for their long-term clinical success. A commonly held assumption that an equivalent of 16 J/cm² of delivered radiant exposure to a single 2 mm thick increment of RBC material is considered sufficient for adequate RBC polymerization 17,18,19. However, the manufacturers’ recommended minimum radiant
exposures for RBC polymerization can vary to a great extent, depending on intrinsic properties and chemical formulation, as well as the shade of the material and the radiant exitance of the LPUs. Dental practitioners are not able to effectively measure the radiant exposure at the RBC restoration. As a result, dental practitioners can either deliver too much energy to the restoration, which can locally generate heat, or deliver too little energy, which can cause inadequate polymerization. Recent research has found that contemporary LED LPUs with a radiant exitance of more than 1,000 mW/cm², designed for a 10s exposure, often were habitually extended to 20s exposure. There is a plethora of studies on performance of LED LPUs in private dental practices. However, based on earlier studies, LPU assessments were conducted by using dental radiometers and with the microhardness measurements for calculation of relative hardness. A previous study conducted to determine the state of LPUs in Toronto's private dental practices which was based on quartz-tungsten-halogen (QTH) LPUs' assessment, was published in 2005 when QTH LPUs were the primary source for photopolymerization. Current literature indicates that LED LPUs have become the gold standard for the polymerization of RBC materials in experimental research settings as well as the most frequently used light sources in private dental offices. The percentage of clinically unacceptable LPUs found in different dental practices varied considerably, from 10% to as much as 70%. However, these data should be interpreted with caution, since the study designs differed significantly, and all of these studies employed dental radiometers that had proven to exhibit inaccuracies.

This study aimed to examine the incident irradiance of LED LPUs in 100 private dental practices in the Greater Toronto Area, and to evaluate the effect of age and damage of light-guide of these LPUs' measured incident irradiance as recorded by a CheckMARC®
device. The Check MARC® has a built-in laboratory grade UV-VIS spectrometer USB4000 (Ocean Optics, Dunedin, FL), with a spectral range from 365 to 515 nm and a laboratory-grade cosine-corrected sensor. This device can efficiently measure incident irradiance up to 10,000 mW/cm² (integration times are used to enable changes in intensity and prevent saturation). A 16 mm diameter sensor is individually calibrated using a NIST-referenced light source (HL-2000 Tungsten Halogen, Ocean Optics, Dunedin, FL). The objective was to test the following research hypotheses. The first research hypothesis was that LED LPUs tested can deliver 16 J/cm² radiant exposure in a 20s exposure. The second research hypothesis was that neither the age of the tested LPUs nor the damage to the light probe would affect the 16 J/cm² radiant exposure in a 20s exposure cycle.

Materials and methods

Upon receiving the University of Toronto Research Ethics Board approval, private dental practices were recruited to participate in the study. The 2012 listing of dentists published by the Royal College of Dental Surgeons of Ontario was used to identify dental practices in the Greater Toronto area. Over 350 potentially qualified practices were initially contacted via telephone to determine their eligibility to participate in the study. However, only 250 qualified dental practices were provided with the study protocol, along with a letter of consent. Only 100 dental practices were retained for the study.

The recruitment criteria for the study participants included the following: a general practice physically located within the Metropolitan Toronto area, with proficiency in RBCs placement. Testing of LED LPUs was conducted in participating dental practices using a
commercial, laboratory grade light measuring device (CheckMARC®, BlueLight Analytics, Halifax, NS), (Figure 3.1). The device was attached to a laptop computer. One test administrator conducted all the testing in each of 100 participating dental practices. The following LED LPUs information was obtained and entered into the CheckMARC® V2 software: the make and model of the LED, visual and tactile inspection of the light probe for cracks, chips, or debris, use of a physical barrier, and sterilization method. The CheckMARC® uses the planar active area of the light tip to calculate incident irradiance measurements. The planar active area is defined by the area of the light tip from which light exits. When a light tip has a curved lens or no flat surface, the area equivalent to the opening plane is measured such is the case for the Valo LPU (Ultradent, Utah), which has a 9.7 mm diameter opening for the lens. Technically the curved lens has a more extensive area but the plane at the tangential point of the lens to define the area has been used. The terms internal or external diameter is not adequate to explain the area measurements for all light types. Thus, to adequately use this device, proper identification of an external diameter size was required. Several LPUs have more than one size of a light probe diameter. The external diameter was measured using Mitutoyo digital caliper (Mitutoyo Canada, Mississauga ON), in which the corresponding light probe diameter from the CheckMARC® V2 software was selected.

The light probe level of damage and resin build-up was appraised by using an evaluation scale (0-8), where 0 represents no damage, and 8 represents the maximum involvement of the light emitting surface of LPUs. The damage on the probe surface was typically observed as a localized crescent along the margins and represented the glass chipping at the marginal area, due to a fall. The resin build-up was also observed at the
periphery of the light probe, very close to the margin. In many instances, resin build-up was localized at the top of damaged surface, overlapping each other. The light probe of each LPU tested was wiped off with disinfecting wipes to remove any dirt, before commencing the incident irradiance test. The image of the light probe was imported into the photo-editing software (Adobe XD™, Adobe Systems, San Jose, CA). The circle represents the light emitting area of the majority LPUs. The damage location resembled a crescent, and it was always noticed at the margin of the LPU light-guide tip, not passing more than 5 mm towards the center of the probe. The software has an option to cut the imported image circle into eight equal sectors and to calculate the area that represented the damage. Furthermore, the software has a tool which measures and calculates the area of damage along the edge of the light probe, as shown in Figure 3.2. The grey elliptical areas in the figure represent the captured physical damage on the surface of the light probe. However, this pattern did not work with the SmartLite Max (Dentsply), which has an elongated ellipsoid light probe surface. In this situation, the damage level was assessed by dividing the light probe surface into eight equal sectors and then applying the previous methodology. The LPUs have been tested “as-is” to obtain an accurate indication of their photopolymerization potential.

After entering the required information, the CheckMARC® device was attached to the computer. The test administrator conducted the test by applying the LED LPUs light tip directly to the Check MARC® sensor and completing a 10-second test cycle. This was repeated 3 times. The mean of 3 measurements was displayed on the computer screen. The measurements were taken in the standard mode of the LPU and without any protective barrier. The Check MARC® software generated a LED LPU report, which included irradiance (mW/cm²). A 10s radiant exposure was multiplied by 2 to represent a 20s radiant
exposure. The rationale for using the 10s, and not 20s radiant exposure, was only for efficiency purpose in a busy dental office. However, it is well-known that LPUs emit a particular quantity of light after the termination of the process. Thus, the CheckMARC® device could capture the amount of light energy beyond a 10s-recording cycle. Thus, when a report was generated, it often showed the radiant exposure in 10.1s.

A computed 20s average radiant exposure of a reference LED LPU (Bluephase Style, Ivoclar-Vivadent), which generated 21 J/cm², was used as a positive control. The rationale to use a positive control was to determine how the top of the line LPU (at the start of the project) would be scored when comparing the tested LPUs.

• Statistical analysis:

Descriptive statistics were used to evaluate the irradiance of the LED LPUs tested. To assess the association between the LPU light probe damage and age of the LPU effect on radiant exposure, values in the function of the required energy of 16 J/cm², the data were statistically analyzed using the Pearson correlation (alpha of 0.001) and independent-samples t-tests. Furthermore, monowave and multiwave LPUs were compared for the level of damage and their age, using an independent-samples t-test and chi-square test. All statistical tests were conducted using a pre-set alpha of 0.05. Windows-based statistical software (SPSS version 22, SPSS Inc., IBM, Somers, NY) was used for statistical analyses.
Results

The Q-Q plots were used for normality assessment, and the results of the incident irradiance values of multiwave and monowave LPUs data distributions are presented in Figures 3.5 and 3.6.

The Levene's test was employed for testing of homogeneity of variance across the comparison groups. The test was not significant, (p=0.298), thus, homogeneity of variance across the comparison groups was assumed. The power analysis using the G Power program for the independent and paired t-tests revealed that the sample size of 113 was capable of detecting a medium effect size with the independent samples t-tests (Cohen's d=.53), and a small effect size with the paired-samples t-tests (Cohen's d=.23). Additionally, for the Chi-square test of independence, guidelines from an article (Oyeyemi et al., 2010) was used for the power analysis. According to these guidelines, the study sample size of 113 can detect only large effects with the power of .80.

The pool of tested LED LPUs consisted of 32 multiwave and 81 monowave LPUs. In the multiwave group, the Valo (Ultradent, South Jordan, UT) was the most common (57.6%), while Demi Plus (Kerr, Orange, CA) was the most common (26.3%) in the monowave group. The interpolated radiant exposure values ranged between 3.8 and 59.6 J/cm² (M=21.7, SD=8.6), using a 20s radiant exposure. The average computed 20s radiant exposure was 22.3 J/cm² (SD=9.7) for monowave LPUs and 20.4 J/cm² (SD=4.5) for multiwave LPUs. The minimum criterion (16 J/cm²) was reached by the majority of LED LPUs (n=87, 77.0%). Figure 3.3 shows the relationship among all LPUs tested with a cut-off value of 16 J/cm².
The LED LPUs tested were between 1.0 and 5.5 years of age (M=2.6, SD=1.2) and had damage levels (scale 0 to 8) ranging from 0 to 4 (M=1.6, SD=1.2).

The results of the independent-samples t-tests showed that the LED LPUs that were unable to produce the minimum acceptable level of radiant exposure, were older (t (111) =5.2, p<0.001, 95% CI for MD: .78; 1.75), and suffered more damage to the light-guide (t (111) =7.2, p<0.001, 95% CI for MD: 1.11; 1.96).

The average age of LED LPUs that were unable to meet the minimum level of radiant exposure was 3.6 years (SD=1.0), while the average age of the LED LPUs that met this criterion was 2.3 years (SD=1.1). Similarly, the average damage level of the LED LPUs that failed to meet the minimum level of radiant exposure was 2.8 (SD=0.9) as compared to 1.3 (SD=1.0) for those LED LPUs that met this criterion. The age distribution of LED LPUs that were able/unable to meet the minimum radiant exposure criterion, depending on their damage levels is presented in Figure 3.4.

A Pearson correlation analysis was used to explore the relationship between the radiant exposure versus LPU's age and light probe damage level. The results revealed a strong, r=-0.67 (p<.001) negative correlation between the LPUs' radiant exposure and age and damage of LPUs.

Monowave and multiwave LPUs were analyzed according to their age and level of damage. The average age of monowave LPUs in the sample was 2.7 years (SD = 1.2), and the average age of multiwave LPUs was 2.6 years (SD = 1.2). This difference was not statistically significant, (t (111) = 0.15, p = 0.884, CI 95% for MD: -0.46; 0.53), Cohen’s d=0.03 indicating a small effect size. Similarly, the two types of LPUs were not significantly different concerning the level of damage, χ² (4) = 5.43, p = 0.246, Cramer’s V=.22 indicating
a small effect size. Specifically, 17.7% of monowave LPUs and 17.6% of multiwave LPUs had no damage, and 6.3% of monowave and 5.9% of multiwave LPUs had the highest level of damage (level 4).

**Discussion**

Parametric statistical tests used in this study relied on the assumptions of normality and equal variances among the comparison groups. Following these assumptions is especially critical when the sample size used in the study is small. Considering that the sample used in this study consists of 113 cases, parametric statistical tests were employed. However, to investigate the potential impact of the violation of the normality assumption on the results of statistical tests, nonparametric tests were also conducted. Should the results of the parametric and non-parametric tests deviate, then the results of the non-parametric tests should be reported. However, it was discovered that the results of non-parametric tests and parametric tests were always the same. Therefore, for simplicity of the presentation, parametric tests were used.

Three relevant parameters express crucial influence on a clinically acceptable level of RBC photopolymerization: the chemical formulation, the operator's clinical skills, and the LPU's characteristics. The literature shows that the longevity of RBCs has been significantly shorter than that of amalgams, while RBC's failure is often associated with insufficient polymerization. Although the operator's clinical skills have the most critical
influence on RBC's survival, LPU's ability to produce sufficient quantities of light energy at appropriate light spectra is fundamental for the RBC restoration's clinical success.

The first research hypothesis, which stated that LED LPUs in the participating dental practices would be able to deliver 16 J/cm² of light energy, was rejected. The minimum criterion (16 J/cm²) was reached by the majority of LED LPUs (n=87, 77.0%), but not by all. The relationship among all LPUs, tested with a cut-off value of 16 J/cm², can be seen in Figure 3.3. The pool of tested LED LPUs consisted of 81 monowave and 32 multiwave LPUs. The average computed 20s radiant exposure was 22.3 J/cm² (SD=9.7) for monowave LPUs and 20.4 J/cm² (SD=4.5) for multiwave LPUs.

The second research hypothesis, which stated that LPUs` age and its light-probe damage would not affect radiant exposure, was also rejected. It was determined that the LED LPUs that were unable to deliver at least 16 J/cm² were older (t (111) =5.2, p<0.001, 95% CI for MD: .78; 1.75), and exhibited more light-probe damage (t (111) =7.2, p<0.001, 95% CI for MD: 1.11; 1.96). The age distribution of the LED LPUs that were able/unable to meet the minimum radiant exposure criterion, depending on their damage levels, is presented in the Figure 3.4. Furthermore, a strong, r=-0.67 (p<.001) negative correlation between the LPUs' radiant exposure and its age and level of damage was recognized. The study revealed that 23% of LED LPUs used in the participating private dental practices performed below the study-required 16 J/cm² passing criterion, which was in accord with previously published results 25-31.

Some comparisons can be drawn between the 2005 Toronto study 26 and the current study concerning performance differences between QTH and LED LPUs. Back in 2005, QTH LPUs were deemed as a gold standard for photopolymerization and LED LPUs just
started to gain popularity among dental professionals. The 2005 Toronto study used an analog radiometer, the best tool available at that time, to quantify irradiance of QTH LPUs. However, ten years later, the current study used more accurate laboratory-grade spectroradiometer to complete the same task. Although 100 dental practices were selected, the sample size consisted of 113 LED LPUs. The goal was to evaluate only the LPUs that were used daily, rather than all LED LPUs that may have been available in the participating offices. Furthermore, the current study intended to characterize the performance of LED LPUs in the same geographic region and to see the real differences in use among dental practices ten years after the previous study. Instead of incident irradiance measurement, a calculated radiant exposure of all LED LPUs tested was conducted, following the recommendations in the literature, for a minimum requirement of 16 J/cm\(^2\) that is considered as an adequate radiant exposure for the majority of RBC materials \(^{17}\). The study results were quite surprising compared to those of the previous studies \(^{25-31}\). The current study revealed that 23% of LPUs tested were below the study-required passing criterion, much lower than previously reported the study average of 46% (range 12-95%) \(^{25-31}\). From the underperforming LPUs group, only three (11.5%) multiwave LED LPUs were unable to meet the minimum requirement, while 23 (88.5%) of the underperforming LPUs were monowave. It was observed that multiwave LPUs outperformed monowave LPUs by a large margin. Furthermore, by calculating the ratio of substandard LPUs to the total number of LPUs tested (multiwave LPUs [3/32] versus monowave LPUs [23/81]), it was discovered that multiwave LPUs were three times less likely to perform below the study-required standard than monowave LPUs. Although the average computed 20s radiant exposure was similar for both LPU groups, 22.3 J/cm\(^2\) (SD = 9.7) for monowave LPUs and 20.4 J/cm\(^2\)
(SD = 4.5) for multiwave LPUs, double values of SD for monowave LPUs were observed. The double values of SD for monowave LPUs suggest that a significantly higher range of extreme radiant exposure values contributed to values in this group. A possible explanation is that multiwave LPUs represented 3rd-generation LED LPUs, which were introduced relatively recently in dental practice. Thus, the LPUs' age at the time of measurement was significantly lower.

In comparison with a 20s radiant exposure produced by a reference LED LPU (Bluephase Style, Ivoclar-Vivadent), which generated 21 J/cm², 47.8% of LED LPUs tested exhibited lower radiant exposure values. The substantial reduction in reported rate of inadequate LPUs could be attributed to technical advancements in LED light source technology, to the significantly higher accuracy of the spectroradiometer, and to standardization in testing by a single administrator. It is possible that QTH LPUs tested in previous studies could have exhibited some technical issues with the equipment used in the study, which may influence the accuracy of the data reported. Furthermore, the accuracy of irradiance readings depends on the adequate measurement of the light probe. The external diameter was measured using Mitutoyo digital caliper (Mitutoyo Canada, Mississauga ON), in which the corresponding light probe diameter from the CheckMARC® V2 software was selected. Thus, the accuracy to assess the radiant exposure of tested LPUs was at the highest level possible. Using the integrating sphere to measure the radiant power and then to divide this by the tip area is prone to errors because a small error in measuring the active tip diameter will lead to a substantial error in the irradiance value. For example, if the radiant power is 800 mW and the active tip diameter is 7.5 mm, the area is 44.2 mm². The incident irradiance is thus 1,811 mW/cm². If the tip diameter is 7.0 mm, the area is 38.5 mm². Thus,
for just a 0.5 mm error (0.25mm on each side), the incident irradiance is now 2,079 mW/cm$^2$, or approximately 10% more, even though the radiant power is the same.

Other factors may have contributed to the degradation of LED LPUs besides age and damage of the light probe. Some additional factors could be related to the condition of the battery or the diminished power of the LED elements. Not only external, but the internal light probe damage was examined. During the assessment of the light probe for possible damage, the light probe was removed (when possible, depending on the type of LPU) and carefully inspected for any internal cracks, which might affect the light transmission through the light probe. When possible the light patency of the probe was examined for an unobstructed reading of any printed material, from the light probe tip to its end. Thus, internal shatter inside the light probe, although not easily detected, could cause a justified concern for the capacity of the LPU to deliver expected quantities of light energy. Furthermore, it is important to note that more than 80% of the participants had no practical knowledge of how to inspect the light probe for the light transmission patency properly.

In this study, the damage level and age of the LPUs have been included in the function of the study-required radiant exposure of 16 J/cm$^2$, which differs from the design of the previous studies $^{25-31}$. Figure 3.4 shows that the age distribution of the LED LPUs had not met the passing criterion that depended on the damage level. As can be seen from this figure, the minimum level of radiant exposure can only be guaranteed for new LPUs. Even one-year-old LED LPUs might not meet this criterion if their damage level is 2 or above. None of the LPUs that had a damage level of 4 met the minimum criterion. Overall, the results suggested that other factors might also contribute to the radiant exposure of LED LPUs as both groups of LPUs (those that met and those that did not meet the minimum criterion)
exhibited overlapping age and damage level intervals. Further analysis of LED LPUs that were not able to generate the required 16 J/cm² of radiant exposure is shown in Table 3.1. As can be seen from the table, LED LPUs that failed to generate the required energy exhibited a mean age of 3.6 years and light probe damage of 2.8/8 together with their average radiant exposure of 12.03 J/cm².

The limitations of the current project were associated with the LED LPUs' assessment study design, which used the CheckMARC® device for a 10s radiant exposure and subsequently converted recorded values for a 20s radiant exposure. It would have been better if the study design had included a 20s radiant exposure measurement. The primary reason for choosing 10s versus 20s exposure time was based on the fact that choosing the latter would double the experimental time spent in the participating dental practices as this project was a part of an extensive study that required several test procedures in the same dental practice.

Future research using the same methodology should focus on different types of dental practices. For example, it would be interesting to know the performance of LED LPUs used in Toronto's public dental clinics and compare this data with the results of the current study. Furthermore, the assessment of LPUs used by dental professionals in rural areas would shed more light on the possible difference in the quality of dental care between urban and rural private dental practices.

Regardless of the current study's results, the LED LPUs tested in the participating dental practices in the Greater Toronto Area continued to exhibit a relatively high percentage of substandard LPUs, which is a cause for justifiable concern regarding sufficient RBC polymerization.
Conclusions

Within the limitations of this study that characterized the LED LPUs in the participating dental practices in the Greater Toronto Area regarding their capacity to deliver at least 16 J/cm$^2$ of radiant exposure in the 20s, the following conclusions can be reached:

1. 23% of LED LPUs tested did not meet the 16 J/cm$^2$ criterion.
2. Multiwave LPUs showed two and a half times better performance than monowave LPUs.
3. A strong, $r=-0.67$ (p<.001) negative correlation between the LPUs' radiant exposure and age and level of damage of LPUs was observed.
4. It was found that LPUs older than 4 years tended to exhibit a higher level of damage.
5. Rigorous inspection of LPUs is required for early detection of any problems associated with routine use.
6. Failure to meet the study criterion of 16 J/cm$^2$ in the 20s implies that 23% of the LED LPUs tested will not allow the practitioners to produce adequate RBC polymerization.
Acknowledgements

The current study is part of a Ph.D. thesis submitted to the Faculty of Dentistry, University of Toronto. This project was financially supported by grants from the Faculty of Dentistry Research Institute of the University of Toronto, and the American Academy of Esthetic Dentistry. The CheckMARC® device was loaned and technically supported by BlueLight Analytics for which the authors are grateful. The Bluephase Style was graciously provided by Ivoclar-Vivadent. There are no words to express immense appreciation to the project research assistants, Ms. Ana Burilo and Ms. Ivana Orlovic for their extensive contribution to the study.
Figure 3.1 The CheckMARC® spectroradiometer

Figure 3.2. Schematic illustration of light-tip damage index (physical damage and/or irremovable resin build-up) used to assess on the light probe surfaces of LPUs tested. Note that observed damage levels during the LPUs’ assessments were in the range from 0/8 to 4/8.
Figure 3.3 Calculated 20s radiant exposure of 113 LPUs with a minimum passing criterion cut-off of 16 J/cm². Note that 26 LPUs failed to reach the passing criterion.

Figure 3.4 Box and Whisker plots: LED LPUs which did not meet (above) and did meet (below) a passing criterion. Circles and stars represent the outlier data points. The circles are the outliers that are closer to the center of the distribution, and the stars are the outliers that are farther from the center of the distribution. It’s interesting to note a wide range of values at zero damage in respect to the age of LPU, only found with LPUs that met the passing criterion.
Table 3.1 Listed LED LPUs that failed to reach a minimum of 16 J/cm² of radiant exposure in the 20s. The listing includes the LED LPUs’ age, light probe’s damage level, and 20s radiant exposure results. The LPUs were classified by the type of LPU: where d: dual-peak (multiwave), s: single-peak (monowave). The LPUs listing is presented in descendent order according to RE values.
<table>
<thead>
<tr>
<th>LPU brands</th>
<th>Age</th>
<th>Damage</th>
<th>J/cm²</th>
<th>Type</th>
</tr>
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<tbody>
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<td>3</td>
<td>2</td>
<td>15.6</td>
<td>s</td>
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<tr>
<td>SmartLite IQ2</td>
<td>4</td>
<td>4</td>
<td>15.4</td>
<td>s</td>
</tr>
<tr>
<td>Flashlight 1401</td>
<td>4</td>
<td>2</td>
<td>15.2</td>
<td>s</td>
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<td>3</td>
<td>15</td>
<td>d</td>
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<td>2</td>
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Figure 3.5 Q-Q plot showed the multiwave LPUs incident irradiance observed values against normally distributed data (represented by the line).

Figure 3.6 Q-Q plot showed the monowave LPUs incident irradiance observed values against normally distributed data (represented by the line).
References


33. CheckMARC® Scientific documentation April 2015. BlueLight Analytics Inc., Halifax, NS.

Chapter 4

Manuscript 2

Photopolymerization application effectiveness among private dental practices in Toronto, Canada
Photopolymerization application effectiveness among private dental practices in Toronto, Canada

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Abstract

Objectives: To determine the ability of dental practitioners to deliver 8 J/cm$^2$ radiant exposure (RE) in 10s to the MARC® Patient Simulator’s (PS) (BlueLight Analytics, Halifax NS) simulated restorations. Methods: Dental practices from the Greater Toronto Area were recruited. Light-emitting-diode (LED) Light Polymerization Units (LPU) were assessed for their ability to deliver the study-required energy. Dental practitioners used their office's LED-LPUs to deliver light-energy to anterior and posterior PS restorations. Following photopolymerization instructions, participants were retested using the same LED-LPUs. Data were statistically analyzed using mixed ANOVA, Chi-square tests, and paired-samples t-tests with a pre-set alpha of 0.05. Results: Before instructions, 73.6% of participants delivered required-energy to anterior restorations, and 32.2% of participants delivered required-energy to posterior restorations. Following instructions, 94.3% of participants delivered required-energy to anterior restorations, and 73.6% of participants delivered required-energy to posterior restorations. Conclusions: Although LPUs could generate 8.0 J/cm$^2$ in 10s, the percentage of dental practitioners who failed to deliver the study-required energy, even after specific instructions, was 5.7% for anterior restoration and 26.4% for posterior restoration. Clinical significance: It was revealed that a large number of dental practitioners failed to deliver the study-required 8 J/cm$^2$ in 10s to posterior restoration. This finding is alarming as it relates well to early failure of Class-2 RBC restorations due to insufficient polymerization.

Keywords: Light Polymerization Unit (LPU); Irradiance; Radiant exposure; Dental spectroradiometer; the MARC® Patient Simulator.
Introduction

Given the demand for natural-looking restorations, in combination with health and environmental concerns regarding mercury in amalgam restorations \(^1\), \(^2\), resin-based composites (RBC), have become the material of choice for many restorative procedures \(^3\). However, sufficient RBC polymerization requires application of adequate quantities and appropriate spectra of light energy delivered to the surface of RBCs \(^4\). Although RBC placement is a technique-sensitive procedure that requires clinicians’ full attention, polymerization by Light Polymerization Units (LPU) may not receive the same consideration as it should \(^5\), \(^6\). It is well-known that an inadequate polymerization has a profound impact on RBCs longevity, as those unpolymerized residues exhibit health hazards due to their nature to leach into oral fluids, which has been reported in many toxicology studies \(^7\), \(^8\), \(^9\).

Dental practitioners are facing many challenges in their clinical practices when it comes to the polymerization of RBCs, especially in the posterior areas, where correct light probe positioning and alignment involves a significant degree of difficulty, due to limited access. It has been confirmed that an angular change in the light probe positioning would cause a significant impact on energy delivered to the restoration, with a corresponding reduction in RBCs polymerization efficiency \(^10\)–\(^13\). Dental practitioners usually do not have the appropriate resources to evaluate their LPUs, but to use dental radiometers. However, recent studies have warned about erroneous readings associated with dental radiometers \(^14\), \(^15\), \(^16\). Furthermore, dental radiometers measure incident irradiance (mW/cm\(^2\)) at the tip of the surface of the light probe, and thus a small change in the tip diameter will dramatically change the actual incident irradiance values.
Although LPUs irradiance measured with spectroradiometers are considered the most accurate measuring devices, this information cannot provide clinicians with the answer, of how well their RBC restorations were polymerized \textsuperscript{17,18}. Manufacturers of commercially available LPUs report that irradiance values were taken at 0 mm distance between the light probe and the measuring device, which is not a clinically relevant distance. For instance, the measured distance in the molar region between the molar cusp tip and the bottom of Class II proximal box could exceed 8 mm, a distance that would significantly reduce the light energy received by the RBC\textsuperscript{19-23}.

Sufficient polymerization of RBCs depends on several key factors: the capacity of LPUs to generate light energy (appropriate quantities and spectra), intrinsic properties of RBCs, and the technique followed by the dental practitioners to deliver the light-energy to the restorations \textsuperscript{24,25}. The goal for any dental practitioner is to efficiently and adequately polymerize RBC restorations within a clinically acceptable time frame. However, the exact quantity of required light energy for adequate RBCs' polymerization remains unanswered. A commonly held assumption is that an equivalent of 16 J/cm\textsuperscript{2} of received radiant exposure delivered to a single 2 mm thick increment of RBC material was considered sufficient for a satisfactory RBC polymerization \textsuperscript{26}. Nonetheless, in other research reports, a range between 6 and 24 J/cm\textsuperscript{2} was suggested as a minimum energy requirement for a sufficient polymerization of majority commercially available RBC materials \textsuperscript{27,28}.

Manufacturers' recommended minimum radiant exposure values for the polymerization of their RBCs can vary to a great extent, depending on the intrinsic properties of the RBC and its chemical formulations, and shade, as well as, LPU’s irradiance \textsuperscript{24,25}. Dental practitioners are not able to efficiently measure the radiant exposure of their LPUs. As
a result, dental practitioners can either deliver too much energy to the restoration, which can locally generate heat, or deliver too little energy, which can result in insufficient polymerization. Because LPUs produce electromagnetic radiation of specific wavelengths, sufficient radiometric quantities should be used in reporting the features of LPUs. The radiant power is the correct term used to describe the output from LPUs, and its measured value is denoted in units of mW. The radiant power emitted throughout the area of the light probe tip represents the radiant exitance of the LPU, expressed in units of mW/cm². The incident irradiance, an essential term of the LPU performance, often incorrectly reported, accounts for the radiant power incident (energy flux) delivered to the RBC surface, expressed in units of mW/cm². A radiant exposure, which represents a product of irradiance and exposure time, is expressed in units of J/cm².

With the introduction of the MARC® Patient Simulator (PS) (BlueLight Analytics, Halifax NS), researchers have received a new device to accurately measure radiant exposure received by simulated restorations in a mannequin head. The MARC® PS device incorporates a laboratory-grade UV-VIS spectroradiometer (USB4000, Ocean Optics, Dunedin, FL) and two, laboratory-grade cosine-corrected sensors. The sensors are 4 mm in diameter, which is the diameter of the ISO depth-of-cure mold. Light captured by the sensors is forwarded to the spectrometer through a bifurcated fiber-optic cable. The MARC® PS system simulates the patient using the mannequin head and typodont. The maxillary typodont is equipped with two light sensors: an anterior one, located between central incisors, 1mm below the buccal surfaces of central incisors (Class III simulated restoration), and a recessed posterior sensor (Class I simulated restoration), located in the maxillary left second molar. The light detector
is located at the base of a Class I preparation, 2 mm lower than the cavosurface margin and 4 mm below the cusp tip \(^{44}\).

Studies assessing the photopolymerization techniques of dental practitioners utilizing the MARC\(^{\circledR}\)PS have shown a massive difference among the participants to deliver the light energy to the simulated restorations \(^{30-35}\). The idea to explore the efficacy of LPUs in dental practices was a subject of several studies. However, to date, no study was able to measure and compare polymerization techniques of dental practitioners in the participating dental practices \(^{36-43}\).

The purpose of this study was to evaluate the operator's technique in delivering light energy to the MARC\(^{\circledR}\) PS simulated restorations, using LED LPUs in the participating private dental practices in the Greater Toronto Area. The objectives were to test two research hypotheses. The first hypothesis was that a 10s radiant exposure delivered by dental practitioners to the MARC\(^{\circledR}\)PS (anterior and posterior restorations) would produce energy equal to or greater than 8.0 J/cm\(^2\), which was reported to be half the minimum requirement, quoted in the literature \(^{26}\). The second research hypothesis was that, following the individualized photopolymerization instructions, dental practitioners would deliver more radiant energy to the MARC\(^{\circledR}\)PS simulated restorations, and will improve the consistency of energy delivered in a 10s radiant exposure cycle.

**Materials and methods**

Following the University of Toronto Research Ethics Board approval, the private dental practices were recruited. The 2012 listing of dentists published by the Royal College
of Dental Surgeons of Ontario was used to identify dental practices in the Greater Toronto area. Over 350 targeted practices were initially contacted via telephone to determine their eligibility to participate in the study. A total of 250 qualified dental practices were presented with a letter explaining the study purpose, along with a consent form. Only 100 dental practices met the study criteria and agreed to participate, with 113 dental practitioners that took part in the study. The recruitment criteria for the study participants included a general dental practice with proficiency in RBCs placement located within the Greater Toronto Area. Study acceptance was granted exclusively for participants who had never experienced MARC®PS testing before. The assessment of photopolymerization techniques of participants to deliver radiant energy was measured using a commercial testing device (MARC®PS) and was completed in the participating dental practices. Software (MARC®PS version 3.4) provided real-time radiant exposure data display and a calculation of energy delivery within user-defined spectral ranges and exposure time to reach 8.0 J/cm².

The study was a part of a broad project, which examined a total number of 113 LPUs for their ability to deliver at least of 8 J/cm² of radiant exposure during a 10s exposure. The assessment was completed by using a commercial, laboratory-grade light measuring device (CheckMARC®, BlueLight Analytics, Halifax, NS). A total number of 87 LPUs was found capable of delivering required energy. Therefore, 87 participating dental practitioners with their LPUs were assessed for their ability to deliver the study-required 8 J/cm² of radiant exposure in 10s to the MARC®PS.

However, to acquire all relevant information for this study, the participating dental practitioners (n=113) (female and male dentists, and dental assistants) were asked to deliver a 10s radiant exposure, using their LPUs, to the MARC®PS simulated restorations. The
practitioners were asked to use their LED LPUs in the way they perform the polymerization on a patient. The participants were tested using the MARC®PS by choosing to use eye protection (hand-held screens, protective glasses, or no protection at all). Participants applied LED LPU’s light tip directly to the MARC®PS anterior sensor (Class III) and completed a 10-second test cycle, performing this test three times. The same procedure was performed on the posterior sensor (Class I). After providing individualized instructions for proper photopolymerization, participants were retested, using the same protocol and the same LPU. The following instructions were given to participants after their initial testing: demonstration of proper hand positioning during light exposure, mandatory use of protective glasses, proper positioning and stabilization of the light probe, and visual inspection at each stage of the process. The test results were shared with the participants after the test procedure. A positive control group consisted of three graduate dental students who were tested in the same way as the participating dental professionals using a reference LPU (Bluephase Stylus, Ivoclar-Vivadent).

Statistical analyses

Mixed-design analysis of variance (Mixed ANOVA) was used to test for differences between three independent groups (male dentists, female dentists, and dental assistants) while subjecting participants to repeated measures (before and after instructions). Following this, Fisher's post hoc multiple comparison tests were conducted using a pre-set alpha of 0.05. Chi-square tests of independence were conducted using a pre-set alpha of 0.05 to investigate whether delivering the minimum acceptable level of radiant energy depends on the dental practitioner (male dentist, female dentist, or dental assistants). Paired-samples t-
tests were conducted to investigate the influence of individualized instructions (before/after) on light energy delivered to simulated restorations by all participating dental professionals (n=113), using a pre-set alpha of 0.05. The SPSS software for Windows, version 22 (SPSS Inc., IBM, Somers, NY), was used for all statistical analyses.

Parametric statistical tests used in this study (such as paired t-tests, chi-square tests, and ANOVA) rely on the assumptions of normality and equal variances among the comparison groups. According to the central limit theorem, when the sample size is greater than 30 cases per group, normal distribution of the sample means can be assumed if the sample data are not normally distributed. Considering that the sample used in this study consisted of 87 (113) cases, parametric statistical tests were used.

**Results**

The Q-Q plots were used for normality assessment. The average 10s radiant exposure delivered by dental practitioners (n=113) to the MARC®PS anterior and posterior restorations, before and post-instructional, are presented in Figures 4.7 to 4.10.

Equality of variances assumption across the comparison groups was tested with the Levene's test. The test was not significant, (p=0.816), thus, the equality of variances was assumed. A power analysis using the G Power program for independent and paired t-tests revealed that the sample size of 113 could detect a medium effect size with the independent samples t-tests (Cohen's d=.53), and a small effect size with the paired-samples t-tests (Cohen's d=.23). A power analysis for Mixed ANOVA used a reference (Green et al., 2010) 45, which states that each cell in design should have at least 15 cases to express the minimum
power of .80, and that criterion was met for the current study. Additionally, for the Chi-square test of independence, a reference (Oyeyemi et al., 2010) was used for the power analysis. According to the guidelines, a study sample size of 113 can detect only large effects with the power of .80.

The majority (73.6 percent) dental practitioners delivered the study-required energy to the anterior restoration before instructions. Eighteen participants (20.7 percent) did not deliver required energy before instructions but were able to deliver it post-instructional. Only three participants (3.4 percent) were not able to deliver this energy at all. The change in the number of dental practitioners able to deliver (before and after instructions) the required energy minimum to anterior restoration, as measured by McNemar test, was significant (p<.001).

Only twenty-eight dental practitioners (32.2 percent) were able to deliver the study-required energy to the posterior restoration before instructions. An additional thirty-six more participants (41.4 percent) were able to deliver required energy post-instructional. The change in the number of dental practitioners able to deliver (before and after instructions) the study-required energy to the posterior restoration, as measured by McNemar test, was significant (p<.001). The average levels of radiant exposure delivered by dental practitioners to the MARC® PS anterior and posterior restorations, before and post-instructional, are presented in Table 4.1, Figure 4.2, and Figures 4.3 to 4.6.

To investigate whether delivering the acceptable level of radiant energy depends on a dental practitioner (n=113) (male and female dentist, or dental assistants), chi-square tests of independence were conducted. The tests disclosed that the experience of dental practitioners to deliver the study-required energy is not related to the restoration location. Thus, for
anterior restoration before instructions ($\chi^2(2)=2.57, p=0.277$, Cramer’s $V=0.17$), post-instructional ($\chi^2(2)=4.95, p=0.084$, Cramer’s $V=0.24$), or posterior restoration before instructions ($\chi^2(2)=1.15, p=0.562$, Cramer’s $V=0.12$), or post-instructions ($\chi^2(2)=3.65, p=0.162$, Cramer’s $V=0.21$) were recorded.

The average levels of radiant energy delivered to anterior and posterior restorations before and after instructions for all dental practitioners ($n=113$) regardless the ability of their LPUs to deliver the study-required energy are presented in Table 4. Paired-samples t-tests were conducted to investigate whether the average energy level delivered by dental practitioners was changed post-instructional. The results of these tests were significant for both anterior ($t(112) = -10.26, p < .001, 95\%CI for MD: -3.14; -2.13$) and posterior ($t(112) = -12.26, p < .001, 95\%CI for MD: -3.17; -2.29$) restorations.

Mixed ANOVA was used to analyze whether practitioners' consistency of energy delivery was changed post-instructional. The results of this analysis showed a significant effect of time (baseline or post-instructional), Wilk's $\Lambda=0.91$, $F(1,110) =10.42$, $p=0.002$. On average, regardless of location (anterior/posterior), and type of dental practitioner, the consistency of energy delivery improved after the instructions: $M$ (before) =1.2 compared to $M$ (after) =0.9 (95%CI for MD: 0.115; 0.480). However, the effect size of this difference, as measured by partial $\eta^2$, was small (.09).

The average light-energy that the positive control group participants delivered to the MARC®PS restorations was: 9.8 J/cm$^2$ to the anterior restoration, and 9.9 J/cm$^2$ to the posterior restoration before instructions, and 12.6 J/cm$^2$ to the anterior restoration, and 11.1 J/cm$^2$ to the posterior restoration, post-instructional.
The average 10s radiant exposure (J/cm\(^2\)) that dental practitioners (n=113) delivered to simulated MARC\(^\circledR\) PS restorations, using monowave (n=81) and multiwave (n=32) LED LPUs is presented in Figure 4.11. No significant difference in performances between monowave and multiwave LPUs was observed, except in only one cluster, at posterior restoration, post-instructional (p=.022).

**Discussion**

The first research hypothesis was that the light energy delivered by dental practitioners (n=87) in the Greater Toronto Area private dental practices, during the 10s radiant exposure would be equal or higher than 8.0 J/cm\(^2\), was rejected. The majority, (73.6 %) of participants delivered the study-required energy to anterior restoration and only 32.2% of participants delivered required energy to posterior restoration, before instructions. Following instructions, 20.7 % of participants deliver the study-required energy to anterior restoration, and 41.4 % of participants delivered required energy to posterior restoration. Based on the MARC\(^\circledR\)PS results, it is clear that photopolymerization skills of some dental practitioners at the baseline, before they received individualized instructions, were not at the level that would allow them to pass the study-required criterion. Thus, the percentage of participants that delivered required energy to anterior restoration was 70.2%, while only 32.2% participants were able to deliver the study-required energy to posterior restoration. Consequently, the percentage of participants that failed to deliver required energy to the MARC\(^\circledR\) PS simulated restorations was 29.8% to the anterior and 67.8% to the posterior restoration, respectively.
The second research hypothesis was that, following individualized instructions on proper photopolymerization, participants (n=113) would deliver more radiant energy to simulated restorations, and they would improve the consistency of energy delivered during a 10s radiant exposure, was accepted. Because of individualized instructions, participants’ average for energy delivered to the anterior restoration increased by 22.6% and to the posterior restoration by 30.4%. Furthermore, they improved the consistency of delivered energy (smaller SD) during a 10s radiant exposure, 25.9% on average, regardless of a restoration location or type of dental professional: M (before) =1.2 compared to M (after) =0.9.

Dental practitioners (n=113) were asked to perform photopolymerization on the MARC® PS simulated restorations, using their LPUs most frequently used for all daily clinical procedures. The rationale for using all participating LPUs regardless of their capacity to deliver the study-required energy was to discover how two different location of simulated restoration changed the magnitude of delivered light energy. Further, to strengthen the data on the advantage of individualized polymerization instructions on improved consistency and quantity of energy delivered by dental practitioners, the participants had three attempts to deliver light energy in a 10s radiant exposure cycle, first to anterior and then posterior restoration using their choice of eye protection (or not at all). Participants were given individualized instructions on proper photopolymerization, before they were asked to repeat the test using mandatory eye protective glasses and the same LPUs, the anterior restoration first, followed by the posterior restoration. The LPU in each dental practice was characterized by the CheckMARC® spectroradiometer device to ensure the capacity of the LPU to generate at least 8.0 J/cm² of radiant exposure during a 10s-time interval.
Although results acquired by the CheckMARC® were accurate, the smaller diameter size of the sensor at the MARC® PS (4 mm) increased the irradiance values depending the differences between the LED LPUs’ light probe diameter and the MARC® PS sensor. Due to the inhomogeneity of the light-beam profile, where the LPU’s central beam exhibits higher exitance irradiance values compared to the periphery, yielding a 4 mm the MARC® PS sensor to capture inflated irradiance values, resulting in an increase of the MARC® PS readings values by 10% to 20% on average. That could explain the CheckMARC® results that twenty-six LED LPUs could not produce 8.0 J/cm² of radiant exposure, while the MARC® PS results showed that eight LED LPU’s could deliver the study-required energy to at least one of the MARC® PS restorations.

A positive control group consisted of three graduate dental students who were tested in the same way as the participating dental professionals using a reference LPU (Bluephase Stylus, Ivoclar-Vivadent). The control LPU’s ability to produce a minimum energy requirement was validated by the CheckMARC® (incident irradiance of 1,077 mW/cm²). In addition, the graduate students that represented a control group had no prior experience with the MARC® PS before were tested. The rationale to use a control LPU for the assessment of photopolymerization skills of graduate students was that a single LPU would exhibit fewer variations during the light energy production cycle, therefore, the focus was on the light-delivering technique, not on the LPU per se. Thus, the quantity of energy delivered to the MARC® PS represented precisely photopolymerization skills of subjects tested. The average energy levels delivered by the control group in the 10s radiant exposure were 9.8 J/cm² to the anterior restoration, and 9.9 J/cm² to the posterior restoration before instructions, and 12.6
J/cm² to the anterior restoration, and 11.1 J/cm² to the posterior restoration, post
instructional.

The average radiant exposure that dental practitioners delivered to the MARC® PS
truly represented the state of affairs in the participating dental practices in the Greater
Toronto Area. The average baseline radiant exposure values recorded using the MARC® PS
were lower in comparison with post instructional values because participants tried to avoid a
direct eye exposure to the LPU’s light source, which prevented them from correctly
positioning and stabilizing the LPUs on top of the simulated restoration. The participants that
were using the hand-held screens for eye protection exhibited insufficient stabilization of the
light probe over the simulated restoration, which resulted in substantially lower radiant
exposure values. In addition, some participants experienced jitters because they were
somewhat apprehensive. However, during the second and third attempt to deliver light
energy they gradually increased confidence, which was shown by improved values of
delivered energy. After individualized instructions on proper photopolymerization, which
also included mandatory use of protective glasses, the participants on average, delivered a
significantly higher energy level to the MARC® PS. The research conducted in the
participating dental practices measured polymerization techniques of practitioners who were
not entrusting the photopolymerization to their assistants. All LPUs were tested without
infection control because a variety of infection control methods were used among the
participating practices, and some practices were not using any infection control at all. For
that reason, the LPUs were tested without any protective barriers, to make meaningful
comparison among LPUs tested in all participating dental practices.
Post-instructional data showed a significant increase in delivered light energy, dental practitioners on average, increased the energy delivered to anterior restoration by 22.6% and posterior restoration by 30.4%. At baseline testing, most of dental practitioners employed a single-hand polymerization, using the hand-held protective screens or no eye protection. However, following the instructions and the mandatory use of eye protective glasses, dental practitioners using the two-hand polymerization technique improved delivered energy to simulated restorations by 26.5% on average.

A significant difference in delivered light-energy that was observed between the anterior restoration and the posterior restoration may be related to the light probe design and the limited practitioners’ ability to access the posterior restorations. There are many difficulties in the posterior area access. A light probe design, which shows a notable curvature on its end, usually stands for a substantial source of challenges in limited interocclusal space, during the light application. Furthermore, the absence of visual control during proper light probe positioning creates a struggle in keeping immovable light probe tip, as well as keeping it at the right angle to the axis of the tooth. The MARC® PS results revealed that the LPUs with a more curved light probe delivered, on average, less light energy to the posterior restoration, in comparison to the LPUs with a less curved light probe. The explanation for this phenomenon could be in the fact that a curved light probe usually needs more space for its proper positioning.

This study tested the ability of dental practitioners to deliver light energy to simulated restorations (anterior and posterior) using the MARC® PS. It was unveiled that the average amount of energy delivered to each simulated restoration, was similar among the three professional groups. However, female dentists were the most consistent in energy delivery
(expressed in lowered standard deviation values), followed by male dentists and dental assistants, respectively. Although the pool of dental assistants was indisputably larger than any other group, it can be safely assumed that the highest standard deviation values could be associated with the larger pool size (Figure 4.2). However, the difference among the energy values delivered by dental practitioners was not significant.

The current results presented in this study that proper light polymerization instructions have significantly increased energy delivered to the simulated restorations on the MARC® PS were in accord with the findings from the earlier studies\textsuperscript{30-35}. The unique perspective of the current study was the ability to characterize incident irradiance of LPUs tested, to assess the radiant exposure that dental practitioners delivered to the MARC® PS restorations, as well as to make a comparison between the two LPU types, monowave, and multiwave. The study results overwhelmingly refute the view that significant improvement has occurred as a result of individualized instructions that dental practitioners received and use of protective goggles and a two-hand polymerization technique.

Bias can occur in any phase of a research project, from planning, data collection, and analysis to the publication phase. This study exhibited selection bias to some extent because those dental practices with the possible lower quality of LPUs or questionable proficiency in RBC placements refused to participate in this study. As mentioned before, over 350 targeted practices were initially contacted via telephone/email to determine their eligibility to participate in the study. Although it was concluded that 250 practices satisfy the criteria, 100 dental practices were only recruited with a total of 113 dental practitioners. Many factors led to low study recruitment outcome.
The study exhibited standardized protocols for data collection and data entry. A single administrator completed the entire study, which substantially reduced any possible inter-observer variability and performance bias while, at the same time, enabling the test administrator to evaluate internal validity during the entire research process efficiently.

Another potential limitation of this study was a possible conceptual problem with a 10s radiant exposure using the MARC® PS. If the passing criterion of 16 J/cm² radiant exposure during a 20s exposure was performed, the results might be more pronounced and probably could bring a much more comprehensive margin of passed/failed polymerization skills. Further, the 16 J/cm² radiant exposure represented an arbitrary value that was more commonly cited in the literature.²⁶, ²⁷

The direction of future research could include a change in the research population, thus to see how rural dental practitioners differ from the urban practitioners and possible include the assessment of Dental Public Health professionals. The study findings will be most useful to researchers, as well as to dental practitioners, as well as possibly to regulatory agencies.

Conclusions

Within the limitations of this study, which used the MARC®PS to quantify energy delivered to simulated restorations by dental practitioners, the following conclusions can be reached:
1. Before instructions, 73.6% of participants delivered required-energy to the anterior restoration, and 32.2% of participants delivered required-energy to the posterior restoration.

2. Following instructions, 94.3% of participants delivered required-energy to the anterior restoration, and 73.6% of participants delivered required-energy to the posterior restoration.

3. Participants on average increased energy delivered to the anterior restoration by 22.6% and the posterior restoration by 30.4% because of instructions.

4. Specific instructions and the mandatory use of eye-protective glasses demonstrated that two-hand polymerization technique (post-instructional) is significantly better than one-hand technique engaged at baseline.

5. Following specific instructions, and because of the two-hand polymerization technique, dental practitioners improved the consistency of delivered energy to the simulated restorations on average by 25.9%.

6. A significant percentage of dental practitioners (26.4%) were unable to deliver the study-required energy to the posterior restorations, even when given instructions.

7. No significant difference in performances between monowave and multiwave LPUs was observed, except in only one cluster, at posterior restoration, post-instructional.
Acknowledgements

The current study is part of a Ph.D. thesis submitted to the Faculty of Dentistry, University of Toronto. This project was financially supported by grants from the Faculty of Dentistry Research Institute of the University of Toronto, and an American Academy of Esthetic Dentistry. The CheckMARC® device was loaned and technically supported by BlueLight Analytics, for which the authors are grateful. The Bluephase Style was kindly provided by Ivoclar-Vivadent. There are no words to express immense gratitude to the project research assistants, Ms. Ana Burilo and Ms. Ivana Orlovic for their contribution to the study.
Figure 4.1 The MARC® Patient Simulator system with a light probe positioned to deliver light energy to the posterior (Class I) restoration. The front sensor, representing the anterior restoration (Class III), between the upper central incisors, is depicted in the picture.

Figure 4.2 A 10s radiant exposure (Mean and SD) that all participants (n=113) delivered to the MARC® PS restorations, separated by each professional group, (Male and Female Dentists, and Assistants). No statistically significant difference among 3 professional groups was found.
Table 4.1 Descriptive Statistics for a10s radiant exposure (J/cm²) delivered by 113 dental practitioners using their LPUs to the MARC® PS restorations, in 4 sequences: anterior and posterior restorations before instructions, and anterior and posterior restorations post-instructional. The results were recorded by the MARC® PS v.3.4 software.

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Figure 4.3 10s Radiant Exposure delivered by dental practitioners (n=113) to the MARC® PS anterior restoration, before instructions, with respect to 8 J/cm² cut-off value.

Figure 4.4 10s Radiant Exposure delivered by dental practitioners (n=113) to the MARC® PS anterior restoration, post-instructional, with respect to 8 J/cm² cut-off value.
Figure 4.5 10s Radiant Exposure delivered by dental practitioners (n=113) to the MARC® PS posterior restoration, before instructions, with respect to 8 J/cm² cut-off value.

Figure 4.6 10s Radiant Exposure delivered by dental practitioners (n=113) to the MARC® PS posterior restoration, post-instructional, with respect to 8 J/cm² cut-off value.
Figure 4.7 Q-Q plot showing the average energy quantities that dental practitioners (n=113) delivered to the MARC®PS anterior restoration before instructions. The observed values are plotted against normally distributed data (represented by the line).

Figure 4.8 Q-Q plot showing the average energy quantities that dental practitioners (n=113) delivered to the MARC®PS posterior restoration before instructions. The observed values are plotted against normally distributed data (represented by the line).
Figure 4.9 Q-Q plot showing the average energy quantities that dental practitioners (n=113) delivered to the MARC®PS anterior restoration, post instructional. The observed values are plotted against normally distributed data (represented by the line).

Figure 4.10 Q-Q plot showing the average energy quantities that dental practitioners (n=113) delivered to the MARC®PS posterior restoration, post-instructional. The observed values are plotted against normally distributed data (represented by the line).
Figure 4.11 a 10s radiant exposure (J/cm$^2$) (Mean and SD) that dental practitioners (n=113) delivered to simulated MARC® PS restorations, using monowave (n=81) and multiwave (n=32) LED LPUs. *A significant difference was observed between two LPU types in only one group, at posterior restoration, post-instructional (p=.022).
References


Chapter 5

Manuscript 3

Relative Hardness of Resin Based Composites Polymerized by LED Light-Polymerization Units in Toronto’s Private Dental Practices
Relative Hardness of Resin Based Composites polymerized by LED Light-Polymerization Units in Toronto’s Private Dental Practices

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Abstract

Objectives: To assess relative-hardness (RH) of two brands of resin-based composites (RBC), polymerized using Light-emitting-diode (LED) light-polymerization units (LPUs) in private dental practices, Toronto, Canada. Methods: 100 dental practices were recruited. In participating dental practices, disc-specimens (2mm-thick/4mm-diameter) (n=6) were fabricated from TPH Spectra (Dentsply) (camphorquinone (CQ) photoinitiator) and Tetric EvoCeram (Ivoclar-Vivadent) (CQ/Lucirin-TPO photoinitiators). Using the office's LPU, specimens were polymerized for the 20s from the top surface, at 1mm (n=3) and 4mm tip-to-target distance (n=3). Specimens were stored (distilled-water/37°C/24h), dried for 1h, before microhardness-testing. Knoop-hardness number (KHN) for each specimen was recorded from 8 measurements (4lower/4upper), using microhardness tester with Knoop indenter (Tukon 300, Bridgeport, CT), and applying 50g load/30s dwell-time. Calculated RH ratios data were statistically analyzed using Pearson correlations, Chi-square tests, and independent-samples t-tests with a pre-set alpha of 0.05. Results: Both RBCs polymerized at 1mm had average ratios greater than the .80 level of RH (ratio of mean lower/upper surface hardness), but not at 4mm tip-to-target distance. A significantly higher percentage of LED LPUs achieved the 0.80 ratio of hardness with TPH Spectra, compared to Tetric EvoCeram RBC with both, 1mm ($\chi^2(1) =27.32, p<.001$) and 4mm tip-to-target distance ($\chi^2(1) =15.48, p<.001$). Conclusions: The RH profiles of RBCs tested demonstrated a strong, inverse correlation between the tip-to-target distance and average RH values. The incident irradiance and LPUs’ beam dispersion, had a significant effect on Knoop hardness profile and mechanical properties of RBCs.
Keywords: Light Polymerization Unit; Irradiance; Knoop hardness, Degree of conversion; polymerization; Resin-Based Composite; CheckMARC®;
**Introduction**

There are several testing procedures available to characterize RBCs polymerization efficiency. During a free-radical photopolymerization reaction, double bonds in the vinyl groups of the RBCs are converted into single covalent bonds, thus further enhancing the conversion of monomers into the linear and cross-linked polymers. The degree of conversion (DC), a significant determining factor of the polymerization kinetics, is highly associated with mechanical, physical, and chemical properties of direct restorative RBC materials, and represents the ratio of converted single bonds to the total number of starting double bonds. Several analytical methods are available for measurement of RBC conversion. For instance, differential scanning calorimetry provides a measure of methacrylate conversion based on the enthalpy of the exothermic polymerization process. The majority of analyses done to evaluate conversion of RBCs have been based on the use of spectroscopy, which gives a direct measure of reacted and unreacted methacrylate groups. Although these methods exhibited an elevated level of accuracy and sophistication, they are always related with high-costs.

The most efficient methods to determine a RBC polymerization level include DC, depth of polymerization (DoP), the degree of crosslinking (DoC), and microhardness. Researchers prefer to use reliable and easy to use microhardness tests, rather than more elaborate tests, such as FTIR or Raman spectroscopy preferentially used for DC. Furthermore, Knoop microhardness testing has proven to be a reliable and a relatively simple method to characterize RBCs’ mechanical properties after polymerization. The Knoop test gained popularity among researchers, primarily due to its good correlation with DC, which has been confirmed in numerous studies. Monomer conversion could not provide a
complete characterization of the polymer structure, because polymers with similar DC may exhibit a different degree of crosslinking and consequently different mechanical properties \(^{17}\). The commonly held assumption before the introduction of bulk-fill RBC materials, was that an equivalent of 16 J/cm\(^2\) of received radiant exposure to a single 2 mm tick increment of RBC material is considered satisfactory for adequate RBCs polymerization \(^{18}\). However, manufacturers' recommended minimal radiant exposures for sufficient RBC polymerization can vary to a great extent, depending on intrinsic properties and chemical formulation, as well as on the material shade and the radiant exitance of the LPUs \(^{19-21}\).

Hardness (H), represents an important parameter in the characterization of the surface properties of a material on a microscopic scale, which is defined as the ratio of the applied load (P), to the contact area (A), which resulted in the subsequent indentation impression:

\[
H = \frac{P}{A} = \beta \frac{P}{d^2}
\]  

(1)

Where \(d\) represents the size of attributed resultant indentation, and \(\beta\) represents the constant related to the geometry of a given indenter \(^{22}\). Vickers and Knoop are the most frequently employed micro-hardness tests for characterization of RBC materials by utilizing a pyramid-based indenter. The Vickers hardness number (VHN) is defined by using the contact area of the indentation impression and the parameter \(d\) in Eq. (1), is described as an average of the two diagonals of the resultant square-shaped impression. Thus, the \(\beta\) constant for VHN calculation is set to be 1.8544. Knoop microhardness test uses a pyramid-based indenter with the length to width ratio of 7:1 and with corresponding face angles of 172.5 degrees for the long edge and 130 degrees for the short edge, as shown in Figure 3.1. Furthermore, Knoop hardness number (KHN) calculation considers the projected area of the
indentation impression, and the parameter $d$, which is determined by the length of the long diagonal of the resultant rhombic impression and $\beta$ constant set to be 14.229. Based on Eq. (1), it can be implied that microhardness represents an indentation area corresponding variable. The literature has shown, especially with RBC materials that the inequality between a plastic zone beneath the indentation and a surrounding elastic matrix exists. Therefore, that phenomenon is described as the elastic recovery of the given material after the removal of the indenter. The elastic recovery is highly related to the surface geometry of an indenter, which differentiates the elastic recovery of Vickers indentation in comparison to Knoop indentation. The elastic recovery attributed to Vickers indentation usually develops along the depth of the indentation, while the diagonal length of the surface impression remains unchanged, contrary to the Knoop indentation, where the elastic recovery appears as a result of a minor diagonal contraction of the indenter. The elastic recovery is highly related to the surface geometry of an indenter, which differentiates the elastic recovery of Vickers indentation in comparison to Knoop indentation. The elastic recovery attributed to Vickers indentation usually develops along the depth of the indentation, while the diagonal length of the surface impression remains unchanged, contrary to the Knoop indentation, where the elastic recovery appears as a result of a minor diagonal contraction of the indenter. The Knoop microhardness computation only considers the length of the longer diagonal into the calculation of KHN, and thus makes this method preferential for its reliability over other methods. A linear correlation between Knoop microhardness and mechanical properties of RBC and Knoop microhardness and irradiance of LPUs have been shown to exist.

Although the scraping test has been considered as a depth of polymerization measure in the ISO 4049 standardization for RBCs, microhardness tests were perceived to be more reliable. The test is based on top and bottom hardness measurements; however, it is common to calculate the ratio of the bottom/top hardness, and the arbitrary minimal values of 0.80 would represent a ratio of sufficient RBCs polymerization. "Relative hardness" term represents the average bottom-to-top hardness ratio.
The project objective was to evaluate relative hardness (RH) of RBCs polymerized using LED LPUs, which were in use in participating private dental practices in the Greater Toronto Area. The test parameter for RH was the bottom-to-top Knoop microhardness values. The study objectives were to test the following research hypotheses: the first hypothesis was that the LED LPUs, from the participating dental practices, capable of producing the radiant exposure of 16 J/cm², would be positively correlated with the RH values of RBCs tested. The second hypothesis was that 1mm and 4mm material-to-probe distance, would not affect the average 0.80 RH values of 113 LED LPUs tested.

**Materials and methods**

From all participating private dental practices in the Greater Toronto Area, a total of number of 113 LED LPUs were included. Specimens were fabricated using an opaque plastic mold (Figure 5.1) from the A2 shade of two conventional RBC materials: TPH Spectra HV (Dentsply, Milford DE) and Tetric EvoCeram (Ivoclar-Vivadent, Amherst NY). TPH Spectra exhibits a camphorquinone (CQ) photoinitiator system, while Tetric EvoCeram has a mix of CQ and a small amount of Lucirin TPO photoinitiators.

With each LPU, a total number of 12 specimens were prepared (6 per material) with 4 mm diameter and 2 mm thickness. The specimens were covered with celluloid matrices on both sides and with a glass slide on the top. A 20s exposure was administered to the top surface of the specimen (n=3) by applying the LPU available in the visited dental practice LED LPU directly through a 1mm glass slide. A 2 mm-metal spacer with a 20 mm diameter was placed on the top of the glass slide that covered the specimen, then 1mm glass slide
covered the metal spacer. This setup created a 4mm material-to-probe distance. A 20s exposure of the top specimens ‘surface (n=3) by the same LED LPU was conducted. The same protocol was implemented to the other brand of RBC. Following the light exposure, specimens were stored in dark containers in distilled water medium at 37°C for 24h before microhardness testing. The next day, all specimens were dried for 1h, before commencing the tests. Knoop Hardness Numbers (KHN) were obtained at 10X magnification from eight surface measurements, as shown in Figure 5.2. Thus, each side of the specimens received four indentations in North-South and East-West direction, using a microhardness tester (Tukon 300, Wilson Instrument Division, Bridgeport, CT), and an applied load of 50g and, during a 30s dwell time. RH ratio for each specimen was calculated from the specimen’s bottom mean KHN values divided by the specimen’s top mean KHN values. A reference, multiwave LPU (Bluephase Style, Ivoclar-Vivadent, Amherst NY) was used as a positive control. The assessment of 113 LPUs in the participating dental practices was completed by using a commercial, laboratory-grade light measuring device (CheckMARC®, BlueLight Analytics, Halifax, NS).

- Statistical analysis

  Descriptive statistics were used to evaluate irradiance values of LED LPUs tested. The 10s radiant exposure data obtained by the CheckMARC® were multiplied by 2 to produce 20s radiant exposure values, which were correlated to the minimum passing criterion of 16 J/cm². To evaluate whether the association between the RH values and LED LPU radiant exposure values, concerning the minimum required the energy of 16 J/cm² exists, the Pearson correlation analysis was used, significant at the 0.001 level. Furthermore, the same
analysis was used to evaluate the relationship between the irradiance values of LPUs (n=113) and obtained Knoop hardness b/t ratio of two RBC materials, polymerized at 1 mm and 4 mm material-to-probe distance. Chi-square tests of independence were used to examine a possible relationship between LED LPUs with the capacity to deliver 16 J/cm² energy and the minimum level of RH (0.80) for each type of specimen. The results of these tests for all four testing groups (two brands of RBCs and two tip-to-target distance levels) at the 0.05 level of significance were plotted. All statistical analyses were conducted using the Statistical software (SPSS for Windows, version 22, SPSS Inc., IBM, Somers, NY).

Parametric statistical tests used in this study relied on assumption of normality of data and equal variances among the comparison groups. Following these assumptions is especially critical when the sample size used in the study is small. Considering that the sample used in this study consists of 113 LED LPUs, parametric statistical tests were used. However, to investigate the potential impact on the normality assumption violations, nonparametric tests were also conducted. In case of discrepancies that arise by using non-parametric tests, the results of the non-parametric tests would be reported. However, it was discovered that the results of non-parametric tests and parametric tests were identical.

**Results**

The Q-Q plots were used for normality assessment, and the results of the average RH values in four data distributions are presented in Figures 5.7 to 5.10. Equality of the variances assumption across the comparison groups was tested with the Levene’s test. The tests were
not significant, Tetric EvoCeram at 1 mm (p=0.351), and 4 mm (p=0.829) material-to-probe distance, and TPH Spectra at 1 mm (p=0.114), and 4 mm (p=0.067) material-to-probe distance, respectively. Thus, the equality of the variances was assumed. A power analysis using the G Power program for the independent and paired t-tests revealed that the sample size of 113 was capable of detecting a medium effect size with the independent samples t-tests (Cohen's d=0.53). Additionally, for the Chi-square test of independence, a reference (Oyeyemi et al., 2010) was used for the power analysis. According to the reference, the study sample size of 113 can detect only large effects with the power of 0.80.

The descriptive statistics for RH levels of two RBC's brands obtained from the specimens polymerized at 1 mm and 4 mm material-to-probe distance are presented in Table 5.1. The average 0.80 level of RH (ratio of the mean bottom/top surface) was accomplished for both RBC brands, polymerized at 1 mm material-to-probe distance. However, the specimens polymerized at 4 mm material-to-probe distance were not able to produce an average 0.80 level of RH regardless of the RBC brand. The percentage of dental practices that reached the 0.80 level of RH for each type of specimens is displayed in Figure 5.3. Significant differences were observed between 1 mm and 4 mm tip-to-target distances for the two RBC brands, and their RH results (inter-brand and intra-brand).

The pool of LPUs tested consisted of 32 multiwave and 81 monowave units. The average RH values of two LPU types and two RBC brands polymerized at 1 mm and 4 mm material-to-probe distance are presented in Figure 5.4. The results of the independent-samples t-tests did not show any statistically significant difference between the average RH values of two RBC brands and a type of LPU used at material-to-probe (1 mm and 4 mm) distance. The following results were observed for Tetric EvoCeram at 1 mm material-to-probe
distance $t_{(113)} = -0.94, p= 0.351$ (95%CI for MD: -0.03; 0.01), and at 4 mm material-to-probe distance $t_{(113)} = 0.22, p= 0.829$ (95%CI for MD: -0.02; 0.03), while the results for TPH Spectra at 1mm material-to-probe distance were $t_{(113)} = -1.59, p= 0.114$ (95%CI for MD: -0.04; 0.00), and at 4 mm material-to-probe distance were $t_{(113)} = -1.85, p= 0.067$ (95%CI for MD: -0.06; 0.00).

The average RH ratios produced by the reference LPU (Bluephase Style, Ivoclar-Vivadent) were 0.85 at 1 mm, and 0.80 at 4 mm material-to-probe distance for Tetric EvoCeram, and 0.84 at 1mm and 0.83 at 4 mm material-to-probe distance for TPH Spectra.

**Discussion**

The first research hypothesis, which stated that the participating dental practices LED LPUs, capable of producing a 20s radiant exposure of 16 J/cm², would be positively correlated with the Knoop hardness b/t ratio values of RBCs tested, was accepted. A positive, weak-to-moderate, but significant (an average $r=0.36$, $p<.001$), correlation was found between the average 0.80 RH level of the two RBC brands and a 20s radiant exposure of LED LPUs capable of delivering at least of 16 J/cm² radiant energy.

During the course of this project, wide variations of LED LPUs were tested, along with possible temperature differences (different weather conditions), and other contributing factors that may happen during the specimens' preparation in the participating dental practices that could cause these results. For instance, the correlation factor is not consistent among RBC materials and the material-to-probe polymerization distance. Although TPH Spectra and Tetric EvoCeram are popular brands of the Bis-GMA based nanohybrid RBCs,
which exhibit the presence of pre-polymerized filler particles in their compositions, they differ in a total filler load values, being 60-62 volume percentage for TPH Spectra and 53–55 volume percentage for Tetric EvoCeram. Furthermore, TPH Spectra exhibits a camphorquinone (CQ) photoinitiator system, while Tetric EvoCeram has a mix of CQ and Lucirin TPO photoinitiators. Thus, the effect of polymerization distance in combination with chemical properties of RBCs tested resulted in a wide range of correlation values. Tetric EvoCeram exhibited a moderate correlation factor of $r=0.43$ at 1 mm material-to-probe distance, but at 4 mm material-to-probe distance the correlation factor was reduced to $r=0.33$, where in an opposite direction with TPH Spectra ($r=0.44$ at 4 mm material-to-probe distance and $r=0.26$ at 1 mm material-to-probe distance) was detected. The magnitude of these relationships suggests that other factors are contributing to RBC microhardness, such as LPU’s spectral irradiance output (monowave vs. multiwave), as well as a beam profile differences, apart from the confirmed LED LPUs capacity to deliver at least 16.0 J/cm$^2$ of energy.

The second hypothesis, which anticipated that 1mm and 4mm material-to-probe distance, would not affect the average 0.80 RH values of the two brands RBC tested, was rejected. The average 0.80 level of RH polymerized at 1mm material-to-probe distance was obtained by 69.0% of Tetric EvoCeram specimens and 82.3% of TPH Spectra specimens, respectively. However, at 4 mm material-to-probe distance, the average 0.80 level of RH values was not achieved by any RBC material (0.77 for both materials). Furthermore, it was discovered that at 4 mm material-to-probe distance, only 28.3% of Tetric EvoCeram specimens and 37.2% of TPH Spectra specimens be able to obtain the minimum RH ratios. Therefore, a recorded RH ratio drop over the 3 mm material-to-probe distance was 59% for
Tetric EvoCeram and 54.8% for TPH Spectra, respectively. The results are in line with previous finding that light energy diminishes considerably with an increased material-to-probe distance, which is observed as reduced microhardness profile values \textsuperscript{35, 36, 37}. The results could be associated with the interactions of light polymerization energy with the microscopic slides, Mylar strips, and a 2 mm span of plastic mold lateral walls. Furthermore, a metal spacer which was used to produce 4 mm distance between the light probe and the RBC specimens, could also influence the RH values. However, the current test set up design was employed for its simplicity, quick set up time, and its ability to use in any participating dental practice.

The participating dental practice LED LPUs capable of delivering at least of 16 J/cm\textsuperscript{2} radiant exposure, produced the 0.80 level of RH only by 61.1% Tetric EvoCeram specimens polymerized at 1 mm material-to-probe distance and by 25.7% polymerized at 4 mm material-to-probe distance. A similar pattern was observed with TPH Spectra, where the requirement was achieved by 70.8% specimens, polymerized at 1mm material-to-probe distance and with only 34.5% specimens polymerized at 4 mm material-to-probe distance. It was evident that specimens at 4mm material-to-probe distance, regardless of RBC brand performed notably below what was found when the light was held at an only 1mm material-to-probe distance. Therefore, the percentage of LPUs that exhibited insufficient polymerization at 4 mm material-to-probe distance was greater than 60%. The material-to-probe distance of 4 mm or more is clinically relevant because most of the polymerization locations in posterior teeth can exceed 7 mm material-to-probe distance \textsuperscript{37}. 

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The current study tested RBC specimens of A2 shade, because of the following facts: A2 shade is the most commonly employed shade in clinical practice\textsuperscript{30}, and the composition of pigments and other colorants has the minimum effect on photopolymerization\textsuperscript{31}.

The pool of tested LED LPUs consisted of 32 multiwave and 81 monowave LPUs. In the multiwave group, the Valo\textsuperscript{®} (Ultradent, South Jordan, UT) was the most common (38.7\%), while the Demi Plus\textsuperscript{®} (Kerr, Orange, CA) was the most common (26.2\%) in the monowave group. Due to the possible variations among participating light sources, the assessment was carried on all LPUs by measuring their irradiance and radiant exposure with a laboratory-grade spectrometer, the CheckMARC\textsuperscript{®} system. The rationale was that all tested LPUs had to be examined whether they had the capacity of delivering at least 16 J/cm\textsuperscript{2} radiant exposure, to correlate the produced energy data with averaged 0.80 RH ratios of two RBC materials.

The results of an analysis which compared Tetric EvoCeram (an alternative photoinitiator system) and TPH Spectra (a conventional CQ photoinitiator system) with multiwave and monowave LPUs, showed no statistically significant difference among those four variables (see Figure 5.4). The multiwave LPUs outperformed monowave lights in all tests except with the Tetric EvoCeram 4 mm material-to-probe distance, where the average RH values of both LPUs type were identical. Interestingly, multiwave LPUs performed better on TPH Spectra specimens, regardless of the material-to-probe distance. Although TPH Spectra exhibited a higher filler load content and a conventional CQ photoinitiator system, apparently these parameters did not produce significant Rayleigh scattering, often seen with the multiwave LPUs violet light spectrum.
This project was the first study that correlated the minimum-required level of radiant exposure of LED LPUs in the participating dental practices using the average 0.80 level of RH to test two RBC materials. The majority of published studies test a selected number of RBCs using yet a variety of LPUs. This study design differed significantly from all previous studies. Microhardness values were taken 24h after exposure and stored in 37°C water to mimic the oral environment. One hour before the hardness testing, the specimens were dried using a paper towel and left in the ambient temperature, after which KHN measurements were obtained. The RBC materials complied with the Water Sorption (ISO 4049) standards. Based on results from a pilot study which used the same two brands of RBCs, no statistically significant difference in microhardness was seen when each of the two RBC materials during the 24h storage in either distilled water or dry containers.

A reference LPU (Bluephase Style, Ivoclar-Vivadent) produced sufficient hardness, regardless of the polymerization material-to-probe distance or the RBC tested. In comparison with RH values for Tetric EvoCeram obtained by the reference LPU (0.85 at 1 mm and 0.80 at 4 mm material-to-probe distance), 108 participating LPUs (95.6%) were below that RH level at 1 mm material-to-probe distance, and 81 LPUs (71.7%) did not produce that RH level at 4 mm material-to-probe distance. Similarly, in comparison with RH values for Spectra TPH obtained by a reference LPU (0.84 at 1 mm and 0.83 at 4 mm material-to-probe distance), 97 LPUs (85.8%) were below that RH value at 1 mm material-to-probe distance, while 101 LPUs (89.4%) did not reach that RH level at 4 mm material-to-probe distance. Furthermore, the reference LPU exhibits relatively homogeneous beam profile distribution of its spectral irradiance, which is the part of the latest LED generation development. Thus, it
was observed that the reference LPU exhibited more uniform Knoop hardness profile with all materials and polymerization material-to-probe distances.

Limitations of the current project were associated with the current set-up that the polymerization light is passing through glass slides, Mylar strips, and bouncing from the lateral walls of the metal spacer, which probably affect the RH values to a certain degree. However, metal sectional matrices that are used in clinical settings may similarly influence RBC polymerization. It would be better if the current set-up had included an opaque plastic spacer, preferably from the same material as the mold used for the specimens’ production.

Future research should be focused on bulk-fill RBC evaluation, using a similar method as was used in this project. Furthermore, to create a clinically relevant scenario, using the same methodology, the irradiation distance could be increased to 6 mm, because most of the polymerization locations in posterior teeth can exceed 7 mm material-to-probe distance. 37

Conclusions

Within the limitations of this study, the following conclusions can be reached:

1. Relative hardness ratios of the two RBC brands demonstrated a weak-to-moderate correlation between the light probe distance to the material surface and 20s radiant exposure.

2. The 0.80 RH ratio of two RBC brands was achieved by the majority of LED LPUs at 1 mm material-to-probe distance.
3. The 0.80 RH ratio of two RBC materials was obtained by a minority of LED
   LPU's at 4 mm material-to-probe distance.
4. The percentage of LPUs that exhibited inadequate polymerization at 4 mm
   material-to-probe distance was observed to be higher than 60%.
5. The average relative hardness reduction over a 3 mm material-to-probe
   distance, expressed by the RH profile, was 59% for Tetric EvoCeram and
   54.8% for TPH Spectra, respectively.
Acknowledgements

The current study is part of a Ph.D. thesis submitted to the Faculty of Dentistry, University of Toronto. It was supported by grants from the Faculty of Dentistry Research Institute of the University of Toronto, and an American Academy of Esthetic Dentistry. The CheckMARC® device was loaned and technically supported by BlueLight Analytics, while material donations were provided by Ivoclar-Vivadent and Dentsply for which the authors are very grateful. In addition, the Bluephase Style was graciously loaned by Ivoclar-Vivadent. The authors are immeasurably thankful to our research assistants Ms. Ana Burilo and Ms. Ivana Orlovic for their contribution to this project.
Figure 5.1 Plastic mold used for the specimens’ production

Figure 5.2. Specimen ready for Knoop microhardness testing
Table 5.1 Descriptive statistics for RH ratios recorded for two RBC’s specimens polymerized at 1mm and 4mm tip-to-material distance. The assumptions of normality and equal variances among the comparison groups was assumed.

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Figure 5.3 Percentages of LPUs that reached the .80 ratios of RH for each RBC brand. Significant differences were observed between 1mm/4mm tip-to-target distances for the two RBC brands, and their RH results (inter-brand and intra-brand).
Figure 5.4 Average Knoop hardness b/t ratios (Mean and SD) produced by multiwave (n=32) and monowave (n=81) LPUs for the two brands of RBCs (Tetric EvoCeram and TPH Spectra HV), irradiated for 20s from 1 mm and 4 mm tip-to-target distance. No statistically significant difference among the groups was found.

Figure 5.5 Average RH ratios for Tetric EvoCeram polymerized at 1 mm and 4 mm tip-to-target distance, using a total of 113 LED LPUs.
Figure 5.6 Average RH ratios for TPH Spectra polymerized at 1 mm and 4 mm tip-to-target distance, using a total of 113 LED LPUs.

Figure 5.7 Q-Q plot showing the average RH ratios of Tetric EvoCeram at 1 mm tip-to-target distance observed values against normally distributed data (represented by the line).
Figure 5.8 Q-Q plot showing the average RH ratios of Tetric EvoCeram at 4 mm tip-to-target distance observed values against normally distributed data (represented by the line).

Figure 5.9 Q-Q plot showing the average RH ratios of TPH Spectra at 1 mm tip-to-target distance observed values against normally distributed data (represented by the line).
Figure 5.10 Q-Q plot showing the average RH ratios of TPH Spectra at 4 mm tip-to-target distance observed values against normally distributed data (represented by the line).
References


Chapter 6

Manuscript 4

Assessment of Diametral Tensile Strength of Resin Based Composites Polymerized by LED Light-Polymerization Units in Private Dental Practices in Toronto, Canada
Assessment of Diametral Tensile Strength of Resin Based Composites polymerized by LED Light-Polymerization Units in Private Dental Practices in Toronto, Canada

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Abstract

Objectives: To evaluate Diametral Tensile Strength (DTS) of two resin-based composites (RBC), polymerized using LED light-polymerization units (LPUs) in participating private dental practices. Methods: A 100 dental practices from the Greater Toronto Area, were recruited. Specimens were made of TPH Spectra (Dentsply), (camphorquinone (CQ) photoinitiator) and Tetric EvoCeram (Ivoclar-Vivident), (CQ/Lucirin-TPO photoinitiators). A plastic mold was used to produce cylindrical specimens (4mm-thick/6mm-diameter). Each specimen's surface received a 20s radiant exposure. Specimens (n=5) were stored in dry/dark container (37°C/24h). The DTS was conducted in a universal testing machine (model 8501 Instron Corp), using a cross-head speed at 0.5 mm/min. Fracture load (N) was recorded, and the DTS was calculated. The DTS data of Tetric EvoCeram and TPH Spectra were analyzed with a paired-samples t-test and a mixed ANOVA. All statistical tests were completed using a pre-set, α of 0.05, and Pearson correlations, using a pre-set, α of .001. Results: No significant difference in average DTS values between the two materials (t (113) =-.72, p=.475) was found. The mean DTS observed for Tetric EvoCeram was 40MPa (SD=5) and for TPH Spectra 39.9MPa (SD=4). The DTS values were highly correlated between the two materials (r=.71, p<.001) and the corresponding LPUs radiant exposure. Conclusions: Although DTS averages two RBCs were not significantly different, moderately-strong correlations between the 16 J/cm² of radiant exposure in 20s and DTS levels of Tetric EvoCeram (r=.54, p<.001) and TPH Spectra (r=.53, p<.001) were observed.

Keywords: Light Polymerization Unit; Irradiance; Radiant exposure; Diametral Tensile Strength test; Degree of conversion; Resin-Based Composite; CheckMARC®.
Introduction

Adequate RBC photopolymerization is a critical factor in predicting clinical success and the longevity of direct restorations. Insufficient RBC polymerization is highly correlated with a substantial reduction in their mechanical properties \(^1\).

The efficient methods to determine the level of RBC polymerization are the degree of conversion (DC), depth of polymerization (DoP), the degree of crosslinking (DoC), compressive strength (CS) test, and the diametral tensile strength (DTS) test. Some mechanical testing procedures have been examined to address the complexity of loading in clinically relevant situations. Based on literature findings, a positive correlation between CS and DTS has been observed \(^2\), \(^3\), \(^4\), \(^5\). Furthermore, the fracture resistance (FS) test has frequently been used for the evaluation of flexural strength and a flexural modulus of RBC materials by performing a three-point bending test, included in the ISO 4049:2009 standardization testing procedures \(^6\). Although DTS test is not a part of the ISO 4049:2009 standards, it was recognized as technically reliable and a straightforward test for the assessment of RBC mechanical properties. The DTS test was defined by the ADA/ANSI Specification No.27 for the RBCs evaluation. The DTS has been designed to test brittle materials by utilizing a cylinder-type specimen that is subject to compressive load across its diameter. It has been observed that materials which exhibit plastic deformation would produce false DTS values. Moreover, they would be anticipated to reveal strain rate sensitivity \(^7\).

There are some controversies associated with the DTS test, as per experimental observation that resultant shear forces acting at the apex of the diametral plane have been suggested to complicate the interpretation of strength, with the possibility that reported data
from different studies would not be challenging to interpret. However, DTS test can provide useful information about the effectiveness of RBC polymerization and in conjunction with other measuring methods can provide meaningful data on the mechanical properties of given materials.

The study aimed to assess specific mechanical properties of two RBC brands, polymerized by LED LPUs in the participating private dental practices, by conducting a DTS test. The study objectives were to test the following research hypotheses. The first hypothesis was that the average DTS values of Tetric EvoCeram and TPH Spectra polymerized using the participating LED LPUs would not show any difference. The second hypothesis was that LED LPUs with the capacity to produce a 20s radiant exposure of 16 J/cm² would be positively correlated with the DTS values of the materials tested. The third hypothesis was that DTS values of the two RBC brands, polymerized by multiwave LPUs would not be different from the DTS values polymerized by monowave LPUs.

Materials and methods

Specimens for the DTS test were made in the participating practices, by a single administrator. However, before the specimens’ preparation, the assessment of LPUs in the participating dental practices was completed by using a commercial, laboratory-grade light measuring device (CheckMARC®, BlueLight Analytics, Halifax, NS). A 10s radiant exposure obtained by the CheckMARC® device was multiplied by 2 to represent a 20s radiant exposure. The study criterion required all LPUs to generate a minimum of 16 J/cm² of
radiant exposure in a 20s cycle. The specimens were fabricated using an opalescent, cylindrical, and plastic mold (4 mm thick and 6 mm in diameter) (Figure 6.1). Furthermore, five specimens per BC brand were prepared from the A2 shade of each of two nanohybrid RBC materials: TPH Spectra (high viscosity) HV (Dentsply, Milford DE) and Tetric EvoCeram (Ivoclar-Vivadent, Amherst NY). TPH Spectra exhibits a camphorquinone (CQ) photoinitiator system, while Tetric EvoCeram consists of CQ and Lucirin TPO photoinitiators.\(^2\) The RBC material was inserted into the mold and overlaid with a polyester strip and a 1 mm microscopic glass-slide on both sides, and then light polymerized by the LED LPU from the participating dental practice, for the 20s at the top and 20s at the bottom surface. The polymerized specimens were extracted from the mold and stored in dark containers at 37\(^0\)C and tested after 24h storage. Specimens were measured with a digital caliper (Mitutoyo Canada, Mississauga, ON) before testing into a universal testing machine (Model 8501, Instron Corp, Canton, MA). Each specimen was tested by placing the specimen on its longitudinal side on the platens of the universal testing machine. The load was applied vertically on the lateral portion of the cylinder at a crosshead speed of 0.5 mm/min, producing tensile stress perpendicular to the vertical plane passing through the center of the specimen (Figure 6.2). The specimens were loaded to failure in compression, and the fracture load was recorded in Newton (N). Following the compressive test, each specimen was visually inspected to determine whether the specimen fractured into two halves. Those specimens fractured into unequal sizes were excluded from the analysis. The DTS was calculated based on fracture load (F) expressed in Newton (N), diameter, and height of the specimen, calculated using the formula from the Phillips’ Science of Dental Materials:\(^3\)

\[
s_t = \frac{2F}{dh\pi}
\]  

(1)
where are: d: diameter (6 mm); h: height (4 mm) of specimens; \( \pi: 3.14 \)

To obtain average DTS values of the positive control group (n=5 per each RBC brand), a reference, multiwave LPU (Bluephase Style, Ivoclar-Vivadent) was used.

- **Statistical analyses**

  Considering that the sample used in this study consisted of 113 light-units, normality was assumed. Therefore, parametric statistical tests were employed. However, to investigate the potential impact of the violation of the normality assumption on statistical tests results, nonparametric tests were also conducted. Whether the results of the parametric and non-parametric tests deviated, then the results of the non-parametric tests would be reported. However, it was discovered that the results of non-parametric tests and parametric tests were identical. Thus, parametric tests were reported.

  A paired-samples t-test was used to investigate whether average DTS values were different between Tetric EvoCeram and TPS Spectra specimens. To further examine whether LED LPUs with the capacity to deliver at least 16 J/cm\(^2\) of radiant exposure had higher levels of DTS on average, a mixed ANOVA was conducted. The DTS levels of the two RBC brands were used as a within factor in this analysis, and an indicator of LED LPUs capable of delivering a minimum radiant exposure level, (yes/no) was used as a between factor. The analyses were conducted using a pre-set alpha of 0.05.

  The 10s radiant exposure data obtained by the CheckMARC® device were multiplied by 2 to produce the 20s radiant exposure values, which were correlated to the study-required minimum criterion of 16 J/cm\(^2\). It was determined that (n=87) LPUs could satisfy the
criterion. Thus, to evaluate whether the association between the DTS values of two RBC tested and LED LPU radiant exposure values, concerning the study-required energy of 16 J/cm² exists, the Pearson correlation analysis was used, significant at the 0.001 level. The SPSS software for Windows, version 22, (SPSS Inc., IBM, Somers, NY) was used for all statistical analyses.

Results

The results of Shapiro-Wilk tests for normality of the average DTS values were not significant for Tetric EvoCeram (p=0.081) and TPH Spectra (p=0.097), confirming that data were normally distributed. Furthermore, the Q-Q plots were also used for normality assessment, and they are presented in Figures 6.4 and 6.5.

The Levene’s test was used for the assessment of equality of variances across the comparison groups. The results of Levene’s tests were not significant for all tests (p>0.05), indicating that assumption of equal variances was satisfied. However, the postulate of equal variances was violated once, in the independent-samples t-test analysis, where the appropriate action was taken (by adjusting the degree of freedom). A power analysis using the G Power program for the paired t-tests revealed that the sample size of 113 was capable of small effect size with the paired-samples t-tests (Cohen's d=.23). A reference from the SPSS manual (Green et al., 2010)²¹ was used to calculate a power analysis for mixed ANOVA. According to the reference, each cell in the design should have at least 15 cases to be able to express the minimum power of .80. Thus, the criterion was met in the current study.
A paired-samples t-test showed no significant differences in the average DTS values (MPa) between two RBC brands ($t_{112} = -0.72$, $p=0.475$, 95% CI: -0.92; 0.43). The mean BTS values (Table 6.1) were 39.7 (SD=5) for Tetric EvoCeram and 39.9 (SD=4) for TPH Spectra. It was observed that DTS levels were highly correlated between the two RBC brands ($r=0.71$, $p<.001$), indicating that LED LPUs which produced higher DTS values on Tetric EvoCeram specimens, also produced higher DTS values on TPH Spectra specimens.

A mixed ANOVA analysis showed that regardless of RBC brand, the LED LPUs that were capable of delivering at least 16 J/cm$^2$ of radiant exposure, also produced higher DTS levels, $F_{(1, 111)} = 18.00$, $p<.001$. A partial $\eta^2=0.14$ was indicating a medium-to-large effect size (95% CI: -5.66; -2.06). Specifically, the average DTS values for LED LPUs that did not meet the criterion was 36.8 MPa (SD=0.8) and for LED LPUs that met the criterion was 40.7 MPa (SD=0.4).

The pool of LED LPUs tested consisted of 32 multiwave and 81 monowave LPUs. The majority of LED LPUs ($n=87$, 77.0%) could deliver at least of 16 J/cm$^2$ radiant exposure in 20s exposure. The average DTS values of the control group were 42.9 MPa for Tetric EvoCeram, and 43.9 MPa for TPH Spectra.

The Pearson correlation analyses ($n=113$) showed moderately strong correlations between the incident irradiance values of LED LPUs and DTS values of Tetric EvoCeram ($r=0.54$, $p<.001$) and TPH Spectra ($r=.053$, $p<.001$) RBCs. Furthermore, small-to-moderate, but significant, correlations were found between LED LPUs capable of delivering at least 16 J/cm$^2$ of radiant exposure ($n=87$), and average DTS values of Tetric EvoCeram and TPH Spectra ($r=0.37$, $p<.001$, and $r=0.31$, $p<.001$), respectively.
An independent-samples t-test showed no significant differences in the average DTS values of Tetric EvoCeram ($t(112) = 0.07$, $p=0.943$, 95% CI: -1.70; 1.83), and TPH Spectra ($t(112) = 1.07$, $p=0.289$, 95% CI: -0.68; 2.25), polymerized with multiwave and monowave LPUs (Table 6.1). The Levene’s tests were significant ($p<0.05$), therefore, the assumption of equal variances was violated, however, the tests with adjusted degrees of freedom were used.

**Discussion**

Adequate photopolymerization is crucial for the expected longevity of RBC restorations. For a quick and straightforward assessment of polymerization efficiency, the BTS test is frequently used to quantify the tensile strength of brittle dental restorative materials. The appropriateness and reliability of this method to successfully analyze the capacity of RBC materials to withstand strong masticatory forces in clinically appropriate situations has been reported.

The first research hypothesis, that the average DTS values of Tetric EvoCeram and TPH Spectra, polymerized LED LPUs in the participating dental practices would not show any significant difference, was accepted. The results of a paired-samples t-test were not significant, ($t(112) = -0.72$, $p=0.475$), indicating no difference in the average level of BTS between the two materials. The 95% confidence interval of the difference in the average DTS level was in the range from -0.92 to 0.43. The mean DTS value observed in the sample for
Tetric EvoCeram was 39.7 MPa (SD=5), (95% CI for MD: 38.7; 40.6), and for TPH Spectra was 39.9 MPa (SD=4), (95% CI for MD: 49.1; 40.7).

Although TPH Spectra and Tetric EvoCeram are Bis-GMA based nanohybrid RBCs, which exhibit the presence of pre-polymerized filler particles in their compositions, they differ in the total filler load values, being 60-62 volume percentage for TPH Spectra and 53–55 volume percentage for Tetric EvoCeram. Furthermore, TPH Spectra exhibits a camphorquinone (CQ) photoinitiator system, while Tetric EvoCeram has a mix of CQ and Lucirin TPO photoinitiators. Thus, an alternative, Lucirin TPO photoinitiator system exhibits its maximum peak absorption spectra below 420 nm, in the violet spectral range. It would be expected that an extended light spectrum of multiwave LPUs yield the higher average BTS values for Tetric EvoCeram, due to the presence of Lucirin TPO, and its affinity for the violet range of multiwave LPUs spectral irradiance. However, experimental data could not support that postulate, as the average DTS values of Tetric EvoCeram were 39.7 MPa, while the average DTS values of TPH Spectra were 39.9 MPa. Although Tetric EvoCeram exhibits a blend of photoinitiators, which included the Lucerin TPO, and a lower filler load percentage than of TPH Spectra, the occurrence of the Rayleigh scattering could be associated with the lower average DTS values of Tetric EvoCeram.

The second hypothesis, that LED LPUs capable of producing at least of 16 J/cm² radiant exposure in a 20s exposure cycle, would be positively correlated with the average DTS values of Tetric EvoCeram and TPH Spectra, was accepted. A positive, significant, but small-to-moderate correlation between LED LPUs (n=87) capable of producing at least of 16 J/cm² radiant exposure and the average DTS values of Tetric EvoCeram (r=0.37, p<.001), and TPH Spectra (r=0.31, p<.001), was observed. Furthermore, the moderately strong
correlations between a 40s radiant exposure delivered by LED LPUs (n=113), and the average DTS values of Tetric EvoCeram (r=0.54, p<.001), and TPH Spectra (r=0.53, p<.001), were noted. A further analysis unveiled that the average DTS levels were highly correlated between the two RBC materials (r=0.71, p<.001), indicating that higher or lower DTS values were observed on both materials depending on the radiant exposure generated by the participating office’s LPU. Currently, this was the first study that correlated a minimum level of radiant exposure of LED LPUs in the participating dental practices to the average DTS level of two RBC materials. Many of published studies have tested a number selected RBCs with a selected number of LPUs 8-16.

The third research hypothesis, that the average DTS values of two RBC brands, polymerized by multiwave LPUs would not be different from the DTS values polymerized by monowave LPUs, was accepted. An independent-samples t-test showed no significant differences in the average DTS values of Tetric EvoCeram (p=0.943), and TPH Spectra (p=0.289), polymerized with multiwave and monowave LPUs, as presented in Figure 6.3. Although it would be expected that multiwave LPUs produce better results with Tetric EvoCeram, that assumption was not observed. The average DTS values produced by multiwave LPUs were 39.6 MPa for Tetric EvoCeram, and 39.4 MPa for TPH Spectra, while the average DTS values produced by monowave LPUs were 39.7 MPa, and 40.1 MPa for TPH Spectra, respectively.

The current project was the first study that explored DTS test values on a large sample size of LED LPUs. This study design was dissimilar to all previous studies 8-13. The decision to use 6mm x 4mm cylindrical specimens was based on a methodology that was borrowed from previous studies, which, however, was not in full accordance with the
ADA/ANSI Specification No.27. Specimens, following the polymerization were stored in dry containers, instead of the distilled water, as advocated in the ADA specification. The RBC materials tested complied with the Water Sorption (ISO 4049:2009) standards. According to a pilot project data, no statistically significant difference was found between two RBC material specimens during the 24h storage in either distilled water or dry containers, followed by the DTS testing. Furthermore, the compressive load that was applied in a universal testing machine, with a crosshead speed of 0.5 mm/min. There is no precise agreement on the employment of different crosshead speed to the specimens for DTS evaluation. However, the ADA/ANSI Specification No.27 recommends a crosshead speed of 0.75 mm/min. The test selection for 0.5 mm/min of crosshead speed, was based on the premise that most of reported studies used the same parameter, and the study results showed that the crosshead speed variations between 0.5 and 1 mm/min were not statistically significant.

When compared with the average DTS values of the control group (42.9 MPa for Tetric EvoCeram, and 43.9 MPa for TPH Spectra), and the average DTS values produced by the LPUs tested, it was found that 77.9% LPUs produced lower average DTS values with Tetric EvoCeram. Similarly, for TPH Spectra, 87.6% LPUs had the average DTS values below the value of the reference LPU.

The broad spectrum of values recorded in this study could be attributed to a more substantial number of LED LPUs that were applied for specimens` polymerization. Furthermore, because travel distance between the participating dental practices was sometimes reasonably long, the RBC materials could have been exposed to the ambient temperature during the cold winter season. Thus, the RBCs temperature fluctuation could
have some influence on test results. Very shallow concentric grooves on the working faces of the platens (universal testing machine) were used to prevent specimen’s slipping during the compressive loading, which eliminated a need for paper slips. Although, paper-points were not used to prevent contact points due to imperfection of cylindrical shape of the specimens, however, any specimen fractured into unequal sizes was excluded from the analysis.

Limitations of the current project were associated with the current set-up where the polymerization light was passing through glass slides, and Mylar strips, which could affect the recorded DTS values to a certain degree. It would be better if the current set-up supported the ADA/ANSI Specification No.27 recommendations for specimen's dimension and storage. However, since the nature of this study was largely comparison of two restorative materials and a current slight variation in specimen dimensions has little or no effect on the outcome.

Future research should include bulk-fill RBC restoratives evaluation, using similar approach used in this project. Furthermore, to create a clinically relevant scenario, using the same methodology, the radiant exposure should follow manufacturers’ recommendation values for the RBC, in respect to the incident irradiance of LPUs tested.

Conclusions

Within the limitations imposed by this study, it may be concluded that:

1. The average DTS values of Tetric EvoCeram and TPH Spectra, polymerized with LED LPUs in participating dental practices, did not show a statistically significant difference. The mean DTS values observed in the sample for Tetric
EvoCeram was 39.7 MPa (SD=5), and for TPH Spectra, it was 39.9 MPa (SD=4).

2. A positive, significant, but small-to-moderate correlation between LED LPUs (n=87) capable of producing at least of 16 J/cm² radiant exposure in the 20s and the average DTS values of Tetric EvoCeram (r=0.37, p<.001), and TPH Spectra (r=0.31, p<.001), was observed.

3. Moderately strong correlations between the 40s radiant exposure delivered by LED LPUs (n=113), and the average DTS values of Tetric EvoCeram (r=0.54, p<.001), and TPH Spectra (r=0.53, p<.001) were discovered.

4. The average DTS levels were highly correlated between the two RBC materials (r=0.71, p<.001), indicating that higher or lower DTS values were observed with both materials, depending on the radiant exposure applied by the LPUs in the participating dental practices.

5. No significant differences were observed in the average DTS values of Tetric EvoCeram (p=0.943) and TPH Spectra (p=0.289) polymerized with multiwave and monowave LPU.
Acknowledgements

The current study is part of a Ph.D. thesis submitted to the Faculty of Dentistry, University of Toronto. It was supported by grants from the Faculty of Dentistry Research Institute of the University of Toronto, and an American Academy of Esthetic Dentistry. The CheckMARC\textsuperscript{®} device was loaned and technically supported by BlueLight Analytics, while material donations were made by Ivoclar-Vivadent and Dentsply for which the authors are very grateful. Further, many thanks to Ivoclar-Vivadent for loaning the Bluephase Style as a study reference LPU. Special thanks to our research assistants Ms. Ana Burilo and Ms. Ivana Orlovic for their participation in this project.
Figure 6.1 A DTS Specimen 4mm thick and 6mm in diameter

Figure 6.2 DTS testing in a universal testing machine.
Figure 6.3. The average DTS values (Mean ± SD) of Tetric EvoCeram and TPH Spectra RBCs polymerized by multiwave (n=32) and monowave (n=81) LPUs, following the 40s radiant exposure. No significant difference among the groups was found.

Table 6.1 Average BTS values of Tetric EvoCeram and TPH Spectra, polymerized by monowave (type 0) and multiwave (type 1) LPUs. *Levene’s tests for homogeneity of group variances were significant for both tests (p<0.05), indicating that assumption of equal variances was not assumed.

<table>
<thead>
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<th>RBC Type</th>
<th>LPU Type</th>
<th>Mean</th>
<th>SD</th>
<th>Levene’s test</th>
<th>t</th>
<th>p-value</th>
<th>95% CI for the mean difference</th>
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<td>4.10*</td>
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<td>0.943</td>
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<td></td>
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<tr>
<td>TPH Spectra</td>
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<td>5</td>
<td>8.68*</td>
<td>1.07</td>
<td>0.289</td>
<td>Lower -0.68 Upper 2.25</td>
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<td></td>
<td>Multi</td>
<td>39.4</td>
<td>3</td>
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</table>
Figure 6.4 Q-Q plot showing the average BTS values of TPH Spectra against normally distributed data (represented by the line).

Figure 6.5 Q-Q plot showing the average BTS values of Tetric EvoCeram against normally distributed data (represented by the line).
References


Chapter 7
Findings, Analyses, Discussion, Limitations, and Future Directions, and Conclusions
7.1 Findings

This thesis analyzed the efficacy of 113 LED LPUs used by general dental practitioners in 100 private practices in the Greater Toronto Area, by conducting a quantitative assessment of LPUs and polymerization skills of dental professionals, as well as the characterization of the surface and bulk-properties of two RBCs polymerized with same LED LPUs. Within the limitations of each of the four studies that this project comprised of, the following conclusions were made:

1. The study characterized the LED LPUs in 100 participating dental practices concerning their ability to generate at least 16 J/cm² of radiant exposure in the 20s computed exposure time, measured by the Check MARC®.

   • The 20s calculated radiant exposure ranged between 3.8 and 59.6 J/cm² (M=21.7, SD=8.6).

   • The pool of tested LED LPUs consisted of 32 multiwave and 81 monowave LPUs. In the multiwave group, the Valo (Ultradent, South Jordan, UT) was the most common (57.6%), while Demi Plus (Kerr, Orange, CA) was the most common (26.3%) in the monowave group.

   • The minimum criterion for radiant exposure of 16 J/cm² in 20s was met for the majority of LED LPUs (n=87, 77.0%), where 29 were multiwave LPUs and 58 were monowave LPUs.

   • There were 26 underperforming LPUs (3 multiwave and 23 monowave)
• By calculating the ratio of substandard LPUs to a total number of LPUs tested, (multiwave LPUs (3/32) versus monowave LPUs (23/81)), monowave LPUs exhibited three times higher possibility to fail the study-required standard of 16 J/cm² per 20s than multiwave LPUs from the same sample.

• In comparison with a computed 20s, radiant exposure of the reference LED LPU (Bluephase Style, Ivoclar-Vivadent), which generated 21 J/cm², 47.8% of LED LPUs tested, delivered lower radiant exposure values.

• The LED LPUs in the sample were between 1.0 and 5.5 years of age (M=2.6, SD=1.2) and had damage levels ranging from 0 to 4.0 (M=1.6, SD=1.2).

• The average age of LED LPUs that did not pass the criterion was 3.6 years (SD=1), while the average age of LED LPUs that passed the criterion was 2.3 years (SD=1).

• The average damage level of LED LPUs that did not pass the criterion was 2.8 (SD=1), compared with 1.3 (SD=1) for LED LPUs that passed the criterion.

• The average age of monowave LPUs was 2.7 years (SD = 1), and the average age of multiwave LPUs was 2.6 years (SD = 1).

• Similarly, the two types of LPUs were not significantly different on their level of damage. Specifically, 17.7% of monowave LPUs and 17.6% of multiwave LPUs had no damage, and 6.3% of monowave and 5.9% of multiwave LPUs had the highest level of damage (level 4).

• A strong, r=-0.67 (p<.001) negative correlation between the LPU radiant exposure and its age and a level of damage, was observed.
2. The study evaluated the ability of dental practitioners to deliver at least eight J/cm² of radiant exposure, in a 10s exposure cycle to the MARC®PS simulated restorations (before/after instructions), using their LED LPUs.

- Before instructions, 73.6% of practitioners delivered required-energy to anterior restoration, and 32.2% of practitioners delivered required-energy to posterior restoration.
- Following instructions, 94.3% of practitioners delivered required-energy to anterior restoration, and 73.6% of practitioners delivered required-energy to posterior restoration.
- Dental practitioners, on average, increased delivered energy to the anterior restoration by 22.6% and the posterior restoration by 30.4% because of instructions.
- Following specific instructions, dental practitioners improved the consistency of delivered energy to simulated restorations on average by 25.9%.
- The positive control group (graduate students) delivered the following quantities of energy to the MARC® PS: 9.8 J/cm² to the anterior restoration, 9.9 J/cm² to the posterior restoration before instructions, and 12.6 J/cm² to the anterior restoration, and 11.1 J/cm² to the posterior restoration, post-instructional.

3. The study evaluated relative hardness ratios (RH) of Tetric EvoCeram and TPH Spectra, polymerized at 1 mm and 4 mm tip-to-target distance with the participating LPUs.
- The relative hardness ratios of the two RBC brands demonstrated a weak-to-moderate correlation (average $r=0.36$, $p<.001$) between the light probe tip-to-target distance, and a 20s radiant exposure.
- The majority of LED LPUs reached the 0.80 RH level of two RBC brands at 1 mm tip-to-target distance.
- The majority of LED LPUs did not obtain the 0.80 RH level of two RBC materials at 4 mm tip-to-target distance.
- The percentage of LPUs that exhibited insufficient polymerization at 4 mm tip-to-target distance was observed to be higher than 60%.
- The average RH ratio reduction over a 3 mm tip-to-target distance, was 59% for Tetric EvoCeram, and 54.8% for TPH Spectra, respectively.
- In comparison with RH ratio for Tetric EvoCeram obtained by the reference LPU (0.85 at 1 mm and 0.80 at 4 mm material-to-probe distance), 108 participating LPUs (95.6%) were below that RH level at 1 mm material-to-probe distance, and 81 LPUs (71.7%) did not produce that RH level at 4 mm material-to-probe distance.
- Similarly, in comparison with RH ratios for Spectra TPH obtained by a reference LPU (0.84 at 1 mm and 0.83 at 4 mm material-to-probe distance), 97 LPUs (85.8%) were below that RH level at 1 mm material-to-probe distance, while 101 LPUs (89.4%) did not yield that RH level at 4 mm material-to-probe distance.

4. The study examined the Diametral Tensile Strength (DTS) of Tetric EvoCeram, and TPH Spectra RBCs polymerized with the participating LPUs.
• The average DTS values of Tetric EvoCeram and TPH Spectra, polymerized with LED LPUs in the participating dental practices did not show any significant difference.

• The mean DTS value observed in the sample of Tetric EvoCeram was 39.7 MPa (SD=5), and for TPH Spectra was 39.9 MPa (SD=4).

• A positive, significant, but small-to-moderate correlation between LED LPUs (n=87) capable of producing at least of 16 J/cm² radiant exposure in 20s exposure, and the average DTS values, produced during a 40s radiant exposure of Tetric EvoCeram (r=0.37, p<.001), and TPH Spectra (r=0.31, p<.001), were observed.

• A moderately strong correlation between a 40s radiant exposure delivered by LED LPUs (n=113), and the average DTS values of Tetric EvoCeram (r=0.54, p<.001), and TPH Spectra (r=0.53, p<.001), were noted.

• The average DTS levels were highly correlated between the two RBC materials (r=0.71, p<.001), indicating that higher or lower DTS values were observed on both materials depending on the radiant exposure applied by the participating offices’ LPU.

• No significant differences were observed in the average DTS values of Tetric EvoCeram (p=0.943), and TPH Spectra (p=0.289), polymerized with multiwave (n=32) and monowave (n=81) LPUs.

• The average DTS values obtained with a control LED LPU were 42.9 MPa for Tetric EvoCeram, and 43.9 MPa for TPH Spectra.

• 77.9% LPUs tested produced lower average DTS values with Tetric EvoCeram, in comparison to the average DTS values of the control LPU.
• 87.6% LPUs tested had lower average DTS values with TPH Spectra, in comparison to average DTS values of the control LPU.

### 7.2 Analysis

Numerous studies reported that LPUs used in private practices exhibited a substantial number of clinically unacceptable outputs. The percentage of clinically underperforming LPUs reported in the literature ranged from 30.3% to 55.5%, depending on the study specific testing criteria\(^\text{308-316}\). Although all of these studies indicated that LPUs employed in dental practices included a relatively large number of LPUs that produce insufficient irradiance levels, it was evident that LED LPUs have shown much better results than QTH LPUs.

Although geographic variations, different methodologies, and differences in study designs presented challenges in making meaningful comparisons, the analysis of a similar 2005 Toronto study would shed some new light on the effectiveness of LPUs in the same geographic region. Many changes happened in private dental practice, since then the principal change was the disappearance of QTH LPUs and their replacement with LED LPUs. The following are the highlights:

• The sample size in the 2005 study involved a total of 214 QTH LPUs. The present study consisted of only 113 LED LPUs.
• There was a tendency of single dental offices becoming aggregated into a group dental practice. Thus, the current study included 100 dental practices as the 2005 study did.

• The mean reported irradiance in the 2005 study was 526 mW/cm². The current study reported 1,082 mW/cm², which indicated that the irradiance values almost doubled in the past ten years. The 2005 study reported that LPUs' mean age was 5.6 years, while the current study reported just being 2.6 years.

• In the 2005 study, an analog radiometer with a range of 0 to 1,000 mW/cm² (Optilux, model 100, Kerr, Orange, CA) was used. The current study used a more sophisticated the CheckMARC®, a laboratory-grade spectroradiometer with a range of 0 to 10,000 mW/cm², which has a scientific-grade accuracy (an accuracy of +/- 5%).

• In the 2005 study, an incidence irradiance level of 400 mW/cm² and above was considered adequate, while the current study promotes that the incident irradiance level of 800 mW/cm² or above as appropriate.

• Based on the research criterion from the 2005 study, a total of 30.3% of the LPUs generated less than the sufficient irradiance values, while the current study exhibited 23% of LPUs that were below the study-required criterion.

• The present study adequately evaluated the optical diameter of the light probe, by measuring an outer tip diameter using Mitutoyo digital caliper (Mitutoyo Canada, Mississauga ON) and inputting those values to the CheckMARC® software, which automatically selected the appropriate active diameter values for the corresponding incident irradiance calculations.
• Evaluation of the level of damage observed on the surface of the light-probe was completed by using an evaluation scale (0-8), where 0 represents no damage, and 8 represents 100 percent of the damaged light probe.

• The 2005 study used an analog radiometer. However, there are a plethora of reports associating dental radiometers with erroneous measurements and questionable results.

Comparison of raw data presented in both studies, ten years apart, showed that LED LPUs, compared with QTH LPUs in the same demographics area, demonstrated, on average, significantly better performance. This improvement could be credited to advances and significant innovations with LED light sources.

7.3 Discussion

The study identified specific problems associated LPUs among the dental practitioners in private dental practices in the Greater Toronto Area. The first issue was associated with the ability of LED LPUs to generate the study-required energy minimum. The age and level of light probe damage had a significant effect on the required quantities of energy being produced. A regular test for damage and debris on the light probe should be part of daily practice routine. Furthermore, a regular incident irradiance test should be conducted using certified measuring equipment. LED LPUs with a service record of four years or more should be tested more frequently, as they exhibited the highest potential for failure.
The second issue that this study focused on was the ability of dental practitioners to deliver adequate quantities of light energy to simulated restorations. To achieve this goal, the MARC® PS was employed in the participating dental practices. The participants were assessed for their clinical skills to deliver at least 8 J/cm² radiant exposure in 10s to simulated anterior and posterior restorations. The test was conducted in their regular office settings, which included their choice of eye protection, if used, as a part of their typical daily routine. Following customized instructions on proper polymerization, participants were retested using provided blue-light protective glasses. The study revealed that a significant number of dental practitioners exhibited inadequate polymerization skills, especially when they delivered light energy to the posterior restoration. It was found that a substantial number of study participants did not use appropriate eye protection. The post instructional results proved that the use of protective glasses, along with individualized instructions had substantial effects on improved photopolymerization technique among dental practitioners tested. It was observed that a low level of awareness about the importance of photopolymerization among dental practitioners had a critical effect on their ability to deliver sufficient energy to restorations.

7.4 Limitations and Future Directions

Bias can occur in any phase of a research project, from planning, data collection, and analysis to the publication phase. The way in which subjects were identified, approached, and respond to invitations to participate in research can be a significant source of bias, and, therefore, it is essential for researchers to evaluate selection bias. Upon approval by the University of Toronto Research Ethics Board, the participating private dental practices were recruited. The 2012 listing of dentists published by the Royal College of Dental Surgeons of
Ontario was used to detect prospective dental practices in the Greater Toronto Area. Over 350 targeted practices were initially contacted by a single test administrator via telephone using the same telephone script approved by the University of Toronto Research Ethics Board, to determine their eligibility to join the study. However, a total of 250 suitable dental practices were presented with the research protocol, along with a letter of consent. The recruitment goal was to secure at least of 100 dental practices for the study. The recruitment criteria for the study participants included: a general dental practice with proficiency in RBC placement and physically located within the Greater Toronto Area. The study acceptance was granted exclusively for participants who have never experienced MARC®PS before. To proportionally include dental practices in the Greater Toronto Area, the target area of Toronto was divided into four quadrants with a similar number of dental practices recruited within each quadrant.

This study may had some inclusion issues to some extent because those dental practices with possible lower quality of LPUs or questionable proficiency in RBC placements may have refused to participate in order to avoid embarrassment. The main excuse for those practices to decline participation was their inability to find time to accommodate the research. The study exhibited standardized protocols for data collection and data entry. A single administrator completed the entire study, which substantially reduced any possible inter-observer variability and performance bias while, at the same time, enabling the test administrator to evaluate internal validity during the entire research process.

Another potential limitation of this study was a possible conceptual problem with the 10s radiant exposure with the MARC® PS device. If the passing criterion of 16 J/cm² with a 20s radiant exposure was performed, the results may have been slightly but not significantly
different. Furthermore, the 16 J/cm² radiant exposure per 20s represented the typical value that was more frequently cited in the literature.\(^{16, 94, 188}\)

The specimens (6 mm diameter and 4 mm height) for DTS test were prepared based on preceding studies protocols\(^ {177, 181, 183, 187, 189}\), not the ADA/ANSI Specification No. 27 (6 mm diameter and 3 mm height). Although the study results were in line with that of published findings, by using the ADA/ANSI Specification No. 27, the outcome may have been more up-to-date, however, the comparative nature of this work places less value on this aspect.

Future research directives should include the examination of bulk-fill materials (packable and flowable) using the methodologies outlined in the current study, except for DTS specimens’ specification, which would include ADA/ANSI Specification No. 27 (6 mm diameter and 3 mm height). Furthermore, it would be useful to change research population, thus to see how rural dental practitioners differ from the urban ones and possibly to include assessment of Dental Public Health professionals in the future projects.

### 7.5 Conclusions

The findings from the study suggested that improvements in polymerization skills are required and justified in a large number of participating dental practices. The results showed that some dental professionals have been delivering insufficient quantities of light energy to the simulated posterior restorations, which would have a detrimental effect on posterior RBC polymerization and long-term longevity in clinical settings. Furthermore, clinicians should be aware that their LPUs may not perform as expected, unless a rigorous maintenance protocol is implemented, including close inspection of their LPU’s light probe and efficient
measurement of their LPU's incident irradiance. LED LPUs with a service record of four years or more, should be tested more frequently as they exhibit the highest potential for failure.
Appendices
Appendix I
### Table 1. Studies on survival of RBC restorations

<table>
<thead>
<tr>
<th>Principal author, year</th>
<th>Evaluation period/study design</th>
<th>Number of restorations/studies</th>
<th>Evaluated restorations</th>
<th>Survival rate/Annual Failure Rate (AFR)</th>
<th>Factors associated with RBC failure</th>
</tr>
</thead>
</table>
| Manhart 298, 2004      | 2-14 years, 18 studies         | Class I and II, amalgams, RBCs, GICs, compomers | AFR: amalgams 3.0%
RBCs 2.2%, GICs 7.2%, compomers 1.1% | secondary caries, fracture, marginal deficiencies, wear and postoperative sensitivity |
| Demarco 300, 2012      | 5-22 years, 34 studies         | Class I and Class II posterior RBCs | AFRs of vital teeth 1% to 3%.
AFRs of non-vital teeth 2% to 12.4% | tooth type and location, operator, socioeconomic, demographic, and behavioral elements |
<p>| Opdam 301, 2014        | 6-22 years, 25 studies 2,816 restorations | Class I and Class II RBCs | high/medium caries risk, with 10-year AFR of 4.6/4.1% compared with 1.6% for low-risk patient | Secondary caries and tooth fracture |
| Lempel 302, 2014       | 10-year retrospective study 701 restorations | 4 microhybrid RBCs of Class II | 10-year survival rate of &gt;97.8% | Number of surfaces, molars vs premolars |
| Pallesen 303, 2015     | 27-year prospective study 99 restorations | 60 premolars 39 molar Class II of 3 RBCs | 27-year survival rate 56.5% | Secondary caries (54.1%) Wear (21.6%) Fracture (18.9%) |</p>
<table>
<thead>
<tr>
<th>Study</th>
<th>Duration</th>
<th>Study Design</th>
<th>Sample Size</th>
<th>Outcomes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rasines Alcaraz 304, 2014</td>
<td>5-7 years</td>
<td>Retrospective</td>
<td>7 RCT of 3,265 RBCs and 1935 amalgams</td>
<td>Amalgam vs RBC: Failure rate RR 1.86, Secondary caries RR 2.14, Fracture RR 0.87</td>
</tr>
<tr>
<td>Beck 305, 2015</td>
<td>1-17 years</td>
<td>Prospective RCTs</td>
<td>88 studies</td>
<td>AFR: 1.46% short-term studies, 1.97% long-term studies</td>
</tr>
<tr>
<td>Borgia 306, 2017</td>
<td>11.5 years</td>
<td>Retrospective</td>
<td>61 patients, 105 RBC Restorations</td>
<td>Statistically higher mean survival time of premolars. Caries-risk factor shown to be crucial.</td>
</tr>
<tr>
<td>Palotie 307, 2017</td>
<td>13-year</td>
<td>Retrospective</td>
<td>5,542 restorations RBC (93%) and amalgam (7%)</td>
<td>Median survival time of all restorations 9.9 years. No statistical difference between RBC/amalgam restorations</td>
</tr>
</tbody>
</table>

Table 1. Studies on survival of RBC restorations (continued)
Appendix II
<table>
<thead>
<tr>
<th>Principal author, year, country</th>
<th>Type of LPUs</th>
<th>Number of LPUs assessed</th>
<th>Methodology</th>
<th>Passing criterion</th>
<th>Conclusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dunne ³⁸⁸, 1996, UK</td>
<td>QTH</td>
<td>49</td>
<td>Depth of polymerization (DOP), analog “LampChecker” radiometer</td>
<td>5.0 to 7.0 on analog scale</td>
<td>&lt;50% of LPUs tested were substandard</td>
</tr>
<tr>
<td>Burke ³⁹⁰, 1997, UK</td>
<td>QTH</td>
<td>98</td>
<td>Assessment of DOP (Heliotest and Z100)</td>
<td>DOP 2.6 mm</td>
<td>43.5% of LPUs tested were substandard</td>
</tr>
<tr>
<td>Martin ³¹⁰, 1998, Australia</td>
<td>QTH</td>
<td>214</td>
<td>Analog radiometer Demetron</td>
<td>400 mW/cm²</td>
<td>47.7% of LPUs tested were substandard</td>
</tr>
<tr>
<td>Pilo ³¹¹, 1999, Israel</td>
<td>QTH</td>
<td>130</td>
<td>Analog radiometer Demetron, Knoop hardness (KH)</td>
<td>300 mW/cm²</td>
<td>55% of LPUs tested were substandard; 46% of LPUs failed when KH data were applied</td>
</tr>
<tr>
<td>Solomon ³¹², 1999, South Africa</td>
<td>QTH</td>
<td>35</td>
<td>Analog radiometer</td>
<td>300 mW/cm²</td>
<td>45.7% of LPUs tested were substandard</td>
</tr>
<tr>
<td>El-Mowafy ³¹³, 2005, Canada</td>
<td>QTH</td>
<td>214</td>
<td>Analog radiometer Knoop hardness</td>
<td>400 mW/cm²</td>
<td>30.3% of LPUs tested were substandard</td>
</tr>
</tbody>
</table>
Table 2. Effectiveness of LPUs in dental practices (continued)

<table>
<thead>
<tr>
<th>Study</th>
<th>QTH</th>
<th>LED</th>
<th>Radiometer Type</th>
<th>Radiometer Power (mW/cm²)</th>
<th>Substandard Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Santos 314, 2005, Brazil</td>
<td>310</td>
<td>120</td>
<td>Analog radiometer</td>
<td>300</td>
<td>56%</td>
</tr>
<tr>
<td>Hedge 315, 2009, India</td>
<td>QTH</td>
<td>120</td>
<td>Digital radiometer</td>
<td>400</td>
<td>88%</td>
</tr>
<tr>
<td>AlShaafi 316, 2012, Saudi Arabia</td>
<td>QTH</td>
<td>140</td>
<td>Laboratory-grade spectroradiometer</td>
<td>QTH: 300, LED: 600</td>
<td>59.5%</td>
</tr>
<tr>
<td>Maghaireh 317, 2013, Jordan</td>
<td>QTH</td>
<td>295</td>
<td>Digital radiometer</td>
<td>300</td>
<td>73.8%</td>
</tr>
<tr>
<td>Sadiku 318, 2010, Switzerland</td>
<td>QTH</td>
<td>220</td>
<td>Integrating sphere</td>
<td>Not available</td>
<td>40%</td>
</tr>
<tr>
<td>Kassim 319, 2013, Kenya</td>
<td>QTH</td>
<td>83</td>
<td>Digital radiometer, DOP, hardness</td>
<td>300</td>
<td>48.2%</td>
</tr>
<tr>
<td>Hao 320, 2015, China</td>
<td>QTH</td>
<td>196</td>
<td>Digital radiometer</td>
<td>300</td>
<td>42.4%</td>
</tr>
<tr>
<td>Kopperud 17, 2017 Norway</td>
<td>LED</td>
<td>713</td>
<td>Self-reporting questionnaire</td>
<td>Reported irradiance 1,000 to 2,000 mW/cm²</td>
<td>78.3%</td>
</tr>
</tbody>
</table>
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