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VISIBLE LIGHT CURING OF FIBER-REINFORCED IMPACT-RESISTANT COMPOSITES

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VISIBLE LIGHT CURING OF FIBER-REINFORCED IMPACT-RESISTANT COMPOSITES

by

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LIST OF COMMON ACRONYMS/SYMBOLS

ATR	Attenuated Total Reflection
ABS	Acrylonitrile Butadiene Styrene
CQ	Camphorquinone
DMAEMA	Dimethylaminoethyl Methacrylate
EB	Electron Beam
EHPA	Enhanced Hurricane Protection Areas
FRCs	Fiberglass-Reinforced Composites
FRIRPs	Fiberglass-Reinforced Impact-Resistant Panels
FTIR	Fourier-Transform Infrared Spectroscopy
HEA	Hydroxyethyl Acrylate
IBOA	Isobornyl Acrylate
LED	Light Emitting Diodes
MMA	Methyl Methacrylate
PI	Photoinitiator
PE	Polyethylene
QTH	Quartz Tungsten Halogen
RTM	Resin Transfer Molding
TMDI	Trimethylhexamethylene Diisocyanate
TPGDA	Tripropylene Glycol Diacrylate
UV	Ultraviolet Light
VOC	Volatile Organic Compound

ABSTRACT

Y. Bi Visible Light Curing of Fiber-Reinforced Impact-Resistant Composites, 80 pages, 25 tables, 26 figures, 2017. Manuscript format used.

Visible light curing technology was used to fabricate fiber-reinforced polymer composites. This project started with designing and constructing a visible light curing unit – a multi-LED array and investigating its optical characteristics. Visible light curable formulations were developed and studied using Fourier-transform infrared spectroscopy (FTIR) to optimize curing efficiency as well as to validate the feasibility of curing through a thick laminate. A third study was conducted to develop test methods and evaluate the impact resistance of visible light cured fiber-reinforced 1/2-inch-thick ballistic panels and 1/4-inch and 1/8-inch-thick storm panels. The results showed a great success in using visible light to cure thick laminated composites. In addition, the visible light cured composites have demonstrated comparable impact strength with commercial ballistic panels.

Key Words: visible light curing, photopolymerization, impact resistance, fiber-reinforced composites

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CHAPTER 1 INTRODUCTION

1.1 Fiber-Reinforced Composites

Fiber-reinforced composites consist of fibers of high strength and modulus incorporated into an organic polymer matrix. The principal fibers in commercial applications include various types of glass and carbon, as well as Kevlar. Fiberglass is the most common of all reinforcing fibers because of its low cost, high tensile strength, high chemical resistance, and excellent insulating properties (Mallick 2007). Many fiberglass-reinforced composites (FRCs) exhibit comparable or better mechanical properties than traditional metallic materials, such as high specific strength and stiffness, superior corrosion resistance, and improved fatigue properties (Cantwell and Morton 1991), as well as the advantage of lower density and higher strength-weight ratio. FRCs have emerged as important structural materials in aerospace, automotive, and construction applications.

Fiberglass-reinforced composites are especially used for high impact-resistant panels because of their low cost, wear down resistance, and high energy absorbing capability. Stratford et al. (2004) studied strengthening masonry walls using glass-fiber reinforced polymer sheets, showing that sheet FRP strengthening increases the load capacity of masonry subjected to in-plane shear loading. Much research has also been done on seeking out other reinforcements to improve mechanical properties of fiberglass-reinforced panels. Wrzesien (1972) investigated the impact properties of other forms of glass fiber composites - woven glass cloth and unidirectional glass sheet, either alone or in combination with wire sheet and carbon fiber. Results showed that wire sheet had a significant improvement in impact resistance and damage containment of glass fiber reinforced plastics.

Fiberglass-reinforced impact-resistant panels (FRIRPs), constructed of about 80% E-glass fiber and 20% thermosetting resin matrix such as phenolic, polyester, and vinyl ester, are widely used in residential and commercial applications. There are two types of FRIRPs, storm panels and impact-resistant ballistic panels. Storm panels are designed to prevent windborne debris from penetrating into constructions to protect occupied areas. Extreme weather such as hurricanes and tornados have repeatedly caused human injury and property damage along the United States east coast from Maine to Texas (Pielke et al. 2008). According to Hurricanes: Science and Society (Scowcroft et al. 2011), the decade of 1996 to 2005 was the one of the most destructive decades in the last century, with total hurricane damage of $198 billion. Hurricane Sandy alone in 2012 caused 286 deaths and $75 billion in damage (Scowcroft et al. 2011). This has driven an increasing growth in the demand for impact-resistant storm panels.

Impact-resistant ballistic panels are intended to stop bullets from entering a protected area, providing protection for fixed structures such as police stations and courtrooms, or for the occupants of vehicles. With the increasing repeated occurrence of gun violence and mass shootings, today's combat scenario is no longer limited to traditional open battlefields. Ballistic panels have quickly made their way into the general public sector, where reasonable and affordable ballistic materials are in increasingly high demand.

1.2 Traditional Manufacturing Method of FRIRPS - Thermal Curing

In the fiber-reinforced composite industry, FRIRPs are manufactured by transforming uncured or partially cured fiberglass-reinforced thermosetting polymers into composite parts or structures, which involves curing the materials at elevated temperatures and pressures for a predetermined length of time. High cure temperature is required to initiate and sustain the chemical reactions that transform the uncured materials into fully cured solids. High cure pressures are used to provide the force needed for the flow of the highly viscous fiber-resin mixture in the mold, as well as for the consolidation of individual unbonded plies into a bonded laminate. The magnitude of these two important process parameters, as well as their duration, significantly affects the performance of the product (Mallick 2007).

According to Lopata et al. (1999), the thermal-curing process typically requires a complex heating and pressure cycle that ultimately must reach temperatures ranging from 150 to 250 °C and pressure as high as 700 KPa for epoxy resins. Yuhazri and Dan (2008) developed high impact hybrid composite panels using a hydraulic hot press. In the process, the mold was heated to melt Acrylonitrile Butadiene Styrene (ABS). The pressure was used to remove bubbles and to ensure bonding between the matrix material and the filler. Once the temperature reached 230°C, a pressure of 2 tons was put on the mold (10” x 12”). A cooling process followed, still under pressure, until the press reached room temperature.

As a result of lengthy heating and cooling cycles, the traditional thermal curing process requires substantial energy consumption and long processing times, as well as inevitable volatile organic compound (VOC) emission.

1.3 Radiation Curing Process for Manufacturing FRIRPs

The radiation curing process, instead of using thermal energy (heat), uses radiation energy (photons or electrons) to activate polymerization, turning liquid resin into solid polymer rapidly at ambient temperature. Research has been conducted on using electron beam (EB) or ultraviolet light (UV) to cure fiber-reinforced composites. Such studies have showed positive results, along with limitations such as high capital cost of instruments, the safety of the working environment, and the limited depth of cure (Patacz et al. 2000; Berejka & Eberle, 2002; Decker 2001). Visible light, considered as a relatively low energy radiation compared to UV and EB, is able to address all of the above issues. It is currently widely used in dentistry to cure restorative resins. However, its industrial application has been minimal. It would be of great value to investigate the feasibility of its industrial utilization and push forward the technology, particularly in today's world where we are on close watch for climate change and advocate reduction in carbon footprint. Visible light curing process could potentially become a new low cost/energy-effective and environmentally friendly green technology.

1.4 Objectives

The overall goal of the research presented in this dissertation is to investigate the feasibility of visible light LED curing of fiber-reinforced composites and to develop bench-scale fabrication procedures, formulations, and mechanical tests. The specific objectives are:

1. To develop a curing unit that can be used to deliver visible light with a spectrum matched to the photoinitiator in the resin formulation. Meanwhile, the light curing unit is expected to meet the following specifications:

a. The curing unit should provide a large enough curing surface area to be able cure a moderate sized panel for testing and evaluating impact resistance.

b. A large number of LEDs potentially increase the overall power input but develop significant heat generation over time. An effective cooling system was needed to provide sufficient heat dissipation to maintain LED junction temperature below 135C and allow constant safe operation.

c. The third goal was to quantify and qualify the distribution and uniformity of irradiance from the LED array and to evaluate how it affects degree of polymerization and depth of cure, that is, the number of layers of fiberglass that can be cured within a certain period of time.

d. Curing time is another factor that determines depth of cure. The fourth goal was to measure the minimum time required to cure through half the panel based on the maximum recommended operating current of the LEDs.

2. To develop a visible light curable resin system that consists of oligomers, monomers, photoinitiators, and co-photoinitiator, and to study how a variety of factors, that is, the concentration of photoinitiator, types of oligomer, and curing time, affect the degree of polymerization and mechanical strength.

This objective required analysis of oligomers in the resin systems because oligomers form the backbone of a polymer matrix, and directly affect the adhesion between polymer and fibers. In general, fibers provide high strength and modulus, while the polymer matrix spreads the load and offers resistance to weathering and corrosion. For impact properties, the polymer matrix influences the impact damage mechanism because delamination, debonding, and fiber pullout energies depend on fiber-matrix interfacial shear strength (Schwartz, 1997). The different functional groups of oligomers result in different cure speeds, degree of polymerization, as well as adhesion to the fibers.

3. To develop laboratory impact test procedures and instrumentation to examine impact properties of visible light cured panels at thicknesses of 1/2” and 1/4” that would simulate standadized impact tests, but in a laboratory setting. Panels ½” thick are designed for ballistic protection, and were subjected to lab impact tests as well as actual shooting tests according to Underwriters Laboratory UL 752 level III ballistic standards. The results were compared with

commercially available ballistic panels. One-quarter-inch thick panels are designed to be used as storm panels, on which lab impact tests were carried out.

4. To conduct a comparative analysis on the energy consumption and processing time of the visible light curing process and thermal cure process for making ½" - thick ballistic panels and to demonstrate the feasibility and advantages of the visible light curing process for industrial applications.

This research started with an extensive preliminary study on the ability of visible light (blue LEDs with the wavelength of 470 nm) to cure through fiberglass sheets. This is the first study of this kind to adapt visible light curing of resin composites from dentistry to an industrial application.

1.5 Organization of Report

The introductory chapter provides an overview of FRIRPs and the traditional manufacturing thermal curing method with its limitations and then briefly introduces a state-of-the-art visible light curing process for manufacturing FRIRPs that could potentially address the issues that the former was facing, and the need to develop such technology in light of today's environmental challenges. The chapter concludes with the objectives of this study.

Chapter 2 presents an overview of pertinent literature on radiation curing technology, covering basic principles and applications of different types of radiation sources as well as a detailed review over visible light curing mechanism and general considerations. This is essential to facilitate better understanding of advantages and limitations of visible light curing which in turn provides guidelines in the design and analysis of experiments.

Chapter 3 contains the materials and methodology for constructing the visible light curing unit and developing visible curable resin system. It also describes the composites fabrication and test methods that were used to meet the objectives of this study.

Chapter 4 includes three manuscripts intended to be published in peer-reviewed journals, titled: manuscript 1 - “Design of a Blue LED Array for Curing Fiber-Reinforced Composite”; manuscript 2 - “Visible Light Curing of Fiber-Reinforced Composites Based on Epoxy Acrylate Resins”; manuscript 3 - “Impact Properties of Visible Light Cured Fiber-Reinforced Composites”.

Chapter 5 presents the results of each stage of experiments and discussions on the major observations and the validation of research methodology.

Chapter 6 summarizes the conclusions of this study and presents thoughts and suggestions for future considerations in this field.

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CHAPTER 2 REVIEW OF LITERATURE

2.1 Radiation Curing Process

Radiation curing of composites is a fast and effective way of converting a liquid resin into a solid material using radiant energy with a solvent-free formulation at ambient temperature (Koleske 2002). Radiation curing takes place by either radical polymerization for acrylate-based resins or cationic polymerization for epoxies and vinyl ethers. Free-radical initiation is achieved either by use of an electron beam or other suitable means that generates ionizing radiation capable of generating free radicals, or by use of ultraviolet radiation and a photoinitiator that will produce free radicals. Cationic initiation is achieved by photochemical means and requires the use of a photoinitiator that will photolyze to form Lewis or Bronsted acids (Koleske 2002). Radiation curing takes place at ambient temperature, and offers a number of advantages, such as low energy consumption, reduced cure time, and little to no VOC emission. As a result, higher productivity, a safer work environment, and higher energy and cost-efficient manufacturing can be achieved. Ultraviolet radiation and electron beam energy are more commonly used for radiation curing, while coherent radiation and visible light are also used.

2.2 Radiation Sources

2.2.1 Electron Beam (EB) and X-ray Radiation

Electron beam technology has been used for many end use applications and is mostly used for high volume production because of the large equipment cost and size (Koleske 2002). Electron beam curing of fiber-reinforced composites was developed over 30 years ago (Berejka and Eberle 2002).

Curing occurs when high-energy electrons initiate free-radical or cationic polymerization and crosslinking in the irradiated material. Compared to ultraviolet radiation, electron beam radiation transfers a higher energy density to the irradiated object with deeper penetration, even into thick or opaque materials (Patacz et al. 2000). In addition to industrial coatings, electron beams have found important utility in the curing of fiber-reinforced composites. EB curable epoxies are a unique class of resins that can be cured rapidly (cross-linked) thorough cationic polymerization using electrons or x-rays to produce composite materials (Janke et al. 1996). According to Berejka and Eberle (2002), for carbon fiber-reinforced composites, accelerator voltages of > 3 MeV are needed to penetrate the tooling and to cure practical composite structures. A typical carbon fiber composite structure with a 1.6 g/cm^3 density can be penetrated with 10 MeV electrons with equal entrance-equal exit dose to approximately 2.0 cm. EB cured composites were found to have comparable mechanical properties to thermally cured products, with the advantages of great reduction in curing time and energy consumption.

The development of high current electron beam accelerators makes x-ray processing possible in industrial applications. Despite the inefficiency in converting electron beams to X-rays, it still affords better overall process efficiency when compared with historic thermal processes (Berejka et al. 2005). The converted x-rays from electron beams allows penetration depths greater than 20cm (Saunders et al. 1994).

2.2.2 UV Radiation

UV radiation is limited in terms of penetration into matter, because most of the events initiated by UV radiation occur near the surface, while the advantages are lower costs for the equipment and lower energy consumption compared to thermal curing (Endruweit et al. 2006).

Due to this limitation, UV polymerization is commonly used for curing thin polymer films in applications such as fast drying of varnishes, paints, printing inks and adhesives, as well as in the production of printing plates, microcircuits, and optical disks (Decker 2001). Additional major fields of application are dental prosthetics and rapid prototyping by means of stereolithography (Narayanan and Scranton 1997).

Commonly used UV radiation sources are mercury arc lamps or electrodeless microwave-powered mercury lamps (Endruweit et al. 2006). Composites must be transparent to illumination for the polymerization to proceed throughout the thickness of the laminates. For UV radiation curing, polymerization mainly takes place in the top resin layer. The optical properties of the resin change as the polymerization proceeds. The absorbing photoinitiator forms transparent photoproducts, so that the incident radiation can penetrate deeper into the material (Decker 1998).

2.2.3 Visible Light Curing

Visible light radiation occurs between 400 and 750 nm. The energy from visible light is less powerful than that from ultraviolet light. For that reason, it has advantages in certain applications such as dentistry and orthopedic cast or device areas (Koleske 2002).

Quartz tungsten halogen (QTH) light has been used for curing dental composites for many years, but recently, light emitting diodes (LED) have proven to be a more efficient light curing unit, with blue LED light offering the highest photopolymerization efficiency (Neumann et al. 2006). Bennett and Watts (2004) found that compared with quartz tungsten halogen light, LED units have lower irradiance, but are more reliable, maintenance free, and are more energy efficient. They recommended increasing light irradiance to enable greater depth of cure, especially when curing from a distance.

Light curing is facilitated by the latest generation LED units providing light intensities of up to 2,000 mW/cm^2 (Kramer et al. 2008). They reported that the cure time for a 2 mm resin composite layer can be limited to 20 seconds to obtain durable results and that curing depth is fundamentally dependent on the distance of the resin composite from the light source. Lindberg et al. (2005) found that increasing the light tip-resin composite distance or decreasing the exposure time decreased the depth of cure. With variable light sources, a 6mm distance and 20s exposure duration resulted in the median depth of cure between 2.0 and 3.5 mm, 40 s resulted in between 3.0 and 4.5 mm depth.

2.2.4 Other Radiation Sources - Gamma Ray and Microwave

Gamma radiation

Gamma radiation is one of main radiation-initiated polymerization methods used to cure monomers in wood (Li 2011; Meyer 1965; Siau, Meyer, and Skaar 1965). Schaudy and Proksch (1982) investigated the improvement of dimensional stability and toughness with a broad variety of monomers and resin solutions. Experiment results showed that methyl methacrylate (MMA) and the reactant (hydroxyethyl acrylate (HEA) and trimethylhexamethylene diisocyanate (TMDI)) at a ratio of 7:3 provided the wood polymer composite the best impact bending strength.

Microwave

Microwaves are electromagnetic waves with wavelengths ranging from 1mm to 1m, or frequencies between 300 MHz to 300 GHz. (Mallakpour and Rafiee 2008). Microwaves can generate heat directly within the sample through molecular interactions with the electromagnetic field, avoid the conduction of heat through the processing equipment, and thus result in fast cure cycles and enhanced overall quality (Thostenson and Chou 1999; Mijovic and Wijaya 1990).

Papargyris et al. (2008) incorporated microwave heating into the resin transfer molding (RTM) technique, showing that microwave heating reduced by half the cure cycle time with similar mechanical properties of the cured products. Lee and Springer (1984) reported that microwaves were able to couple well with glass fiber composites, but would only be able to process relatively thin unidirectional carbon fiber composites due to the high dielectric loss of the carbon fiber. Mijovic and Wijaya (1990) compared the kinetics of cure of an epoxy formulation by microwave versus thermal energy. They found that cure proceeded slightly faster in thermal than in microwave field at a given temperature interval (115-195°C) used in the study and that the glass transition range is broader in the microwave field.

2.3 Visible Light Free Radical Polymerization

2.3.1 Photoinitiator

A photoinitiator is a molecule that absorbs light and, as a result, either directly or indirectly, generates a reactive species that can then initiate polymerization (Fouassier 1995). A photoinitiator molecule is excited into the singlet state by the absorption of a photon. The absorbed radiation causes bond breakage to take place between a carbonyl group and an adjacent carbon (Drobny 2010). There are two types of photoinitiators. Type I photoinitiators are compounds that upon irradiation undergo a cleavage reaction (α- or β- cleavage) to generate two radicals (Figure 1), both of which have the potential to initiate polymerization.

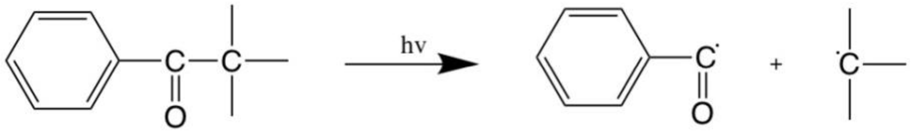

Figure 1. Type I Photoinitiator

Type II photoinitiators require the use of co-initiators, usually tertiary amine synergists, for an efficient polymerization process to occur (Drobny 2010). A co-initiator does not absorb light, but interacts with an activated photoinitiator to produce a reactive species that begins polymerization. Camphorquinone is an example of a type II photoinitiator (Figure 2). In this case, the tertiary amine provides the reactive radicals.

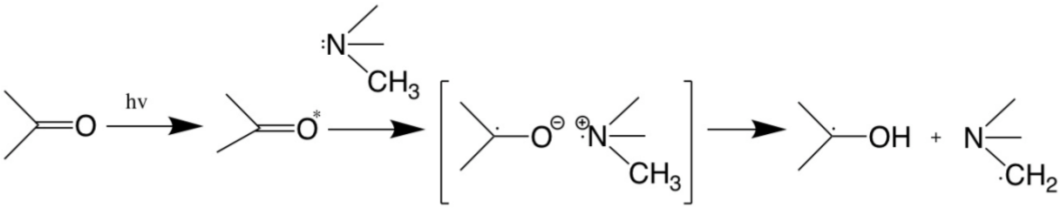

Figure 2. Type II Photoinitiator

CQ-tertiary amine initiators have been the standard in dental composite restoratives. A number of studies have been undertaken to understand the photoinitiation mechanism and the parameters that affect photoinitiation. Yoshida & Greener (1993) examined the effect of the CQ/amine ratio on initiator efficiency by the measurement of conversion in unfilled resin. It was found that, at a fixed CQ concentration, conversion increased monotonically to approximately a 1:2 or 1:3 molar ratio of CQ to amine and then plateaued with additional amine. Another study by Yoshida & Greener (1994) focused on the influence of varying concentrations of CQ and amine reducing agent, 2- (N, N-dimethylamino) ethyl methacrylate (DMAEMA), on the degree of conversion (DC). It showed that at low CQ concentration (0.5 mol.%, 1.0 mol.%), a CQ/amine molar ratio of 1:2 gave the most distinct improvement in maximum DC. At high CQ concentration (2.0 mol.% and above), no additional improvement was observed, but it discolored polymer specimens.

For dental restoration, CQ should be as little as possible because of the yellowness of resin for aesthetic considerations. For industrial applications, CQ concentration is expected to be the same for economic considerations, as well as the yellowness of resin, which may affect the light transmission into the composite.

2.3.2 Curing Time, Curing Depth, and Degree of Conversion

Curing time

A review study (Krämer et al. 2008) has stated that with high-power LED units of the latest generation, curing time of 2-mm thick increments of resin composite can be reduced to 20 seconds to obtain durable results. At energy densities > 17,000 mW/cm^2, no further improvement of mechanical properties was achieved.

Curing depth

Curing depth is fundamentally dependent on the distance from the resin composite to the light source (Krämer et al. 2008). Lindberg et al. (2004) demonstrated a linear relationship between light intensity of LED lamps and curing depth, and even prolonged curing times did not guarantee greater curing depths (Lindberg et al. 2004; Lindberg et al. 2005). They found that if the light tip was placed at a distance of more than 6 mm from the resin composite surface, polymerization depth was affected (Lindberg et al. 2005).

Degree of conversion

Degree of conversion is commonly measured by Fourier transform infrared reflectance spectroscopy - attenuated total reflection (FTIR-ATR). The absorbance peak area ratio of cured to uncured material provides the percentage of converted double bonds. It has generally been observed that the higher the conversion in resin composites, the higher the polymerization shrinkage will be (Silikas et al. 2000).

Studies (Koran & Kurschner 2001; Asmussen & Peutzfeldt 2001) have shown that energy density played an important role in the polymer structure, thus the final mechanical properties. A reduced intensity polymerization is probably associated with relatively few growth sites of polymerization, which may result in a relatively low crosslinked structure. In contrast, high light intensity in the initial phase of the irradiation period will initiate a multitude of growth sites, resulting in a higher crosslinking density. Less crosslinked polymer composite may be still more sensitive to crack initiation or visco-elastic degradation even with a high degree of conversion. Additionally, different monomers used in the formulation may result in different crosslinking density as well. Vaidyanathan & Vaidyanathan (1992) have found a significant increase in degree of conversion for UDMA compared to BisGMA monomers.

2.3.3 Curing Unit

Visible light curing of dental materials was introduced in the 1970s (Rueggeberg, 2011). Since then, a variety of curing units were developed. Quartz-tungsten-halogen (QTH) lamps were first put into clinical practice. QTH has a remarkably low efficiency and a limited lifespan with continuous degradation of the lamp because of the heat being produced during operation. The argon-ion laser requires less time to achieve equal physical properties as compared to QTH units; meanwhile, the polymerization shrinkage was considered problematic (Fleming & Maillet,1999). It became outdated in a short time due to various reasons, such as the high expense of a typical unit, the inability to replace the source by office personnel, and the increased temperature from operation (Rueggeberg, 2011). Plasma arc lights are pulsed and performed based on multiple 3-s exposures. These units must be highly filtered, since they generate tremendous amounts of infrared light and ultraviolet, which may cause biological damage.

The invention of blue LEDs in the early 1990s represents a significant and practical advance in dentistry, since blue LED emissions match well with the absorption by Camphorquinone. LEDs are more energy-efficient, lightweight, narrow-banded requiring no filter, and have a lifespan of several thousands of hours without a significant intensity loss. These advantages led to its extensive use in dentistry over the last decade.

Compared to UV LEDs, visible light LEDs offer additional advantages such as deeper penetration, higher outputs, lower input power (high energy efficiency), lower prices, and a safer work environment.

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CHAPTER 3 EXPERIMENTAL

3.1 Materials

3.1.1 LED array

The LED assemblies were purchased from Luxeon Star LEDs (Brantford, Canada). Each assembly contained 7 blue (470 nm) LED chips soldered onto a 40 mm round Coolbase. The specifications of a single LED assemble are shown in Table 1.

Lumens @700mA	490 lm
Typical Wavelength @ 350 mA	470 nm
Wavelength Range	460 to 485 nm
Recommended Operation Current	700 mA
Maximum Forward Voltage	24.57 Vf
Dimensions Diameter x H	40 mm x 5 mm

Table 1. The Specifications of LEDs

For each assembly, the LEDs were powered in series at a recommended operating current of 700mA. Twenty-eight assemblies, powered in parallel, were fastened to a heat sink using double-sided thermal tape. The heat sink contained five cooling channels, connected with plastic hoses to a circulating water bath, to form a closed-loop water cooling system. More details can be seen in Chapter 4 - Paper 1.

3.1.2 Plexiglas Pressing Mold

A pressing mold was made of two pieces of 12” x 12” x 1 1/8” clear Plexiglas sheets bolted together on three sides (Figure 3). The fourth side was not bolted in order to provide space for the excess resin to flow out. The Plexiglas sheets transmitted visible light and UV without absorption.

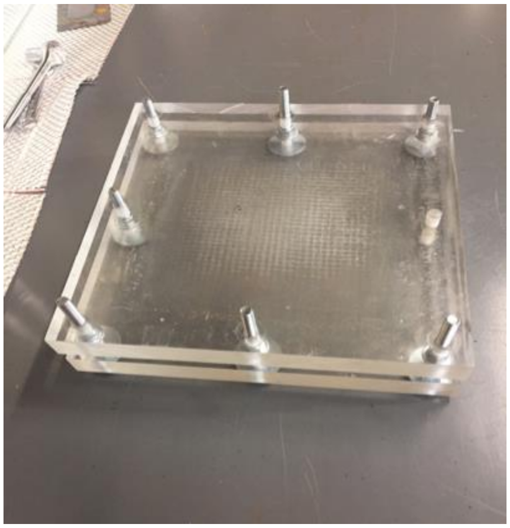

Figure 3. Plexiglas Pressing Mold

Shims (Figure 4) of the appropriate height (1/2”, 1/4”, 1/8”) by 0.5” wide and 4” long were placed between the bolts on three sides (two on each side) inside the mold to provide desired thickness of the panels.

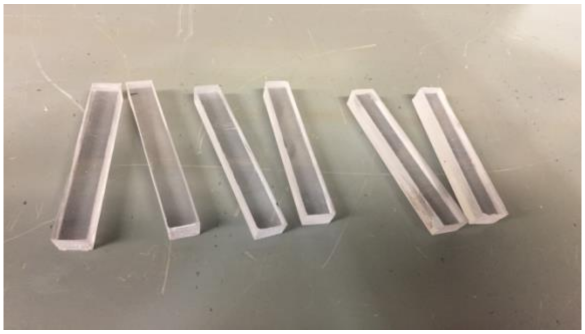

Figure 4. Plexiglas Shims (0.5-inch-thick)

3.1.3 Fiberglass

Fiberglass is the predominant fiber used in structural reinforcement composites. Fiberglass contributes high tensile strength, flexural, and impact properties. E-glass fiber is known for relatively high strain to failure and inexpensive cost, and is the most widely used fiberglass in the composite industry.

The fiberglass used in this project was E-glass woven roving, at a density of 24 ounces per square yard and a width of 50 inches, purchased online from http://www.fiberglasssupply.com. The woven roving fiberglass sheets were cut to a size of about 9.0” x 9.0”.

3.1.4 Resin System

Resin formulations in this study consisted of 5.89:1 mixture by mass of Bisphenol A Diglycidyl Ether Acrylate diluted with 25% Tripropylene Glycol Diacrylate (TPGDA) and Isobornyl Acrylate (IBOA) (Table 2). The oligomer Bisphenol A Diglycidyl Ether Acrylate forms the backbone of the polymer network, while IBOA, monofunctional acrylate monomer, was used as a reactive diluent, both of which were donated by Rapid Cure Technologies (East Syracuse, NY). Camphorquinone (CQ) was used as a photoinitiator with a concentration of either 1.0 wt % or 3.0 wt % (Table 2). The molar ratio of CQ to tertiary amine, Dimethylaminoethyl Methacrylate (DMAEMA)was 1:2.

Resin was mixed in a dark room, and heated in an oven at 40°C for 12 hours for dissolution of photoinitiator until the resin mixture appeared homogeneous. The resin mixture was then stored in dark bottles in a closed closet at room temperature.

Formulation ID	Bisphenol A Epoxy Diacrylate (wt %)	Bisphenol A Epoxy Methacrylate (wt%)	IBOA (wt%)	CQ (wt %)	DMAEMA (wt%)
D1	83	--	14.1	1	1.9
D3	--	83	14.1	1	1.9
M1	77.5	--	13.8	3	5.7
M3	--	77.5	13.8	3	5.7

Table 2. Visible Light Curable Resin Formulations

3.2 Methods

3.2.1 Preparation of Specimens

Preparation of 22-layer fiberglass-reinforced composites (FRCs)

The first ply of fiberglass sheet was placed on a piece of clean polyethylene (PE) plastic. Resin was applied repeatedly onto the fiberglass using a brush, until the sheet appeared to be fully wet. Another ply of fiberglass sheet was placed on top, followed by another layer of resin. This process was repeated until the top (22nd) layer of laminates was formed.

After the wet lay-up process, the unpolymerised laminated FRC were packed into a clean transparent PE bag and then placed between two clear Plexiglas sheets 1 1/8 - inch thick. On the three sides of Plexiglas, screws were tightened down to secure the composite materials in place.

A Wabash MPI electric compression press, which provides maximum clamping force of 30 tons with two 15" x 15" platens, was used to subject 2 tons of pressure onto the Plexiglas assembly (12" x 12"). Panels were pressed to stops, using one-half-inch thick Plexiglas shims. The screws were tightened so that the Plexiglas sheets would not spring back, maintaining 1/2" space after pressure was released. The pressure was released after 5 minutes' compression, during which time excess resin was squeezed out and trapped air bubbles were removed. The unpolymerised FRC, together with the Plexiglas mold, was placed on top of the LED array, and irradiated with blue light for 10 minutes on each side.

Preparation of light cured thin film - Film-C

Film-C was cured in the center of the 22-layer FRC. After the 11th layer of resin was applied, a piece of plastic sheet was placed instead of fiberglass. A pipette was used to add one to two drops of resin, covered by another plastic sheet. The hand lay-up process was resumed till 22 layers of laminates were formed. After the laminate was cured and separated by the plastic films, Film C was obtained for analysis.

Preparation of light cured thin films

For each formulation, one drop of resin was placed between two transparent PE plastic films. The uncured resin was brought to the center of the LED array and irradiated with blue light for 5s, 10s, or 60s (Table 3). After irradiation, the cured or partially cured resin formed a thin film, and was stored in a dark environment.

Formulation ID	Oligomer	PI (wt %)	Curing Time	Film ID
D1	Epoxy Diacrylate	1%	5s	D105
			10s	D110
			60s	D160
D3	Epoxy Diacrylate	3%	5s	D305
			10s	D310
			60s	D360
M1	Epoxy Methacrylate	1%	5s	M105
			10s	M110
			60s	M160
M3	Epoxy Methacrylate	3%	5s	M305
			10S	M310
			60s	M360

Table 3. Visible Light Cured Thin Film Specimens Based on Four Formulations

3.2.2 Fourier Transform Infrared Spectroscopy (FTIR)

An IR spectrum was recorded using a Bruker's ALPHA FTIR spectrometer with a single reflection diamond ATR (Attenuated Total Reflection) accessory. Twenty-four scans were taken at 4 cm^{-1} resolution, obtaining an absorbance spectra ranging from 4000 to 400 cm^{-1}. The curing behavior was analyzed by observing the changes in the peaks of carbon-carbon double bonds. A decrease in the peaks at approximately 1635 cm^{-1} and 810 cm^{-1} were observed for the cured resin.

The peak around 1720 cm^{-1} originating from C=O groups remained unchanged during polymerization, and was considered as an internal standard.

The degree of conversion of each specimen was determined by the comparison of the ratio of the aliphatic carbon-carbon double bond (C=C) peak at 1635 cm^{-1} and the internal standard peak (C=O bond around 1735 cm^{-1}) for the cured and uncured specimens, using the formula:

Degree of conversion = $\{1- (A_{t=0}/A_{It=0})/(A_t/A_{It})\}$ x 100%

Where $A_{t=0}$ is the area of peak 1635 cm^{-1} of the uncured resin. A_t is the area of peak 1635 cm^{-1} of the specimen when curing time is t. $A_{It=0}$ is the area of peak 1735 cm^{-1} of uncured resin. A_{It} is the area of peak 1735 cm^{-1} of the specimen when curing time is t.

The peak areas were obtained using peak fitting analysis after a baseline correction.

3.3 Impact Tests

3.3.1 Low Velocity Impact Test for Ballistic Panels

Resistance of FPIRPs to bullets was simulated in a laboratory setting by using a low-velocity drop impact test that imparted the correct force on the panel. A drop impact (low velocity impact) tester was designed to simulate a speeding bullet by dropping a weight of 250 lb from a preselected height onto the specimen (Figure 5). The preselected height was calculated based on Formula (1). The projectile (Figure 6, A) was made from a 7/16” x 3” non-deforming hard steel bolt, welded in a grade 8 bolt, attached to the bottom of the weight. The 7/16” diameter simulate the cross section of the specified SWC bullet (Figure 6, B) in the shooting test. The impact tester lifted and dropped the weight through electromagnetic control.

Test Energy (Ft lb) = Falling Weight x Preselected Height (ft) (1)

Where Falling Weight = 250 lb

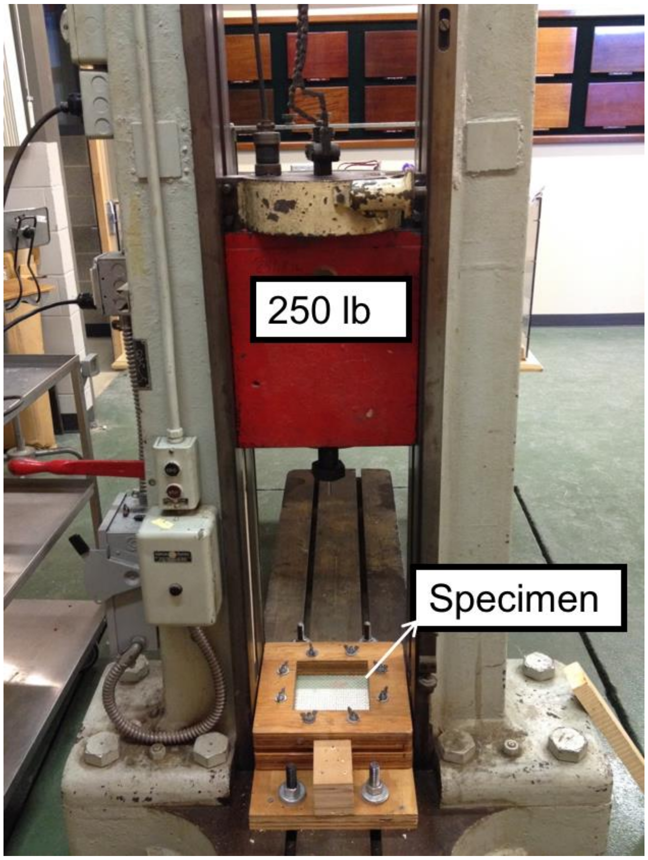

Figure 5. Low Velocity Impact Tester with Wooden Holding Frame

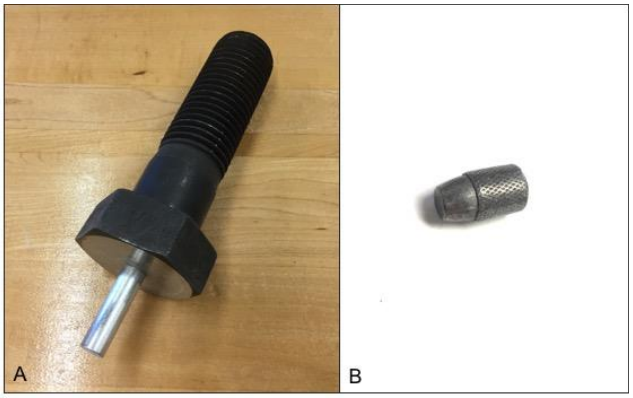

Figure 6 (A, B). Low Velocity Impact Test Projectile for Ballistic Panels (A) and Semi-Wadcutter Bullet for Shooting Test (B)

Two types of specimen holders were used throughout the study. A new aluminum holding frame was fabricated in replacement with the old wooded one, after the wooden frame showed signs of damage. Test data have been carefully organized so that only the results under the same test condition were analyzed.

The panel was clamped horizontally in a wooden frame type fixture by nuts and bolts on four sides as shown in Figure 5. The fixture held the panels in a manner such that the panel edges were constrained from slipping out of the frame. The clamped area was 1.5 inches from all the sides. The total exposed area was 6” x 6”.

After a strike, the specimen was examined to determine whether it passed or failed the test based on the criteria in Table 4, as well as the extent of penetration and delamination.

Fail	The projectile penetrates through the panel.
Pass	The projectile stops before reaching the bottom layer.

Table 4. Pass/Fail Criteria for Drop Impact Test

3.3.2 Low Velocity Impact Test for Storm Panels

Storm panels are designed to be used as reinforcing sheathing of walls and doors for the protection of building occupants. The reinforcement adds extra impact protection to the original wall structures from windborne flying objects and debris that result from a hurricane or tornado.

Enhanced Hurricane Protection Areas (EHPA) criteria (Floridadisaster, 2012), also known as the public shelter design criteria, was developed by Florida State legislation to regulate new educational facilities to be used as public hurricane evacuation shelters. The 1/8 -inch-thick storm panels were tested using low velocity impact test level 1 (Table 6) and an impact energy of 349 ft lb to simulate the energy of a 9-pound 2 by 4 propelled at 34 mph (ASTM E 1996 Level D, Table 5). Level D is the minimum code requirement for EHPA criteria.

The 1/4-inch- thick storm panels were tested using lab low velocity impact test Level 2 (Table 6) and an impact energy of 894 ft lb to simulate the energy of a 9-pound 2 by 4 propelled at 55 mph (ASTM E 1996 Level E, Table 5).

Storm panel specimens were made 1/4” and 1/8” - thick with resin loading in the range of 25% - 30%. The projectile used in the derived Level 1 and 2 were a 1-foot-long 2 by 4 lumber. The projectile was placed at the center of the specimen before dropping the weight.

Standards	Missile	Impact Energy
ASTM E 1996 Level D	9 lb 2x4 propelled at 34 mph	349 ft lb
ASTM E 1996 Level E	9 lb 2x4 propelled at 55 mph	894 ft lb

Table 5. ASTM E 1996 S Level D and E Test Specifications

Panel Thickness	Level	Impact Energy
1/8"	1	349 ft lb
1/8"	2	894 ft lb
1/4"	1	349 ft lb
1/4"	2	894 ft lb

Table 6. Storm Panel Impact Test Standard

3.2.3 High Velocity Impact Test - Ballistic test

Ballistic tests were conducted based on the Underwriters Laboratory (UL) 752 Bullet Resistant Testing Standard Level 3. The Level 3 standard requires a 0.44 Magnum pistol firing a lead semi-wadcutter gas checked bullet with a weight of 240 grains, i.e. about 15.6 g, from a distance of 15 ft. The velocity of the projectile should be recorded and must be within 1350 - 1484 ft/s. The temperature is to be 72 +/- 5 F. The specifications of projectiles and panels are shown in Table 7.

Due to the relevant New York State Regulations, the ballistic testing setups (particularly the gun and the ammunition) were unable to be acquired. The ballistic tests were conducted at the ballistic testing laboratory at Armortex, Inc., Schertz, TX.

Two visible light cured ballistic panels were made with Bisphenol A Epoxy Diacrylate and Bisphenol A Epoxy Methacrylate resins, respectively, and tested by Armortex. The thickness of the panels was 0.5 inch, and the resin loadings were both around 30%.

UL 752 Level 3 Standard	
Projectile Caliber	0.44 Magnum
Cartridge Type	240 grains SWC
Velocity range	1350 to 1485 ft/s
Panel Size	12 x 12”

Table 8. Underwriters Laboratory (UL) 752 Level 3 Standard

CHAPTER 4 MANUSCRIPTS

1. Bi, Y., Driscoll, M., Meyer, R. W., Larsen, L. S. “Design of a Blue LED Array for Curing Fiberglass-Reinforced Composites”. RadTech UV+EB Expo & Conference, Rosemont, IL, May 2016
2. Bi, Y., Driscoll, M., Meyer, R. W., Larsen, L. S. “Visible Light Curing of Fiber-Reinforced Composites Based on Epoxy Acrylate Resins”.
3. Bi, Y., Driscoll, M., Meyer, R. W., Larsen, L. S. “Impact Properties of Fiber-Reinforced Impact-Resistant Panels”.

Design of a Blue LED Array for Curing Fiberglass-Reinforced Composites

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Abstract

The development and continued evolution of Light-Emitting-Diodes (LEDs) represents a significant advance in the lighting industry. In addition to conventional illumination applications, LEDs have shown to be promising in many new applications such as the radiation curing industry. In this study, a LED array for curing fiberglass-reinforced panels is designed, as well as an efficient cooling system to maintain constant operation. To evaluate the effectiveness in inducing photopolymerization, the intensity and uniformity of the LED irradiance were investigated. Furthermore, this paper demonstrates the optical effect of Plexiglas on the irradiance distribution.

1. Introduction

Radiation-induced polymerization has contributed to advancements in sustainable materials and manufacturing field around the world. Ultraviolet light (UV) has been widely used in industrial applications such as inks, coatings, adhesives, and sealants. Electron Beam (EB) and X-ray processing have been the subject of extensive research in advanced composites, such as for automobile and aerospace manufacturing.

The primary application of visible light curing process is seen in dental composite restoratives. Visible light curing of dental materials was introduced in the 1970s (Rueggeberg 2011). Since then, a variety of curing units were developed. Quartz-tungsten-halogen (QTH) lamps were first put into clinical practice. QTH has a remarkably low efficiency and a limited lifespan with consecutive degradation of the lamp because of the heat being produced during operation. Argon-ion lasers require less time to achieve comparable physical properties as compared to QTH units; meanwhile, the polymerization shrinkage was considered problematic (Fleming & Maillet 1999). It became outdated in a short time due to various reasons, such as the high expense of a typical unit, the inability to replace the source by office personnel, and the increased temperature from operation (Rueggeberg 2011). Plasma arc lights are pulsed and performed based on multiple 3-s exposures. These units must be highly filtered, since they generate tremendous amounts of infrared and ultraviolet light, which may cause biological damage.

The invention of blue LEDs in the early 1990s represented a significant and practical advance in dentistry, since blue LEDs have emissions matching well with the absorption by Camphorquinone, which in combination with an amine, forms the conventional photoinitiator system in dental restorative resins. LEDs are more energy efficient, lightweight, narrow-banded requiring no filter, and have a lifespan of several thousands of hours without a significant intensity loss (Kraemer et al. 2008). These advantages allow its extensive use in dentistry for the last decade. However, its application in industry has been minimal.

This study proposes an innovative industrial application using visible light (blue LEDs) to photocure fiberglass-reinforced impact-resistant panels (FRIRPs). In this study, an 8 ⅛” x 10 ⅜” blue LED array curing device with an efficient cooling system was designed and fabricated.

Photopolymerization is initiated by blue LEDs emitting light at 470nm. To achieve adequate polymerization, light-cured composites rely on sufficient energy. Previous studies (Yoon et al. 2002; Mills et al. 2002) have shown that the degree of polymerization of the resin composite is significantly influenced by the energy density of the light curing unit. Energy density can be approximated if the irradiance and the time of exposure are known. It should be noted that the amount of energy required to totally cure differs for various resin systems, photoinitiating systems and light sources. In addition, in order to manufacture FRIRPs in large sizes, a uniform irradiance distribution is desired. Thus, this study also investigated the uniformity and distribution of the irradiance of the LED array to evaluate its effectiveness in inducing photopolymerization.

2. Experimental

2.1 Fabrication of LED Array

The LED assemblies were purchased from Luxeon Star LEDs (Brantford, Canada). Each assembly includes 7 blue (470nm) LED chips soldered onto a 40mm round Coolbase. The specifications are shown in Table 1.

Lumens @700mA	490 lm
Typical Wavelength @ 350 mA	470 nm
Wavelength Range	460 to 485 nm
Recommended Operation Current	700 mA
Maximum Forward Voltage	24.57 Vf
Dimensions Diameter x H	40 mm x 5 mm

Table 1. Specifications of an LED Assembly

Twenty-eight LED assemblies were connected in parallel, mounted to an aluminum heat sink (approximately 206 mm x 264mm x 25mm) with thermal conductive adhesive tape. The assemblies were oriented such that the distribution of LED chips was the most uniform (Figure 1). A 1/8”- thick piece of Plexiglas protecting the LED panel was supported by four rubber spacers on each corner of the panel (Figure 2). The LED array was driven by two DC power supplies (9.8A, 23.1V; HY3010E-3, MASTECH).

2.2 Cooling System

The LED array, especially on long exposure at high power, generates a significant amount of heat, which could potentially damage the LEDs. To ensure a longer LED lifetime and better color stability, an efficient heat dissipation system is needed.

A closed-loop water cooling system consists of a refrigerated bath and an aluminum heat sink (Figure 3) thermally attached to the LEDs with thermal adhesive tape. The refrigerated bath and heat sink are connected using plastic hoses. Cooled water was circulated through passages (Figure 3) drilled through the heat sink to maintain LED junction temperature below 90°F.

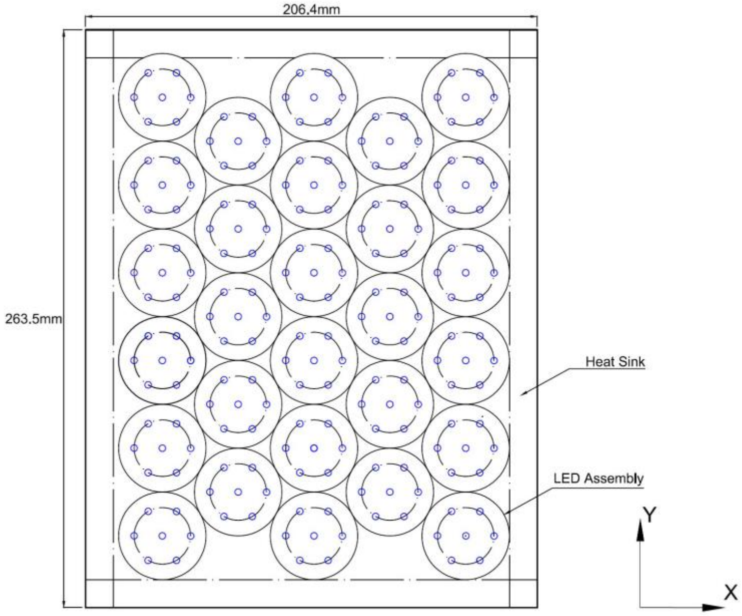

Figure 1. Layout of the LED Units on an Aluminum Heat Sink

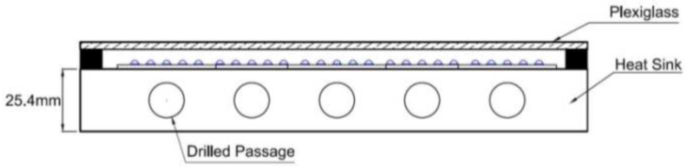

Figure 2. Schematic Representation of a Customized LED Array Curing Panel

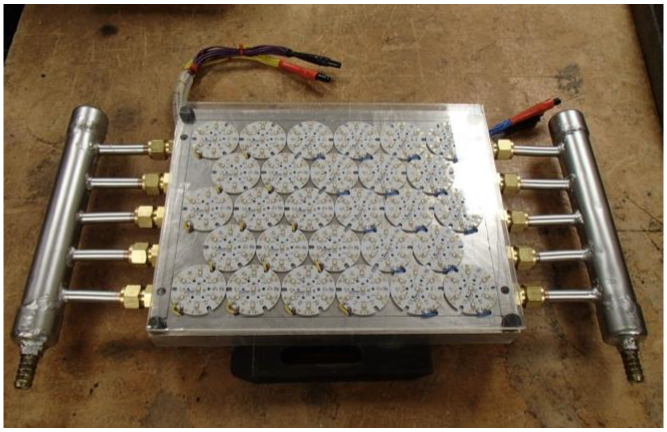

Figure 3. LED Array with Water Cooling Fixture

2.3 Irradiance Uniformity and Distribution Measurement

UV-V Radiometer Dosimeter (Loctite, Rocky Hill, CT) (Figure 4) was used for the measurement of light intensity. Readings were recorded at 10mm intervals in the X and Y direction (Figure 1), in mW/cm^2, representing the optical power received across the X-Y plane. The light intensity readings were then plotted as an intensity distribution map in Excel.

To observe and compare the irradiance uniformity across the LED array, the radiometer was placed at three positions: 1. right above the array, 2. 1 ⅛ -inch away from the array, and 3. right above 1 ⅛”-thick Plexiglas (Figure 5).

The temperature of the radiometer increased due to the radiated light from the LEDs, causing a slight decrease in the reading. To eliminate measurement error, a 10-minute waiting period was adopted after each 5 minutes of operation. In addition, a cooling fan was used to facilitate air flow over the LED array and radiometer.

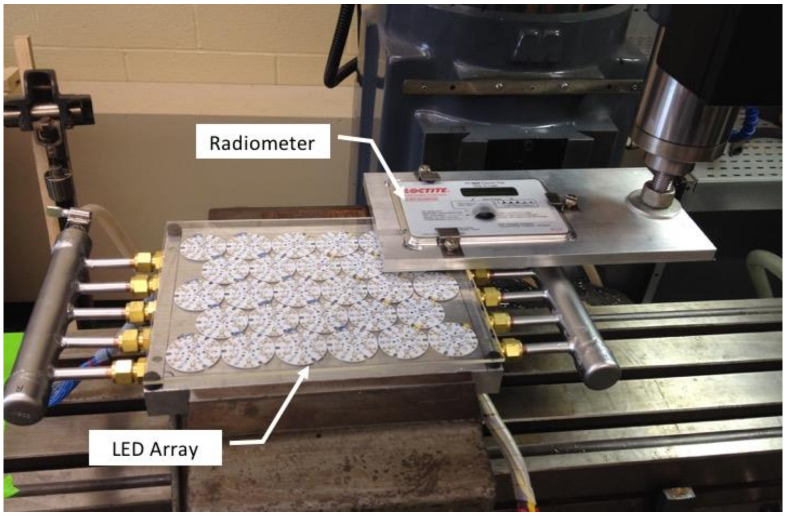

Figure 4. Suspended Radiometer over the LED Array

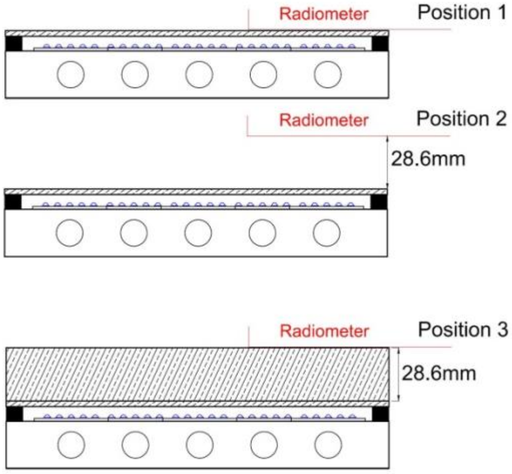

Figure 5. Irradiance Measurements Taken at Three Positions

3. Results

Irradiance distribution of the LED array measured at the three positions are displayed in Figures 4-a, 5-a, and 6-a. As can be seen in Figure 4-a, a number of high intensity peaks across the array represent the areas where individual LED assemblies are located. Figure 7-a and Figure 8-a show much more uniformed irradiance distributions, compared to Figure 6-a. This can be attributed to light divergence and scattering. When measured above 1 ⅛" thick Plexiglas, a larger high intensity area (800-1000 mW/cm^2, Figure 7-b) was observed but only a small area of 800-1000 mW/cm^2 was observed 1 ⅛" away from the array without Plexiglas in between (Figure 8-b).

Statistical analysis of the irradiance distribution is shown in Table 2. The highest average irradiance (880.3 mW/cm^2) was detected at the shortest distance from the array. The average irradiance was 707.5 mW/cm^2 when measured 1 ⅛" away from the LED array without Plexiglas (position 2) and 759.9 mW/cm2 with Plexiglas, representing an increase of 7% when Plexiglas is used.

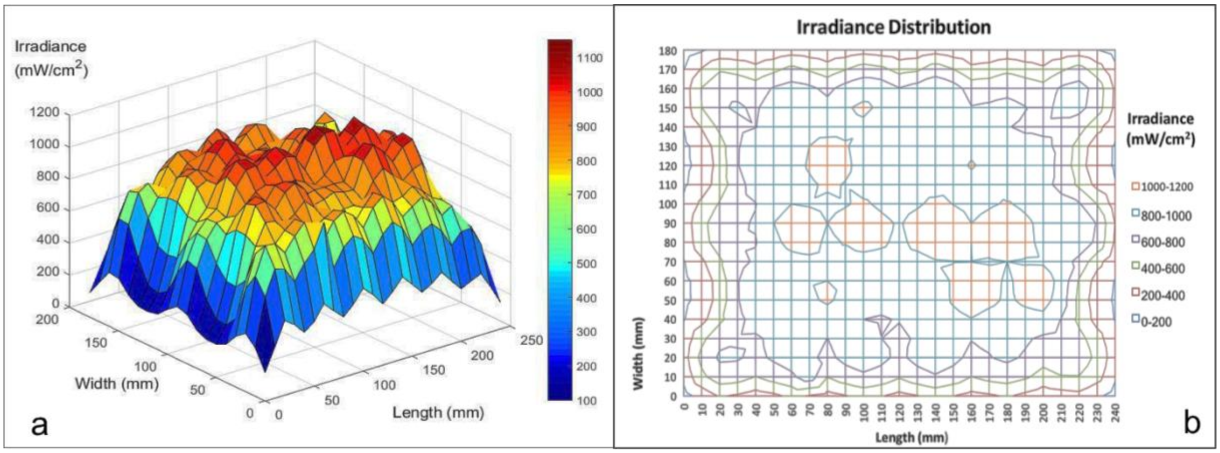

Figure 6 (a, b). Irradiation Distribution at Position 1 – Measured on Top of LED Array

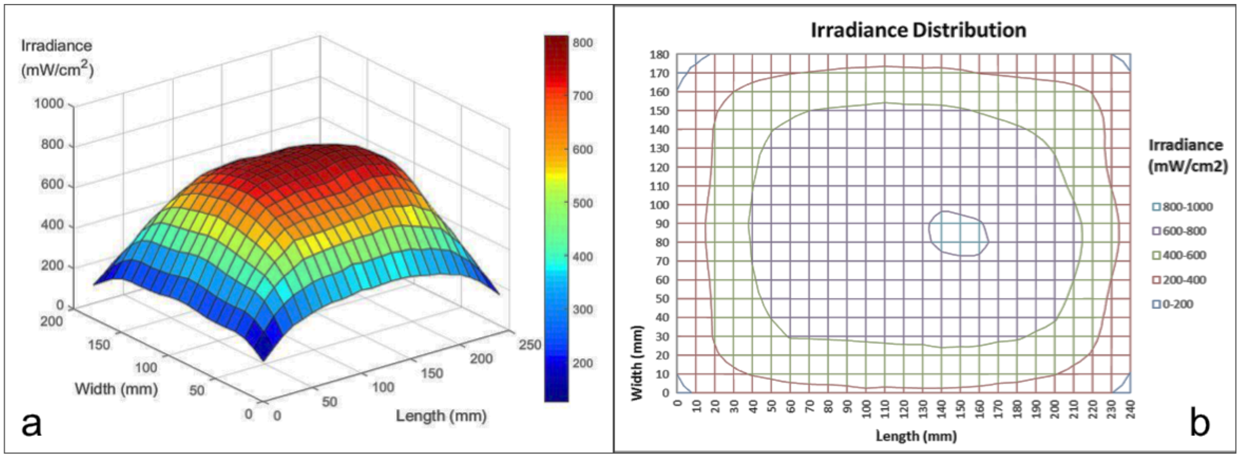

Figure 7 (a, b). Irradiance Distribution at Position 2 – Measured from 1 1/8” (28.6mm) Away from the LED Array

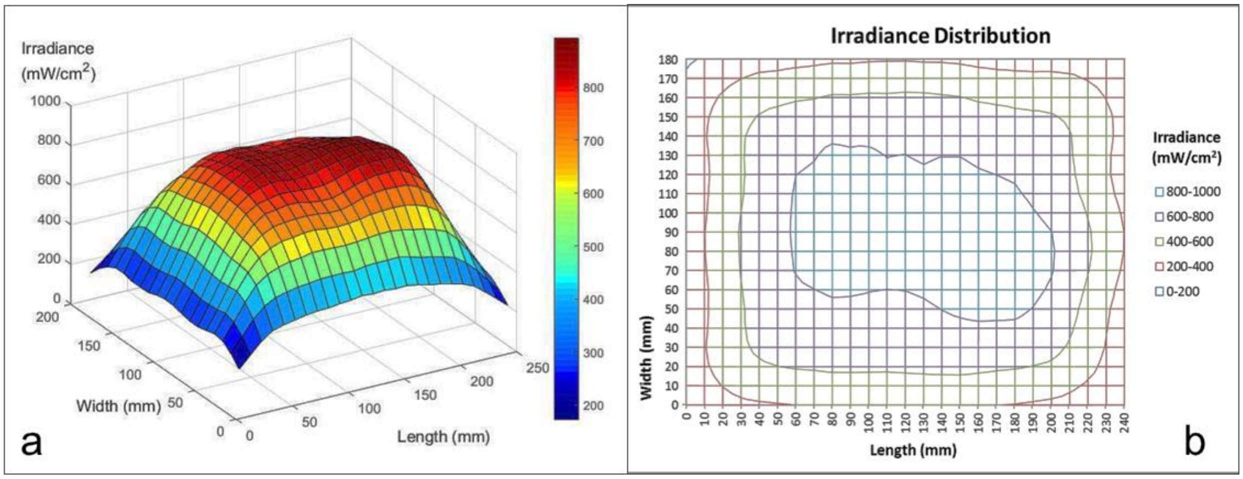

Figure 8 (a, b). Irradiance Distribution at Position 3 – Measured Through a 1 1/8” (28.6mm) Thick Plexiglas

Position	**Min (mW/cm^2)**	**Max (mW/cm^2)**	**Median (mW/cm^2)**	**Average (mW/cm^2)**
1	602	1150	886	880.3
2	600	810	712	707.5
3	600	892	774	759.9

Table 2. Statistical Analysis of the Irradiance from 600 to 1150 mW/cm^2 at Three Positions

4. Discussion

4.1 Cooling System

Heat dissipation is an integral part to assure required operation stability and a long lifetime of LEDs. Heat is produced within the LED itself when current flows across the junction and becomes considerable when a number of LEDs are packed together. The key factor to optimize heat transfer is the thermal path from the LED junction to ambient temperature. In this design, water cooling efficiently brings down the junction temperature to enable constant operation.

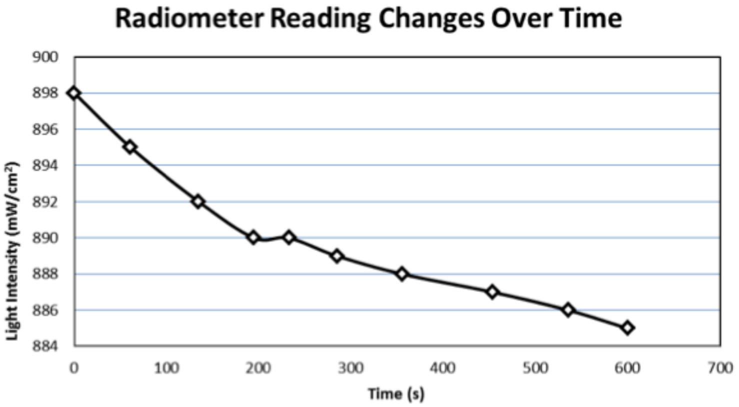

Figure 9. Radiometer Reading Changes over Time at (110mm,110mm)

In addition to the heat generated by LED itself, heat is given off when light is absorbed by the radiometer. The heat accumulates over time, causing the reading of radiometer drop slightly (Figure 9). A cooling fan was placed at one side of the array, providing a forced convection of air flow to accelerate heat transfer. To maintain a no more than 1% error, the array was turned off for 10 minutes to cool down after each 5 minutes operation.

4.2 Irradiance Uniformity

In radiometry, intensity is the amount of radiant power per solid angle, while irradiance is the amount of radiant power per unit area. In this study, intensity and irradiance are used interchangeably, representing the amount of visible light arriving at a surface per square centimeter (cm^2).

Irradiance of the light source and time of exposure, determine energy density. Since energy density is important for the total cure of the resin material (Mills & Raymont 2009), it is important to know the distribution of irradiance of the light source.

It is believed that the perceived irradiance homogeneity largely depends on the distance of the cure surface from the array unless lenses are used. The closer it is the stronger and less uniform the irradiance is. Figure 6-a, Figure 7-a, and Figure 8-a agreed with the prediction. Table

2 shows the Plexiglas enhanced the overall irradiation, especially the central high intensity area. One possible explanation is that when light travels through Plexiglas, part of it is reflected from the four side surfaces. Compared to air as the medium, more light is trapped in the Plexiglas, and is subsequently measured by the radiometer. Another explanation is with a higher refractive index of 1.49 than air (1.00), Plexiglas performed as refractive lens focusing light to the center of the array, resulting in a higher concentration of irradiance.

5. Conclusions

This study demonstrated a procedure for designing a LED array and its heat dissipation system. Water cooling is essential for constant operation of multiple LEDs. Additional fan cooling is required for measuring irradiance to minimize error, because the radiometer is affected by heat buildup from the light.

The distribution of irradiance is more uniform as the distance increases from the array. Plexiglas placed over the array further increases the uniformity of the distribution and enhances the irradiance. These results are desirable, since Plexiglas will be a part of the mold fixture in future curing process.

Acknowledgement

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Visible Light Curing of Fiberglass-Reinforced Composites Based on Epoxy Acrylate Resins

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Abstract

Visible light curing of composites is predominantly used in dentistry. This paper introduces a novel industrial application of using blue (470nm) LEDs to photocure fiberglass-reinforced polymer composites that are traditionally manufactured by heat curing. Photopolymerization takes place under blue light radiation from a customized LED array. The curing mechanism was investigated with a focus on the effect of oligomers, concentration of photoinitiator, and curing time on the degree of conversion of a Bisphenol A Epoxy Diacrylate/Methacrylate based resin system. Fourier Transform Infrared Spectroscopy (FTIR) was used to record the curing profile. This study also validated the ability of the blue LED array to cure through a 0.5-inch-thick fiberglass-reinforced polymer composite.

1. Introduction

Fiberglass-reinforced polymer composites (FRPCs) have been playing important roles in both civil and military applications. FRPCs are usually made of woven fiberglass and a polymer matrix system, traditionally manufactured by thermal curing, which involves a substantial amount of energy and time, and Volatile Organic Compound (VOC) emissions. Radiation curing process is based on radiation (photons or electrons) activated polymerization at ambient temperature, which effectively solves the energy, time and emission problems since it significantly reduces energy consumption and processing time with little to no VOC emissions.

Research on Ultraviolet light (UV) and Electron Beam (EB) cured composites has been conducted for various applications, while visible light polymerization is predominantly seen in dentistry for anterior and posterior restorations since it was first introduced in 1970s (Rueggeberg 2011). Visible light offers several significant advantages over UV and EB, such as lower cost of equipment and a non-hazardous environment during operation. Along with these benefits come the need to develop a visible light curing unit and associated resin system to achieve desired physical and mechanical properties of the finished product compared to commercially manufactured (thermal cured) products.

Visible light curing of epoxy acrylate resin is based on free radical polymerization, which involves the same three steps - “initiation”, “propagation”, and “termination” as in any polymerization. Unlike thermal curing systems, polymerization is initiated by free radicals generated by a photoinitiator. When radiation (photons) strikes the resin system, photoinitiators absorb the energy and directly or indirectly generate reactive species that can initiate polymerization (Fouassier, 1995). There are two types of photoinitiators. Type I photoinitiators undergo homolytic decomposition and directly form free radicals. Type II photoinitiators form free radicals by hydrogen abstraction or electron extraction from a co-initiator that becomes the actual initiating free radicals (Koleske, 2002). Camphorquinone (CQ) is a type II photoinitiator, and is by far the most widely used in biomedical applications (Kamoun et al., 2014). The absorption range of CQ is between 370-500mm with a peak at 468 nm which falls into the blue region of the visible spectrum and matches well with the blue LEDs (470nm), and thus were used in this study as a photoinitiator.

The lifetime of the initiated excited species is very short, generally less than 10^{-6}s (Drobny, 2010). For the photoinitiator to react correctly, the light must carry enough intensity at the correct wavelength. Adequate curing time can ensure a high degree of conversion especially when curing through a thick material. Studies have shown that higher light density, to some degree, can reduce curing time. Kramer et al. (2008) found that with high-power LED units of the latest generation providing output levels consistently between 1500-2000 mW/cm^2, curing time of 2 mm thick increments of resin composite can be reduced to 20 seconds to obtain durable results. At energy densities > 17000 mW/cm^2, no further improvement of mechanical properties was achieved.

Acrylate reins, based on acrylate/methacrylate unsaturation, are the most widely used light-curable oligomers. In general, methacrylates are less toxic than acrylates, but are also less reactive (Mehnert et al., 1998). Among acrylate resins, epoxy acrylate oligomers are the most widely used for high reactivity, good adhesion and producing chemically resistant films. It should be noted that in the radiation curing industry, the term “epoxy acrylate” means acrylated epoxides since there is no epoxy functionality in the molecules. “Acrylate” in this context can mean both acrylate and methacrylate. Monofunctional or multifunctional monomers are usually added later to dilute the formulation to a suitable application viscosity and to create cross-links between segments of the oligomer, so they act as reactive diluents.

The objective of this study was to develop a visible light curable resin formulation for FRPCs and to assess the ability of blue LEDs with the wavelength of 470 nm to cure deeply through epoxy acrylate/methacrylate resin systems and through multiple layers of woven fiberglass prepregs. An 8” x 10” blue LED array designed and constructed in the previous study was used as the light source. In addition, it was also desired to investigate the formulation parameters involved in the visible light (blue LEDs) curing process of FRPCs and to study their effect on the degree of conversion. This study has its own importance and provides a fundamental understanding of the visible light curing process for application to the FRPC manufacturing technique.

2. Materials

Four different formulations consisting of an oligomer, a monomer, a photoinitiator, and an amine synergist were prepared (Table 1). Two types of oligomers were used in this study - Bisphenol A Epoxy Diacrylate (Photomer 3016 25R, IGM resins) and Bisphenol A Epoxy Methacrylate (PE250, Miwon), both of which were diluted with 25 wt% Tripropylene Glycol Diacrylate (TPGDA). Isobornyl acrylate (IBOA, Sartomer) is a monofunctional acrylate monomer and was used as a reactive diluent. A photoinitiator and a tertiary amine, Camphorquinone (CQ, Esstech) and Dimethylaminoethyl Methacrylate (DMAEMA, Esstech), were used with a molar ratio of 1:2 (CQ/ DMAEMA). Two concentrations of CQ were tested - 1% and 3%. The composition of the formulations is given in Table 1. All chemicals were used as received without further purification.

Formulation ID	Bisphenol A Epoxy Diacrylate (wt %)	Bisphenol A Epoxy Methacrylate (wt%)	IBOA (wt%)	CQ (wt %)	DMAEMA (wt%)
D1	83	--	14.1	1	1.9
D3	--	83	14.1	1	1.9
M1	77.5	--	13.8	3	5.7
M3	--	77.5	13.8	3	5.7

Table 1. Visible Light Curable Resin Formulations

3. Methods

3.1 Preparation of resin system

The resin mixture was blended at room temperature. The blending process was performed in a dark room with yellow lighting to avoid incident polymerization induced by ambient light. The mixture was then heated in an oven at 40 degrees C for 12 hours to accelerate the dissolution of Camphorquinone and to remove air bubbles.

3.2 Preparation of specimens

3.2.1 Preparation of Light Cured Thin Films

For each formulation, one drop of resin was placed between two transparent plastic sheets. The uncured resin was brought to the center of the blue LED array where the light intensity was in the range of 900 - 1090 nW/cm^2 for 5s, 10s, or 60s (Table 2). After irradiation, the cured resin formed a thin film, and was stored in a dark environment immediately after curing.

Formulation ID	Oligomer	CQ (wt %)	Curing Time	Film ID
D1	Epoxy Diacrylate	1%	5s	D105
			10s	D110
			60s	D160
D3	Epoxy Diacrylate	3%	5s	D305
			10s	D310
			60s	D360
M1	Epoxy Methacrylate	1%	5s	M105
			10s	M110
			60s	M160
M3	Epoxy Methacrylate	3%	5s	M305
			10s	M310
			60s	M360

Table 2. Specimens Based on Four Formulations

3.2.2 Preparation of Light Cured Thin Film - Film-C

To make fiber-reinforced polymer composites, commercial E woven roving fiberglass with a density of 24 ± 10% oz per square yard was used as the composite filler. The composite was fabricated using a hand lay-up process in which each ply was impregnated with resin using a brush and stacked on the top of each other, until the 22nd layer of fiberglass was applied.

Film-C was formed in the middle of the 22-layer Fiber-reinforced polymer composite (Figure 1). After the 11th layer of fiberglass was applied, a piece of plastic sheet was placed instead of fiberglass. One drop of resin was applied in the center of the plastic sheet, and covered by another plastic sheet. The hand lay-up process was resumed until the 22 layers of laminates were formed.

The unpolymerised laminate was then put into a transparent PE bag and placed inside a Plexiglas mold which was comprised of two 1 1/8- inch-thick Plexiglas plates (Figure 2). Together with the Plexiglas mold, the laminate was taken to a Wabash MPI electric compression press to press to the desired thickness (0.5 inch). After 5 minutes' compression, bolts connecting the edges of the Plexiglas plates were tightened to maintain the 0.5-inch-thickness, the compression was then released. The FRPC was then placed on top of the LED array, and irradiated with blue light for 15 minutes on each side. The irradiance of blue light around the center of the array was in the range of 800 - 1000 mW/cm^2. Since Film-C was cured in the middle of the 22-layer composites, its received irradiance was much lower than 800 mW/cm^2. After the laminate was separated by the plastic films, Film C was obtained for analysis.

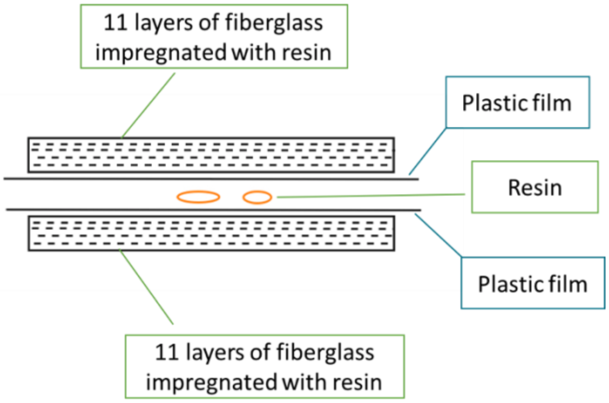

Figure 1. Schematic Illustration Showing the Formation of Film-C

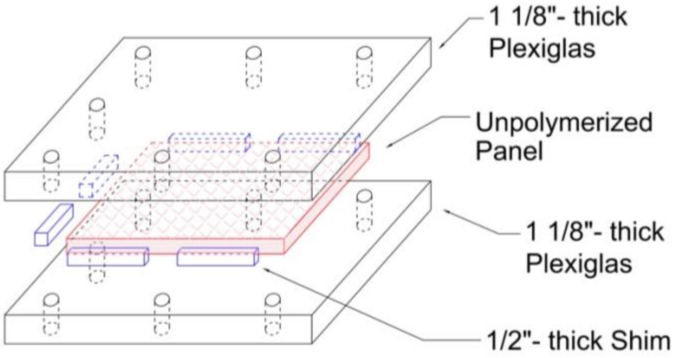

Figure 2. Schematic Illustration of an Unpolymerized Panel Inside the Plexiglas Mold

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The curing mechanism of visible light induced polymerization was studied by FTIR. IR spectra were recorded using a Bruker's ALPHA FTIR spectrometer with a single reflection diamond Attenuated total reflectance(ATR) accessory. Twenty-four scans were taken at 4 cm^{-1} resolution, obtaining an absorbance spectrum ranging from 4000 to 400 cm^{-1}.

The curing behavior was analyzed by observing the changes in the peaks of carbon-carbon double bonds (Figure 3). A decrease in the peaks of approximately 1635 cm^{-1} and 810 cm^{-1} were observed for the cured resin. The peak around 1735 cm^{-1} originating from C=O groups remained unchanged during polymerization, and was adopted as an internal standard.

The degree of conversion of each specimen was determined by the comparison of the ratio of the unreacted aliphatic carbon-carbon double bond (C=C) peak at 1635 cm^{-1} and the internal standard peak (C=O bond) at around 1735 cm^{-1} for each specimen, using the formula:

Degree of conversion = $\{1- (A_{t=0}/A_{It=0})/(A_t/A_{It})\}$ x 100%,

where $A_{t=0}$ = the area of peak at 1635 cm^{-1} of uncured resin,

A_t = the area of peak at 1635 cm^{-1} of the specimen when curing time is t,
$A_{It=0}$ = the area of peak at 1735 cm^{-1} of uncured resin,
A_{It} is the area of peak at 1735 cm^{-1} of the specimen when curing time is t.

The absorbance spectra were analyzed by exporting raw FTIR profile data to OriginPro software. The peak areas were obtained using conducting peak fitting analysis with a baseline correction. Three specimens were tested for each formulation.

4. Results

4.1 FTIR Spectrum

The curing profile was monitored by following the decrease in the absorbance intensity of acrylate bonds (C= C). For example, Figure 3 shows the FTIR spectra of M3 formulations (Bisphenol A Epoxy Methacrylate with 3% photoinitiator) as a function of time. It was found that all formulations showed decreases in the intensity of the acrylate group (C=C) peaks at around 1635 cm^{-1} and 810 cm^{-1} with increasing curing time. This is because the C=C bonds in the oligomers and reactive monomers underwent polymerization and cross-linking reaction.

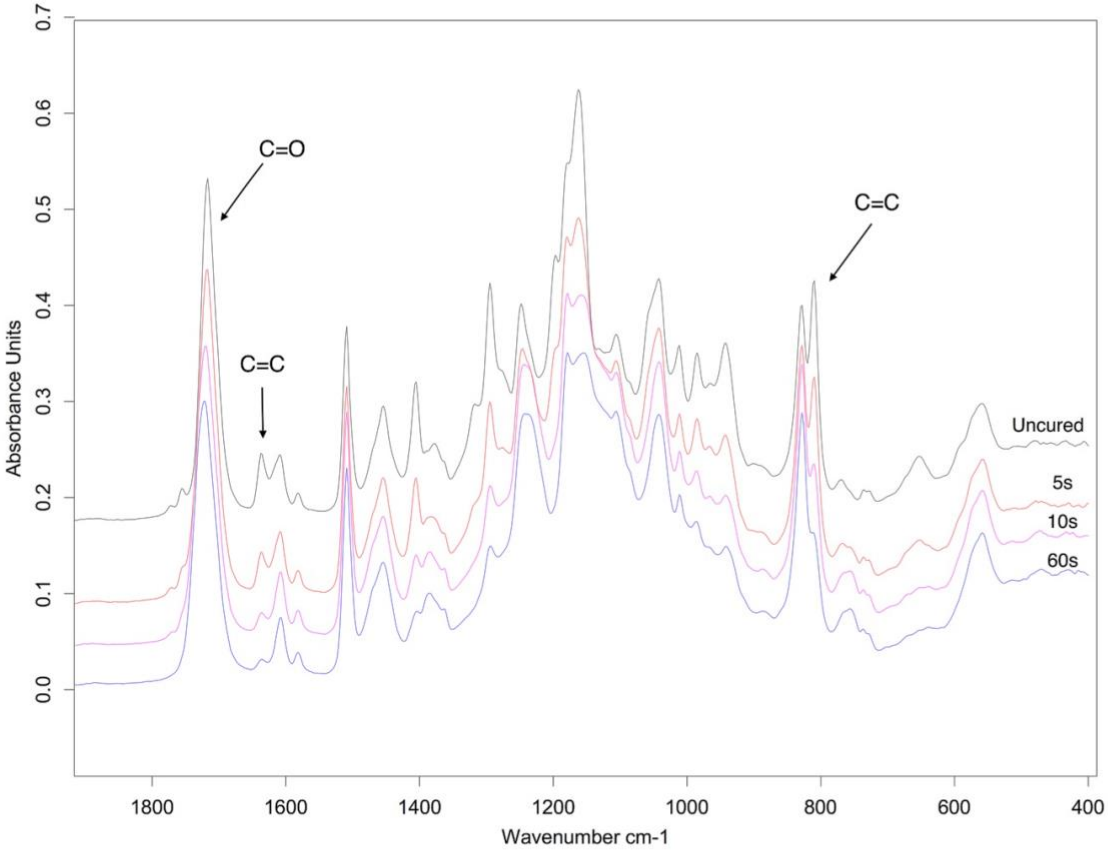

Figure 3. FTIR Spectra of Bisphenol A Epoxy Methacrylate with 3% Photoinitiator formulation (M3)

4.2 Impact of Oligomer and Photoinitiator Concentration on the Degree of Conversion

The conversion of acrylate bonds for four formulations as a function of curing time is presented in Figure 4. As can be seen from Figure 4, as curing time increased, the degree of conversion increased rapidly during the first 5 seconds, and then slowed down until 10 seconds. The rate of change continued to decrease till 60 seconds. This observation was in agreement with other studies (Kunwong, et al., 2011; Yang, 2005). From 10 seconds to 60 seconds, the conversion increased extremely slowly. For M1 and D3 formulations from 10 seconds to 60 seconds, the degree of conversion reached plateaus at 70± 1% and 65 ± 1%, respectively.

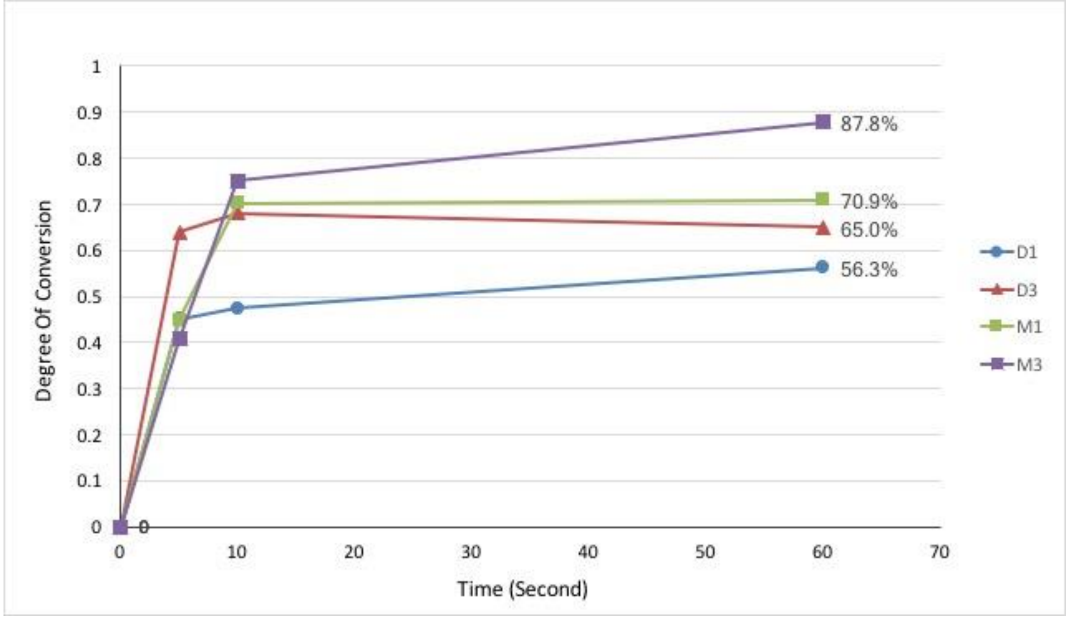

Figure 4. Degree of Conversion of Two Types of Oligomers: Bisphenol A Epoxy Diacrylate (D1; D3) and Bisphenol A Epoxy Methacrylate (M1; M3) with 1% and 3% of Photoinitiator

Figure 4 also shows that with 1% photoinitiator, the Bisphenol A Epoxy Methacrylate formulation (M1) achieved a remarkably higher degree of conversion (70.9%) than Bisphenol A Epoxy Diacrylate (D1, 56.3%) at 60s, an increase of about 26%. A similar observation was found with 3% photoinitiator: Bisphenol A Epoxy Methacrylate formulation (M3) having a 87.8% conversion compared to 65.0% for Bisphenol A Epoxy Diacrylate (D3) at 60s, showing a 35% increase.

The amount of photoinitiator is usually a small percentage in a light curable resin system, but it plays a critical role in affecting curing efficiency and the degree of final conversion. It is obvious to see from Figure 4 that both oligomers with 3% photoinitiator concentration achieved higher final conversion at 60s than that with 1% photoinitiator. For Bisphenol A Epoxy Methacrylate formulation, the 1% and 3% concentration did not show distinct differences in the conversion rate at 5s and 10s. For Bisphenol A Epoxy Diacrylate formulation, 1% concentration showed a slightly higher conversion rate at 5s.

4.3 Film-C

Film-C was based on M1 formulation (Bisphenol A Epoxy Methacrylate with 1% photoinitiator) cured in the middle of the 22 -layer FRPC for a total of 30 minutes. Compared to the rest of the specimens, Film-C was cured with lower irradiance but for a longer curing time. Three replicates were tested. The average of the degree of conversion reached 88.3%, the highest among all the films.

5. Discussion

The light-curable formulation consists of three essential ingredients: an oligomer, a monomer, and a photoinitiator. The base reactive oligomer imparts most of the properties to the cured materials, while the viscosity of the oligomers is typically high, thus often requiring a diluent. Many commercial oligomers are diluted with 20 - 30% of low viscosity monomeric acrylates as marketed (Koleske, 2002). In this study, M3 formulation (epoxy methacrylate resin with 3% photoinitiator) achieved the highest degree of conversion. Other factors, such as cost of raw materials and fiber-polymer interaction, must be considered to decide the best combination for the industrialization of visible light curing of FRPCs. To improve the performance of light cured materials, novel oligomers have been developed by many researchers (Tasic et al., 2004; Xu et al., 2006). Park et al. (2009) studied dual-cure adhesives based on epoxy acrylate oligomers and found that the extent of C=C bond contents of the epoxy acrylate oligomers do affect the extent of curing. The structures and formulations of diluent monomers are selected based on particular applications and property requirements (Allen, 1996). The functionality of monomers impacts cure speed and crosslinking. In general, viscosity, cure speed, and crosslink density increase with the functionality of monomers, while adhesion and flexibility decrease with monomer functionality.

In dental composite restoratives, CQ is frequently used with a tertiary amine co-initiator. A number of studies on the CQ-amine photoinitiation process have been undertaken to investigate the initiation mechanism and the parameters that affect photopolymerization (Cook, 1992; Mateo et al., 1994; Yoshida & Greener, 1993). It was found that the degree of conversion was optimal with approximately 1:2 or 1:3 molar ratio of CQ to amine.

For economic considerations, a lower concentration of CQ is preferred for FRPC manufacture because CQ is the single most expensive component in the formulation and takes up more than 70% of the cost of the entire formulation with 1% concentration and more than 87% with 3% concentration. Therefore, within the range of acceptable conversion, the CQ concentration should be as little as possible.

Based on a cost/benefit analysis, M1 (epoxy methacrylate resin with 1% photoinitiator) was selected to be the preferred formulation to make FRPCs. The final 88% of conversion of Film-C cured in the middle of a 22-layer PRPC based on M1 formulation means that 0.5-inch-thick FRPC was fully cured. This is because as light passes through the FRPC, it is absorbed and scattered, attenuating the intensity and reducing the effectiveness of the light for inducing photopolymerization (Vargas et al., 1998). The middle layer(s) of the 22-layer FRPC received the least intense radiation but achieved even higher degree of conversion than that of film M160 (71%). This result demonstrated the ability of the blue LED array to cure though a 0.5-inch-thick

22-layer FRPC panel. The conversion for M1 formulation had increased from about 71% to 88% from 1 minute to 30 minutes with an extremely low conversion rate compared to the first 1 minute when the conversion already reached 71%. It is safe to say that thirty minutes of curing time is more than adequate to cure through a 0.5-inch-thick composite, and it is known that even for prolonged curing times, the degree of conversion will not reach 100%. This is because as the polymerization and crosslinking reaction took place rapidly, the glass transition temperature of the resin quickly increased, causing the rapid loss of the residual acrylate double bonds (Yang, 2005).

6. Conclusion

This study investigated the curing mechanism of visible light polymerization for fabricating FRPCs. Degree of conversion of acrylate bonds obtained from FTIR spectra was used as a measure of degree of cure. A blue LED (470nm) array was used as the light source providing the irradiance of 800-1000 nW/cm^2 around the central area where the resin mixture was cured. With the limit of the study, the following conclusions can be reached:

- Bisphenol A Epoxy Methacrylate based thin films achieved higher final conversion than Bisphenol A Epoxy Diacrylate at 60 seconds.
- 3% photoinitiator concentration resulted in higher final conversion than 1% photoinitiator concentration for both Bisphenol A Epoxy Diacrylate and Bisphenol A Epoxy Methacrylate formulations.
- Based on the above findings, M3 formulation (Epoxy Bisphenol A Methacrylate with 3% photoinitiator) achieved the highest conversion, followed by M1, D3, and D1. Taking economic factors into consideration, as well as the comparable results, M1 (Epoxy Bisphenol A Methacrylate with 1% photoinitiator) is the preferred formulation for fabricating FRPCs.
- Film-C achieved higher conversion than M160 at 60 seconds, which proved that 0.5-inch-thick composites based on M1 formulation was fully cured under current curing protocol.

Acknowledgement

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Impact Properties of Visible Light Cured Fiberglass-Reinforced Composites

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Abstract

Visible light cured fiber-reinforced polymer composites were made in three different thicknesses – 0.5-inch-thick for ballistic panels; 1/4-inch and 1/8-inch-thick for storm panels. The ballistic panels and the commercial panels (control panels) were compared in low velocity drop impact test and high velocity impact ballistic test (using Underwriters Laboratory (UL)752 Bullet Resistant Testing Standard Level 3. The Storm panels were tested in low velocity impact test using a devised ASTM E 1996 standard. The results have shown that the visible light cured ballistic panels demonstrated 73% critical impact energy of control panel in low velocity impact test, while in ballistic test, both panels passed the UL Level 3 Standard. The storm panels in a similar low impact test also showed positive impact resistance.

1. Introduction

In the last few decades, the use of composite materials in structural applications has become increasingly popular for their excellent weight/strength and weight/stiffness properties. The advantage of composite materials is that they can have the best qualities of the original materials and some qualities that neither element possesses (Safri et. al., 2014). Fiber-reinforced composites (FRCs) have long been considered as advanced materials for many applications, especially as a structural material in military vehicles where a high strength and low weight is preferred. Lower weight requires lower energy consumption and reduces wear and tear which could potentially extend a vehicle's' service life. On a broader scale, high impact resistant panels can not only be utilized in military force protection and to protect government buildings for homeland security, but also can improve earthquake, hurricane and tornado resistance in residential and commercial construction.

FRCs are usually made of woven fiberglass and a polymer matrix system, traditionally manufactured by thermal curing. Traditional thermal curing systems require a substantial amount of energy and time for controlled heating and cooling ramps during manufacturing cycles, along with inevitable Volatile Organic Compounds (VOCs) emission due to the solvents used in the resin formulation. However, the radiation curing process significantly minimizes these problems. Radiation curing process uses radiation energy, for example visible light, to activate polymerization. Visible light activated free radical polymerization takes place at ambient temperature using nearly 100% solid formulation, thus no excess energy and curing time is required for heating and cooling and little to no VOCs are emitted.

In FRC materials, E-glass fibers and various carbon fibers are the two most common fibers for structural applications, where E-glass fiber is the heaviest reinforcing fiber and is the most widely used due to its low cost and good mechanical properties. Normally the strength and stiffness of the composites is provided by the fiber, while the rigidity and environmental resistance of the composite is provided by the resin matrix.

Impact resistance is affected by a combination of factors including projectile (shape, size, hardness), the panel (type of fiber and polymer), and the impact loading condition (such as impact velocity) (Safri et. al., 2014). Impact loading can be categorized in three groups: low velocity impact, high/ballistic impact, and hyper velocity impact (Siva Kumar & Balakrishna 1998). As the velocity of the projectile varies, there are changes in energy transfer between the projectile and the target, energy dissipation, and damage mechanism (Naik & Shrirao 2004). Low velocity impact could be a large falling mass; the high velocity impact can be a projectile from a weapon; the hyper velocity impact are jets from shape-charge warheads or space debris travelling at several kilometers per second.

In this study, the impact behavior of two types of visible light cured FRCs was investigated. The ballistic panels were made 0.5 - inch - thick, and were compared with traditional thermal cured FRCs in both low and high velocity impact tests. The effect of curing time and oligomer type on impact resistance of the cured composites were also studied. The storm panels were made with a thickness of 1/4 and 1/8 inch, and were subjected to low velocity tests derived from ASTM E 1996 - Standard Specification for Performance of Exterior Windows, Curtain Walls, Doors, and Impact Protective Systems Impacted by Windborne Debris in Hurricanes.

2. Materials and Method

2.1 Preparation of Specimens

2.1.1 Formulations and Fabrication Procedure

The composite panels were made of E-fiberglass and Bisphenol-A epoxy acrylate based visible light curable resin systems. The formulations can be seen in Table 1.

	Epoxy Diacrylate Based Resin Formulation	**Epoxy Methacrylate Based Resin Formulation**
Oligomer	Bisphenol A Epoxy Diacrylate diluted with Tripropylene Glycol Diacrylate (TPGDA)	Bisphenol A Epoxy Methacrylate diluted with Tripropylene Glycol Diacrylate (TPGDA)
Monomer	Isobornyl Acrylate (IBOA)	Isobornyl Acrylate (IBOA)
Photoinitiator	Camphorquinone (CQ)	Camphorquinone (CQ)
Co-photoinitiator	Dimethylaminoethyl Methacrylate (DMAEMA)	Dimethylaminoethyl Methacrylate (DMAEMA)

Table 1. Visible Light Curable Resin Formulation Components

The FRC panels were fabricated using a hand lay-up process. Each panel consisted of 22 plies of fiberglass for ballistic panels; 6 and 11 plies for storm panels.

The unpolymerized assemblies were put into a transparent plastic bag and placed into a Plexiglas mold (Figure 1, Figure 2), which was then taken to Wabash MPI electric compression press. Spacers were used between the Plexiglas mold and the electric press platens. The Wabash press exerted a loading of 3 tons, pressing to stops for the desired thickness. After the platen contacted the shims, the bolts were tightened to maintain pressure; the press load was then released. The panels were then cured using a customized LED array on each side for certain time. Each panel was cut into 7.5” x 7.5” square specimens for impact testing.

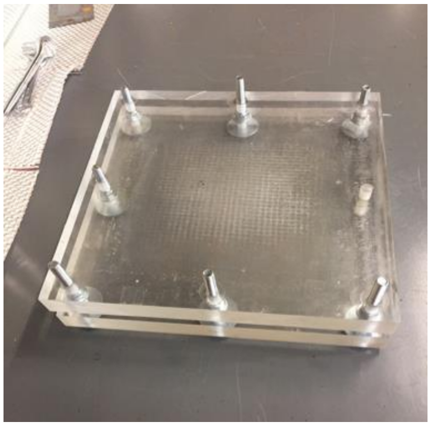

Figure 1. Plexiglas Mold Shown with Bolts in Place

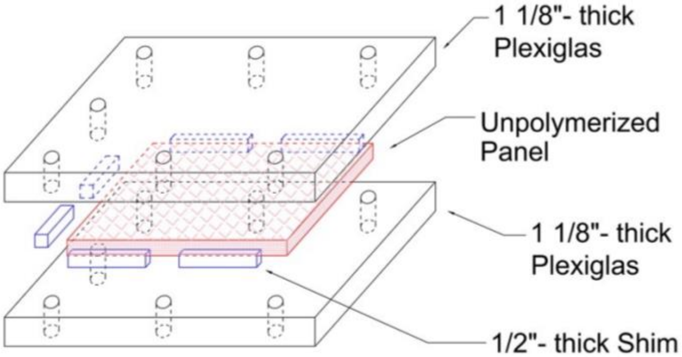

Figure 2. Schematic Illustration of a Unpolymerized Panel Inside the Plexiglas Mold

2.1.2 Resin Loading

Resin loading was defined as the percentage of resin in the panel by weight. It was calculated using the following formula:

$\text{Resin Loading} = (\text{Weight}_{\text{Panel}} - \text{AD}_{\text{Fiber}} * A * n)/\text{Weight}_{\text{Panel}} \times 100\%$

Where
$\text{Weight}_{\text{Panel}}$ = the weight of the sample panel.
AD_{Fiber} = the area density of fiberglass sheet (24 oz/ yard^2).
A = the area of the panels = width * length
The width and length of the panels were measured after trimming using an electronic caliper.
n = the number of layers of fiberglass

The resin loading was determined after the panels were made. Therefore, some variance was inevitable. The factors that affect resin loading include the amount of resin applied to the fiberglass during hand lay-up process, and the viscosity of resin.

2.2 Low Velocity Impact Test

A drop impact (low velocity impact) tester was designed to simulate a speeding bullet by dropping a weight of 250 lb from a preselected height onto the specimen (Figure 3). The preselected height was calculated based on Formula (1). The projectile (Figure 4, A) was made from a 7/16” x 3” non-deforming hard steel bolt, fixed in a grade 8 bolt, attached to the bottom of the weight. The impact tester lifted and dropped the weight through electromagnetic control.

$$\text{Test Energy (Ft lb)} = \text{Falling Weight (250 lb)} \times \text{Preselected Height (ft)} \quad (1)$$

Where Falling Weight = 250 lb

The panel was clamped horizontally in a wooden holding frame by nuts and bolts on four sides as shown in Figure 3. A new aluminum holding frame was later fabricated in replacement with the wooded one, after the wooden frame showed signs of damage. The fixture held the panels in a manner such that the panel edges were constrained from slipping out of the frame. The clamped area was 1.5 inch from all the sides. The total exposed area was 6” x 6”.

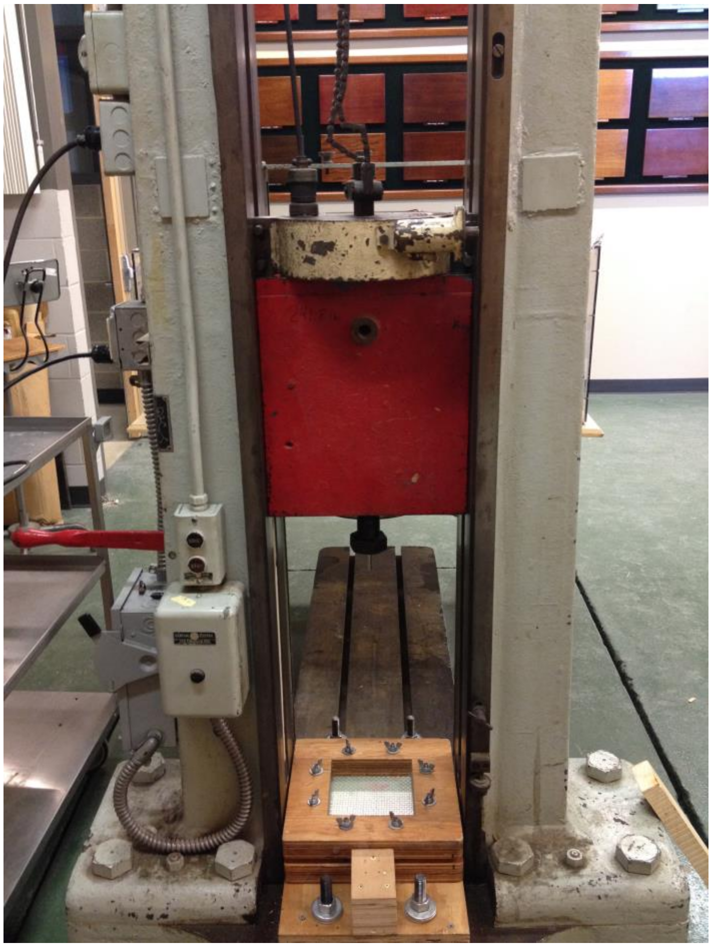

Figure 3. Low Velocity Impact Tester with Wooden Holding Frame

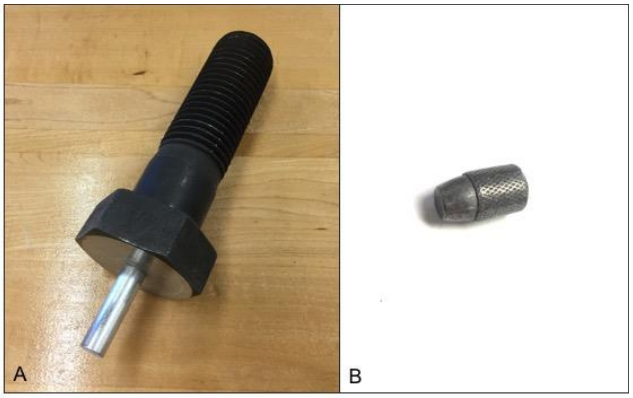

Figure 4 (A, B). Low Velocity Impact Test Projectile for Ballistic Panels (A) and Semi-Wadcutter Bullet for Shooting Test (B)

Fail	The projectile penetrates the panel.
Pass	The projectile stops before reaching the bottom layer.

Table 2. Pass/Fail Criteria for Drop Impact Test

2.2.1 Visible light Cured Ballistic Panels and Control Panels

The visible light cured ballistic panels (Figure 5, A) were made with resin loading ranging from 25% - 30% and a thickness of 0.5 inch (Table 3). The control panels (Figure 5, B) were made with woven roving fiberglass cloth impregnated with a thermoset polyester resin through a thermal curing process. They are commercially available and were donated by the manufacturer, Armortex (Schertz, TX). The specifications of the control panels are shown in Table 3.

	Control Panel	**Visible Light Cured Ballistic Panel**
Area Density of Fiber	24 oz per square yard	24 oz per square yard
Resin Loading	30%	25 - 30%
Panel Thickness	0.5 inch	0.5 inch

Table 3. Specifications of Control Panels and Visible Light Cured Panels

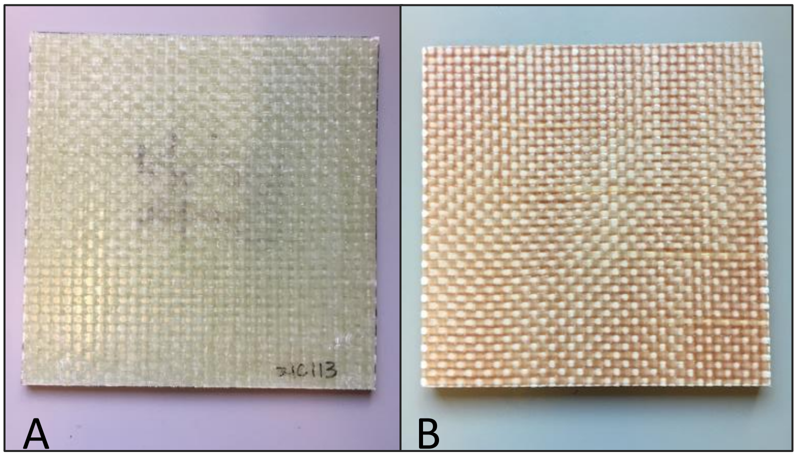

Figure 5. Visible Light Cured Panel (A) and Control Panel (B)

Impact energy is the dominant cause of penetration in impacted structures. When a projectile strikes the targeted area, it is the impact energy of the projectile that causes the target to deform or for the projectile to penetrate the panel. Therefore, it is important to study the critical impact energy required to cause penetration. A low velocity impact test procedure was developed to determine the minimum required impact energy to cause penetration of the specimen. The impact tests were started with an impact energy of 700 ft lb. The procedures are shown in Figure 6.

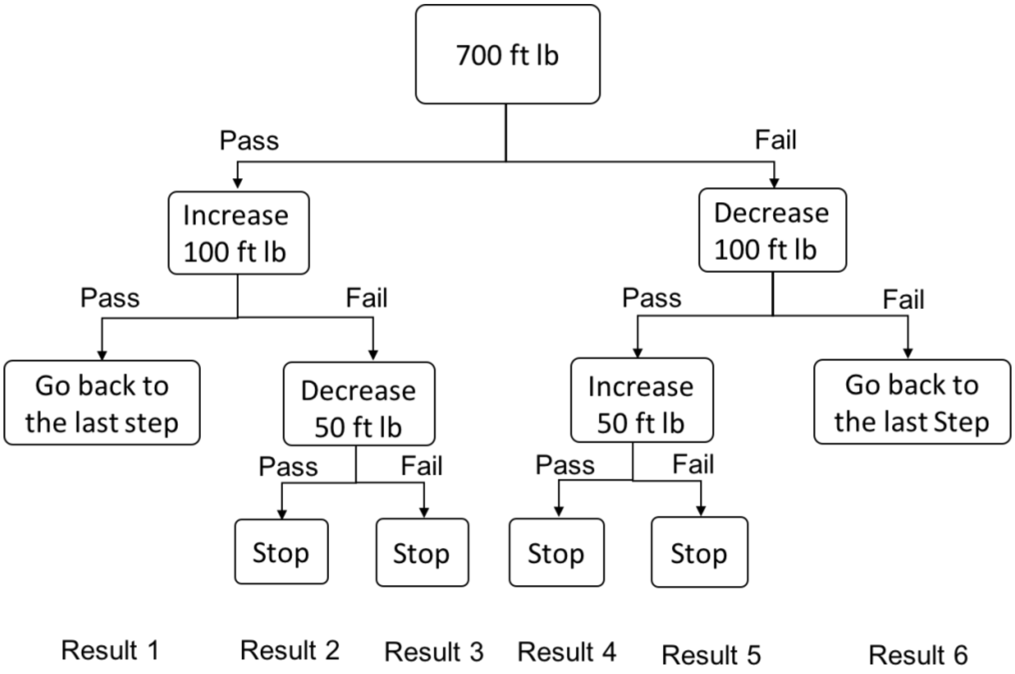

Figure 6. Impact Test Procedures to Determine Critical Impact Energy

According to Figure 6, there can be 6 possible results. For each impact test, a new specimen was used which required a large number of panels.

Result 1:

Step 1.

If the specimen passes at 700 ft lb, and passes n times after increasing 100 ft lb until it fails at {700 + (n +1) x 100} ft lb, decrease 50 ft lb of impact energy.

Step 2.

If the specimen passes {700 + (n+1) x 100 -50} ft lb, the critical impact energy is (750 + 100n) ft lb;

Or if the specimen fails {700 + (n+1) x 100 -50} ft lb, the critical impact energy is (700+100n) ft lb.

Result 2:

If the specimen passes at 700 ft lb, fails at 800 ft lb, and passes at 750 ft lb, the critical impact energy is 750 ft lb.

Result 3:

If the specimen passes at 700 ft lb, fails at 800 ft lb, and fails at 750 ft lb, the critical impact energy is 700 ft lb.

Result 4:

If the specimen fails at 700 ft lb, passes at 600 ft lb, and passes again at 650 ft lb, the critical test energy is 650 ft lb.

Result 5:

If the specimen fails at 700 ft lb, passes at 600 ft lb, and fails at 650 ft lb, the critical test energy is 600 ft lb.

Result 6:

Step 1.

If the specimen fails at 700 ft lb, and fails m times after decreasing 100 ft lb each time until it passes {700 - (m+1) x 100} ft lb, increase 50 ft lb of impact energy.

Step 2.

If the specimen passes at {700 - (m+1) x100 + 50} ft lb, the critical test energy is {650 - 100m} ft lb;

Or if the specimen fails at {700 - (m+1) x100 + 50} ft lb, the critical test energy is {600 - 100m} ft lb.

For the visible light cured panels impact test, the critical impact energy of control panels was used as the starting impact energy. The similar test process was followed.

2.2.2 Comparison of Curing Time and Oligomer

Ballistic panel samples for the comparison of curing time and oligomer were made with resin loading ranging from 10-15% and a thickness of 0.5 inch. Both epoxy diacrylate and epoxy methacrylate panels were cured 10 minutes on each side and 15 minutes on each side. The test steps were based on Figure 6 with impact energy ranging from 550 ft lb to 600 ft lb. The specifications of visible light cured panel samples are shown in Table 4.

Oligomer	**Curing Time (Minutes)**
Epoxy Diacrylate	10+10
	15+15
Epoxy Methacrylate	10+10
	15+15

Table 4. Ballistic Panel Samples for Impact Test for Comparison of Curing time and Oligomers

2.2.3 Storm Panels

Storm panels are designed to be used as reinforcing sheathing of walls and doors for the protection of buildings. The reinforcement adds extra impact protection to the original wall structures from windborne flying objects and debris that result from a hurricane or tornado.

Enhanced Hurricane Protection Areas (EHPA) criteria (Floridadisaster, 2012), also known as the public shelter design criteria, was developed by Florida State legislation to regulate new educational facilities to be used as public hurricane evacuation shelters. The 1/8 -inch-thick storm panels were tested using low velocity impact test level 1 (Table 6) which were devised from ASTM E 1996 Level D (ASTM E1996-14a) (Table 5). Level D is the minimum code requirement for EHPA criteria and specifies that 9 lb 2 by 4 sawn lumbers to be propelled at 34 mph with an impact energy of 349 ft lb.

The 1/4-inch- thick storm panels were tested using low velocity impact test Level 2 (Table 6) devised from ASTM E 1996 Level E (Table 5). The Level E test specifies the same large missile as Level D propelled at 55 mph with impact energy of 894 ft lb.

Storm panel specimens were made ¼” and ⅛” - thick with resin loading in the range of 25% - 30%. The projectile used in the devised Level 1 and 2 was a 1-foot-long 2 by 4 lumber. The projectile was placed at the center of the specimen before dropping the weight. Only the aluminum holding frame was used in the impact tests for storm panels.

Standards	**Missile**	**Impact Energy**
ASTM E 1996 Level D	9 lb 2x4 propelled at 34 mph	349 ft lb
ASTM E 1996 Level E	9 lb 2x4 propelled at 55 mph	894 ft lb

Table 5. ASTM E 1996 S Level D and E Test Specifications

Panel Thickness	**Level**	**Impact Energy**
1/8"	1	349 ft lb
1/8"	2	894 ft lb
1/4"	1	349 ft lb
1/4"	2	894 ft lb

Table 6. Storm Panel Impact Test Standard

2.3 Ballistic Test

Ballistic tests were conducted based on the Underwriters Laboratory (UL) 752 Bullet Resistant Testing Standard Level 3. The Level 3 standard requires a 0.44 Magnum pistol firing lead semi-wadcutter gas checked bullet (Figure 4, B) with a weight of 240 grains, i.e. about 15.6 g, from a distance of 15 ft. The velocity of the projectile should be recorded and must be within 1350 - 1484 ft/s. The temperature is to be 72 +/- 5 F. The specifications of projectiles and panels are shown in Table 7.

Due to the relevant New York State Regulations, the ballistic testing setup (particularly the gun and the ammunition) was unable to be acquired. The ballistic tests were conducted in the ballistic testing laboratory at Armortex, Inc. (Schertz, TX).

Two visible light cured ballistic panels were made with Bisphenol A Epoxy Diacrylate and Bisphenol A Epoxy Methacrylate resins, respectively. The thickness of the panels was 0.5 inch, and the resin loadings were both around 30%.

UL 752 Level 3 Standard	
Projectile Caliber	0.44 Magnum
Cartridge Type	240 grains SWC
Velocity range	1350 to 1485 ft/s
Panel Size	12 x 12”

Table 7. Underwriters Laboratory (UL) 752 Level 3 Standard

3. Results

3.1 Sample Size

There are three types of impact tests in this study – the low velocity impact test for control panels and visible light cured ballistic panels, the ballistic test for visible light cured ballistic panels, and the low velocity impact test for visible light cured storm panels. In the first two types of tests, one specimen was used for each test condition. A small sample size was used because this study is highly exploratory. New samples were designed and fabricated after evaluating previous test results. In order to quickly find out whether a specific method worked or not and decide the next step, a small sample size was preferable to improve the efficiency of the experiment design. Secondly, the resin loading of the specimens was calculated after the specimen were made. It was not practical to replicate specimens with the exact resin loadings. Third, the test result was either pass or fail, rather than quantitative measures, which is subject to a higher risk of errors and inaccuracy. In the third type of test for storm panels, two replica specimens were made. This is because two ¼”-thick panels or four 1/8”-thick panels can be made at one cure. This approach allowed almost the same resin loading for the two ¼”-thick panels or four 1/8”-thick panels.

3.2 Visible Light Cured Ballistic Panels and Control Panels

As can be seen in Table 8, the control panels (commercial panels) failed at 700 ft lb and 600 ft lb, but passed at 500 ft lb and 550 ft lb. The critical impact energy for control panel is 550 ft lb. The impact tests on visible light cured panels started with 500 ft lb. The test failed at 500 ft lb, passed at 400 ft lb, but failed at 450 ft lb (Table 9). Therefore, the critical impact energy for visible light cured panel is 400 ft lb.

Samples	**Impact Energy**	**Result**	**Sample Size**
Control 1	700	Fail	1
Control 2	600	Fail	1
Control 3	500	Pass	1
Control 4	550	Pass	1

Table 8. Impact Test Results for Control Panels (Tested with Aluminum Holder)

Samples	**Impact Energy**	**Result**	**Sample Size**
Light Cured Panel 1	550	Fail	1
Light Cured Panel 2	500	Fail	1
Light Cured Panel 3	400	Pass	1
Light Cured Panel 4	450	Fail	1

Table 9. Impact Test Results for Visible Light Cured Panels (Tested with Aluminum Holder)

3.3 The Effect of Curing Time and Oligomer

Curing time is one of the factors that affects degree of polymerization, which subsequently influences the adhesion between resin matrix and fibers. The 10+10 minutes cured epoxy diacrylate panels failed at 550 ft lb impact test, while the 15+15 minutes cured epoxy diacrylate panels showed slightly better impact resistance, as the fiber on the bottom layer just shown signs of breakage with no penetration observed. For epoxy methacrylate panels, different curing times did not make a difference within the impact energy range of 500 ft lb to 600 ft lb.

Oligomer	Impact Energy (Ft lb)	Test Result	Curing Time (Minute)	Sample Size
Epoxy Diacrylate	550	Fail	10+10	1
	550	Pass/Fail	15+15	1
Epoxy Methacrylate	600	Pass	10+10	1
	600	Pass	15+15	1

Table 10. Low Velocity Impact Test Results for Comparing the Effect of Curing Time (Tested with Aluminum Holder)

When comparing oligomers, Table 11 shows Epoxy Methacrylate panels provided better impact resistance than Epoxy Diacrylate panels when both cured for 10 minutes on each side and 15 minutes on each side. In addition, the Epoxy Methacrylate panels showed severe delamination when cured for 15 + 15 minutes, while Epoxy Diacrylate panels exhibited slight delamination (Figure 7). When curing time was 10 + 10 minutes, Epoxy Methacrylate showed more delamination than Epoxy Diacrylate as well.

Curing Time (Minute)	Impact Energy (Ft lb)	Test Result	Oligomer	Sample Size
10 +10	550	Fail	Epoxy Diacrylate	1
	550	Pass	**Epoxy Methacrylate**	1
15 +15	600	Fail	Epoxy Diacrylate	1
	600	Pass	**Epoxy Methacrylate**	1

Table 11. Low Velocity Impact Test Results for Comparing the Effect of Oligomers (Tested with Aluminum Holder)

Figure 7. Epoxy Diacrylate panel and Epoxy Methacrylate Panel Showing Different Delamination after Impact Test (600 ft lb) When Cure Time was 15 + 15 Minutes

3.4 Storm Panels

As shown in Table 12, the 1/8 -inch-thick storm panels passed Level 1 test that specifies the same impact energy (349 ft lb) as ASTM E1996 Level D. Level D represents the standard for providing basic protection from ground-level debris and structural debris in wind zone 3 and 4 (Table 13).

The 1/4-inch- thick storm panels passed Level 2 test that specifies the same impact energy (894 ft lb) as ASTM E1996 Level E. Level E represents the standard for providing enhanced protection from ground-level debris and structural debris in wind zone 3 and 4 (Table 13).

Panel Thickness	Level	Impact Energy	Results	Sample Size
1/8"	1	349 ft lb	Pass	1
1/8"	2	894 ft lb	Fail	1
1/4"	1	349 ft lb	Pass	1
1/4"	2	894 ft lb	Pass	1

Table 12. Impact Test Results for Storm Panels

Wind Zone	Wind Speed (mph)	Impact
3	130 ~ 140	349 ft lb
4	> = 140	894 ft lb

Table 13. Wind Zone Specifications (ASTM E1996)

3.5 Ballistic Test

The Epoxy Diacrylate panels failed the UL 752 Level 3 Ballistic standard test. All three shots within the velocity range penetrated the panel with spalling. However, the Epoxy Methacrylate panel passed the UL 752 Level 3 Ballistic standard test.

4. Discussion

4.1 Ballistic Panels

Impact properties represent the capacity of a material to absorb and dissipate energy under low or high velocity impact. When the projectile hits the panel, the fibers under the projectile start to fail. As the impact proceeds through the laminate, stress is exerted on the fibers in the surrounding area, causing deformation. The fibers at the impact point are pushed forwards by the projectile, which eventually exits from the panel if the bottom layer is broken. The projectile stopes if all the kinetic energy is absorbed. Delamination or cracks usually occur during the impact event and play the major role in absorbing impact energy.

Due to the unavailability of ballistic testing setup and a 72 +/- 5 °F temperature required in the Underwriters Laboratory (UL) 752 ballistic testing Level 3 standard, a low velocity impact tester was designed and used to simulate the force of a bullet. The low velocity impact test results have shown that the control panels provided better impact resistance than the visible light cured panels. This was not unexpected because the light cured panels are based on a basic Bisphenol A Epoxy Methacrylate resin system, one of the most commonly used UV curing oligomers. The oligomer was selected to test panel fabrication and testing methods for this feasibility study, rather than to optimize impact performance, whereas the commercially available control panels on the market have undergone complete product life cycle and performance optimization. Thus, they exhibited excellent impact resistance. The control panels were made of woven roving fiberglass cloth impregnated with a thermoset polyester resin compressed into flat rigid sheets using pressure and heat curing process.

4.1.1 Oligomers

To further improve the impact resistance of visible light cured panels, other oligomer and monomer options should be investigated. Oligomers form the backbone of the polymer network and govern some basic physical and mechanical properties. Acrylate-based resins have become standard in energy curing formulations, mainly because of their high reactivity and toughness. Epoxy acrylates are most widely used, particularly in inks, varnishes, and adhesives. Monomers are used to reduce viscosity of the mixture to a certain level for ease of application and facilitating the materials to be drawn around the fibers. The functionality of monomers can impact cure speed and crosslinking. In general, viscosity, cure speed, and crosslink density increase with monomer functionality, while adhesion and flexibility decrease with monomer functionality. It is highly possible that better impact properties can be achieved by experimenting with more options of oligomers and monomers, especially with customized resin by industrial raw materials manufacturers.

In this paper, two types of oligomers - Bisphenol A Epoxy Diacrylate and Bisphenol A Epoxy Methacrylate were compared using a low velocity impact tester. The epoxy methacrylate panels exhibited better impact resistance with more delamination than epoxy diacrylate panels, which demonstrated that epoxy diacrylate based formula has better adhesion to the fiberglass than epoxy methacrylate based resin. This is due to the fiber-matrix interaction was playing a key role in influencing impact energy. At high level of adhesion, the failure mode is brittle and relatively little energy is absorbed by fiber failure, and at low levels of adhesion, multiple delamination may occur to absorb higher impact energy (Schwartz, 1997). Therefore, lower adhesion is preferred to promote progressive delamination, which in turn produces high impact energy absorption. In addition to altering resins, fiber surface treatment, customized fiber sizing, and adhesion adjusting additives are other ways to achieve the same result.

4.1.2 Curing time

Adequate curing time ensures the delivery of the amount of energy required to cure composites. Twenty minutes (10 minutes on each side) and thirty minutes (15 minutes on each side) of curing time were used to demonstrate how time affects impact performance. It was found that for Epoxy Diacrylate panels, thirty minutes curing time has shown slightly better impact resistance than twenty minutes. Epoxy Methacrylate panels shown the same test results within the range of 500 to 600 ft lb. It was found that in this study curing time was not a significant factor affecting impact properties. This was probably due to the mechanism of the free radical photopolymerization which takes place extremely rapidly in a fraction of second. Studies (Kunwong, et al. 2011; Schneider, et al. 2008) have shown the rate of polymerization increased very fast during the first 5 seconds and then decreased. The rate of conversion of acrylate bonds almost became constant after 10 seconds. Twenty and thirty minutes curing time was adequate for curing 0.5-inch-thick composite panels.

4.1.3 Ballistic Test

The high velocity ballistic tests have a range of velocity from 50 m/s to 1000 m/s (Safri et al., 2014). The UL 752 Level 3 Standard (Underwriters' Laboratories, 2005) specifies the velocity of the projectile within the range from 411 m/s to 453 m/s (1350 ft/s to 1485 ft/s). It is said that ballistic impact tests often resulted in different failure modes as compared to low velocity impact tests. Lee et al. (1993) found that in ballistic impact, the damage is localized and clearly visible by external inspection, while a low velocity impact involves long contact time between the projectile and target, which produces global structure deformation. Similar observations were found in this study.

Another finding is that there is no direct correlation between the low velocity drop impact test results and ballistic tests results due to the following reasons. First, the sizes of specimen are different. For low velocity impact test, 7.5” x 7.5” specimens were used, while 12” x 12” samples were used for ballistic tests. Secondly, the lead-tipped bullets in ballistic tests absorbed part of impact energy when they become deformed upon hitting the specimen, and extra impact energy was required for the widened tip to push through the specimen. However, given such differences, one might be able to establish a correlation between the two sets of tests or use one to predict the other if controlled resin loading of specimens can be obtained with a large enough statistical test data.

4.2 Storm panels

Storm panels are designed to be used as reinforcing sheathing for walls and doors for the protection of buildings. The reinforcement adds extra impact protection to the original wall structure from windborne flying objects and debris that result from hurricanes or tornados. The 1/4-inch and 1/8- inch - thick storm panels passed impact test Level 1 and 2 with the same impact energy of 349 ft lb and 894 ft lb required in Level D and E of ASTM E 1996, respectively. These preliminary impact tests have shown promising results, as in ASTM E 1996, the specimen size is 2.5 times larger than that in this study, which will allow better energy dissipation. In addition, when testing the actual reinforced wall panels, the crushing failure of the original structure will absorb a large amount of impact energy upon impact of the projectile, leaving less energy exerted on the storm panels.

4.3 Limitations of the Study

4.3.1 Resin Loading

In this project, when fabricating the panels, the resin loading of specimens can only be estimated rather than predetermined due to the nature of the hand lay-up process and curing procedure. The actual resin loading was calculated after the specimen was fabricated and trimmed. It has been observed that different resin loading exhibited apparent different impact test results in low velocity impact tests for both Epoxy Diacrylate and Epoxy Methacrylate panels. One of the examples is shown in Table 14. With this limitation, only the specimens with resin loading within 5% difference were used in one type of test. For each test, the resin loading of specimens were clearly stated. In other words, the test results of specimens with a different range of resin loading should not be compared to draw conclusions.

Samples	Impact Energy	Result	Resin Loading
Epoxy Methacrylate Panels	500	P	12.19%
	450	F	27.13%
Epoxy Diacrylate Panels	500	P	11.92%
	500	F	27.86%

Table 14. Visible Light Cured Panels with Different Resin Loadings Showing Different Impact Test Results (Tested with Aluminum Holder)

4.3.2 Test Fixture (Specimen Holder) in Low Velocity Impact Test

Two types of specimen holders were used throughout the study. After the wooden holding frame showed signs of damage, it was replaced with a new aluminum holder. The effect of the aluminum holder was unexpected and significant. By allowing the specimen to flex, the wooded holder absorbed part of the impact energy, causing less energy impacting on the specimen, while the rigid aluminum stopped the flexing, resulting in more energy impacting on the specimen and causing damage. In this study, the test data have been carefully organized so that only the results under the same test condition were analyzed.

5. Conclusions

In this study, the impact resistance of visible light cured panels (1/2-inch-thick) were characterized and compared with commercial ballistic panels. The visible light cured ballistic panels demonstrated an energy of 73% of critical impact energy of the control ballistic panels in a low velocity impact test. However, they achieved comparable ballistic resistance as control panels, as they both passed UL 752 Level 3 Ballistic Standard.

A preliminary low velocity impact test on visible light cured storm panels (1/4- and 1/8-inch-thick) was carried out, and have shown positive results. As the storm panels were designed to be attached or mounted to an original structure as reinforcement, an actual reinforced structure should be constructed and tested with ASTM E 1996 standard in future study.

With comparable impact strength of visible light cured panels presented in this study, visible light curing of composites has shown great potential and can be a big driving force in composite material development and manufacturing, considering the significant economic and environmental benefits compared to thermal curing of composite materials.

Acknowledgement

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CHAPTER 5 RESULTS AND DISCUSSION

5.1 Visible Light Curing Unit

5.1.1 The Construction and Optical Characteristics of the LED Array

The LED array consisted of 28 LED assemblies. The LEDs produce a large amount of heat, so they were mounted on an aluminum heat sink through which cooling water was circulated. This allowed the LED array to operate for a prolonged time while maintaining the junction temperature (the highest operating temperature of LEDs) below the recommended value (135C).

The second heating problem occurred during the measurement of the irradiance of the LED array. Heat was given off when light was absorbed by the radiometer, causing the reading of radiometer drop slightly. To maintain a less than 1% error on the irradiance measurement, a cooling fan was used on the side of the LED array to provide forced convection of airflow to accelerate heat transfer. The array was turned off for cooling for 10 minutes after each 5 minutes' operation.

Irradiance distribution of the LED array was measured at three positions (Figure 3, Manuscript 1). The measurement at position 1 (on top of the LED array) provided a basic understanding of the overall intensity based on the packing density and the array configuration of LEDs. As expected, the overall intensity was the highest and the least uniform. Moving 1 1/8" away from the array, the irradiance at position 2 was much more uniform than that at position 1. The average intensity across the array reduced about 20% and the highest intensity decreased about 30% (Table 2, Manuscript 1). The comparison of position 2 and position 3 (through 1 1/8-

inch-thick Plexiglas) indicated the optical effect of the Plexiglas. Illumination from the LED array passed through a 1 1/8-inch-thick block of Plexiglas further enhanced the overall intensity and uniformity compared with no Plexiglas, as shown in Figure 4, 5, and 6 in Manuscript 1.

5.2 Visible Light Curable Resin System

5.2.1 Formulations

The light-curable formulation consists of three essential ingredients: oligomers, monomers, and photoinitiators. Oligomers impart the basic properties of the cured materials and are usually high in viscosity. Monomers are used as diluent reactants to reduce viscosity of the resin system. The functionality of monomers impacts cure speed and crosslinking. In general, diluting monomers improve cross-linking, reactivity, mechanical and chemical resistance, and cause more shrinkage with increasing functionality of the diluting acrylate, while flexibility and adhesion decrease. Photoinitiator absorbs photons and directly or indirectly produces reactive species that initiates polymerization. In CQ/amine system, the carbonyl group in CQ absorbs light and am promoted to an activated triplet state. The CQ triplets react with amine molecules to produce aminoalkyl radicals that initiate polymerization (Stansbury, 2000).

Epoxy acrylates are the most widely used oligomers for their high reactivity and producing hard and chemically resistant films (Drobny, 2010). In this study, Bisphenol A Epoxy Diacrylate and Bisphenol A Epoxy Methacrylate were used and compared with respect to the degree of cure. It was found that during the first 5 seconds the degree of conversion increased rapidly (Figure 4, Manuscript 2). During the next 5 to 10 seconds, the conversion kept increasing but at a slower rate. After 10 seconds, the conversion of D3 and M1 formulations remained at plateaus, and the D1 and M3 formulation increased extremely slowly. At 60 seconds, the conversion rate of Bisphenol A Epoxy Methacrylate formulation achieved a higher degree of cure than Bisphenol A Epoxy Diacrylate.

The concentration of photoinitiator was studied by comparison 1% and 3% concentrations. The results showed that for both oligomers, 3% photoinitiator resulted in a higher degree of cure after 60 seconds than 1% photoinitiator. Among four formulations, M1 (Bisphenol A Epoxy Diacrylate with 1% photoinitiator) formulation had the greatest conversion rate in the first 5 seconds; and M3 (Bisphenol A Epoxy Methacrylate with 3% photoinitiator) formulation had the highest degree of cure at 60 seconds.

To choose the optimal formulation for FRPCs manufacture, other factors, such as cost of raw materials and fiber-polymer interaction, must be considered as well. For economic considerations, a lower concentration of CQ is preferred for FRPC manufacture because CQ is the single most expensive component in the formulation.

5.2.2 Film-C

Based on a cost/benefit analysis, M1 (epoxy methacrylate resin with 1% photoinitiator) was selected to be the preferred formulation to make FRPCs. The final 88% of conversion of Film-C based on M1 formulation cured in the middle of a 22-layer PRPC indicated that the 0.5-inch-thick FRPC was fully cured. The criteria for “fully cured” in this experiment is whether the Film-C cured in the middle of the panel exceeded the maximum conversion of a thin film cured at 60 seconds. This is because as light passes through the FRPC, it is absorbed and scattered, attenuating the intensity and reducing the effectiveness of the light for inducing photopolymerization. The middle layer(s) of the 22-layer FRPC received the least intense radiation but achieved higher degree of conversion than that of film M160 (71%). This result demonstrated the ability of the blue LED array to cure though a 0.5-inch-thick 22-layer FRPC panel.

The conversion for M1 formulation had increased from about 71% to 88% from 1 minute to 30 minutes at an extremely low conversion rate compared to the first 1 minute when the conversion already reached 71%. It is safe to say that thirty minutes of curing time is more than adequate to cure through a 0.5-inch-thick composite, and it is known that even for prolonged curing times, the degree of conversion will not reach 100%. This is because as the polymerization and crosslinking reaction took place rapidly, the glass transition temperature of the resin quickly increased, causing the rapid loss of the mobility of the residual acrylate double bonds (Yang, 2005).

5.3 Impact Properties of Fiberglass-Reinforced Composites

The impact properties of a material represent its capacity to absorb and dissipate energy under impact or shock loading (Schwartz, 1997). Impact loading can be categorized in three groups: low velocity impact, high/ballistic impact, and hyper velocity impact (Siva Kumar & Balakrishna 1998). Low velocity impact could be a large falling mass; the high velocity impact can be a projectile from a weapon; the hyper velocity impact are jets from shape-charge warheads or space debris travelling at several kilometers per second, and will not be discussed in this study. When the projectile hits the panel, the fibers under the projectile start to fail. As the impact energy proceeds, stress is exerted on the fibers in the surrounding area, causing deformation. The fibers at the impact point are pushed forwards by the projectile, which eventually exit from the panel if the bottom layer is broken. The projectile stops if all the kinetic energy is absorbed.

The ballistic impact response of FRPCs is complicated. Other than the physical properties of the projectile (shape, size, hardness) and impact loading, it also depends on the mechanical characteristics of the fiber, resin system, and fiber/resin interaction.

E-glass fiber is known for relatively high strain to failure and inexpensive cost, and is the most widely used fiberglass in the composite industry. Glass fibers come in strands (collections of continuous fiber filaments), chopped strands, or in woven form, such as woven roving. Woven roving is a course drapable fabric in which continuous roving are woven in two mutually perpendicular directions (Mallick 2007), used in most cases to increase flexural and impact strength. In this study, E-glass woven roving was used to manufacture FRPCs, the same with the commercial panels.

Fiber-matrix interfacial shear strength is influenced by fiber sizing and resin system (matrix). The adhesion of the resin system plays a significant role in energy dissipation and failure mode. Studies (Yeung & Broutman,1978; Bader et al., 1973) have shown that, at high levels of adhesion, the failure mode is brittle and relatively little energy is absorbed, while at very low levels of adhesion, multiple delamination may occur without significant fiber failure. High impact energy absorption is produced at intermediate levels of adhesion when the failure mode is a combination of fiber failure and delamination.

5.3.1 The Evaluation of Visible Light Cured Ballistic Panels (0.5”- Thick)

This study used a low velocity impact test to investigate the impact resistance of visible light cured composites compared with control panels. Each test/strike requires a new panel; therefore, a large number of panels were made and tested to conduct the impact testing as well as to optimize the impact resistance by experimenting different curing time, number of layers and adjusting resin loading at the same time. This has resulted in a number of out-of-spec panels that may have too low resin loadings or too many layers of fiberglass, or possible inadequate cure. These panels were still tested but were not used for later data analysis. The drop impact test (with wooden frame) originally started with 1000 ft lb and proceeded by dropping 100 ft lb or increasing 50 ft lb at a time depending on the test result. Eventually the control (commercial) panels passed 750 ft lb (critical impact energy) and the visible light cured panels (Epoxy Diacrylate with 1% PI based formulation) passed 700 ft lb (critical impact energy). A couple of out-of-spec panels with low resin loadings even passed 800 ft lb. After the wooden holding frame showed signs of damage and replaced with an aluminum holding frame, a different set of critical energies were observed – 550 ft lb for the control panels and 400 ft lb for the visible light cured panels (Epoxy Methacrylate with 1% PI based formulation). Repetitive testing was conducted on both the control panels and light cured panels to verify the changed results. It was finally confirmed and understood that the aluminum frame stopped the flexing of the panels which was previously allowed by the wooden frame that subsequently absorbed part of the impact energy.

Another observation was the Epoxy Methacrylate panels significantly outperformed Epoxy Diacrylate panels and showed more delamination (Figure 7, Manuscript 3). Twenty-minute or thirty-minute curing time did not make a distinct difference in impact resistance. Therefore, the Epoxy Methacrylate formulation was then selected to fabricate FRPC panels that were compared with the control panels, with a curing time of thirty minutes.

In short, in the low velocity impact test, the control panels exhibited better impact resistance having a critical impact energy of 550 ft lb than visible light cured FRPCs (Epoxy Methacrylate) with a critical impact energy of 400 ft lb. However, in the shooting test, both control panels and the visible light cured FRPCs passed the Underwriters Laboratory (UL) 752

Bullet Resistant Testing Standard Level 3. The difference in the two test results was a result of different impact loadings and test conditions. Naik and Shrirao (2004) found that as the velocity of the projectile varies, there are changes in energy transfer between the projectile and the target, energy dissipation, and damage mechanism.

5.3.2 The Evaluation of Visible Light Cured Storm Panels (1/4”-Thick and 1/8” - Thick)

The storm panels were fabricated using the same visible light curing procedure with a different thickness - ¼” - and ⅛” - thick. Impact resistance was evaluated in the low velocity impact test using a revised ASTM E 1996 Standard, which was designed for evaluating the performance of exterior windows, curtain walls, doors impacted by windborne debris in hurricanes. The results showed that the 1/8 -inch-thick storm panels withstood an impact energy of 349 ft lb specified in the ASTM E1996 Level D test; the 1/4-inch- thick storm panels withstood an impact energy of 894 ft lb specified in the ASTM E1996 Level E test. Level D and Level E represent the standard for providing basic and enhanced protection, respectively, from ground-level debris and structural debris in wind zone 3 and 4 where the wind speed was greater than 130 mph (ASTM E1996).

5.4 Limitations of the study

5.4.1 Resin Loading

Resin loading was calculated after the specimens were fabricated and trimmed. Impact test results were affected by resin loading in low velocity impact tests for both Epoxy Diacrylate and Epoxy Methacrylate panels. In Table 14 (Manuscript 3), 12% resin loading performed better than resin loading of 27%. With this limitation, only the specimens with resin loading within 5% difference were used in one type of test. For each test, the resin loading of specimens were clearly stated. In other words, the test results of specimens with different ranges of resin loading should not be used for comparison or drawing conclusions.

5.4.2 Test Fixture (Specimen Holder) in Low Velocity Impact Test

A wood specimen holder was used originally for the study. After repeatedly stressing the wood holder, it started to fail. It was then replaced with an aluminum holder. The aluminum holder did not flex as much as the wood holder did. Since the wood holder was able to flex, it absorbed some of the impact energy, so panels tested with the wood holder appeared to be stronger. Therefore, test data have been carefully organized so that only the results under the same test condition were analyzed.

5.5 References

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CHAPTER 6 CONCLUSIONS

6.1 Major findings

- This study demonstrated the procedure for designing a blue LED array. It was found that water cooling is essential for constant operation of multiple LEDs. When measuring irradiance at close distance, fan cooling may be required for additional airflow. Alternating cooling and operation period is helpful to minimize reading error caused by heat built up of the radiometer.
- The distribution of irradiance is more uniform as the distance increases from the array. The Plexiglas placed on the top of the array made the distribution of irradiance more uniform and enhanced the overall irradiance.
- The constructed blue LED (470nm) array was able to cure through 0.5-inch-thick 22-layer fiber-reinforced composite. The preferred formulation is Bisphenol A Epoxy Diacrylate with 1% photoinitiator. The curing time is 30 minutes with 15 minutes each side.
- Adhesion or fiber-matrix interfacial shear strength is crucial for allowing progressive delamination of the composites. Only when adhesion is at the intermediate level and the failure mode is a combination of delamination and fiber failure, a high impact energy can be produced. To manipulate the adhesion, the following should be considered: type of oligomer, adhesion inhibitor/promoter, fiber sizing.

- The visible light cured ballistic panels have shown comparable impact strength with the commercial panels, while consumed less energy and time with no VOC emission. The economic and environmental benefits are significant factors that will affect commercialization of visible light curable composites. It is evident that visible light curing of composites can be a big driving force in composites development and manufacturing.

6.2 Future Research

- In the visible light curable formulation, Camphorquinone, the photoinitiator, was the single most expensive component. To lower the cost of the formulation, other visible light photoinitiators (or combinations) can be explored.
- To further improve the impact resistance of the composites, customized fiber sizing or fiber surface treatment should be considered to adjust the adhesion of the resin system to fiber.
- Resin loading determines the density of the composites, and can also affect the adhesion to fiber by creating voids in the composites if resin loading is too low. Due to the limitation of this study, resin loading was unable to be controlled quantitatively, which has caused distinct difficulty during testing. In future studies, a more standardized procedure should be developed to assure consistent resin loading.
- Another area of research could include integrating particulates into the fiber-reinforced composites. Research have shown that the addition of particles to polymers could lead to a desirable effect on properties such as hardness, wear resistance, and compressive strength, and an improvement in creep resistance and

fracture toughness (Ahmed & Jones 1990; Schwartz 1997). Extensive study on particle loading, size, particle/matrix interfacial adhesion should be conducted because they effectively affect the mechanical properties of the composites.

6.3 References

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Graduate Teaching Assistance – Sustainable Construction Management and Wood Product Engineering, SUNY ESF (2010 - 2014)

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Publications and Conference Presentations

- **Bi**, **Y.**, Driscoll, M., Meyer, R. W., Larsen, L. S. "Stopping Speeding Bullet with Light Cured Fiberglass-Reinforced Ballistic Panels". Poster presentation at the The Composites and Advanced Materials Expo (CAMX), Anaheim, CA, Sept. 2016
- **Bi**, **Y.**, Driscoll, M., Meyer, R. W. "Design of a Blue LED Array for Curing Fiberglass-Reinforced Composites". Paper presentation at the RadTech UV+EB Expo & Conference, Rosemont, IL, May 2016
- **Bi**, **Y.**, Driscoll, M., Meyer, R. W., Larsen, L. S. "Visible Light Curing of Fiberglass-Reinforced Polymer Composites Based on Epoxy Acrylate Resins". Presentation at the RadTech UV+EB Expo & Conference, Rosemont, IL, May 2016
- **Bi**, **Y.**, Driscoll, M. Meyer, R. W., Larsen, L. S. "Mechanical Properties of Visible Light Cured Fiber-Reinforced Impact-Resistant Panels" (Under preparation).

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