Light-Activation Influence on the Thermal Analysis of a Resin-Modified Glass-Ionomer

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LIGHT-ACTIVATION INFLUENCE ON THE THERMAL ANALYSIS OF A RESIN-MODIFIED GLASS-IONOMER

by

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ABSTRACT
LIGHT-ACTIVATION INFLUENCE ON THE THERMAL ANALYSIS OF A RESIN-MODIFIED GLASS-IONOMER

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The acid-base and light polymerization reactions in resin modified glass ionomers (RMGI) have been shown to compete and possibly inhibit one another during early RMGI development. Earlier beginning times of light polymerization initiation may limit the acid-base reaction and if time allowed for the acid-base components to react is increased, the extent of light cure reaction may be lesser. The thermal behavior of a commercially available RMGI was investigated in relation to a light initiation regimen using a differential scanning calorimeter (DSC). The relationship between delay in light initiation or no light initiation and the resultant set matrix of the material was determined by subjecting the material to a dynamic temperature scan between 37^{o}C and 300^{o}C at 10^{o}C/min. Different cure groups (n=10 per cure group for an immediate light cure group, 5 min and 10 min delay light cure groups, and a dark cure group) were stored for specific periods of time (30 min, 1 day, 1 week, 1 month and 3 months; n=10/time group) in an incubator at 100% relative humidity and 37^{o}C. Specimen weight changes due to storage and weight loss due to DSC testing were also computed. The DSC thermograms displayed endothermic peaks reflective of material degradation and thus material structure. All groups of specimens had a characteristic single endothermic peak in the thermograms except the 30 min dark cure specimens which had two endothermic peaks in their thermogram. The endothermic peaks were mainly attributed to the dehydration of bound water in the matrix of the material. Significant differences in endothermic peak enthalpy and peak temperature were observed among the cure and time groups. The results suggest that, in general, the immediately light cured material is of differing structure compared to groups that allow the acid-base reaction to occur either due to delay in light curing or its absence. Additionally, changes in the endothermic peak over time were observed, indicating material maturation occurred and is likely due to changes in the ratio of bound to unbound water in the matrix. Interpretation of weight changes in storage show light curing reduced the moisture sensitivity of the RMGI.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

CONVENTIONAL GLASS IONOMERS

Conventional glass ionomers were first introduced around 40 years ago in 1969 by Wilson and Kent [1]. They are derived from aqueous polyalkenoic acids such as poly(acrylic acid) (PAA) and a glass component that is usually a fluoroaluminosilicate. When the powder and liquid are mixed together, an acid-base reaction occurs which involves neutralization of acid groups on polymeric acids, like poly(acrylic acid), with powdered solid bases (calcium fluoroaluminosilicate glasses). These glasses are bases because they are proton acceptors, even though they are not soluble in water. The hydrogen ions from the acid decompose the glass particles with the liberation of calcium, aluminum, and fluoride ions, and silicic acid. As the reaction continues, the polymer chain unwinds with an increasing negative charge which results in the condensation of cations on the polymer chain forming an insoluble salt precipitate which is a sol at first and then gets converted into a gel [2]. The polymer is used typically as a 40–50% aqueous solution [3]. The attack on the glass particles by the acid is not uniform. It takes place preferentially at the calcium rich sites which is indicated by the presence of calcium in the glass to neutralize the sites in which aluminum has replaced silicon with a network of MO_4 tetrahedra. Calcium is therefore referred to as a "Network Modifier". Since Al is more basic than silica, these parts are more basic. Hence there is preferential dissolution of calcium first, followed by dissolution of aluminum. The early hardening is due to early neutralization reactions leading to the formation of a stiff, ionically cross-linked

polyacrylate matrix [4]. Silica and phosphorous are also present in the matrix of the set cement. As the metallic polyalkenoate salt begins to precipitate, gelation begins and proceeds until the cement sets hard [5]. After the initial set or gelation, the cement continues to harden as cations are increasingly bound to the polyanion chain and the hydration reaction continues. Variables such as the composition of the aluminosilicate glass and the polyalkenoic acid, the particle size of the glass powder, the relative proportion of the constituents (glass/polyacid/tartaric acid/water) in the cement mix, and the type of mixing, are mainly determined by the manufacturer [6]. During the setting of the glass ionomers it is essential for the acid-base reaction to remain dominant because it is through this that the powder becomes bound to the matrix and the matrix in turn binds to the tooth structure. Also the release of fluoride occurs through this acid-base mechanism [7].

Conventional glass ionomers have the main advantages of ion exchange adhesion to the tooth surface and continuous fluoride release which could lead to prevention of further breakdown of tooth structure [8]. Several methods have been implemented to improve the adhesion of glass ionomers to the tooth structure. One such method is the "conditioning" of the tooth structure using 10% poly(acrylic acid) for about 10 seconds to remove the smear layer and other contaminants from the dentinal tubules. This is also shown to alter the surface energy of the tooth structure sufficiently to encourage the adaptation of the cement and to ensure optimum placement of the restoration [9].

Fluoride release in conventional glass ionomers

Fluoride is released from the glass powder at the time of mixing and lies free within the matrix. It can therefore be released without affecting the physical properties of the cement. It can also be taken up into the cement during topical fluoride treatment and released, allowing the cement to act as a fluoride reservoir over a relatively long period. Fluoride ions form fluorapatite in or on the tooth surface and are more resistant to acid attack and therefore inhibit demineralization [10]. The level of fluoride ions in the region of a glass ionomer restoration has been measured to be approximately 10 ppm. There is a halo effect created around the restoration and it is shown to cause remineralization of both enamel and dentin [11].

Classification of conventional glass ionomers

Mount [12] classified glass ionomers based on the usage in restorative dentistry as follows:

Type I: Luting Cement

Type II: Restorative Cements

Type II. 1: Restorative aesthetic-auto cure

Type II.1: Restorative aesthetic-resin modified

Type II.2: Restorative reinforced

Type III: Lining Cement

Clinical applications of conventional glass ionomers

The desirable properties of glass ionomers make them useful materials in the restoration of carious lesions in low stress areas such as smooth surface and small anterior proximal cavities in primary teeth. Glass ionomers are used in a variety of applications in clinical dentistry like as a luting cement in crown and bridge work, lining cement under metallic restorations, a base for composite restorations, a long term sealant over an active carious lesion, etc. [13]. Recently, glass ionomers have also been used as coatings on obturation points.

By bonding a restorative material to tooth structure, the cavity is theoretically sealed, protecting the pulp, eliminating secondary caries, and preventing leakage at the margins. This also allows cavity forms to be more conservative and, to some extent, reinforces the remaining tooth by integrating restorative material with the tooth structure. The coefficient of thermal expansion of conventional glass ionomers is close to that of dental hard tissues and therefore it has good marginal adaptation [14]. Conventional glass ionomers are tooth-colored and available in different shades.

Limitations of conventional glass ionomers

Freshly mixed conventional glass ionomers have been found to be cytotoxic, but the set material had no effect on cell cultures [14]. The main limitation of the glass ionomers is their relative lack of strength and low resistance to abrasion and wear. Conventional glass ionomers have low flexural strength but high modulus of elasticity, and are therefore very brittle and prone to bulk fracture. Although the addition of resin in the modified materials has further improved their translucency, they are still rather opaque and not as esthetic as composite resins. In addition, their surface finish is usually not as good. Conventional glass ionomers are difficult to manipulate as they are sensitive to moisture imbibition during the early setting reaction and to desiccation as the materials begin to harden.

COMPOSITE RESINS

Composite restorative materials are complex blends of polymerizable resins mixed with glass powder fillers. To bond the glass filler particles to the plastic resin matrix, the filler particles are coated with silane, an adhesive coupling molecule. Many modern restorative materials set following irradiation by visible light in the range of 450–480 nm. They require the presence of camphoroquinone (CQ) or a similar photo-initiator to start the polymerization reaction by the formation of free radicals. Other additives also are included in composite formulations to enhance radiographic opacity for better diagnostic identification, optimize esthetics, facilitate curing, and adjust viscosity for

better handling. Composite resins need to be bonded to the tooth surface using bonding agents. Bonding resins typically contain low molecular weight resin monomers. Composite resins can be either light cured or dual cured resins [15].

Light-cured composite resins consist of 2 main components: an organic matrix monomer and a powdered ceramic. Activation of free radicals is used to polymerize the unsaturated methacrylate monomer. Increase in irradiation time and light intensity lead to higher strength because of the formation of a structure with a higher density of cross-links (increased degree of cure) [16]. In dual-cured resin systems, polymerization is initiated by surface exposure to a curing light while the bulk of the material continues to cure by a chemical process. Benzoyl peroxide is used as an initiator, which is activated by a tertiary aromatic amine, and free radicals are formed by a multi-step process.

Polymerization of the resin matrix produces gelation in which the material is transformed from a viscous-plastic phase with flow, into a rigid-elastic phase. A major part of the initial polymerization (pre-gel polymerization), occurs within the first 10 sec of irradiation. The gel point is reached in the first 10 sec from the start of curing. After this, the polymerization reaction continues at a slower rate. As the light source is removed and as the viscosity of the composite becomes greater, the reaction stops by combination of the remaining free radicals [17].

Previous studies on dental composite resins have shown that many characteristics of the material, including hardness, tensile and compressive strength, and flexural modulus depend on the degree of resin polymerization. The greater the degree of polymerization, the greater the mechanical properties of the composite resin [18]. In

particular, degree of cure modulates solubility and degradation, which affects the biological performance of the material. The lower the degree of conversion, the less biocompatible or more cytotoxic the restoration is [19].

Polymerization of composite resin materials results in a temperature rise caused by both the exothermic reaction process and radiant heat from the light curing unit. This may be examined with a differential scanning calorimeter (DSC). Temperature rise during composite resin light curing is a function of the rate and degree of conversion of carbon–carbon double bonds. The exothermic reaction is proportional to the amount of resin available for polymerization and to the degree of conversion of carbon–carbon double bonds. A rapid and marked temperature rise was observed in a study conducted by Al-Qudah et al. which indicates a rapid rate of polymerization (i.e. short exposure times, 5 or 10 s, caused significant activation) [17].

RESIN MODIFIED GLASS IONOMERS (RMGI)

Resin modified glass ionomers are a combination of conventional glass ionomers and composite resins. The resin was added to the glass ionomer to provide a material with improved mechanical properties and a cure on command facility whilst retaining the advantages of the original glass ionomer [20, 21]. Mitra [22] introduced a cement forming system based on graft copolymers of poly(acrylic acid) in which a minor proportion of the functional groups were replaced with crosslinkable branches that were

terminated in vinyl groups [22]. These materials required HEMA to retain all the components in one phase.

Composition

The RMGIs contain not only the components of the glass ionomers; polyacid, acid-degradable glass and water, but also a water-compatible monomer usually 2-hydroxy-ethyl methacrylate (HEMA), or a photocurable side chain grafted onto the poly(acrylic acid), together with suitable polymerization initiators. Some formulations may also contain, an additional photocurable monomer, such as that conventionally used in composite resin filling materials like Bis-GMA. RMGIs usually contain benzoyl peroxide as an initiator, ascorbic acid as an activator, and cupric sulphate as a co-activator in the chemically cured materials. The light cured materials contain camphoroquinone as photoinitiator.

Many marketed RMGIs contain important compositional differences compared to the conventional glass ionomers. Apart from the incorporation of the light curable methacrylate-based monomers and the supporting accelerators and catalysts, polyacrylate derivatization to the methacrylate functionalized analogue has been found in the liquid components of Fuji II LC and Vitremer. Photac-Fil was the only material based on the traditional Ca-Al-F silicate glass powder used in glass ionomers. The other RMGIs contain Sr-Al-F or Ba-Al-silicate glasses to improve the optical properties compared to the more opaque nature of the Ca-Al-F silicates [23].

Classification

McCabe [24] classified the materials formed by mixing composite resins and glass ionomers into 3 categories:

1. Modified Composites: those that set only through polymerization reactions but also contain ion-leachable glasses in an attempt to achieve fluoride release. An example of this material class was the product Variglass (LD Caulk Division, Dentsply International Inc., Milford, DE).

2. Hybrid Type Composites: those that set through an acid-base reaction and through polymerization (light and/or chemically activated). These materials also set under conditions where no polymerization occurs. These are the only cements that can be classified as true "resin modified glass ionomers" because they contain components of both glass ionomer and composite resins. Examples of this material class include Fuji II LC (GC America, Alsip, IL) and Vitremer (3M, St. Paul, MN).

3. Compomers: these materials contain the major ingredients of both glass ionomer and composite resins except water. Exclusion of water prevents the premature setting of the material in the container. It also ensures that the setting of the cement occurs only by polymerization. A limited acid-base reaction occurs later as the material absorbs water. Examples of this material class include Dyract (Dentsply International, York, PA) and Compoglass (Ivoclar Vivadent Inc., Amherst, NY) [24]. The uptake of water by the anhydrous mix results in further crosslinking to the matrix and allows for the diffusion of ionic species [25].

Resin modified glass ionomers have been called "hybrid ionomers" although the former term is much more common. The light-curing system enables the material to be cured on command with a visible light-curing unit. Resin modified glass ionomer (RMGI) materials are described as dual setting materials; upon mixing the liquid and powder the acid-base reaction occurs and the light-initiated free-radical polymerization of resin also occurs. The term resin modified glass ionomer implies that the characteristics of glass ionomers are maintained, but modified by the presence of resin. McLean et al. [26] have proposed that the term “resin modified glass ionomer” should only be used when a substantial part of the setting reaction of the cement involves the acid–base reaction [26]. The modified cements combine the favorable properties of glass ionomers: adhesion to enamel and metal, the ability to absorb and release fluoride, and the ability to chemically bond in the presence of moisture. The modified cements also include the favorable properties of resins: light curing for quick set and increased strength.

The working time of the resin modified glass ionomers can be controlled by light activation but not to the extent of composite resins. There are two reasons for this. Firstly, these cements begin to set through an acid-base reaction immediately after mixing. Secondly they are extremely sensitive to exposure to ambient light [26].

Clinical applications

Resin modified glass ionomers have been used in a variety of applications such as a restoration, lining, base, core build up, and luting agent [24]. Resin modified glass

ionomers can bond to both tooth structure and composite resins and hence they can be used in the sandwich technique instead of conventional glass ionomers. Similarly, they can also bond to amalgam and therefore can be used as a base for amalgam restorations. Because of their adhesive properties, they have been advocated to be used as root canal sealers [27].

Role of HEMA and glasses

HEMA is a hydrophilic monomer added to RMGIs to form the resin matrix upon polymerization along with other multifunctional methacrylates like Bis-GMA or TEGDMA, if present. The addition of HEMA in RMGI makes the aqueous and the organic components miscible acting both as a co-solvent and a polymerizable monomer. The role of multifunctional methacrylates is to introduce covalent cross links to the resin phase after curing. RMGIs contain glasses of the calcium fluoroaluminosilicate type. These glasses have two roles: they act as the source of cross linking ions for the acid–base process, and as filler for the resin phase. Water is included in the formulation to promote the neutralization reaction, but is present at reduced levels compared with the self-curing materials. The curing of the resin part of RMGIs is mainly initiated photochemically using visible light and a camphoroquinone-based photoinitiating system; it may be induced also chemically, by the use of benzoyl peroxide with an amine accelerator in a two paste system or chemically activated RMGI [2].

Effect of co-initiator

Photopolymerization of HEMA induced by CQ in the absence of a co-initiator occurs very slowly. The addition of a co-initiator accelerates the process substantially. Also, when polymerization is carried out in air, the strong inhibitory effect of oxygen under the conditions used, causes HEMA not to polymerize in the absence of co-initiators. Interestingly, HEMA in the presence of 5% PAA solution results in higher polymerization: the rate and the double bond conversion substantially increase [2].

RMGI as a hydrogel

According to studies [28-31], resin modified glass ionomer cements, upon continued exposure to moisture, behave like mild "hydrogels" imbibing water and becoming weaker and more plastic.

Setting reaction of an RMGI

RMGIs have two possible setting mechanisms, the acid–base reaction of the conventional glass ionomers and a free-radical addition polymerization of the monomer. In some RMGIs, a further polymerization reaction involving unsaturated side-chains on the modified polyacid will also take place. Sidhu et al. [32] described the setting reaction

of these materials as a second resin polymerization reaction which supplements the fundamental acid-base reaction [32]. The first reaction that occurs after mixing the material is the acid–base reaction. Free-radical polymerization of the monomeric components is then initiated by visible light irradiation. The set cement then consists of interpenetrating networks of poly(HEMA) and polyacrylate salts [32]. Many of the resin systems used in composite resins are usually not water soluble, so if used in RMGIs they would be immiscible with the liquid of glass ionomers. Therefore, the monomers usually added to RMGI formulations are water soluble (having hydroxyl groups) as in HEMA. However, since the two systems (resin and acid–base component) cannot occupy the same space, the presence of any resin-former will be at the expense or loss of GI acid and vice versa, thus resulting in a "network competition" between the components of the RMGI cements. It was thus found that in RMGIs, if the GI reaction is delayed, the resin network will form more fully, but this will then limit the acid–base reaction; similarly, if the free-radical polymerization is delayed, the formation of the GI network will proceed unhindered, but this will then limit the resin network from forming. This implies that any delay in irradiation limits the extent to which the resin network can form. Also, while light-curing offers the potential for longer working times, it is at the cost of much reduced strength that cannot be compensated for by extra irradiation [33]. The bulk of the polymerization reactions have been found to occur within 10 min [34]. The setting mechanisms in the materials, primarily those of the acid-base reaction, have been shown to continue for about 24 hours [35]. The set RMGI consists of residual glass particles embedded in a mixed polysalt and polymerized monomer matrix. However the presence of the monomeric species in the cement formulation significantly reduces the rate of the

acid–base reaction. Andrzejewska et al. [2] found that the polymerization of HEMA proceeds with a gel effect which results in autoacceleration of the process and sets with nearly 20% double bond conversion. A final degree of conversion of around 90% can be obtained in air or a neutral atmosphere.

Kakaboura et al. [23] conducted a study to determine the extent of free-radical polymerization and the acid-base reaction during the setting of some commercially available RMGIs. They classified the specimens of the different RMGIs (P/L combinations) into 4 groups based on the light irradiation treatments. They found that none of the products tested showed any evidence of salt formation immediately after mixing and light curing. The water containing RMGIs (ex: Fuji II LC and Vitremer) showed an acid-base reaction that progressed at a significantly lower rate than the traditional glass ionomers, while the water-deficient RMGIs (ex: Variglass) did not demonstrate any acid-base reaction even over time. The VariGlass liquid contained a high ionic strength but limited water content. Vitremer specimens were found to have the highest acid-base yield among the materials tested. This difference can be attributed to: the liquid/powder components of Vitremer are thought to be more reactive, the high Al/Si and Sr/Si atomic ratios in the powder component may increase carboxylate salt formation due to increased effective acid ionization, the chemically initiated free-radical polymerization is inefficient and hence does not interfere with the acid-base reaction, and the slow rate of chemically initiated polymerization allows efficient acid neutralization rates. They found that free radical formation rates are slower than those achieved by chemically initiated polymerization but they provide adequate conversion and high carboxylate salt yields. Kakaboura et al. [23] also studied the effects of light curing on

the speed or extent of the acid-base reaction. They found that photo polymerization greatly reduced the acid-base reaction during the early setting stages of resin modified glass ionomers. The free-radical formation rates were slower than those achieved by chemically initiated polymerization, but they produce adequate conversion and high carboxylate salt yields [23].

According to Nicholson and Anstice [30], upon irradiation of the specimen, the setting theoretically occurs rapidly by the photochemical cross-linking reaction and more slowly by the acid-base reaction. However, in practice, the two reactions cannot take place without reference to each other. Therefore, the photochemical reaction will be affected by the polar nature of the acid-base medium and the acid-base reaction will be affected by the presence of relatively hydrophobic entities, and also by the reduced diffusion coefficients of the reactive species through the cross-linked polymer network.

Commercially available RMGI materials like Fuji II LC and Vitremer (which contain acid in the liquid component) have been found to demonstrate the highest ratio of carboxylate salts formed to the remaining unionized carboxyl groups (COOM/COOH). However, non-exposed/non-irradiated specimens of Vitremer demonstrated an additional setting mechanism – a chemically initiated free-radical polymerization of the methacrylate based monomers in addition to the acid-base mechanism which was the only setting mechanism for the non-exposed/irradiated Fuji II LC specimens. Hence, Vitremer can be termed as “triple-cure” cements and Fuji II LC are termed as “dual-cure” RMGIs [23]. McCabe [24] refers to resin modified glass ionomers capable of undergoing chemically activated polymerization in the absence of light as “tri-cure” materials [24].

Exothermic setting reaction

Studies conducted by Al-Qudah et al. [17] to determine the temperature change during the setting of RMGIs found that there was an exothermic temperature rise during setting of an RMGI. RMGI contains polycarboxylic acid, modified with methacrylate groups, as well as HEMA and photo initiators. When the material is mixed and light cured, several types of polymerization can take place. The HEMA will polymerize to form polyHEMA. The modified polycarboxylic acid, because it contains unsaturated groups, will copolymerize with HEMA. In addition, the modified polycarboxylic acid will further polymerize to form a cross-linked polycarboxylic acid, which should increase the strength of the material. These polymerization reactions may explain the greater reaction exotherm observed with RMGI as compared to a conventional hybrid composite. However, the general behavior of RMGIs was found to be similar to that of composite resin [17]. Berzins et al. [36] have also used DSC to study the setting mechanism of RMGI and not only found that the setting reaction is an exothermic one but also that acid-base and light polymerization reactions compete and possibly inhibit one another during early RMGI development [36].

Kanchanavasita et al. [37] observed a temperature rise of up to 20°C during polymerization of light cured resin modified glass ionomers which was greater than that of a microfilled composite resin.

Curing shrinkage

Attin et al. [38] studied the curing shrinkage, volumetric changes, and water content (after water storage) of six commercially available RMGIs and compared it with the results of a traditional glass ionomer and a hybrid composite resin material. Curing shrinkage and volumetric changes were measured using the hydrostatic principle assuming the change in buoyancy of the material in water depends on the volumetric changes of the material. The results of the study showed that the curing shrinkage of most of the RMGI specimens were significantly greater than that of conventional glass ionomers and the hybrid composites. Also, the curing shrinkage of all the materials showed an increase with respect to time after polymerization. The results of volumetric changes showed that the conventional glass ionomers presented with a marked volumetric loss whereas the hybrid composites maintained a nearly constant volume during water storage. The RMGI specimens however, expanded as a function of water immersion duration (28 days). However, the total volumetric change was a net volumetric loss in most materials. Therefore, it was assumed that the expansion from the absorbed water, even after 28 days of water storage, would not cause enough expansion to seal the margins of restorations. Other authors like Feilzer et al. [35] have also found similar curing shrinkage of RMGI materials and composites within the first 24 hours of polymerization. The clinical implications of this curing shrinkage are many and range from marginal gap formation to increased stress in the bulk of the material resulting in cohesive failure of the restoration, although the later is unlikely.

The swelling/expansion of the set cement may cause clinical consequences like pressure against the cavity wall. These types of consequences have been reported for resin composite restorations [39]. Also, the effect of water storage (to simulate the condition in the oral environment) on the mechanical properties has been studied. McCabe found that water storage causes an initial decrease in strength of the cement but does not have any significant long term effects [24]. The presence of HEMA is found to be a major factor for this type of swelling/expansion since it is more hydrophilic than the resins used in composites.

Setting stresses

Feilzer et al**.** [40] conducted a study to determine the setting stresses that developed in some commercially available conventional and resin modified glass ionomers and the influence of water exposure on these stresses. Conventional glass ionomers were found to fracture spontaneously (either cohesively or adhesively) when they were cured in the absence of water (but not dehydrated) due to the development of setting stresses. These stresses were relieved on exposure to water and prevented the spontaneous cracking/fracturing. RMGI specimens on the other hand did not exhibit any spontaneous fractures upon light curing in isolated conditions (no water exposure or dehydration). Water exposure to these specimens reversed the contraction stresses into expansion stresses.

Watts et al. [41] studied the dimensional changes associated with RMGIs in both aqueous and non-aqueous media (silicone fluid) at room temperature (23^{o}C) and oral temperature (37^{o}C). They observed a small amount of setting shrinkage within the first 5 min from the start of fabrication of these materials. Exposure to water (aqueous media) resulted in expansion of these materials. The shrinkage values observed were reasonably small compared to the expansions observed in water. In silicone fluid, however, the RMGI specimens expanded slightly at 23^{o}C but shrank at a higher temperature (37^{o}C) which could be attributable to the further progression of setting reactions. Similar observations were made by Watts and Cash [42] in another study using the silicone filled dilatometer technique.

Phase separation

The liquid components of some commercially available RMGI liner/base materials were found to undergo phase separation on storage. The resulting materials could not undergo acid-base reaction and showed extensive swelling on soaking in water. Thus it can be said that these materials have an inherent thermodynamic tendency to undergo phase separation. The phase separation tendency of these materials as they undergo setting likely could be due to the fact that the product itself contains domains of different phases [30].

Phase separation was also reported by Andrzejewska et al. [2] who studied the effect of aqueous polyacid solutions on the photocuring of RMGIs. They reported that

polyacid aqueous solutions influenced photopolymerization by both physical and chemical effects. Phase separation during polymerization was found to be associated more when a less hydrophilic monomer, like TEGDMA, was a component of the material. Phase separation can lead to turbidity of the polymerizing system, which may result in worse light penetration and in decreased initiation efficiency. The chemical effect could involve the presence of readily abstractable tertiary hydrogens from the polyacid backbone or a change in dielectric constant of the reaction medium, which may affect the initiation process by solvation effects.

Phase separation has also been assumed to be the cause of the lower microhardness found in the RMGIs compared to conventional GIs. [31, 43, 44] The addition of HEMA affects the setting reaction of glass ionomers. The presence of an organic medium reduces the dielectric constant. Therefore the ions of poly(acrylic acid) are dissociated to a much lesser extent in the presence of HEMA than in water as the medium. Methanol also has similar effects on the setting rate of the material. It causes the molecule to coil up more tightly than it does in pure water. With the continuation of the setting reaction, there is a tendency for phase separation of the components. As an increasingly ionic medium begins to develop, there is reduction in miscibility of even the slightly polar organic molecules and this leads to phase separation as the ions cluster into phases that separate from the organic domains [4].

Depth of cure

Some studies have used DSC to determine the setting rates and mechanisms of setting of RMGIs. Bourke et al. found that the depth of cure of these materials was similar to those of composite resins [45]. Others like Mongkolnam et al. [46] found a lower depth of cure of resin modified glass ionomers compared to composite resins [46]. Burke et al. [47] studied the depth of cure of light-cured glass ionomers used as a liner and found that the depth of cure increased progressively after setting and was greater at 12 hours after light curing than it was after immediately light curing. This increased depth of cure was explained as a result of the continued hardening due to the acid-base (glass ionomer) reaction [47]. Hansen and Asmussen [48] found that that the depth of cure (hardness) of composite resins decreased as the distance from the surface increased in a study to study the depth of cure of composite resins using simple scraping tests [48]. The hypothesis of increase in depth of cure over time as a result of chemical curing mechanism (acid-base reaction) within the materials was tested by Swift et al. [49]. They tested the depth of cure of some commercially available RMGIs using microhardness measurements at different depths/levels of the specimen and at different time periods after light curing. They found that at 10 min after light curing, the top layers (0-1 mm) of the materials were significantly harder than the deeper layers (4-5 mm). At the end of 1 day, there was no significant difference in hardness among the layers for most materials (Geristore, Photac-Fil, Vitremer, Fuji II LC). A single 40 s exposure resulted in a 5 mm depth of cure for the materials tested. However, the hardness of VariGlass declined significantly with the distance away from the surface. At the end of 7 days, the materials had their most uniform hardness values. However, immediately after light-activation, all

the materials tested were too soft to be measured at depths greater than 5 mm and the hardness values at 4-5 mm depth were relatively low. Therefore, incremental placement and curing of 2-3 mm increments remains a prudent approach to the clinical use of RMGI cements. Similar results have been found for the depth of cure of composite resin materials. Rueggeberg et al. [50, 51] used FTIR spectrometry to determine the depth of cure of composite resins. They found that the depth of cure decreased with the increased distance from the surface of light exposure, especially in the inner aspects of the material (restoration). Also, the top surface of the light cured materials was not significantly influenced either by the intensity or duration of light exposure. However, in a study by Andrzejewska et al., [2] the polymerization rate and the degree of conversion of double bonds were found to depend on the irradiation time. Even though the manufacturers emphasize the importance of incremental placement and proper light curing duration of RMGIs, the chemical curing ability of these materials could be of significant advantage as it could compensate for the failure of the curing light to penetrate thick or inaccessible regions of the restorations [52]. Swift et al. [49] claim that RMGIs (especially Fuji II LC) have adequate setting maturation of up to 5 mm when they are light cured for 40 s [49]. However, in a study conducted by Roberts et al. [53], it was found that even though there was post light-activation chemically initiated resin polymerization and/or acid-base reaction in RMGIs, the hardness of the materials at different depths suggested that these reactions do not result in adequate polymerization for long term success of the restoration.

MECHANICAL PROPERTIES

Bream et al. [54] measured the elastic modulus of resin modified glass ionomers and found that it was lower than that of composite resins and therefore these materials are less rigid [54]. The compressive strengths of RMGI cements have been found to be higher than that of conventional glass ionomers [55-60]. RMGIs have also been found to have higher flexural and tensile strengths than conventional glass ionomers [20, 57, 60-63].

Effect of water

Cattani-Lorente et al. [64] studied five commercially available RMGIs for the effect of water sorption on the physical properties of the materials like flexural strength, flexural modulus, and microhardness by storing the RMGI specimens in different levels of humidity for various time periods. They found that the conventional glass ionomers absorbed less water compared to RMGIs. Fuji II LC specimens that were stored in a humid environment were found to absorb less water compared to the ones stored completely immersed in water for the same time period. When stored under the same conditions, the RMGI specimens were found to have slightly higher mechanical strengths than the conventional glass ionomers. Hardness of the specimens was also found to be dependent on the storage conditions. Failure tests revealed that the specimens stored in air were brittle and showed little deformation before fracturing whereas specimens stored in water seemed to be more plastic and deformed greatly before fracturing. This was

correlated directly with the amount of water taken up by the specimens. A similar observation was made by Nicholson et al. [28] when they tested the effect of water storage on Vitremer and XR Ionomer RMGIs. They found that the water stored specimens demonstrated a barrel shaped deformation upon loading to failure.

Cattani-Lorente et al. [64] found that RMGI specimens stored in a humid environment presented a higher flexural strength, modulus, and greater hardness when compared to specimens completely immersed in water for the same period of time. This is due to the slower uptake of water in a humid environment and thus consequently a lesser amount of water absorbed by the specimens in a humid environment. Vickers hardness tests revealed that the softening due to water storage was greater at the surface than the core and this behavior follows Fick's laws of diffusion. The chemical composition of these materials is important to their water sorption characteristics. The polar functional groups (in HEMA) found in the polymer chain of RMGIs produce electrostatic interactions (which is responsible for the strengthening effect of the material) that make it more sensitive to water sorption. Upon water sorption, the electrostatic interactions are reduced and the polymer network becomes more flexible leading to a lower elastic modulus and greater plastic deformation upon loading. Therefore, water acts like a plasticizer, however, with reversible effects on the physical properties of the cement. Water also partly dissolves the glass network (glass ionomer part) of these materials, consequently altering the network of the cement. Anstice and Nicholson [29] describe the water sorption behavior of these materials as "hydrogel" behavior. They also argue that the changes that take place in these materials upon placement in distilled water may not exactly mimic the conditions in the oral

environment and the effect of saliva on these cement restorations will be minimized due to the presence of salts and proteins in saliva.

In general, compomers have been shown to have better mechanical properties compared to RMGIs independent of storage conditions, although their physical properties are also influenced by the water content. The elastic moduli of compomers, however, are lower than the RMGIs because of their lower glass filler content [25].

Hardness

Many studies have compared the microhardness characteristics of RMGI and conventional GI cements [43, 58, 60, 65-68]. Some authors [67, 68] studied the microhardness of RMGIs as a function of time and water exposure. Their results showed that the microhardness of RMGIs were lower than the GIs at all measurement times. These results are in agreement with the studies of other authors [60, 43, 66, 69]. Ellakuria et al. [67] found that Vitremer showed a significant increase in microhardness between the first day to 12 months after mixing. The lower hardness of these materials could be due to the incomplete polysalt matrix formation caused by the crosslinked HEMA matrix which prevents the acid-base reaction [28, 45, 67, 70]. The hardness of compomers has been reported to be similar to those of composite resins [71].

Fracture Toughness

Mitsuhashi et al. [72] reported that the fracture toughness of commercial RMGIs were significantly greater than those of conventional GIs by approximately two fold. They found that there was no significant difference in the fracture toughness of materials with different powder/liquid ratios. They also found that the experimental RMGIs with smaller particle sizes (up to 10 μm) had higher fracture toughness values and greater tensile strength. Goldman et al. [73] used the measurement of fracture toughness as a predictor for clinical success of a material. He reported that the conventional glass ionomers have a high modulus of elasticity, but very low fracture toughness and large inherent flaw size compared to composite resins which have medium to small inherent flaw sizes. Similar results were found by Mitchell et al. [74] who found composite resin specimens to have higher fracture toughness values compared to RMGI specimens. Conventional GIs were found to have the lowest fracture toughness values among the three types of materials.

Microstructure

Xie et al. [75] studied the fractured microstructures of some commercially available GIs and RMGIs using scanning electron microscopy (SEM). In general, several voids and cracks were found in the microstructure of both GIs and RMGIs. The fracture surfaces of Fuji II LC showed numerous small glass particles dispersed in the polymer matrix while those of Vitremer and Photac-Fil exhibited a more tightly integrated glass

particle-polymer matrix surface and less exposed glass particles with Vitremer having the best integrated microstructure. This was associated with higher values of flexural strength, diametral tensile strength (DTS), and wear resistance. The RMGI microstructures also exhibited large fractures fragments of the resin matrix. The cracks were found to propagate through microstructural porosities and voids. The large resin fragments are due to the plastic deformation behavior of the RMGIs. They also found that among the RMGIs, the wear resistance behavior of Fuji II LC was the lowest and this was said to be due to the non-uniform distribution of glass particles in the resin matrix where the areas of glass particle fillers and unreacted polymer matrix would offer the lowest wear resistance. SEM images also showed that the wear resistance of the materials was associated with the glass particle sizes with the larger glass particle size having increased wear resistance. Mitsuhashi et al. [72] found that the microstructure of Fuji II and Fuji II LC had a broad distribution of powder particle sizes while Vitremer exhibited a narrow distribution of particle sizes. Also, Fuji II and Fuji II LC had a predominantly larger particle size compared to the Vitremer specimens which consisted of relatively smaller and more uniform particles as seen under the SEM.

Effect of polyacid aqueous solutions on photocuring

It was found that the addition of polyacid solutions causes earlier onset of auto-acceleration and shortens the time when the maximum polymerization rate occurs [2]. This effect increases with the amount of polyacid added (up to 10%). Specifically, the

addition of polyacids to HEMA-based formulations exerts a strong accelerating effect to the polymerization initiated by CQ. However, when the two-component initiating systems are used, the polymerization is much less efficient and the polymerization rates are significantly slower. Despite the increase in auto-acceleration, the addition of polyacids slightly lowers the final conversion of double bonds. Another detrimental effect of adding polyacid is the increase in viscosity of the formulation [2].

Adhesion to tooth surface and bond strength

Chemical bonding to tooth structure is one of the major advantages of glass ionomers. The bond strength of resin modified glass ionomers has been found to be greater than conventional glass ionomers but is lower than that of composite resins [76-78]. Eliades and Palaghias [79] have suggested that the role of HEMA is the primary factor in the bonding to the tooth structure of the resin modified glass ionomers. In addition to the chemical bonding of RMGIs via the glass ionomer components, resin monomers penetrate surface irregularities to produce a micromechanical interlock (bond) after polymerization [80]. Mitra et al. [81] and Coutinho et al. [82] found ionic carboxylate bonding between the carboxyl groups of methacrylated copolyalkeonic acid and the hydroxyapatite of tooth structure using FTIR and XPS analysis.

Fluoride release

Resin modified glass ionomers have been found to release as much fluoride as conventional glass ionomers. The mechanism of fluoride release can be either due to ion exchange or dissolution from the cement/restoration. If the fluoride release occurs by a wash out mechanism, it results in leaching of other ions like calcium from the material and the gradual disintegration of the material [83]. The levels of fluoride release can be increased by topical fluoride applications.

Biocompatibility of RMGI

Concern has been raised regarding the biocompatibility of resin modified glass ionomer materials since they contain unsaturated groups [14]. Conventional glass ionomers have been found to have a minimal setting exotherm, rapid acid neutralization, and slow release of beneficial ions like fluoride ions [84]. In contrast to conventional glass ionomers, the resin modified glass ionomer has been found to set with a significant exotherm [17, 36, 37].

RMGIs have also been found to be more cytotoxic than conventional GI cements in a few studies [85, 86]. Aranha et al. [87] tested the cytotoxicity of RMGI lining cements to an immortalized odontoblastic cell line and found Fuji II lining cement to be less cytotoxic than Vitremer cement. They also found that the duration of light curing did

not affect the toxicity of the cements to the odontoblasts. The cytotoxicity of Vitrebond was also independent of light activation time.

Release of HEMA from RMGI

Palmer et al. [34] studied the effect of curing regimes (irradiation time and maturation time) on the release of HEMA from four commercially available resin modified glass ionomers using high pressure liquid chromatography (HPLC). For Vitremer, under- and over-curing neither increased nor reduced the percentage of HEMA released in comparison to specimens cured for the manufacturer's recommended time. However, Fuji II LC without light curing released a significantly higher percentage of HEMA than the light cured specimens of the same maturation and also, unlike Vitremer, Fuji II LC seemed to benefit from over-curing as observed with over-cured specimens releasing significantly less HEMA than those cured for either the manufacturer recommended time or less. They also found that the percentages of released HEMA from the liner/base grade materials (Fuji Lining LC and Vitrebond) were generally higher than those from the restorative materials (Fuji II LC and Vitremer). This is due to the thinner consistency (lower powder: liquid ratio) required for the liner/base materials. The effect of maturation time was not significant for most specimens. Vitremer specimens had the lowest release of HEMA, even when not light cured, reflecting its greater sensitivity to ambient light. Fuji II LC was found to set without light-curing in only 5 min. Stanislawski et al. [88] found many other components to be released during the setting

reaction of RMGI. Of these, zinc ions were found to be of sufficiently high concentrations to induce cytotoxicity. The reduced free-radical cross-linking reaction in an RMGI material may be associated with more leachable material remaining [33].

SUMMARY

Resin modified glass ionomers were introduced as a combination of conventional glass ionomer and composite resins to result in a material with improved mechanical properties and handling characteristics compared to the conventional glass ionomer whilst retaining their beneficial properties like fluoride release and chemical bonding to the tooth structure. The term “resin modified glass ionomer” implies that the characteristics of glass ionomers are maintained, but modified by the presence of resin. These materials have been found to have improved mechanical properties compared to the conventional glass ionomers, similar to that of composite resins. They have been shown to release similar amounts of fluoride compared to the conventional glass ionomers. The setting reaction of these materials include both an acid-base reaction similar to that seen in conventional glass ionomers and a polymerization reaction often induced by light although some materials have also been shown to exhibit an additional free radical polymerization reaction.

OBJECTIVE

In the current study, the influence of light activation on the setting reaction of a commercially available resin modified glass ionomer (Fuji II LC, GC America, Alsip, IL, USA) was studied using a differential scanning calorimeter (DSC). The objective of the study was to investigate the setting reaction interaction in a resin modified glass ionomer using thermal analysis as a measure when a RMGI is light-activated at specific time intervals after mixing of the material and stored for various periods.

CHAPTER II

MATERIALS AND METHODS

MATERIALS

The materials and equipment used in this study were: a resin modified glass ionomer (Fuji II LC capsules, shade A2, GC America, Alsip, IL, USA) containing the powder and liquid components of the restorative material (Figure 1), Promix^{TM} amalgamator (Dentsply Caulk, DE, USA) used to mix the contents of the capsule, a differential scanning calorimeter (Model 822e, Mettler Toledo, Inc., Columbus, OH, USA) used for thermal analysis of the material, an analytical balance (AG245, Mettler Toledo, Inc.) to weigh the test material at various stages of the experiment, an Optilux 501 light curing unit (SDS Kerr, CT, USA) to initiate the free radical polymerization of the material (Figure 2), and an Isotemp Economy Lab Incubator (Fischer Scientific, Pittsburgh, PA, USA) to store the specimens in 100% humidity at a temperature of 37^{o}C. The materials and equipment used and their respective manufacturers are also listed in Table 1 below. The composition of the powder component of Fuji II LC is listed by the manufacturer as 95% aluminosilicate glass and 5%poly(acrylic acid) liquid component as 30-35% 2-hydroxyethyl methacrylate, 20-25% poly(acrylic acid), 5-15% proprietary ingredient and 1-5% 2,2,4, trimethyl hexamethylene dicarbonate.

Table 1: Materials and equipment with manufacturers.

Material	Manufacturer	Batch no.
Fuji II LC capsules-Shade A2	GC America, Alsip, IL, USA	830141, 807238,810158
Promix™ Amalgamator	Dentsply Caulk, DE, USA	-
Differential Scanning Calorimeter (DSC)	Mettler Toledo, Inc., Columbus, OH, USA	-
Analytical balance	AG245, Mettler Toledo, Columbus, OH, USA	-
Optilux 501	SDS Kerr, CT, USA	-
Isotemp Economy lab Incubator	Fischer Scientific, Pittsburgh, PA, USA	-

Figure 1: Fuji II LC capsules used in the study.

Figure 2: Light initiation unit used in the study.

METHODS

The DSC aluminum crucibles were weighed to the nearest 1/100th of a milligram using an analytical balance (Figure 3) before the RMGI capsules were activated. The Fuji II LC capsules were activated and mixed in the amalgamator shown in Figure 4 at high speed for 10 seconds. A timer was started immediately after the completion of mixing of the RMGI. The mixed RMGI from the capsule was dispensed into the pre-weighed aluminum crucible such that the thickness of the RMGI in the crucible was approximately 2 mm, reflecting the distance from the base of the crucible to the lip of the crucible. For the immediate light cure group, the dispensed RMGI was immediately light cured for 20 seconds upon dispensing by holding the light curing unit tip about 1 mm from the surface of the RMGI. For the 5 min and 10 min delayed light cure groups, the specimen was light cured in the same manner as the previous group but the light cure was initiated 5 or 10 min after mixing. All the specimens were mixed, dispensed, and light cured in a relatively dark room with minimal natural light. The fourth groups of specimens were not light cured and termed “dark cure” specimens. This resulted in four groups of specimens based on the light initiation regimen of the material.

Ten specimens were prepared for each light initiation group. All specimens with or without the light curing were weighed in the analytical balance to determine the weight of the RMGI mix by subtracting the total weight of the crucible with the RMGI material from the weight of the empty crucible recorded earlier. After weighing the specimens, they were placed in labeled plastic containers and stored in the incubator (Figure 5) for specific, allotted periods of time (30 min, 1 day, 1 week, 1 month, and 3 months). The

plastic container was sealed and contained a distilled water-moistened paper towel to ensure adequate humidity to prevent RMGI desiccation. Overall, 5 different time groups were obtained with each group containing 10 specimens of each light initiation group, resulting in a total of 200 specimens.

Figure 3: Analytical balance used to weigh the crucibles and the specimens.

Figure 4: The amalgamator containing the activated RMGI capsule used to mix the material.

Figure 5: Incubator used to store the specimens.

The specimens were removed from the incubator at the prescribed time and weighed in the analytical balance to record the weight of the specimen after storage and the weight absorbed/lost in storage was calculated. The final weight of the RMGI before DSC was recorded and entered into the DSC software.

THERMAL ANALYSIS

Thermal analysis was done using a differential scanning calorimeter (DSC) attached to a liquid nitrogen cooling system as shown in Figure 6. The test specimen, which contained the sample material (resin modified glass ionomer) in an aluminum crucible, was placed carefully on the DSC ceramic sensor using a pair of tweezers at the designated area which read "S" for the sample/specimen position. The specimen was checked for proper positioning on the sensor by gently moving it in place to ensure no excessive movement of the crucible on the sensor. An empty aluminum crucible of the same dimension as the test crucible was used as the reference material and was placed in the same manner on the sensor at the area marked "R" on the sensor. The positioning of the reference crucible and the crucible containing the specimen in the DSC sensor is shown in Figures 7 and 8.

For the thermal analysis of the specimens, the DSC experiment was performed in dynamic scan mode from 37^{o}C to 300^{o}C at a rate of 10^{o}C/min in a closed, air environment. After scanning the specimens in the specified temperature range, they were removed from the scanner and weighed again in the analytical balance to calculate the resultant weight loss due to DSC analysis. The resultant thermogram was integrated

using the Mettler-Toledo STARe software to determine the temperature of the main peaks (in ^{o}C) and the associated enthalpies (in J/g).

Figure 6: DSC connected to the liquid nitrogen cooling system used in the study.

Figure 7: DSC sensor containing RMGI filled sample crucible and an empty reference crucible in their respective positions.

Figure 8: Close-up view of the DSC sensor containing RMGI filled sample crucible and an empty reference crucible in their respective positions.

DATA ANALYSIS

Statistical analyses of the results were done using SPSS software, version 17.0 (Statistical Package for the Social Sciences, Chicago, IL, USA). The mean peak temperatures and mean enthalpies of all groups were recorded with standard deviations. A two-way ANOVA was used to analyze the data obtained from the DSC with time and light cure groups as factors followed by Scheffe post hoc test where indicated. Additionally, the changes in weight with storage and DSC analysis were computed and analyzed.

CHAPTER III

RESULTS

The different groups of specimens were analyzed in the DSC from 37^{o}C to 300^{o}C with a total of 200 specimens tested for their decomposition behavior. The thermal exposure of the RMGI test specimens in relation to the reference crucible (aluminum) resulted in endothermic peaks in the DSC thermograms at different temperatures. STAR-e software was used to analyze these endothermic curves for their peak temperature and enthalpy. The peaks observed in the thermograms are indicative of decomposition of the components of the specimen. One main endothermic peak was observed for all specimens except for the dark cure group analyzed after 30 minutes. The mean peak enthalpies and their respective mean peak temperatures with standard deviations are listed in Tables 2 and 3 for light initiation groups and time groups, respectively.

Two-way ANOVA with cure group and time as factors found significant differences ($p<0.001$) existed for enthalpy and peak temperature among both cure and time groups. Additionally, as mentioned below, a significant ($p<0.001$) interaction was also observed. Scheffe post hoc tests were done to determine the differences in enthalpy and peak temperature within the cure groups and the time groups. Table 4 displays the results of the post hoc test for the different light initiation groups which revealed significant differences between certain groups. In general, the immediate cure and dark cure groups were statistically similar for both enthalpy and peak temperature and were different from the 5 min and 10 min delay groups.

Table 2: Mean enthalpy and mean peak temperatures with standard deviations for the different light initiation groups.

Time Group	Mean Enthalpy (J/g)	Mean Peak Temperature (^{o}C)
Immediate Cure Groups		
30 Min	20.67 (±6.90)	191.1 (±11.2)
1 Day	10.96 (±5.46)	102.5 (±5.6)
1 Week	21.87 (±8.22)	112.5 (±14.9)
1 Month	28.86 (±8.43)	109.9 (±3.6)
3 Month	29.33 (±6.79)	116.4 (±10.8)
5 min Delay Cure Groups		
30 min	35.63 (±11.72)	195.6 (±27.1)
1 day	32.08 (±7.17)	148.2 (±4.2)
1 week	35.35 (±10.33)	146.5 (±4.6)
1 month	64.79 (±11.42)	143.5 (± 2.0)
3 month	45.35 (±5.58)	138.3 (±4.5)
10 min Delay Cure Groups		
30 Min	63.05 (±13.91)	169.6 (±14.5)
1 Day	40.91 (±21.68)	146.7 (±11.3)
1 Week	38.27 (±16.49)	138.9 (±10.3)
1 Month	53.12 (±8.44)	139.8 (±4.0)
3 Month	42.66 (±4.71)	138.6 (±4.0)
Dark Cure Groups		
30 Min	7.215 (±6.59)	103 (±9.2)
	24.21 (±8.49)	165.7 (±11.3)
1 Day	22.2 (±11.19)	136.3 (±6.3)
1 Week	28.187 (±12.91)	136.5 (±13.4)
1 Month	43.713 (±9.36)	126.2 (±6.3)
3 Month	39.305 (±9.87)	136.4 (±8.4)

Table 3: Mean enthalpy and mean peak temperatures with standard deviations for the different time groups.

Light Initiation Group	Mean Enthalpy (J/g)	Mean Peak Temperature (^{o}C)
30 Min Groups		
Immediate Cure	20.67 (±6.90)	191.1 (±11.2)
5 min Delay Cure	35.63 (±11.72)	195.6 (±27.1)
10 min Delay Cure	63.05 (±13.91)	169.6(±14.5)
Dark Cure	7.22 (±6.59)	103 (±9.2)
	24.21 (±8.49)	165.7 (±11.3)
1 Day Groups		
Immediate Cure	10.96 (±5.46)	102.5 (±5.6)
5 min Delay Cure	32.08 (±7.17)	148.2 (±4.2)
10 min Delay Cure	40.91 (±21.68)	146.7 (±11.3)
Dark Cure	22.20 (±11.19)	136.3 (±6.3)
1 Week Groups		
Immediate Cure	21.87 (±8.22)	112.5 (±14.9)
5 min Delay Cure	35.35 (±10.33)	146.5 (±4.6)
10 min Delay Cure	38.27 (±16.49)	138.9 (±10.3)
Dark Cure	28.19 (±12.91)	136.5 (±13.4)
1 Month Groups		
Immediate Cure	28.86 (± 8.43)	109.9 (±3.6)
5 min Delay Cure	64.79 (±11.42)	143.5 (±2.0)
10 min Delay Cure	53.12 (±8.44)	139.8 (±4.0)
Dark Cure	43.71 (±9.36)	126.2 (±6.3)
3 Month Groups		
Immediate Cure	29.33 (±6.79)	116.4 (±10.8)
5 min Delay Cure	45.35 (±5.58)	138.3 (±4.5)
10 min Delay Cure	42.66 (±4.71)	138.6 (±4.0)
Dark Cure	39.31 (±9.87)	136.4 (±8.4)

Table 4: Post hoc test for enthalpy and peak temperature for different light initiation groups.

Light Initiation Group	Light Initiation Group	Enthalpy Significance (p-values)	Peak Temperature Significance (p-values)
Immediate cure	5 min Delay Cure	<0.001	<0.001
	10 min Delay Cure	<0.001	<0.001
	Dark Cure	0.08	0.11
5 min Delay Cure	10 min Delay Cure	0.20	0.004
	Dark Cure	<0.001	<0.001
10 min Delay Cure	Dark Cure	<0.001	<0.001

The post hoc analysis in Table 5 reveals significant differences existed between certain time groups for both enthalpy and peak temperature. In general, the peak temperature of the 30 min specimens was significantly different from all other time groups. For enthalpy, significant differences existed among some groups with 1 week, 1 month, and 3 month groups different from each other.

Table 5: Post hoc test for enthalpy and peak temperature for the different time groups.

Time Group	Time Group	Enthalpy Significance (p-values)	Peak Temperature Significance (p-values)
30 min	1 Day	0.23	<0.001
	1 Week	0.97	<0.001
	1 Month	<0.001	<0.001
	3 Months	0.12	<0.001
1 Day	1 Week	0.58	1.00
	1 Month	<0.001	0.67
	3 Months	<0.001	1.00
1 Week	1 Month	<0.001	0.72
	3 Months	0.02	1.00
1 Month	3 Months	0.02	0.87

As mentioned above, two-way ANOVA showed there was a significant ($p<0.001$) interaction between factors (cure conditions/group and time of evaluation/group). As a consequence, one- way ANOVA was performed to evaluate the individual effects among the different cure and time groups. The next sections will explore the different light initiation groups over time (e.g. immediate cure at 30 min, 1 day, etc.) and then compare the different light initiation groups at specific times (e.g. immediate cure, dark cure, and delay groups at 1 day).

Evaluation of Specimens by Light Initiation Group

Immediate Cure Groups

Table 6 gives the values of the mean enthalpies and mean peak temperatures with standard deviations along with the values of weight change in storage and DSC weight loss for the immediate cure group over time. One-way ANOVA of the immediate cure groups over time revealed significant differences in both the enthalpy and peak values ($p<0.001$). A Scheffe post hoc test was conducted to determine the differences in enthalpy and peak temperatures between the different time groups for the immediate cure specimens and the results are listed in Table 7. The mean enthalpies of the immediate cure groups showed an increasing trend with respect to storage time except for the 30 min group which did not follow this trend as it had a higher mean enthalpy than the 1 day specimens as viewed in Figure 9. However, this difference in enthalpy between the 30 min and the 1 day group for the immediate cure specimens was not statistically

significant ($p=0.139$). The results of the Scheffe post hoc test showed that the enthalpy of the 1 day specimens were significantly lower ($p=0.037$, $p<0.001$, $p<0.001$) compared to the other time groups (1 week, 1 month, and 3 month groups, respectively). There were no significant differences in enthalpy between the other groups.

The mean peak temperatures of the 1 day, 1 week, 1 month, and 3 month immediate cure group specimens were found to be similar at around 100^{o}C except the 30 min group which had a significantly higher ($p<0.001$) mean peak temperature at 191.1^{o}C (Figure 10).

Also observed was a trend for an increase in the weight absorbed in storage of the specimens of the immediate cure group as seen in Figure 11. The DSC weight loss of the 30 min and 1 day specimens should not be compared for the different light initiation groups as the initial experimental protocol consisted of subjecting the specimens to a temperature program of 37^{o}C to 600^{o}C as opposed to a maximum temperature of 300^{o}C that the rest of the specimens experienced. Hence, the DSC weight loss of specimens should be compared for all specimens except the 30 min and the 1 day specimen groups. Typical DSC thermograms of the immediate cure group specimens are shown in Figure 12 below.

Table 6: Mean enthalpy, peak temperature, weight change in storage and DSC weight loss of immediate cure specimens (The standard deviations are given in parentheses).

Immediate Cure Groups				
Time Group	**Mean Enthalpy (J/g)**	**Mean Peak Temperature (^{o}C)**	**Weight Absorbed in Storage (mg)**	**DSC Weight Loss (mg)**
30 min	20.67 (±6.90)	191.1 (±11.2)		
1 day	10.96 (±5.46)	102.5 (±5.6)	0.85 (±0.21)	
1 week	21.87 (±8.22)	112.5 (±14.9)	1.08 (±0.12)	6.65 (±0.91)
1 month	28.86 (±8.43)	109.9 (±3.6)	1.31 (±0.34)	7.04 (±0.79)
3 month	29.33 (±6.79)	116.4 (±10.8)	1.41 (±0.11)	7.13 (±0.75)

Table 7: Results of the Scheffe post hoc test for the immediate cure groups.

P-Values for Enthalpy of Immediate Cure Groups		
30 min	1 Day	0.139
	1 Week	0.998
	1 Month	0.284
	3 Months	0.232
1 Day	1 Week	0.037
	1 Month	<0.001
	3 Months	<0.001
1 Week	1 Month	0.345
	3 Months	0.280
1 Month	3 Months	1.000
P-Values for Peak Temperature of Immediate Cure Groups		
30 min	1 Day	<0.001
	1 Week	<0.001
	1 Month	<0.001
	3 Months	<0.001
1 Day	1 Week	0.304
	1 Month	0.612
	3 Months	0.064
1 Week	1 Month	0.986
	3 Months	0.943
1 Month	3 Months	0.711

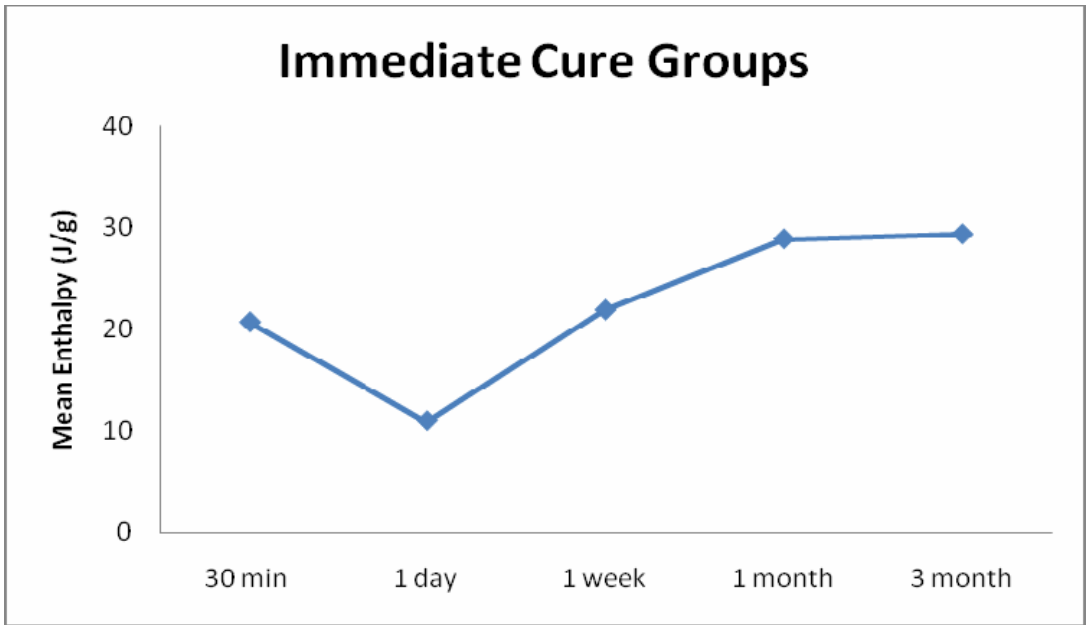

Figure 9: Average enthalpy values for the immediate cure groups.

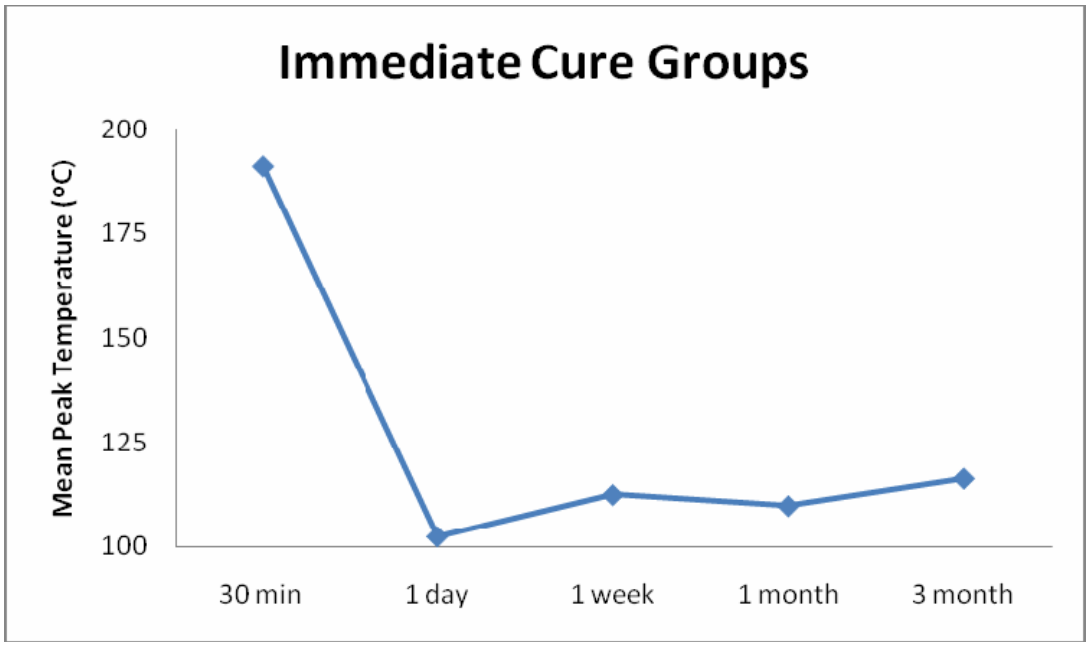

Figure 10: Average peak temperature values for the immediate cure groups.

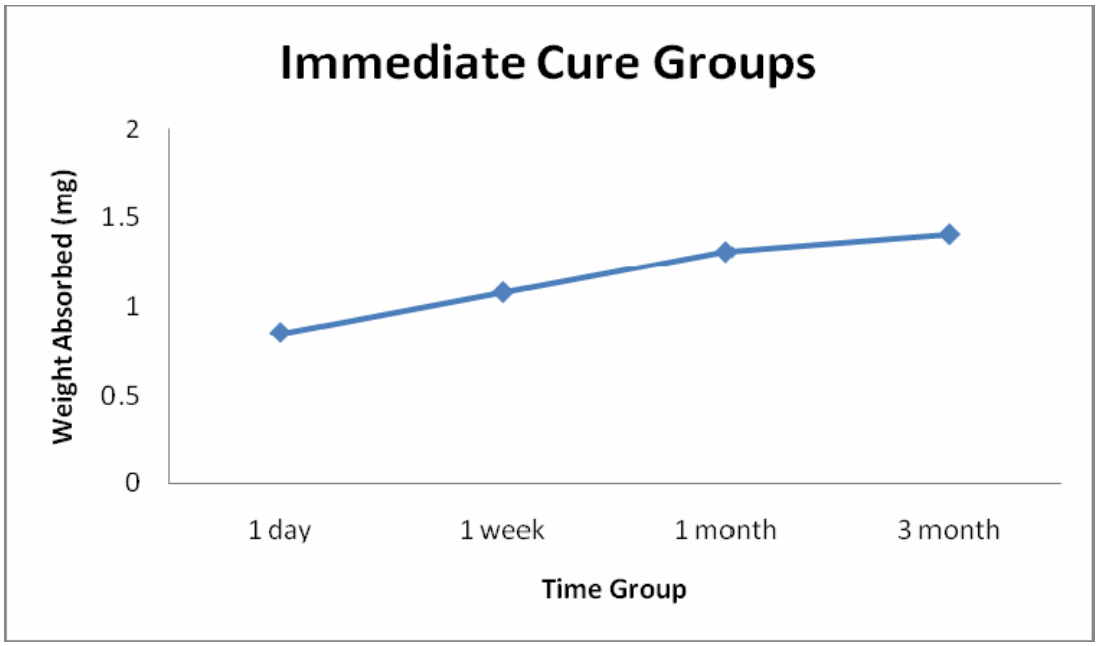

Figure 11: Average weight absorbed in storage for the immediate cure groups.

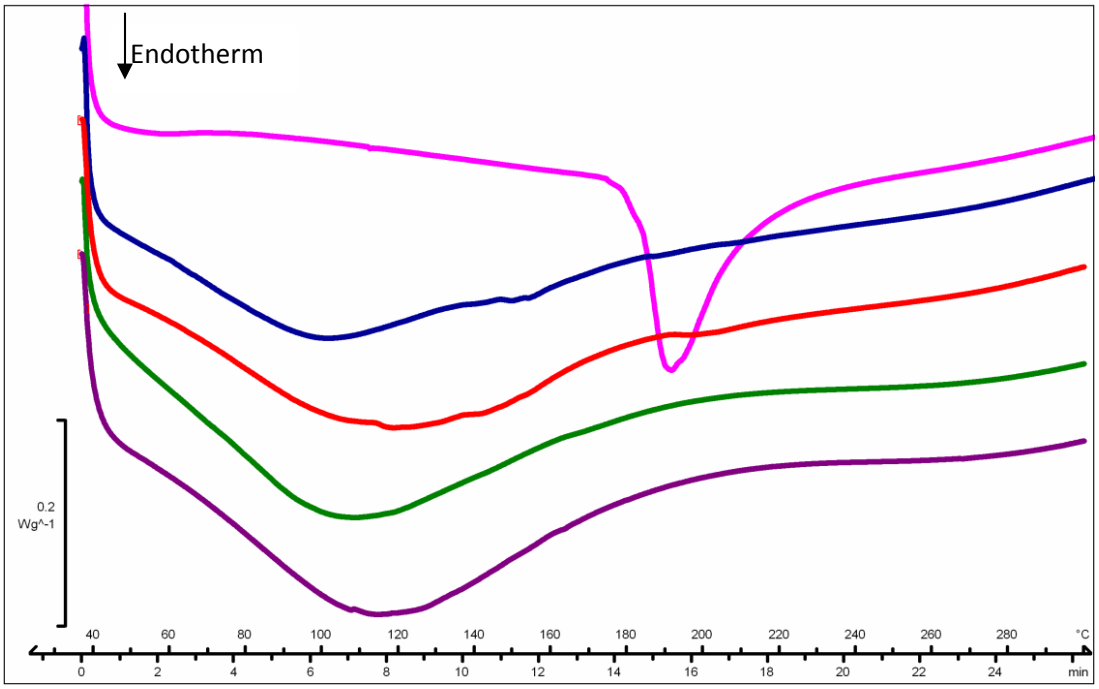

Figure 12: DSC thermogram for the immediate cure groups (Top to bottom, the curves are 30 Min, 1 Day, 1 Week, 1 Month, and 3 Month groups, respectively).

5 min Delay Cure Groups

Table 8 gives the values of the mean enthalpies and mean peak temperatures with standard deviations along with the values of weight change in storage and DSC weight loss for the 5 min delay cure group over time. One-way ANOVA of the 5 min delay cure groups over time revealed significant differences in both the enthalpy and peak temperature values ($p<0.001$). Scheffe post hoc test was conducted to determine the differences between the different time groups for the 5 min delay cure specimens and the results are listed in Table 9. Table 8 shows that the average enthalpy values of all time groups for the 5 min delay cure group were consistently similar except the 1 month group which had the highest enthalpy value (64.79 J/g) ($p<0.001$) compared to the other groups. The 3 month group was also had a higher enthalpy (45.35 J/g) but was not significantly different compared to the 1 month group ($p=0.99$). This can be observed in Figure 13. There were no significant differences in enthalpy between the other time groups for this cure group.

The mean peak temperatures for all the time groups was found to be similar except the 30 min group which had a higher mean peak temperature than the other groups ($p<0.001$) as observed in Figure 14. There were no significant differences in the peak temperatures of the other groups (Table 9).

The weight absorbed in storage of these specimens showed an increasing trend over time except for that of the 3 month group which showed a slightly lower weight gain in storage (1.29 mg) than the 1 month group which absorbed an average of 1.44 mg

(Figure 15). Typical DSC thermograms of the 5 min delay cure group specimens are shown in Figure 16 below.

Table 8: Mean enthalpy, peak temperature, weight change in storage and DSC weight loss of 5 min delay cure specimens (The standard deviations are given in parentheses).

5 Min Delay Cure Groups				
Time Group	**Mean Enthalpy (J/g)**	**Mean Peak Temperature (^{o}C)**	**Weight Absorbed in Storage (mg)**	**DSC Weight Loss (mg)**
30 min	35.63 (±11.72)	195.6 (±27.1)		5.55 (±0.46)
1 day	32.08 (±7.17)	148.2 (±4.2)	0.95 (±0.22)	
1 week	35.35 (±10.33)	146.5 (±4.6)	1.23 (±0.10)	6.92 (±0.43)
1 month	64.79 (±11.42)	143.5 (± 2.0)	1.44 (±0.38)	7.34 (±0.66)
3 month	45.35 (±5.58)	138.3 (±4.5)	1.29 (±0.20)	6.86 (±0.63)

Table 9: Results of the Scheffe post hoc test for the 5 min delay cure groups.

P-Values for Enthalpy of 5 min Delay Cure Groups		
30 min	1 Day	0.972
	1 Week	1.000
	1 Month	0.003
	3 Months	0.220
1 Day	1 Week	0.983
	1 Month	<0.001
	3 Months	0.057
1 Week	1 Month	0.003
	3 Months	0.219
1 Month	3 Months	0.442
P-Values for Peak Temperature of 5 min Delay Cure Groups		
30 min	1 Day	<0.001
	1 Week	<0.001
	1 Month	<0.001
	3 Months	<0.001
1 Day	1 Week	0.999
	1 Month	0.706
	3 Months	0.567
1 Week	1 Month	0.860
	3 Months	0.751
1 Month	3 Months	0.999

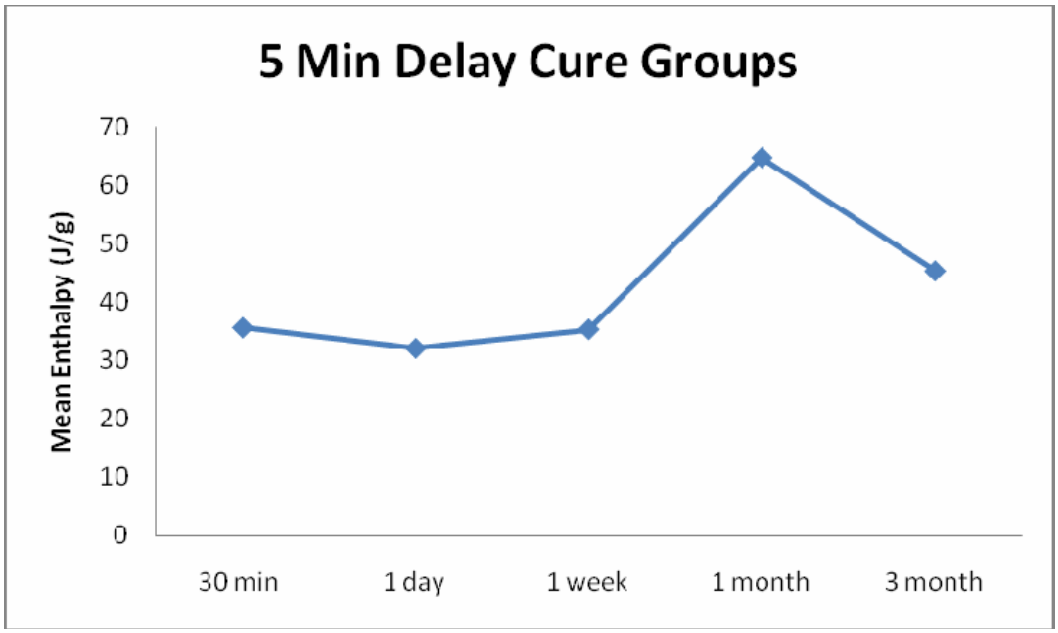

Figure 13: Average enthalpy values for the 5 min delay cure groups.

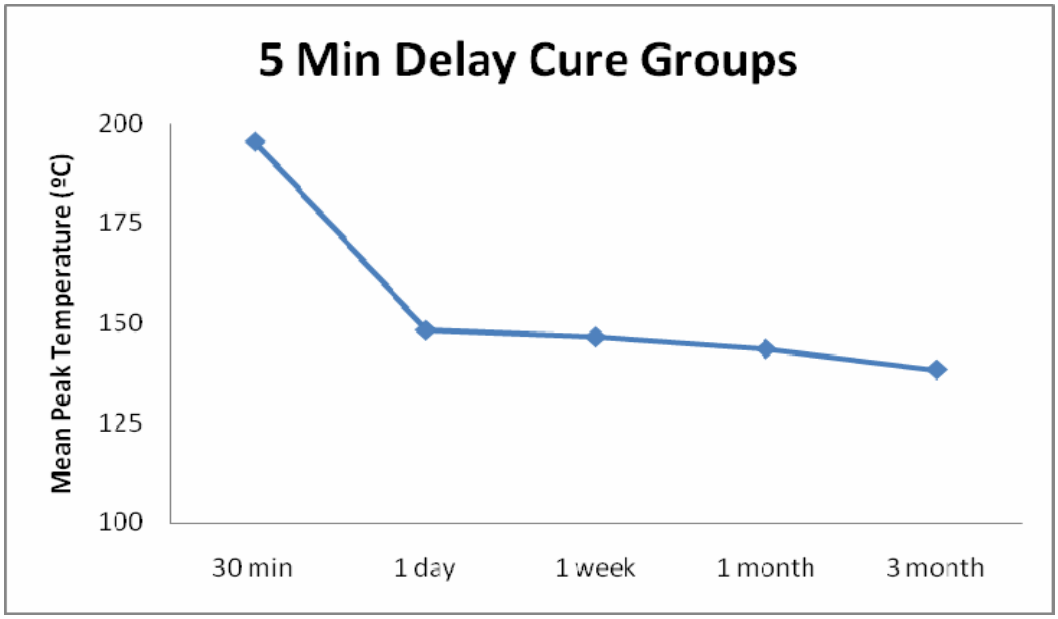

Figure 14: Average peak temperature values for the 5 min delay cure groups.

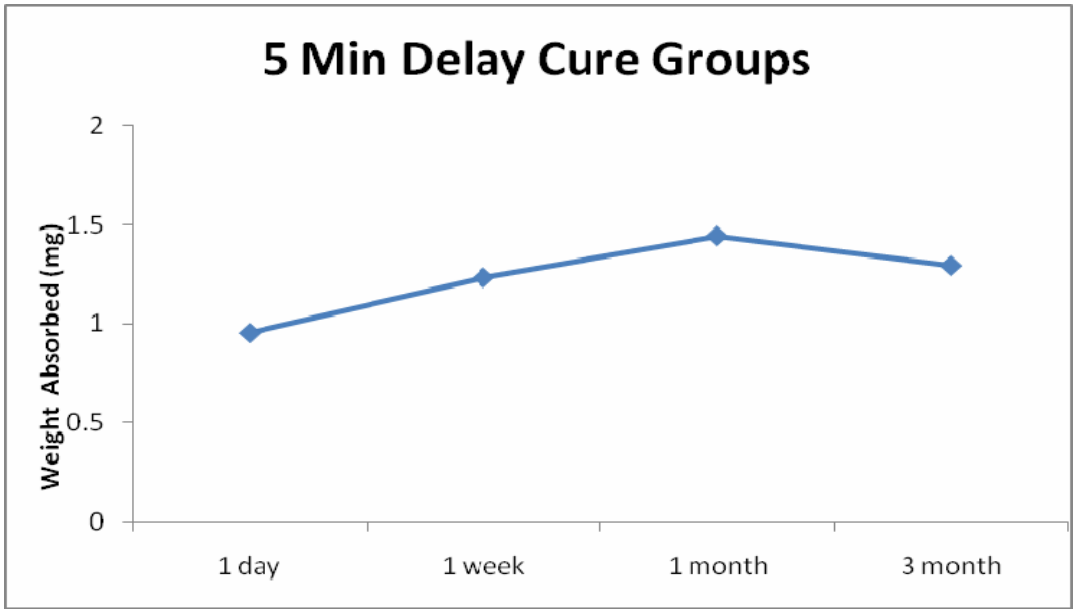

Figure 15: Average weight absorbed in storage for the 5 min delay cure groups.

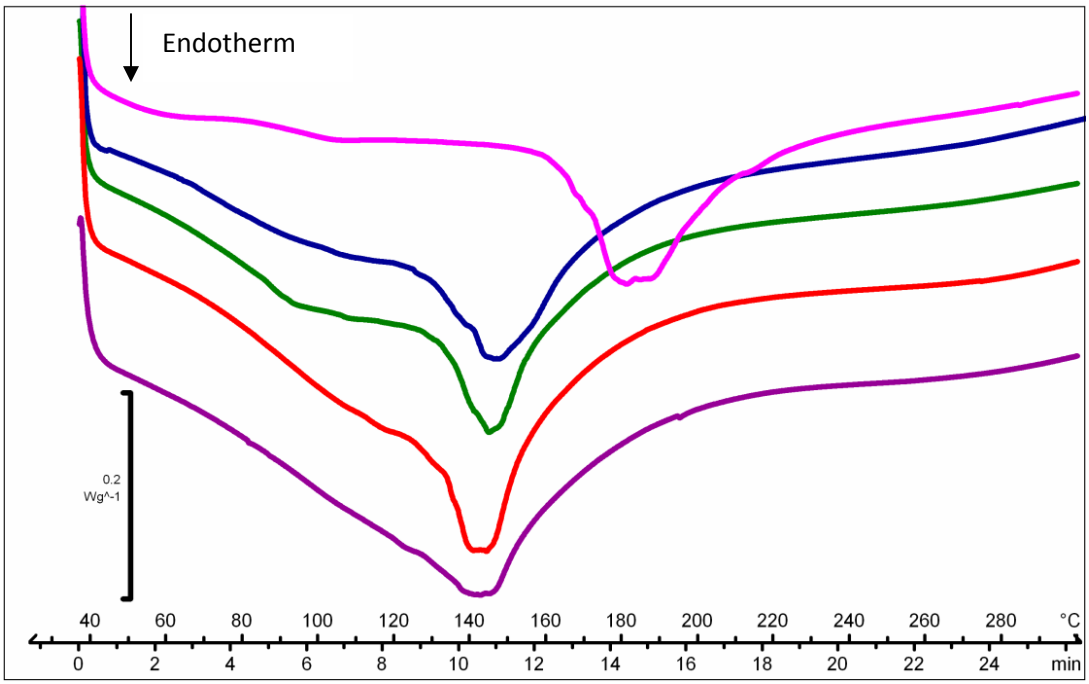

Figure 16: DSC thermograms for the 5 min delay cured groups (Top to bottom, the curves are 30 Min, 1 Day, 1 Week, 1 Month, and 3 Month groups, respectively).

10 min Delay Cure Groups

Table 10 gives the values of the mean enthalpies and mean peak temperatures with standard deviations along with the values of weight change in storage and DSC weight loss for the 10 min delay cure group over time. One-way ANOVA of the 10 min delay cure groups over time revealed significant differences in both the enthalpy and peak temperature values ($p<0.001$). A Scheffe post hoc test was conducted to determine the differences between the different time groups for the 10 min delay cure specimens and the results are listed in Table 11. The mean enthalpies of the 10 min delay cure groups did not seem to follow any increasing or decreasing trend with respect to time as seen in Figure 17. The 30 min specimen group had the highest mean enthalpy of 63.05 J/g compared to the other groups and the enthalpy of the 30 min group was found to be significantly different ($p=0.029$) from the 1 day group and 1 week group ($p=0.011$). There were no significant differences in enthalpy between the other time groups for this cure group (Table 11).

The mean peak temperatures of the 10 min delay cure group decreased from the 30 min specimens to the 1 day and the 1 week specimens but did not show much difference after 1 week of storage as viewed in Figure 18. Statistically, the peak temperatures of the 30 min specimens were found to be significantly higher ($p<0.001$) than all the other time groups but there were no significant differences in the peak temperatures of the other groups.

The weight absorbed in storage of all the time groups was similar with a slight increase in weight gain from the 1 month to 3 month specimens as observed in Figure 19.

Typical DSC thermograms of the 10 min delay cure group specimens are shown in Figure 20 below.

Table 10: Mean enthalpy, peak temperature, weight change in storage and DSC weight loss of 10 min delay cure specimens (The standard deviations are given in parentheses).

10 Min Delay Cure Groups				
Time Groups	**Mean Enthalpy (J/g)**	**Mean Peak Temperature (^{o}C)**	**Weight Absorbed in Storage (mg)**	**DSC Weight Loss (mg)**
30 min	63.05 (±13.91)	169.6 (±14.5)		
1 day	40.91 (±21.68)	146.7 (±11.3)	1.08 (±0.15)	6.46 (±0.90)
1 week	38.27 (±16.49)	138.9 (±10.3)	1.06 (±0.50)	6.47 (±0.62)
1 month	53.12 (±8.44)	139.8 (±4.0)	1.09 (±0.12)	6.51 (±0.96)
3 month	42.66 (±4.71)	138.6 (±4.0)	1.21 (±0.25)	6.49 (±0.68)

Table 11: Results of the Scheffe post hoc test for the 10 min delay cure groups.

P-Values for Enthalpy of 10 min Delay Cure Groups		
30 min	1 Day	0.029
	1 Week	0.011
	1 Month	0.665
	3 Months	0.054
1 Day	1 Week	0.996
	1 Month	0.470
	3 Months	0.999
1 Week	1 Month	0.270
	3 Months	0.976
1 Month	3 Months	0.620
P-Values for Peak Temperature of 10 min Delay Cure Groups		
30 min	1 Day	<0.001
	1 Week	<0.001
	1 Month	<0.001
	3 Months	<0.001
1 Day	1 Week	0.526
	1 Month	0.641
	3 Months	0.495
1 Week	1 Month	1.000
	3 Months	1.000
1 Month	3 Months	0.999

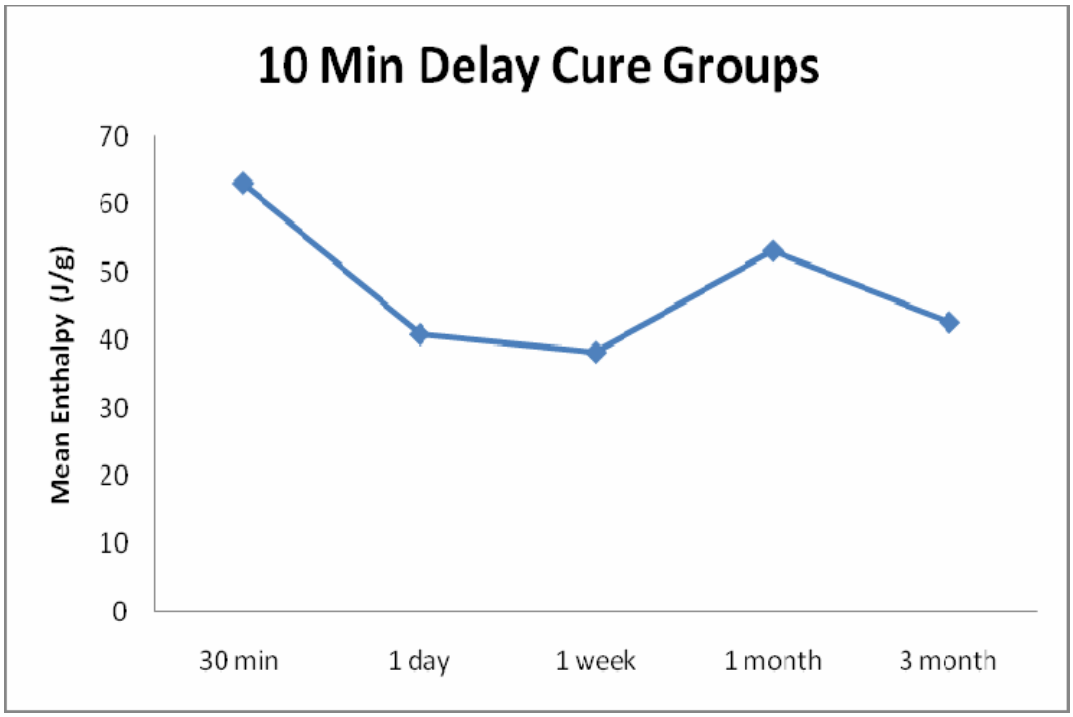

Figure 17: Average enthalpy values for the 10 min delay cure groups.

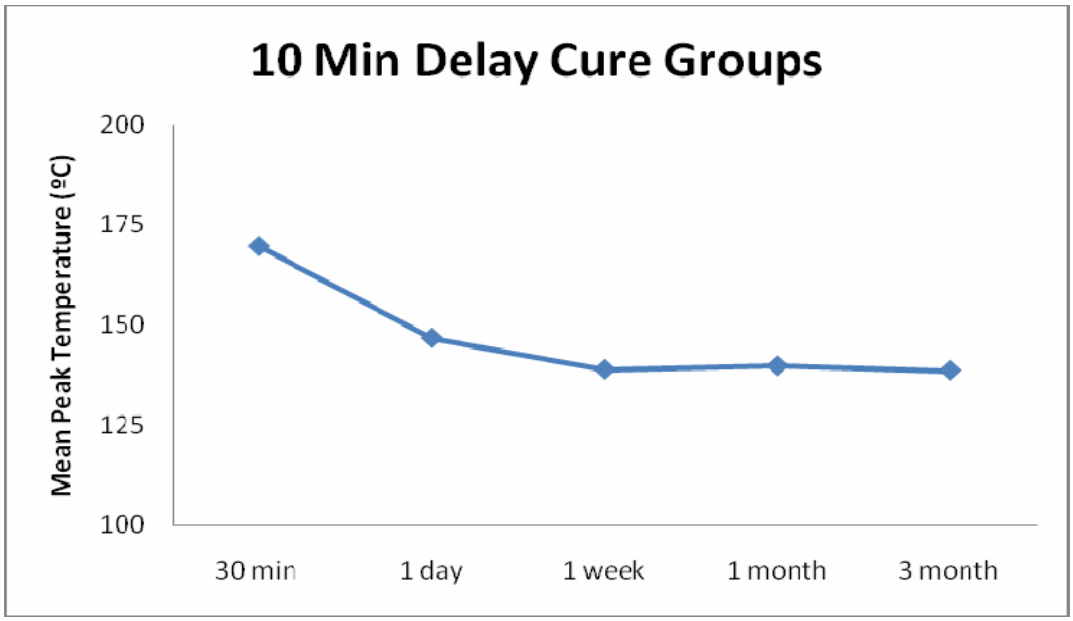

Figure 18: Average peak temperature values for the 10 min delay cure groups.

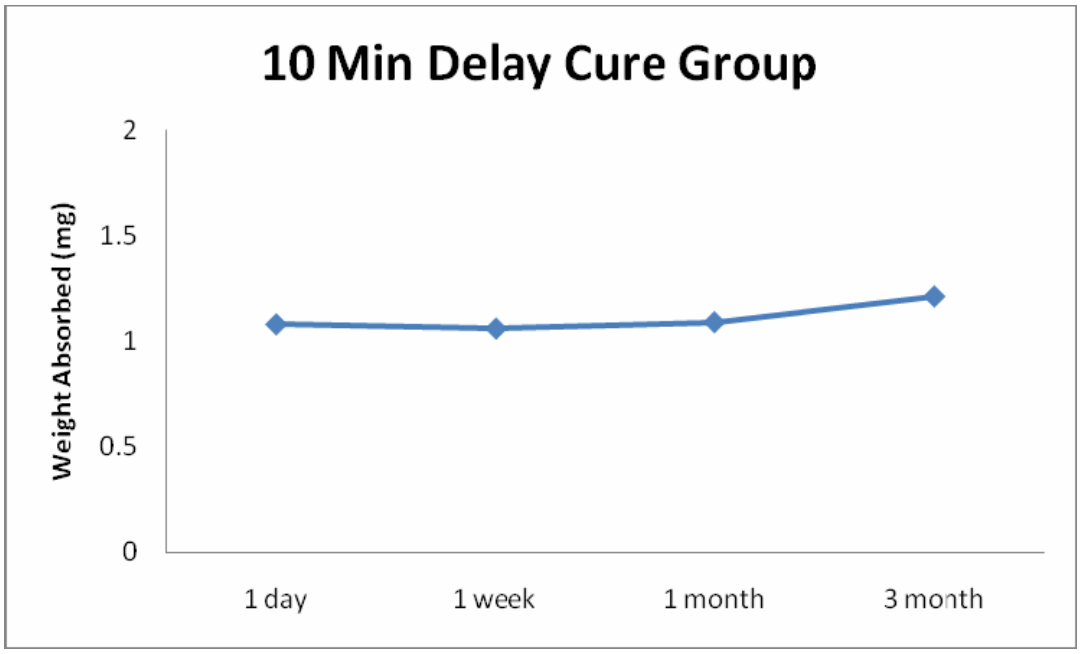

Figure 19: Average weight absorbed in storage for the 10 min delay cure groups.

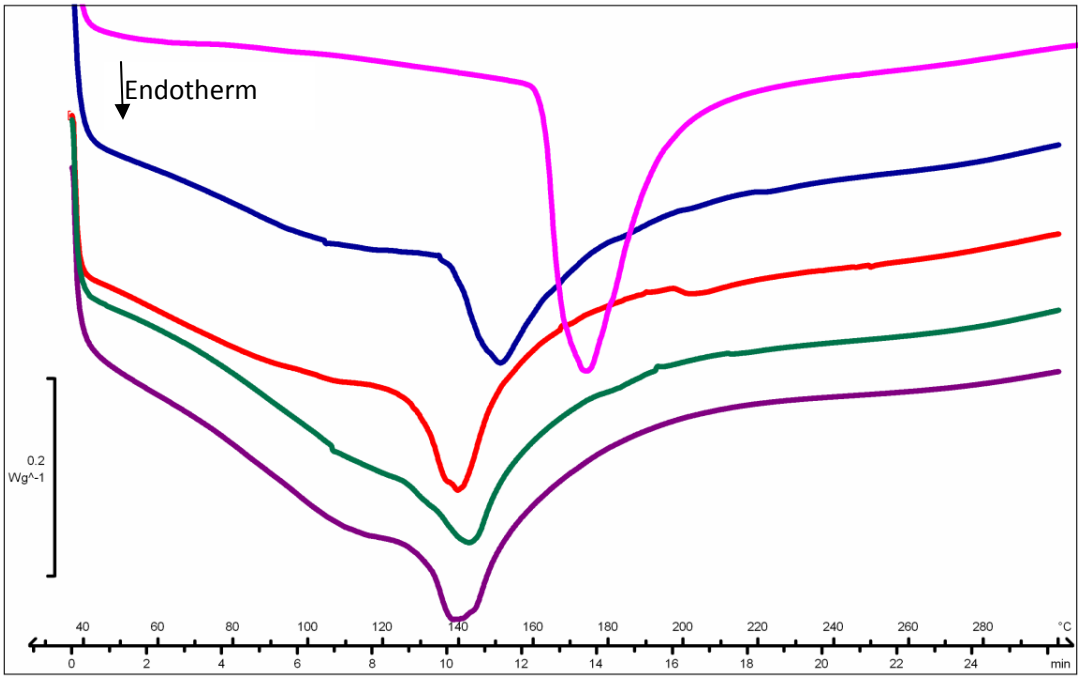

Figure 20: DSC thermograms for the 10 min delay cure groups (Top to bottom, the curves are 30 Min, 1 Day, 1 Week, 1 Month, and 3 Month groups, respectively).

Dark Cure Groups

Table 12 gives the values of the mean enthalpies and mean peak temperatures with standard deviations along with the values of weight change in storage and DSC weight loss for the dark cure group over time. One-way ANOVA of the dark cure groups over time revealed significant differences in both the enthalpy and peak temperature values ($p<0.001$). A Scheffe post hoc test was conducted to determine the differences between the different time groups for the dark cure specimens and the results are listed in Table 13. The enthalpy of the dark cure groups showed an increasing trend with increase in storage time until the 1 month group as seen in Figure 21. A Scheffe post hoc test revealed significant differences in the enthalpy values ($p<0.001$) between the 30 min specimens with the other time groups with the 30 min group specimens having the lowest enthalpy of 7.22 J/g. The enthalpy of the 1 month group was found to be significantly higher ($p<0.001$) than those of the other time groups except the 3 month group which did not have a significantly lower ($p=0.918$) enthalpy compared to the 1 month group. It should be noted that the 30 min group of the dark cure specimens typically contained two endothermic peaks in the temperature range tested and the enthalpy of the second peak was found to be around 24.21 J/g with the mean peak temperature of 165.7^{o}C. Since the temperature scan range was limited, the first peak was used for statistical comparisons to match the other groups where the first (and only visible) peak was used.

The peak temperature of the 30 min dark cure group (103^{o}C) was significantly lower ($p<0.001$) than the other time groups of the dark cure group (Figure 22). This observation was similar to the other light initiation groups (i.e. the immediate cure group,

and 5 and 10 min delay cure groups). There were no significant differences in the peak temperatures of the other groups.

Also noticed was a weight loss during the storage of the specimens unlike the light cured groups which showed a weight gain on storage in a humid environment. This weight loss did not follow any trend and was highest for the 3 month specimens (-1.25 mg) and lowest for the 1 day specimens (-0.65 mg) as seen in Figure 23. Typical DSC thermograms of the dark cure group specimens are shown in Figure 24 below.

Table 12: Mean enthalpy, peak temperature, weight change in storage and DSC weight loss of dark cure specimens (The standard deviations are given in parentheses).

Dark Cure Groups				
Time Groups	**Mean Enthalpy (J/g)**	**Mean Peak Temperature (^{o}C)**	**Weight Absorbed in Storage (mg)**	**DSC Weight Loss (mg)**
30 min	7.22 (±6.59) 24.21 (±8.49)	103.0 (±9.2) 165.7 (±11.3)		
1 day	22.20 (±11.19)	136.3 (±6.3)	-0.65 (±0.53)	
1 week	28.19 (±12.91)	136.5(±13.4)	-0.99 (±0.98)	8.34 (±1.10)
1 month	43.71 (±9.36)	126.2 (±6.3)	-0.7 (±1.40)	7.34 (±1.12)
3 month	39.31 (±9.87)	136.4 (±8.4)	-1.25 (±0.36)	7.36 (±0.78)

Table 13: Results of the Scheffe post hoc test for the dark cure groups.

P-Values for Enthalpy of Dark Cure Groups		
30 min	1 Day	0.043
	1 Week	<0.001
	1 Month	<0.001
	3 Months	<0.001
1 Day	1 Week	0.786
	1 Month	<0.001
	3 Months	0.014
1 Week	1 Month	0.032
	3 Months	0.223
1 Month	3 Months	0.918
P-Values for Peak Temperature of Dark Cure Groups		
30 min	1 Day	<0.001
	1 Week	<0.001
	1 Month	<0.001
	3 Months	<0.001
1 Day	1 Week	1.000
	1 Month	0.210
	3 Months	0.100
1 Week	1 Month	0.187
	3 Months	1.000
1 Month	3 Months	0.195

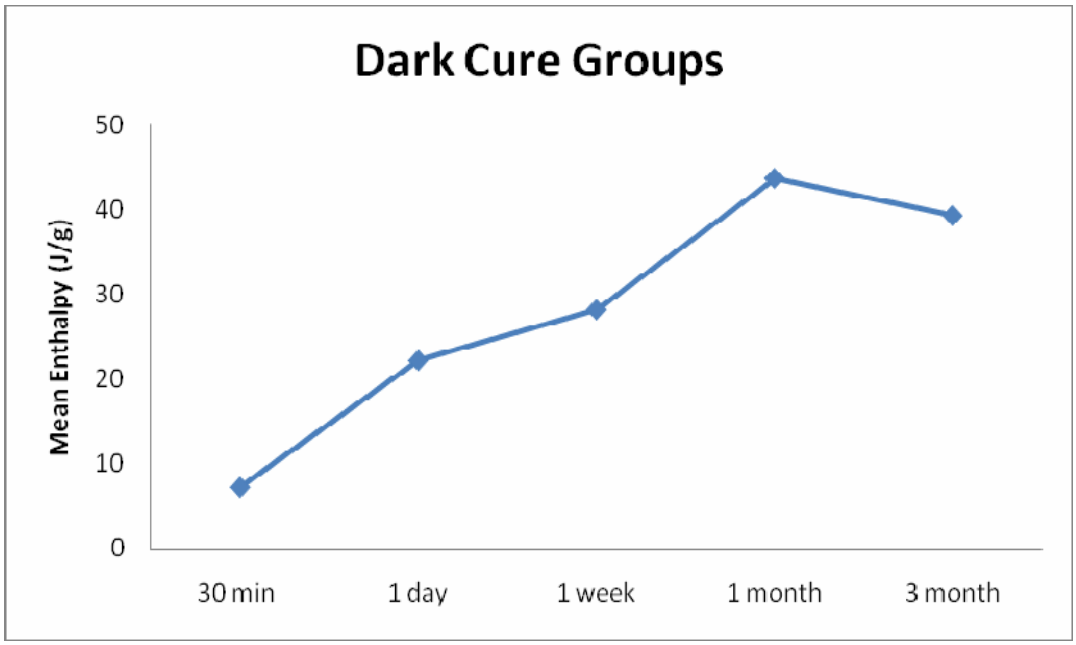

Figure 21: Average enthalpy values for the dark cure groups.

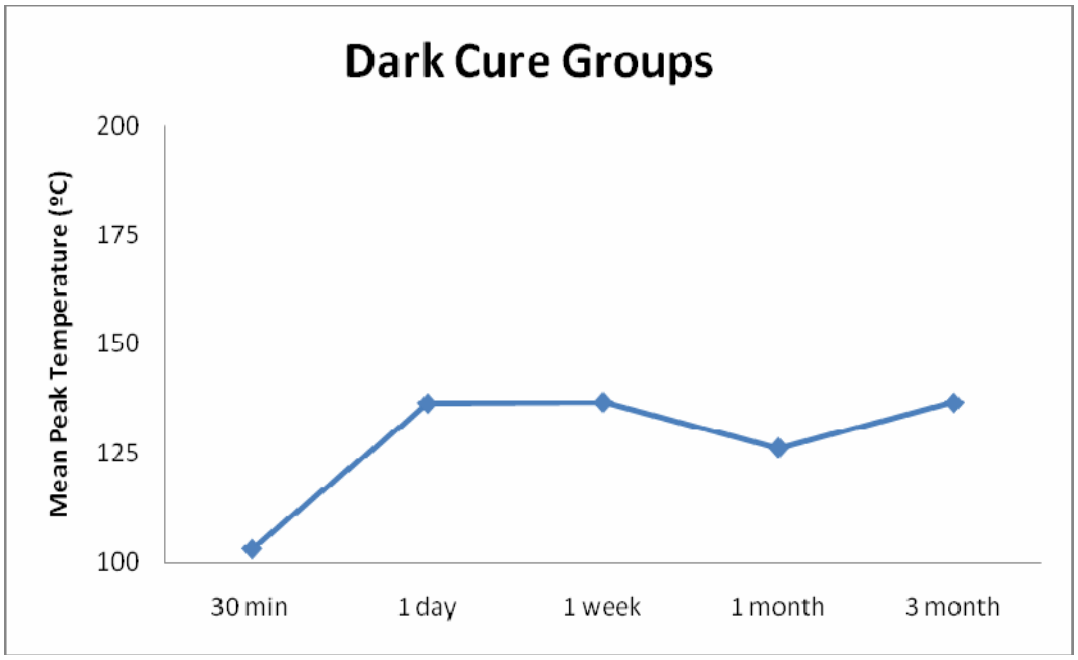

Figure 22: Average peak temperature for the dark cure groups.

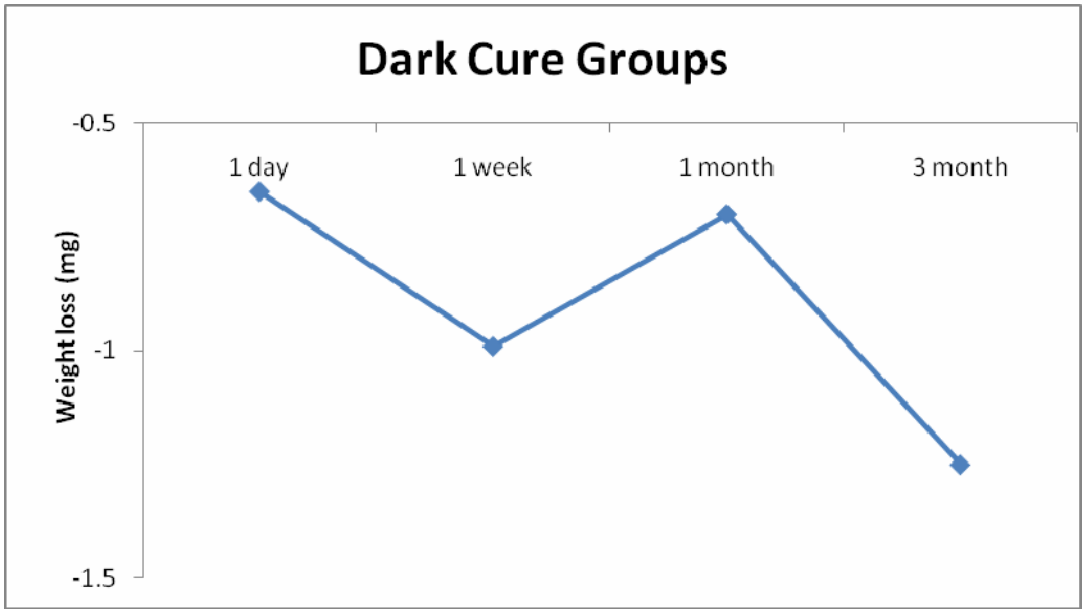

Figure 23: Average weight loss in storage for the dark cure groups.

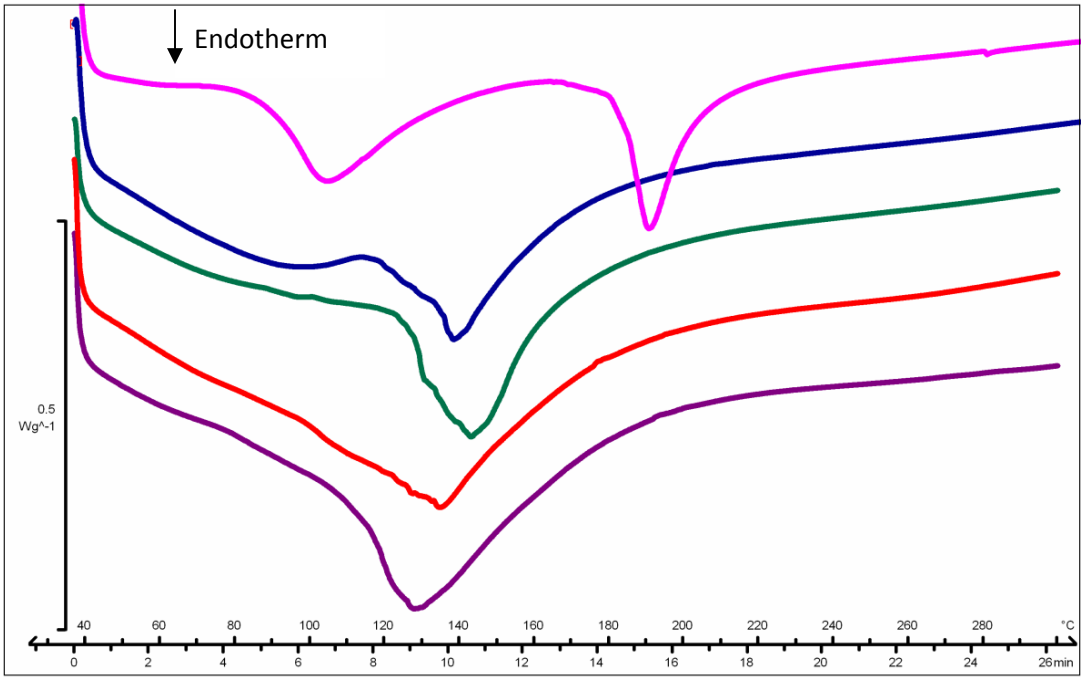

Figure 24: DSC thermograms for the dark cure groups (Top to bottom, the curves are 30 Min, 1 Day, 1 Week, 1 Month, and 3 Month groups, respectively).

Evaluation of Specimens by Time Group

30 Min Specimens

Table 14 gives the values of the mean enthalpies and mean peak temperatures with standard deviations for all the light initiation group specimens of the 30 min group. One-way ANOVA of the 30 min groups revealed significant differences in both the enthalpy and peak temperature values ($p<0.001$). A Scheffe post hoc test was conducted to determine the differences between the different light initiation groups for the 30 min specimens and the results are listed in Table 15. The mean enthalpies of the 30 min specimens were found to be dependent on the light initiation of the specimens. There was an increase in the mean enthalpy with an increase in delay of light initiation as seen in Figure 25. The enthalpy of the 10 min delay cure specimens was significantly greater ($p<0.001$) than the other specimen groups. The dark cure group had the lowest enthalpy of 7.26 J/g which was significantly different from the 5 and the 10 min delay cure groups ($p<0.001$), but was not significantly lower ($p=0.102$) than that of the immediate cure group specimens.

Figure 26 reveals that the mean peak temperature of the 30 min specimens showed a decreasing trend with an increase in delay of light initiation from the 5 min delay cure specimens to the 10 min delay cure specimens. Significant differences in temperatures ($p=0.021$) were found between the 5 min and the 10 min cure groups. The peak temperature of the 10 min delay cure specimens were also significantly lower ($p<0.001$) than that of the immediate cure specimens. The mean peak temperature of the

dark cure groups was found to be the lowest (103^{o}C) which was significantly different ($p<0.001$) from those of all the other groups.

The 30 min group specimens were not accounted for weight change in storage or DSC weight loss because the specimens were examined with different temperatures in the DSC compared to other groups. Typical DSC thermograms of the 30 min group specimens are shown in Figure 27 below. As mentioned above, the dark cure group of the 30 min group specimens typically contained two endothermic peaks in the temperature range tested and the enthalpy of the second peak was found to be around 24.21 J/g with the mean peak temperature of 165.7^{o}C.

Table 14: Mean enthalpy and mean peak temperatures of the 30 min group specimens (The standard deviations for the mean enthalpy and mean peak temperature are given in parentheses).

30 Min Groups		
Cure Group	**Mean Enthalpy (J/g)**	**Mean Peak Temperature (^{o}C)**
Immediate Cure	20.67 (±6.90)	191.1 (±11.2)
5 min delay	35.63 (±11.72)	195.6 (±27.1)
10 min delay	63.05 (±13.91)	169.6 (±14.5)
Dark Cure	7.26 (±6.59)	103.0 (±9.2)

Table 15: Results of the Scheffe post hoc test for the 30 min groups.

P-Values for Enthalpy of 30 Min Groups		
Immediate Cure	5 min Cure	0.057
	10 min Cure	<0.001
	Dark Cure	0.102
5 min Cure	10 min Cure	<0.001
	Dark Cure	<0.001
10 min Cure	Dark Cure	<0.001
P-Values for Peak Temperature of 30 Min Groups		
Immediate Cure	5 min Cure	0.964
	10 min Cure	0.121
	Dark Cure	<0.001
5 min Cure	10 min Cure	0.021
	Dark Cure	<0.001
10 min Cure	Dark Cure	<0.001

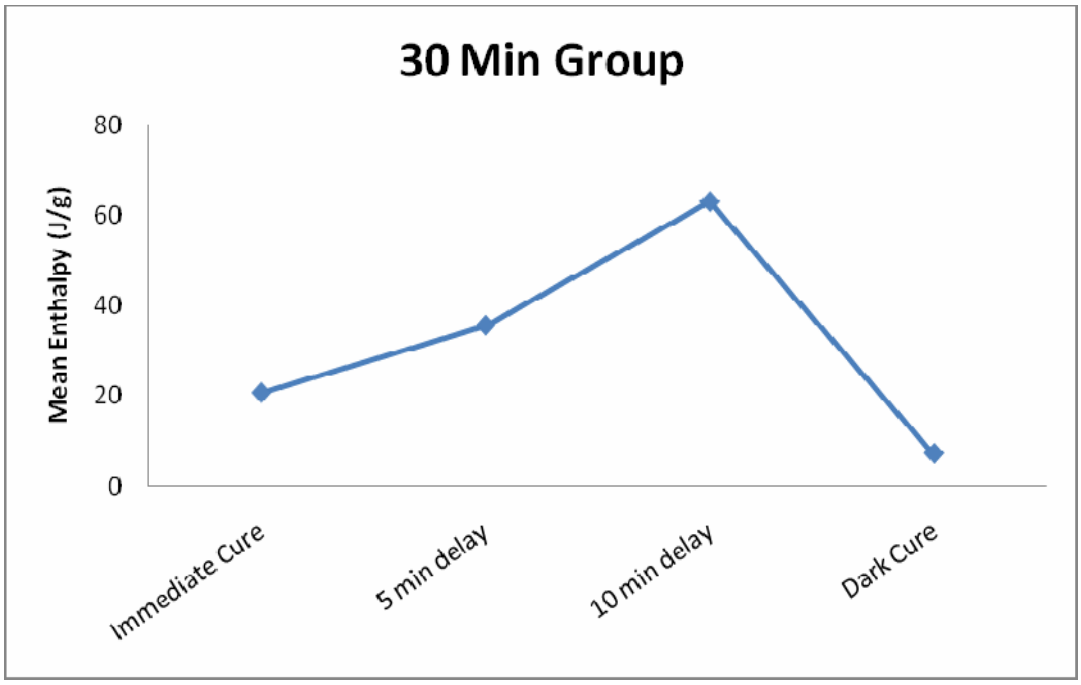

Figure 25: Average enthalpy values for the 30 min groups.

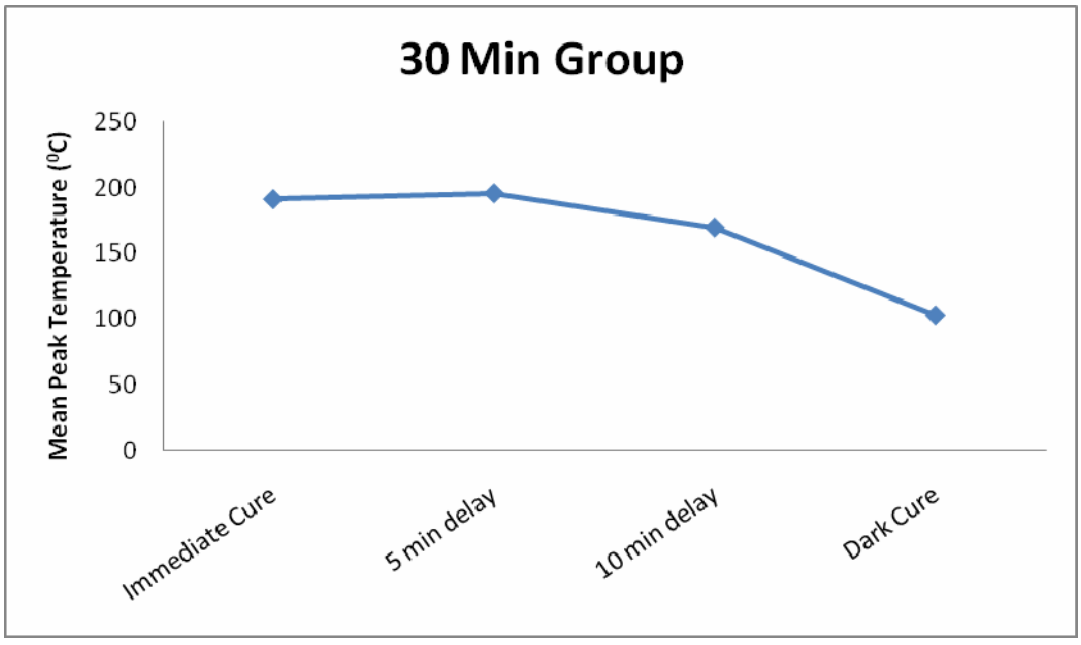

Figure 26: Average peak temperature values for the 30 min groups.

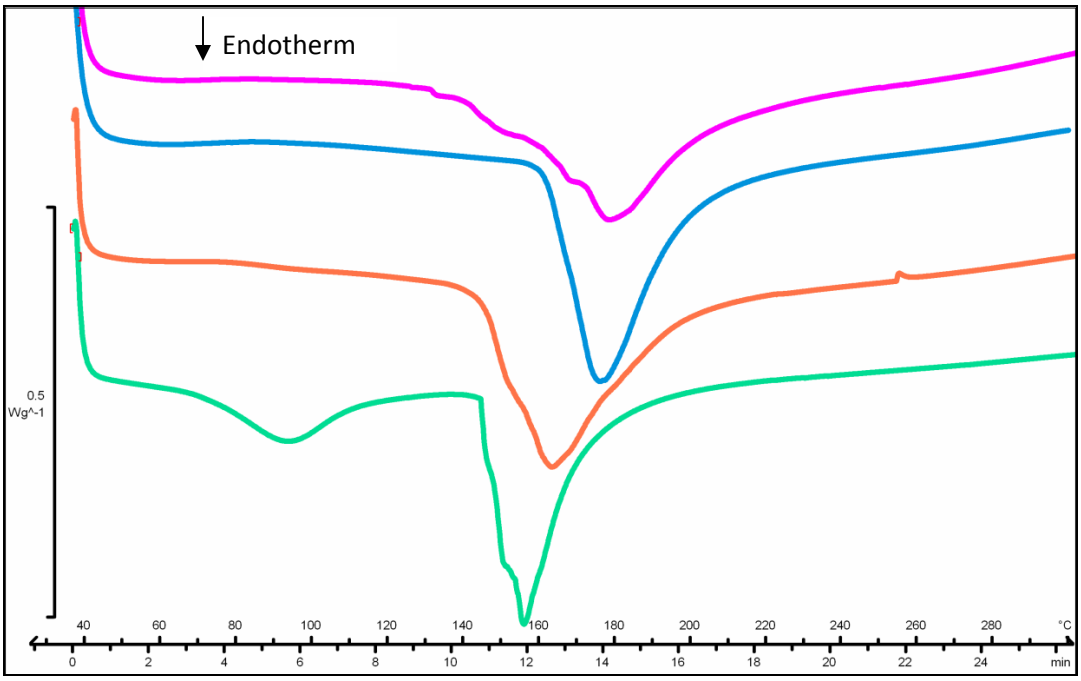

Figure 27: DSC thermograms for the 30 min groups (Top to bottom the curves are the immediate cure, 5 min delay, 10 min delay, and dark cure groups, respectively).

1 Day Specimens

Table 16 gives the values of the mean enthalpies and mean peak temperatures with standard deviations for all the light initiation group specimens of the 1 day group. One-way ANOVA of the 1 day groups revealed significant differences in both the enthalpy and peak temperature values ($p<0.001$). A Scheffe post hoc test was conducted to determine the differences between the different light initiation groups for the 1 day group specimens and the results are listed in Table 17. The mean enthalpies of the 1 day specimens followed a similar increasing trend for enthalpy with respect to an increase in delay in light initiation as that of the 30 min specimens which can be observed in Figure 28, with the enthalpies of the 5 and 10 min delay cure specimens being significantly

higher ($p=0.007$ and $p<0.001$, respectively) than that of the immediate cure specimens. The mean enthalpy of the dark cure specimens (22.2 J/g) was higher than that of the immediate cure specimens (10.96 J/g) but lower than the 5 min and the 10 min cure specimens (32.81 J/g and 40.91 J/g respectively) but was significantly different ($p=0.027$) only from the 10 min delay cure specimens.

Figure 29 shows that the mean peak temperature of the different light initiation groups and the dark cure group did not show any specific increasing or decreasing trend for the 1 day group as it did for the 30 min group although the mean peak temperature increased from the immediate cure group to the 5 min delay cure group. The mean peak temperature of the immediate cure group (102.5^{o}C) was significantly lower ($p<0.001$) than the other groups of the 1 day group specimens. Also, like the 30 min group, the peak temperatures of the dark cure group were found to be significantly different ($p<0.001$) from that of all the other light initiation groups. There were no significant differences in the peak temperatures of the 5 and 10 min cure groups ($p=0.974$).

The weight absorbed in storage showed an increasing trend with respect to delay in light initiation as seen in Figure 30. There was a net weight loss in the dark cure specimens of the 1 day group. Typical DSC thermograms of the 1 day group specimens are shown in Figure 31 below.

Table 16: Mean enthalpy, peak temperature, weight change in storage and DSC weight loss of 1 day groups (The standard deviations are given in parentheses).

1 Day Groups			
Cure Group	**Mean Enthalpy (J/g)**	**Mean Peak Temperature (^{o}C)**	**Weight Absorbed in Storage (mg)**
Immediate Cure	10.96 (±5.46)	102.5 (±5.6)	0.85 (±0.21)
5 min Delay Cure	32.08 (±7.17)	148.2 (±4.2)	0.95 (±0.22)
10 min Delay Cure	40.91 (±21.68)	146.7 (±11.3)	1.08 (±0.15)
Dark Cure	22.20 (±11.19)	136.3 (±6.3)	-0.65 (±0.53)

Table 17: Results of the Scheffe post hoc test for the 1 day groups.

P-Values for Enthalpy of 1 Day Groups		
Immediate Cure	5 min Cure	0.007
	10 min Cure	<0.001
	Dark Cure	0.308
5 min Cure	10 min Cure	0.590
	Dark Cure	0.358
10 min Cure	Dark Cure	0.027
P-Values for Peak Temperature of 1 Day Groups		
Immediate Cure	5 min Cure	<0.001
	10 min Cure	<0.001
	Dark Cure	<0.001
5 min Cure	10 min Cure	0.974
	Dark Cure	0.010
10 min Cure	Dark Cure	0.031

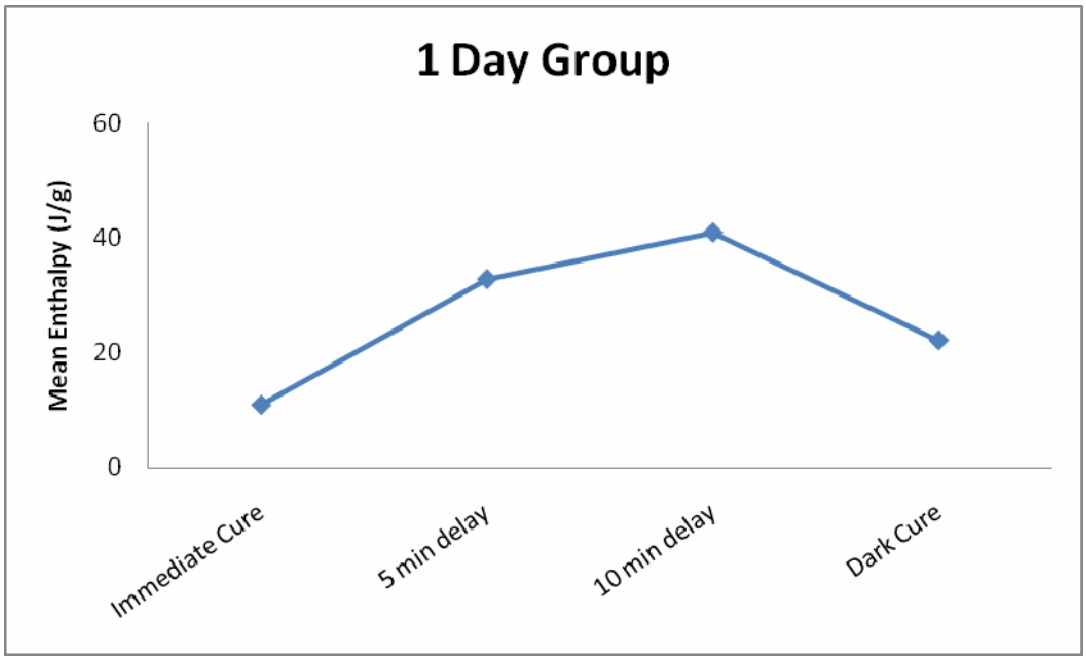

Figure 28: Average enthalpy values for the 1 day groups.

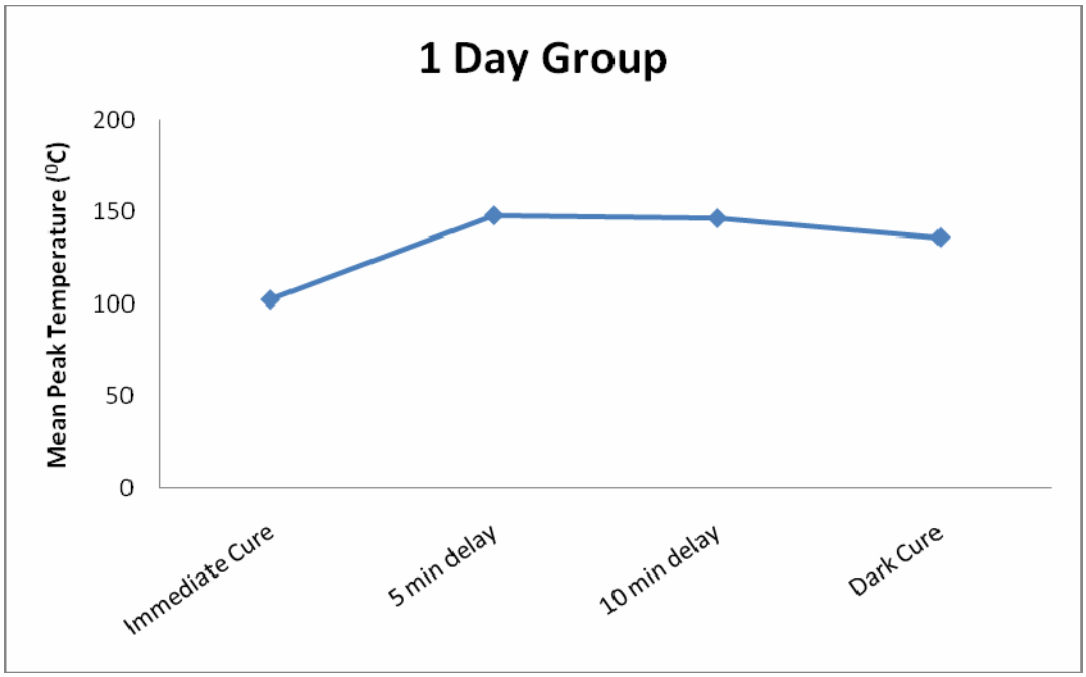

Figure 29: Average peak temperature values for the 1 day groups.

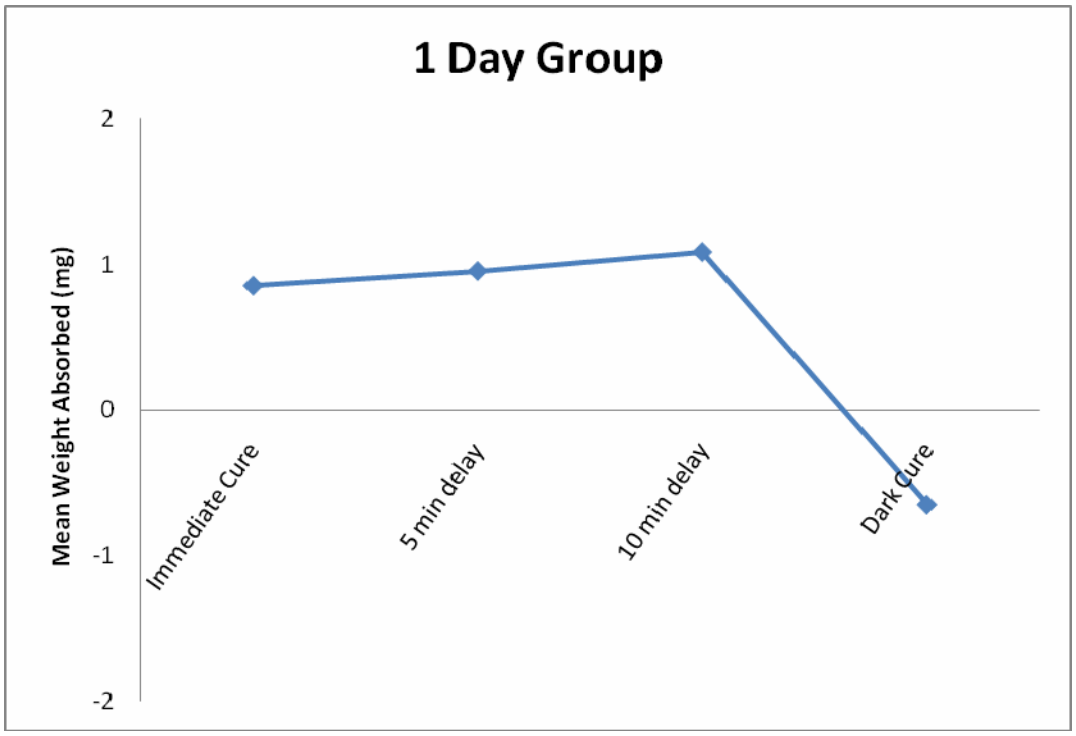

Figure 30: Average weight absorbed in storage for the 1 day groups.

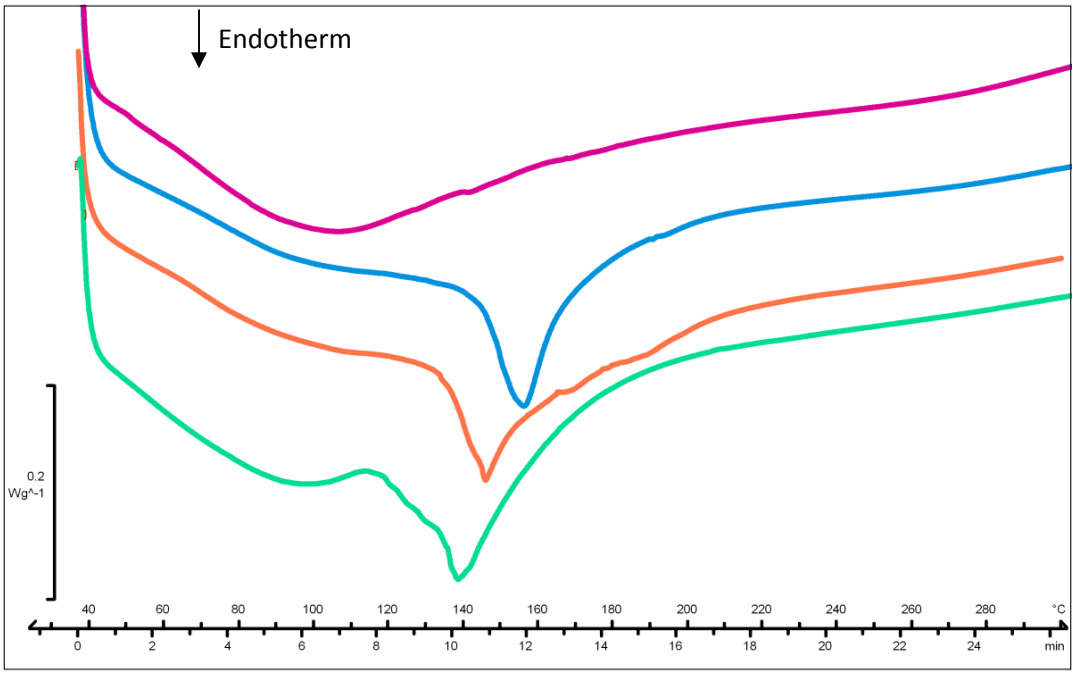

Figure 31: DSC thermograms for the 1 day groups (Top to bottom the curves are the immediate cure, 5 min delay, 10 min delay, and dark cure groups, respectively).

1 Week Specimens

Table 18 gives the values of the mean enthalpies and mean peak temperatures with standard deviations for all the light initiation group specimens of the 1 week group. One-way ANOVA of the 1 week groups revealed significant differences in both the enthalpy and peak temperature values ($p<0.001$). A Scheffe post hoc test was conducted to determine the differences between the different light initiation groups for the 1 week group specimens and the results are listed in Table 19. The 1 week specimen groups behaved in a similar manner in terms of mean enthalpy and mean peak temperature values as the 1 day specimen group. Figure 32 shows that the mean enthalpy values for the 1 week group showed an increasing trend with the increase in delay of light initiation. The mean enthalpy of the 10 min delay cure group (38.27 J/g) was significantly higher ($p=0.049$) than that of the immediate cure group (21.87 J/g). There were no significant differences in enthalpy between the other light initiation groups of the 1 week specimens.

Figure 33 reveals no observable increasing or decreasing trend with the mean peak temperature of the 1 week specimen group. The mean peak temperature of the immediate cure specimens (112.5^{o}C) was observed to be significantly lower ($p<0.001$) than that of the other group specimens of the 1 week group.

The weight absorbed in storage for the 1 week specimens also did not show any increasing or decreasing trend with respect to light initiation as seen in Figure 34. It can be observed in Figure 35 that the mean DSC weight loss for the 1 week specimens are similar for all light initiation groups, with the dark cure specimens having the highest

mean DSC weight loss (-8.34 mg). Typical DSC thermograms of the 1 week group specimens are shown in Figure 36 below.

Table 18: Mean enthalpy, peak temperature, weight change in storage and DSC weight loss of 1 week groups (The standard deviations are given in parentheses).

1 Week Groups				
Cure Group	**Mean Enthalpy (J/g)**	**Mean Peak Temperature (^{o}C)**	**Weight Absorbed in Storage (mg)**	**DSC Weight Loss (mg)**
Immediate Cure	21.87 (±8.22)	112.5 (±14.9)	1.08 (±0.12)	6.65 (±0.90)
5 min Delay Cure	35.35 (±10.33)	146.5 (±4.6)	1.23 (±0.10)	6.92 (±0.43)
10 min Delay Cure	38.27 (±16.49)	138.9 (±10.3)	1.06 (±0.49)	6.45 (±0.60)
Dark Cure	28.19 (±12.91)	136.5 (±13.4)	-0.99 (±0.98)	8.34 (±1.10)

Table 19: Results of the Scheffe post hoc test for the 1 week groups.

P-Values for Enthalpy of 1 Week Groups		
Immediate Cure	5 min Cure	0.155
	10 min Cure	0.049
	Dark Cure	0.733
5 min Cure	10 min Cure	0.967
	Dark Cure	0.668
10 min Cure	Dark Cure	0.364
P-Values for Peak Temperature of 1 Week Groups		
Immediate Cure	5 min Cure	<0.001
	10 min Cure	<0.001
	Dark Cure	<0.001
5 min Cure	10 min Cure	0.572
	Dark Cure	0.343
10 min Cure	Dark Cure	0.978

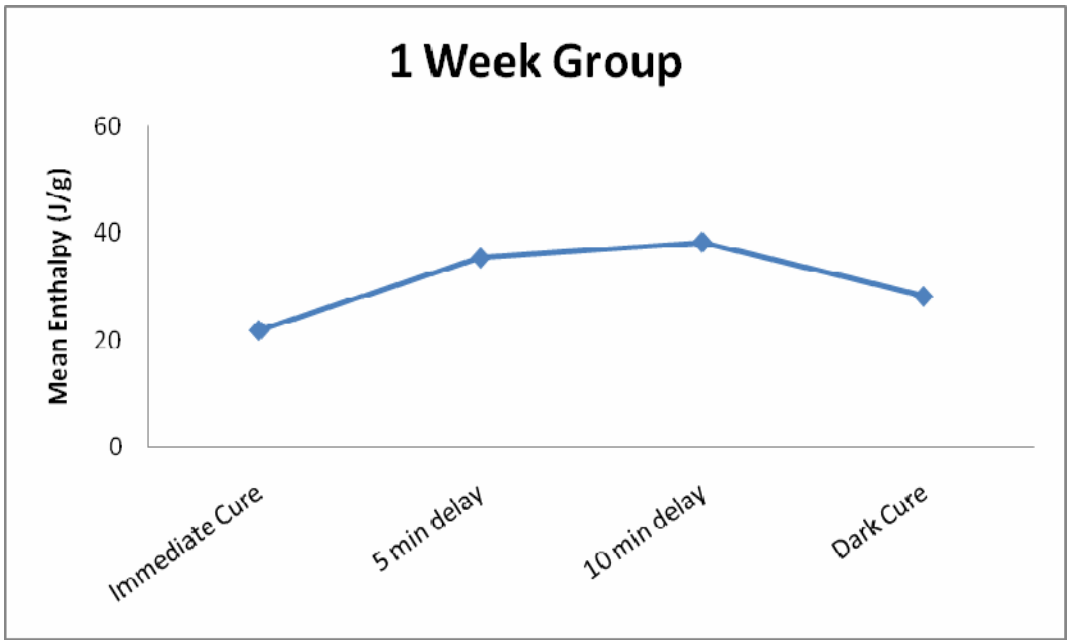

Figure 32: Average enthalpy values for the 1 week groups.

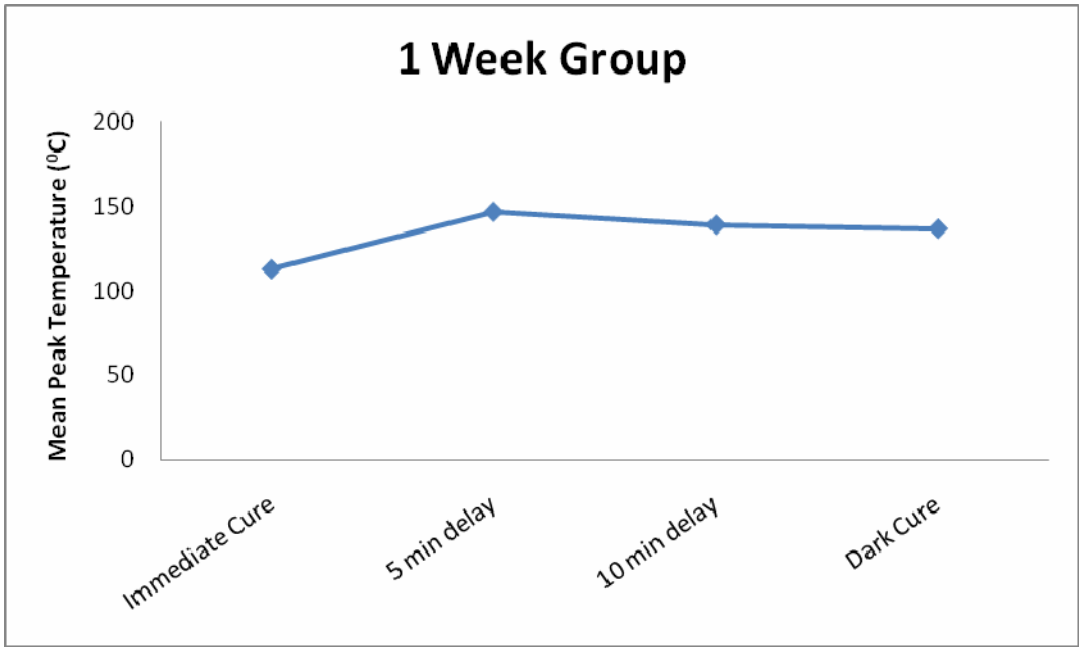

Figure 33: Average peak temperature for the 1 week groups.

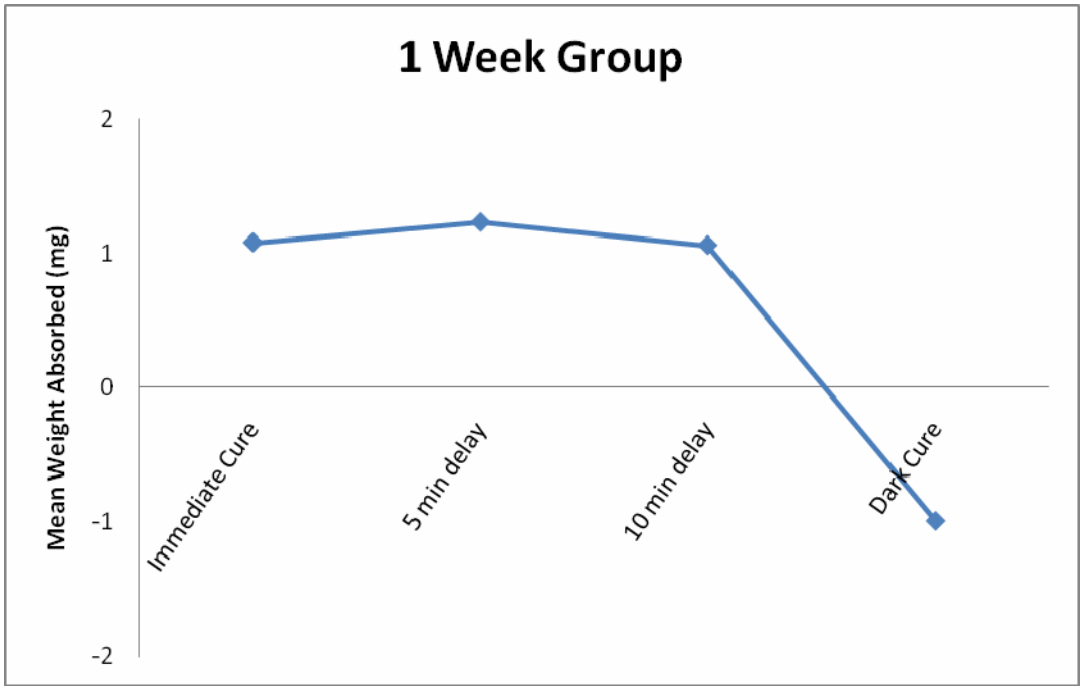

Figure 34: Average weight absorbed in storage for the 1 week groups.

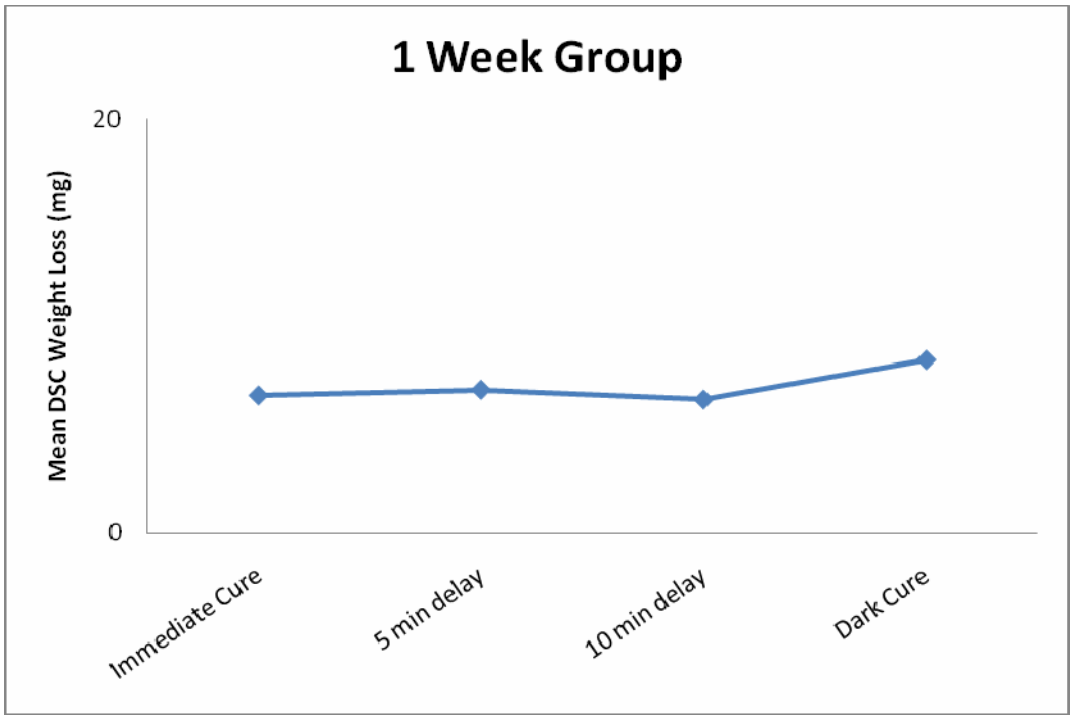

Figure 35: Average DSC weight loss for the 1 week groups.

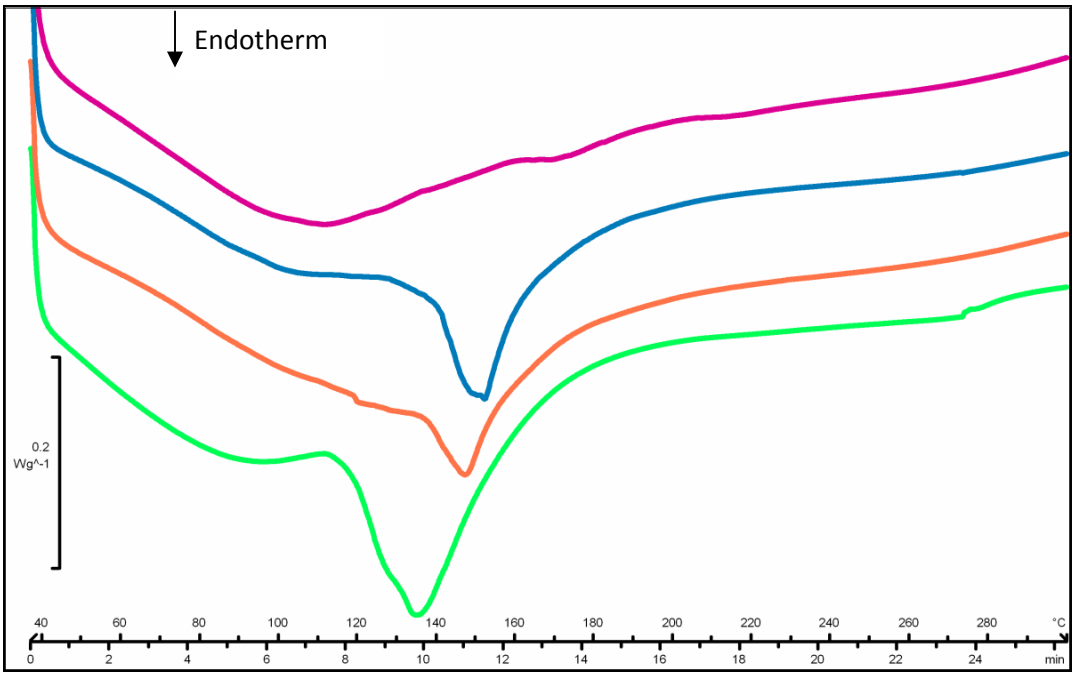

Figure 36: DSC thermograms for 1 week groups (Top to bottom the curves are the immediate cure, 5 min delay, 10 min delay, and dark cure groups, respectively).

1 Month Specimens

Table 20 gives the values of the mean enthalpies and mean peak temperatures with standard deviations for all the light initiation group specimens of the 1 month group. One-way ANOVA of the 1 month groups revealed significant differences in both the enthalpy and peak temperature values ($p<0.001$). A Scheffe post hoc test was conducted to determine the differences between the different light initiation groups for the 1 month group specimens and the results are listed in Table 21. Figure 37 shows that the mean enthalpy of the 1 month specimens did not seem to be affected by the light initiation regimen. The immediate cure group had the lowest enthalpy (28.86 J/g) which was significantly lower ($p<0.001$) than the other light initiation groups and also significantly lower ($p=0.014$) than the dark cure group. A significant difference in enthalpy ($p<0.001$) was also found between the dark cure group and the 5 min delay cure group. There was no significant difference in the enthalpy ($p=0.073$) of the 5 min cure and the 10 min cure groups and also between the 10 min cure and the dark cure group ($p=0.198$).

The mean peak temperature of the immediate cure group was found to be the lowest (109.9^{o}C) as observed in Figure 38. This is significantly lower ($p<0.001$) than the mean enthalpies of the other groups of the 1 month specimens. The peak temperature of the dark cure group was also significantly different ($p<0.001$) from the other light initiation groups. There was no significant difference ($p=0.285$) found in the peak temperatures between the 5 min and the 10 min delay cure groups for the 1 month specimens.

The weight absorbed in storage did not show any specific increasing or decreasing trend related to the light initiation regimen for the 1 month group specimens as observed in Figure 39. The mean DSC weight loss was similar for all light cure groups of 1 month specimens, with the 10 min cure specimens having the lowest value of 6.61 mg (Figure 40). Typical DSC thermograms of the 1 month group specimens are shown in Figure 41 below.

Table 20: Mean enthalpy, peak temperature, weight change in storage and DSC weight loss of 1 month groups (The standard deviations are given in parentheses).

1 Month Groups				
Cure Group	**Mean Enthalpy (J/g)**	**Mean Peak Temperature (^{o}C)**	**Weight Absorbed in Storage (mg)**	**DSC Weight Loss (mg)**
Immediate Cure	28.86 (± 8.43)	109.9 (±3.6)	1.31 (±0.34)	7.04 (±0.78)
5 min Delay Cure	64.79 (±11.42)	143.5 (±2.0)	1.44 (±0.38)	7.34 (±0.66)
10 min Delay Cure	53.12 (±8.44)	139.8 (±4.0)	1.09 (±0.12)	6.51 (±0.96)
Dark Cure	43.71 (±9.36)	126.2 (±6.3)	-0.7 (±1.40)	7.34 (±1.12)

Table 21: Results of the Scheffe post hoc test for the 1 month groups.

P-Values for Enthalpy of 1 Month Groups		
Immediate Cure	5 min Cure	<0.001
	10 min Cure	<0.001
	Dark Cure	0.014
5 min Cure	10 min Cure	0.073
	Dark Cure	<0.001
10 min Cure	Dark Cure	0.198
P-Values for Peak Temperature of 1 Month Groups		
Immediate Cure	5 min Cure	<0.001
	10 min Cure	<0.001
	Dark Cure	<0.001
5 min Cure	10 min Cure	0.285
	Dark Cure	<0.001
10 min Cure	Dark Cure	<0.001

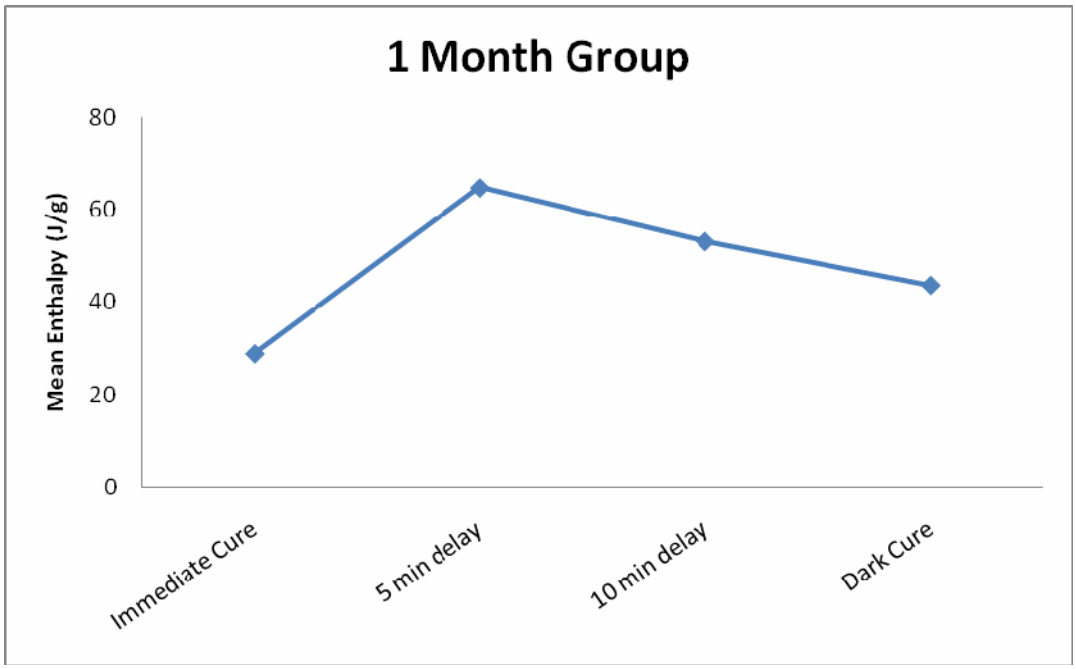

Figure 37: Average enthalpy values for the 1 month groups.

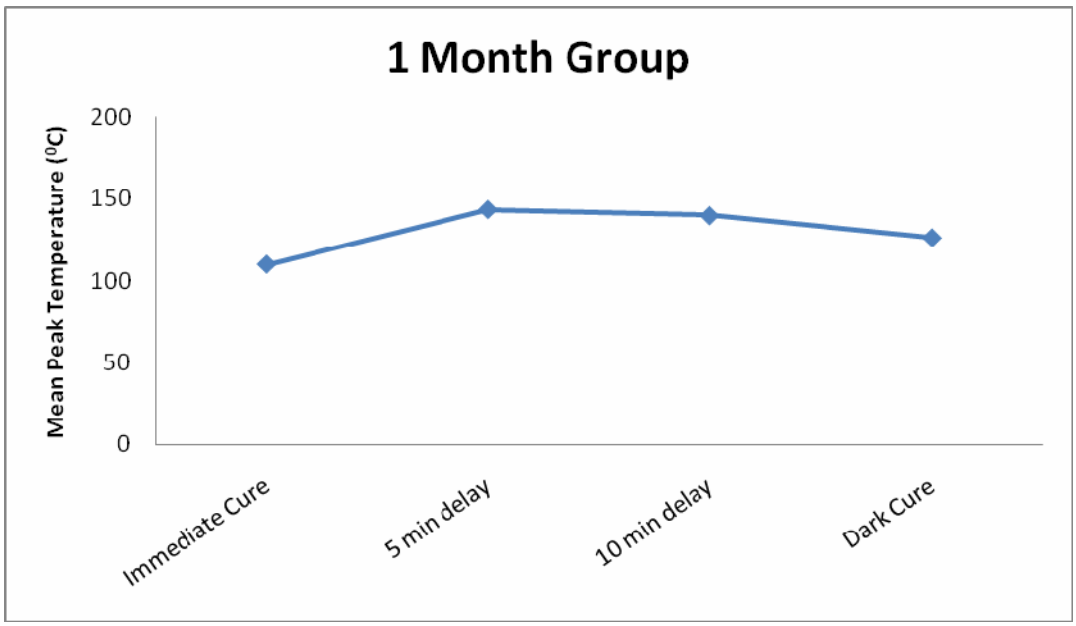

Figure 38: Average peak temperature for the 1 month groups.

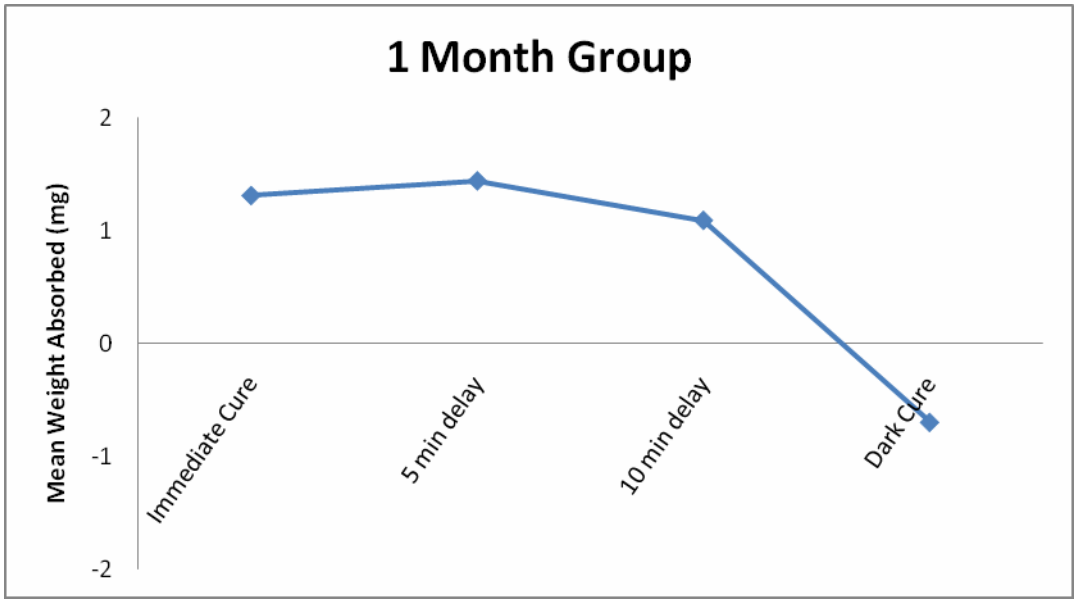

Figure 39: Average weight absorbed in storage for the 1 month groups.

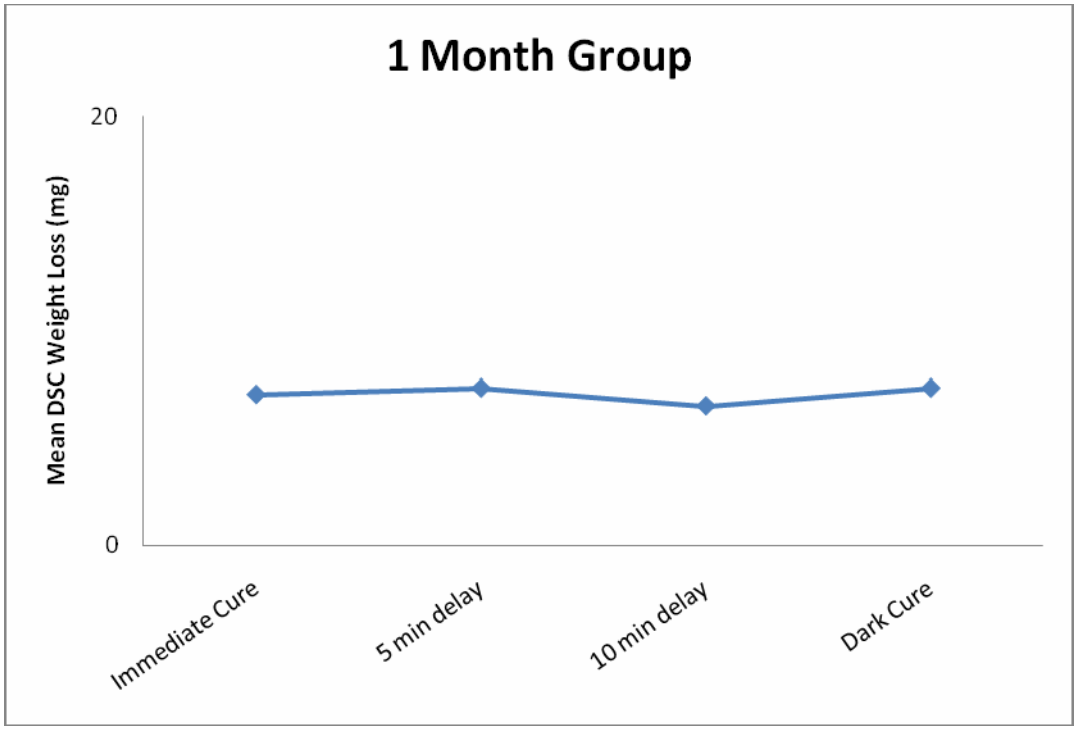

Figure 40: Average DSC weight loss for the 1 month groups.

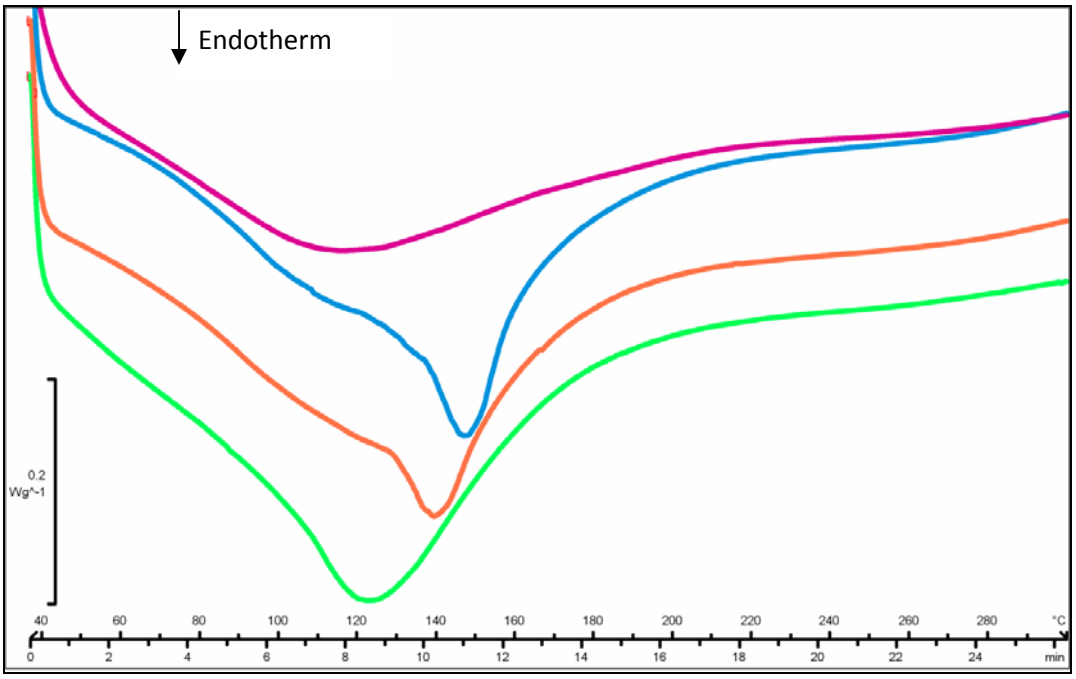

Figure 41: DSC thermograms for 1 month groups (Top to bottom the curves are the immediate cure, 5 min delay, 10 min delay, and dark cure groups, respectively).

3 Month Specimens

Table 22 gives the values of the mean enthalpies and mean peak temperatures with standard deviations for all the light initiation group specimens of the 3 month group. One-way ANOVA of the 3 month groups revealed significant differences in both the enthalpy and peak temperature values ($p<0.001$). A Scheffe post hoc test was conducted to determine the differences between the different light initiation groups for the 3 month group specimens and the results are listed in Table 23. Figure 42 shows that the mean enthalpy of the 3 month specimens increased with an increase in delay of light initiation. The mean enthalpies of the 5 min and the 10 min delay light cured groups were similar ($p=0.864$; 45.35 J/g and 42.66 J/g, respectively). The immediate cure group had the

lowest enthalpy of 29.33 J/g which was significantly lower ($p<0.001$) than those of all the other groups of the 3 month specimens. There was no significant difference in the enthalpy between the other cure groups.

The peak temperature results of the 3 month specimens were similar to that of the 1 week specimens. The mean peak temperature of the different light initiation groups for the 3 month specimens did not follow any trend although the mean peak temperatures increased with the increase in delay of light initiation as viewed in Figure 43. The mean peak temperature of the immediate cure group (116.4^{o}C) was found to be significantly lower ($p<0.001$) than that of the other groups of the 3 month specimens. There was no significant difference found in the peak temperatures between the other groups for the 3 month specimens.

The weight absorbed in storage did not show any increasing or decreasing trend with respect to light initiation regimen and the values were similar for the different groups as observed in Figure 44. The graph for DSC mean weight loss for the 3 month specimens (Figure 45) showed no association with the light initiation regimen of the specimens and again, the 10 min cure specimens had the lowest DSC weight loss of 6.49 mg compared to the other cure groups of the 3 month group. Typical DSC thermograms of the 3 month group specimens are shown in Figure 46 below.

Table 22: Mean enthalpy, peak temperature, weight change in storage and DSC weight loss of 3 month groups (The standard deviations are given in parentheses).

3 Month Groups				
Cure Group	**Mean Enthalpy (J/g)**	**Mean Peak Temperature (^{o}C)**	**Weight Absorbed in Storage (mg)**	**DSC Weight Loss (mg)**
Immediate Cure	29.33 (±6.79)	116.4 (±10.8)	1.41 (±0.11)	7.13 (±0.75)
5 min Delay Cure	45.35 (±5.58)	138.3 (±4.5)	1.29 (±0.20)	6.86 (±0.63)
10 min Delay Cure	42.66 (±4.71)	138.6 (±4.0)	1.21 (±0.25)	6.49 (±0.68)
Dark Cure	39.31 (±9.87)	136.4 (±8.4)	-1.25 (±0.36)	7.36 (±0.78)

Table 23: Results of the Scheffe post hoc test for the 3 month groups.

P-Values for Enthalpy of 3 Month Groups		
Immediate Cure	5 min Cure	<0.001
	10 min Cure	0.002
	Dark Cure	0.029
5 min Cure	10 min Cure	0.864
	Dark Cure	0.310
10 min Cure	Dark Cure	0.767
P-Values for Peak Temperature of 3 Month Groups		
Immediate Cure	5 min Cure	<0.001
	10 min Cure	<0.001
	Dark Cure	<0.001
5 min Cure	10 min Cure	1.000
	Dark Cure	0.958
10 min Cure	Dark Cure	0.936

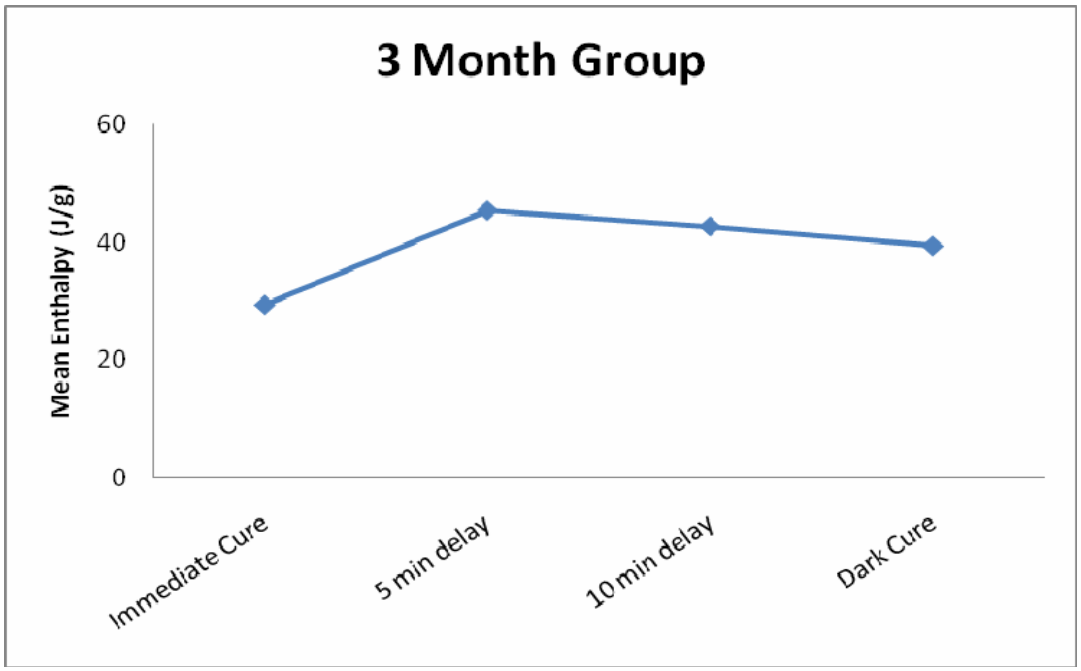

Figure 42: Average enthalpy values for the 3 month groups.

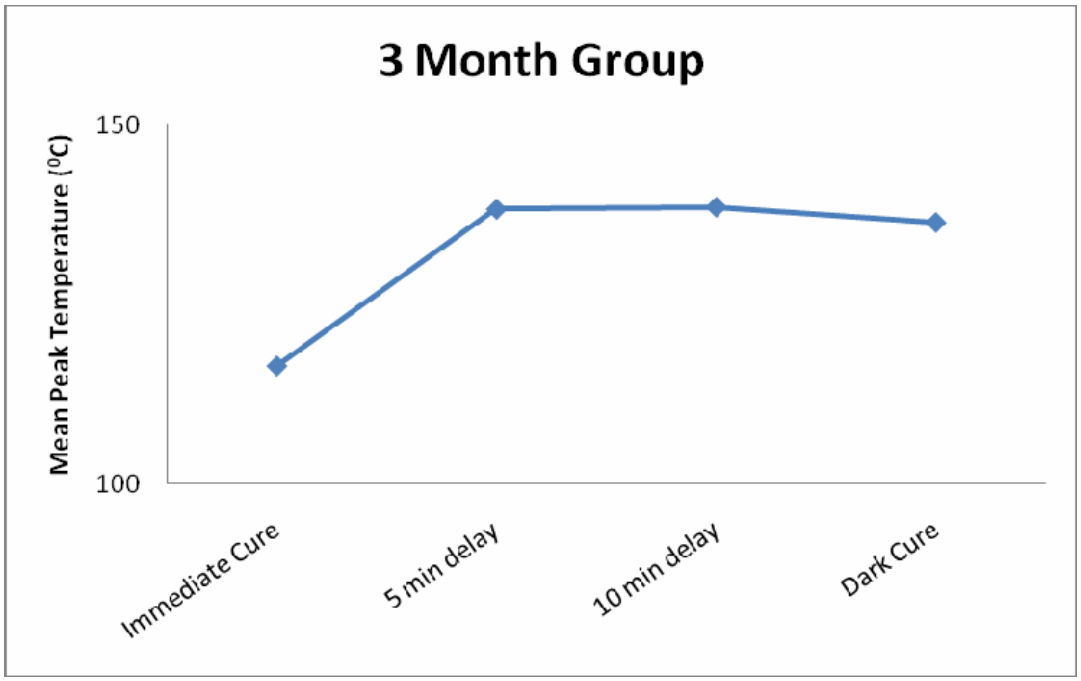

Figure 43: Average peak temperature for the 3 month groups.

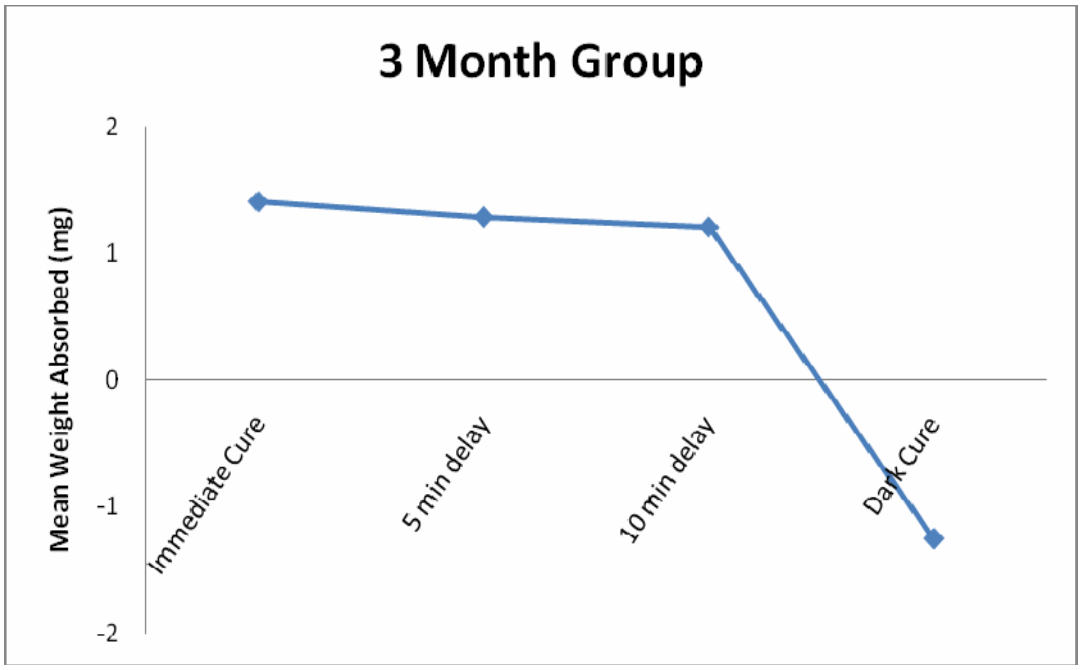

Figure 44: Average weight absorbed in storage for the 3 month groups.

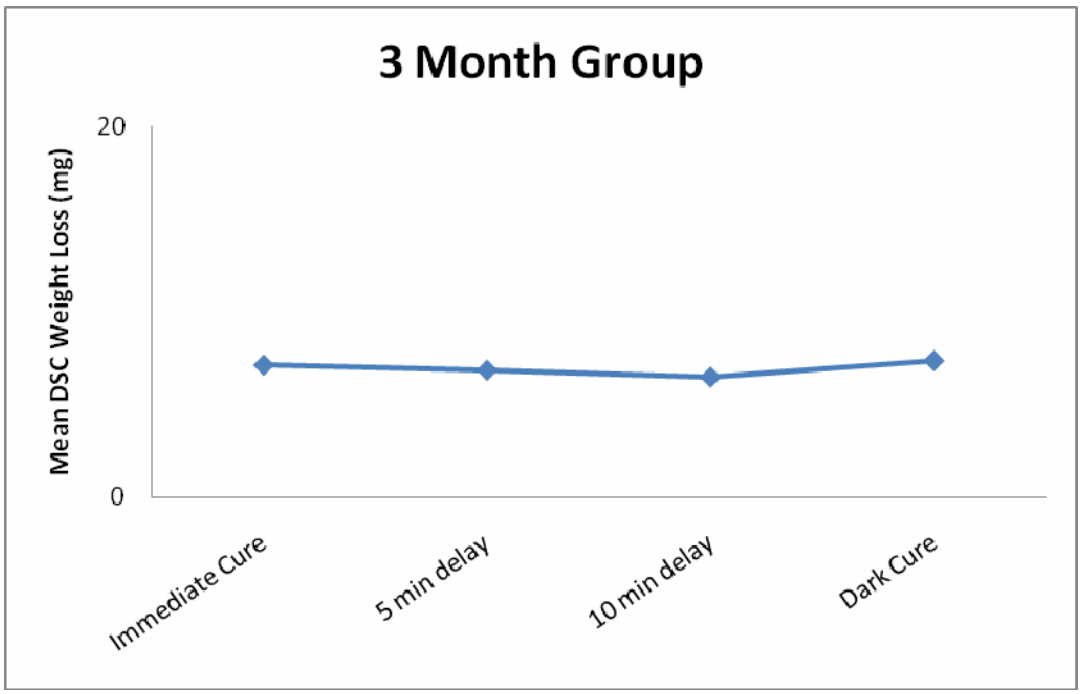

Figure 45: Average DSC weight loss for the 3 month groups.

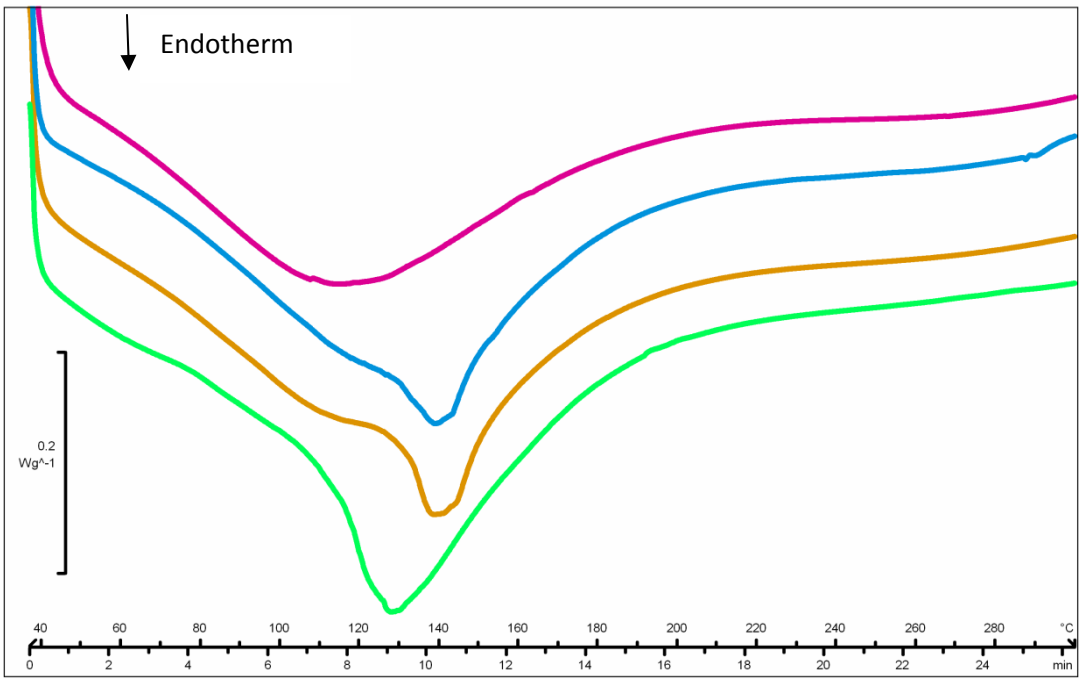

Figure 46: DSC thermograms for the 3 month groups (Top to bottom the curves are the immediate cure, 5 min delay, 10 min delay, and dark cure groups, respectively).

CHAPTER IV

DISCUSSION

A resin modified glass ionomer was studied for its thermal behavior in a DSC and the influence of light activation and time on the same. Although several studies have been conducted on the mechanical properties and biocompatibility of RMGIs, few studies have concentrated on the influence of light activation and time on the setting behavior of the material. The setting of RMGIs is a complex phenomenon and this study was designed to investigate the setting reaction of an RMGI material using DSC analysis.

Differential scanning calorimetry is a very useful thermal analytical method for studying phase transformations and chemical reactions in different materials. It measures the energy (usually in the form of heat) to establish a zero temperature difference between a substance and a reference (an empty aluminum crucible in this study) when they are subjected to identical temperatures in an environment that is heated or cooled at a controlled rate. As the heat flows, changes in the sample may impose a difference in temperature between the sample and the reference. Therefore, more or less heat is required to maintain the sample and the reference at identical temperatures and this energy is the calculated enthalpy of the reaction that occurs in the sample and the changes in temperature or heat flow result in peaks in the DSC thermogram. The peaks observed are either endothermic (downward peaks) or exothermic (upward peaks) depending on the type of reaction that takes place in the sample. A reaction that consumes energy (in the form of heat) results in an endothermic peak and one that liberates energy (in the form of heat) results in an exothermic peak.

DSC has been used to study the photo polymerization reactions of composite resins and RMGI materials. The rate of the polymerization reaction has been studied using DSC by assuming that the heat produced during polymerization in a DSC is proportional to the rate of the reaction (number of monomer units reacted) [89, 90]. In the present study, a DSC was used to determine the effect of light curing (delay/lack of light initiation) on the setting reaction/structure of a commercially available RMGI material over time. Here, by exposing the material to elevated temperature, it will degrade. Insight into the structure of the material is gained by examining the enthalpy and temperature of the endothermic degradation peaks. FTIR analysis of RMGI specimens scanned up to 240^{o}C in a thermogravimetric analyzer by Berzins et al. [36] revealed the most abundant decomposition product was water which was presumed to be primarily from the RMGI bound fractions and partly from poly (acrylic acid) degradation. Additionally, the liberation of residual HEMA was also detected with a higher amount observed in delayed light cure or dark cure groups.

Statistical analysis of the 30 min specimens revealed significant differences between the immediate cure group and the other specimen groups. From the results of the study, it can be seen that the mean peak temperatures of the 30 min group specimens is significantly different from that of the other time group specimens (1 day, 1 week, 1 month and 3 month) for all light initiation groups and the dark cure group. On observation of the DSC thermograms for the immediate cure specimens for the different time groups, it can be seen that the 30 min group resulted in a sharp endothermic peak (191.1^{0}C) whereas the other time groups had broader peaks. This would imply that continued acid–base reaction is occurring in the 5 and 10 min delay cured groups and the

dark cure groups. The mean peak temperature of the 30 min group specimens is significantly higher ($p<0.001$) than that of the other time group specimens for all the light initiation groups and is significantly lower ($p<0.001$) than that of the other time groups for the dark cure specimens. This observation is similar to the results of a study by Berzins et al. [36]. The matrix of the glass ionomer contains two types of water. The "tightly bound" water refers to the water retained in the glass ionomer even after desiccation or setting whereas the "loosely bound" water refers the water in the matrix of the glass ionomer that could be removed easily by desiccation [4]. The higher peak temperature of the 30 min group for the different light initiated specimens is because the set material may contain very little loosely bound water as the photo curing results in a highly cross linked matrix. On the other hand, the matrix of the light initiated specimens of the other time groups (1 day, 1 week, 1 month and 3 month groups) may absorb some water in the humid storage environment resulting in more loosely bound water in the matrix of the specimens. The absorption of water in the matrix of the light initiated specimens could be attributed to the presence of HEMA in the material which is a hydrophilic monomer facilitating the absorption of water into the matrix. This could be observed in the results of this study which showed that the specimens in storage for all the light initiated groups increased in weight after storage. The water absorption characteristics of RMGI materials have been studied by many authors [28, 29, 64]. The lower mean peak temperature of the dark cure group of the 30 min specimens compared to the dark cure groups of the other time group specimens, could be attributed to the unreacted water in the matrix of the material. This could be supported with the lowest peak temperature of decomposition in these materials of $103^{o}C$ which is closer to the

evaporation temperature of water. The dark cure specimens of the other time groups on the other hand, have continued acid-base reaction in the matrix of the material over time with which the water in the matrix is more “bound”.

For the other time groups (1 day, 1 month, 1 week, 1 month and 3 month groups), the enthalpy and the peak temperatures were found to be significantly lower for the immediate cure specimens compared to the other light initiation specimens. This difference in peak temperature could be because of the residual acid-base reaction that occurs in the matrix of the RMGI material during the storage period.

Statistical analysis also revealed that the mean peak temperature of the immediate cure group is significantly lower ($p<0.001$) compared to those of the other light initiation groups for all time groups (1 day, 1 week, 1 month and 3 month) except the 30 min group. This can due to the additional acid-base reaction that takes place during the delay in light initiation (as in the 5 min and 10 min delay cure specimens) or without light curing (as in dark cure specimens). The immediate curing of the specimens traps in the available water in the cross linked matrix as unreacted particles of the acid-base components of the material, which decomposes at a lower temperature in the calorimeter. Water sorption during storage could also contribute to the lower decomposition temperature of these groups of specimens. A majority of the setting reaction in the immediate cure specimens takes place by polymerization reaction and hence the scope for acid-base reaction in this light initiation group is lowered as described by the “network competition” behavior of the RMGI materials by Yelamanchili and Darvell [33]. The dark cure specimens may have continued and residual acid-base reactions in the matrix

that convert loosely bound water to tightly bound water during the different storage times.

The dark cure specimens were found to be the most sensitive to the humid environment as they exhibited a net weight loss during storage over time. The higher peak temperatures of the dark cure specimens over time compared to the 30 min specimens could be attributed to the additional acid-base reaction during storage of the specimens.

In the 30 min group, the mean peak temperature of the dark cure group is significantly lower ($p<0.001$) than that of the mean peak temperatures of other light initiation groups and also the mean peak temperatures of the 5 min delay and the 10 min delay cure groups are significantly different. The dark cure group in the 30 min specimens has no resin polymerization reaction (because of lack of light activation) and incomplete acid-base reaction (due to inadequate storage time) and therefore, has "free" water in the matrix of the set cement which decomposes at a temperature ($103^{o}C$) closer to the evaporation temperature of water ($100^{o}C$). As seen in Figures 24 and 27, the dark cure specimens for the 30 min group typically had two peaks in the temperature range tested at $103^{o}C$ and $165.7^{o}C$. The second peak could be due to the unreacted glass ionomer particles in the matrix. This can be supported by the results of a study by Khalil and Atkins [90] who reported the degradation temperature of the acid-base component of a glass ionomer material to be around $170^{0}C$ and that of water to be around $96.5^{0}C$. It was observed that the temperature of the peaks of the dark cure specimens of the other storage groups decreased over time and this could be attributed to the additional acid-base reaction that would occur in the matrix over time.

From Figures 14 and 18, it can be seen that the peak temperatures of the 5 and 10 min delay cure specimens decreases with storage time with the 30 min group specimens having a significantly higher peak temperature compared to the other time groups. This is similar to the trend observed in the resin modified glass ionomer study by Berzins et al. [36]. The difference in peak temperature from the 30 min specimens to the other time group specimens could be because of the water absorption in the matrix of these specimens and the additional acid-base reaction over time. The 10 min delay cure specimens, however, had a significantly lower peak temperature over time compared to the 5 min delay cure specimens. The significantly lower peak temperature of the 10 min delay cure group compared to the 5 min delay cure group could be explained based on the delay in light initiation of the material, leading to a greater acid-base reaction in the matrix of the 10 min delay cure specimens. The acid-base reaction requires the water component in the RMGI material and thus, the longer the delay in light curing, the greater the amount of bound water in the matrix there is. Yelamanchili and Darvell [33] also stated that the delay in light initiation limits the extent to which the resin network can form in the RMGI matrix. Early initiation of light to cure the material inhibits the extent of acid-base reaction and ultimately the amount of loosely bound water in the matrix of the set cement. The 5 and the 10 min delay cure specimens of the 1 day group however, did not have any significant differences in the peak temperatures which can be explained based on the residual acid-base reaction that occurs in the material for up to 24 hours as mentioned by Feilzer et al. [35]. There was also no significant difference in peak temperatures of the 5 and 10 min delay cure groups of the 1 week, 1 month, and the 3 month group specimens according to the results of this study.

Khalil and Atkins [91] determined the behavior of Fuji II LC in an isothermal DSC scan at 37^{o}C in the absence of light curing. Thermograms showed two distinct but overlapping peaks which they attributed to two different setting reactions i.e., acid-base neutralization and the chemical polymerization reaction in the material. When a previously light cured (for 20 s) Fuji II LC material was scanned at 37^{o}C, it did not result in any peak in the DSC trace. Khalil and Atkins also determined the degradation temperature of a typical glass ionomer material to be around 170^{o}C. When only the liquid component was scanned in a dynamic trace in the DSC, they found an endothermic peak at around 158^{o}C which they attributed to the degradation temperature of the polymeric constituents of the liquid. Thus they found that cross-linking the polymer in the liquid with the glass powder resulted in an increase in the degradation temperature of the material by 12^{o}C or by 7.6 %.

Statistical analysis revealed significant differences in the enthalpies and peak temperatures between the different light initiation groups and time groups. Eden et al. [92] studied the setting behavior of conventional glass ionomer materials using dynamic mechanical analysis (DMA) and also DSC. DSC was used to determine the effect of heating on the distribution of loosely bound water in the glass ionomer material. The authors attributed the energy change in the DSC to the removal of loosely bound water in the glass ionomer. They also reported that younger glass ionomer materials contained more loosely bound water in their matrix and hence required more excitation energy for an endothermic peak [92].

According to Yelamanchili and Darvell [33], a “network competition” exists between the resin matrix and the glass ionomer network in a resin modified glass ionomer

material, meaning that neither of the two can develop fully. They concluded that a hybrid material like a resin modified glass ionomer is ultimately a compromise. Berzins et al. [36] also found that the visible light curing initiation time had a significant influence on the acid-base reaction rate and extent. The immediate implication of these studies being that any delay in light initiation can limit the extent to which the resin network forms.

Based on the previous studies, the DSC behavior of the RMGI materials in the present study can be attributed to the difference in the loosely bound water for the different groups based on delay in light curing or storage time. A greater delay in light curing results in the presence of more loosely bound water in the set material. Another observation can be made based on the higher enthalpies and the greater mean peak temperatures for the specimens stored for a longer period of time in that there seems to be some amount of residual acid-base reaction that occurs in the set material over time. The residual acid-base reaction increases the amount of bound water in the specimens thus increasing the mean enthalpies for degradation of the specimens over time. This behavior is contrasting with the studies of Feilzer et al. [35] who stated that the setting reaction of the RMGI materials, particularly the acid-base reaction, continues for 24 hours after the mixing of the material.

Clinical Significance

In a study similar to the present one, Berzins et al. [36] showed an exothermic peak attributed to the acid-base reaction in the isothermal DSC analysis of Fuji II LC specimens that had delayed light initiation by 5 or 10 min. This peak was typically found around 3-4 min after mixing the specimens. The exothermic peak of dark cure specimens was also found to be around 4.2 min. The immediate cure specimens, however, did not show any exothermic peaks associated with acid-base reaction. The manufacturer stated working time for Fuji II LC is 3 min and 15 sec. If light initiation of Fuji II LC is delayed this amount of time after mixing, the amount of polymerization reaction in the material was calculated to be 85% of that of immediately cured Fuji II LC. The authors state that even though a delay of 10 min before light curing is unlikely clinically, even small delays in light activation could result in various structural and characteristic differences in RMGIs [36].

Berzins et al. [36] also observed that more residual HEMA was present in dark cure and delayed light cure specimens. This could affect the biocompatibility of the material by increasing the cytotoxicity of the RMGI material as RMGI materials have been found to be more cytotoxic than conventional GIs due to the release of HEMA [85, 86]. Aranha et al. [87] found that the cytotoxicity of RMGIs was independent of the duration of light activation. However, the effect of delay in light initiation on the cytotoxicity of RMGI is uncertain at this time.

The inability of the dark cure specimens to absorb water may influence the long term success of the material if used as a restoration. Slight swelling of the restoration due

to water imbibition could result in expansion of the restoration thus sealing the margins of the restoration and possibly preventing secondary caries. The weight loss of the dark cure RMGI material may have effects on the marginal seal of the restoration.

CHAPTER V

CONCLUSION

DSC analysis of the resin modified glass ionomers tested resulted in single endothermic peaks for all the specimen groups except the 30 min dark cure group specimens. Two-way ANOVA tests of groups revealed significant differences ($p<0.001$) with regard to enthalpy and peak temperatures between the different light initiation groups and time groups. Additionally, there was a significant interaction ($p<0.001$), so a one-way ANOVA was done to determine the differences between the different light initiation groups and the time groups.

- The peak temperature of the immediate cure group for all time groups except the 30 min group was significantly lower compared to that of the other light initiation groups
- The peak temperature of the 30 min group specimens were significantly higher compared to the that of the other light initiation group specimens of all the other time groups whereas both the enthalpy and peak temperatures of the 30 min dark cure specimens was significantly lower compared to those of the dark cure specimens of the other time group specimens
- The peak temperatures of the 5 min and the 10 min delay cure specimens of the 1 day group and the 1 month group were significantly higher compared to that of the dark cure group but there were no significant differences in temperatures between the 5 min and the 10 min delay cure specimens

- The enthalpy of the immediate cure specimens for the 1 day group was also significantly lower than the other light initiation groups except the dark cure group
- The enthalpy of the immediate cure specimens of the 1 month and the 3 month groups were significantly lower than that of the other time groups.

It can therefore be conclude from the results of this study that the delay in light initiation has a significant influence on the extent of polymerization reaction and acid-base reaction in the matrix of a resin modified glass ionomer.

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