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Evaluation of the pH of a self-adhesive flowable composite over 3 months

A Thesis

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In Partial Fulfillment of the Requirements for the Degree of  
Master of Science in Oral Biology

By

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April 2016

Evaluation of the pH of a self-adhesive flowable composite over 3 months

A REPORT ON

Research project investigating the effect of varying storage conditions on the pH of  
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## ABSTRACT

**Purpose:** The purpose of this study is to evaluate the pH of a self-adhesive flowable composite under varying storage methods over the course of 3 months.

**Methods:** Vertise Flow®, a self-adhesive flowable composite, shade A2, was ordered and shipped from the manufacturer by normal means. The composite was stored at three different temperatures: room temperature (73F), incubator (131F) and refrigerator (36F). A benchtop pH meter and micro bulb electrode were calibrated prior to each reading using the protocol and solutions provided by the manufacturer. The readings were performed in a dark room under red lighting. A baseline pH reading was taken of each sample prior to initiating their storage. Every 30 days the samples were removed from their various storage methods and allowed to normalize to room temperature prior to taking the next pH reading. The data was gathered and analyzed using statistical analysis.

**Results:** On the ANOVA, there was no statistically significant difference in pH between storage methods ( $p > 0.05$ ). There was a statistically significant difference in pH between times ( $p < 0.001$ ). When the data were plotted as a boxplot, the distribution did not appear to be normal, so the analysis was repeated with a non-parametric Kruskal-Wallis ANOVA. This confirmed the results.

**Conclusions:** Based on the results of this in-vitro study, there is no statistically significant difference between the pH of the self-adhering flowable composite under the varying storage methods. There was a statistically significant difference between the first pH reading and the subsequent readings, regardless of storage method. At a certain temperature and exposure to heat the self-adhesive flowable material began to harden. This temperature and duration is currently unknown. The hardening of the composite under incubator storage was noted at its first 30 day reading and continued throughout the 90 days of evaluation. However, there remained uncured flowable composite surrounding the cured product, allowing the pH to be obtained. The uncured composite maintained a pH that was not statistically significant different ( $p > 0.05$ ) from that of the product stored under the other methods (room temperature and refrigerator). Therefore, it can be concluded that the pH remains similar under varying storage conditions as long as the material maintains its viscous state. It can also be concluded that at some temperature and duration the composite will begin to harden. This temperature and duration remains unknown and could be investigated during future studies.

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## INTRODUCTION

The field of dental materials is constantly advancing, especially in the area of adhesive dentistry. For nearly a century, dental amalgam was the direct restorative material of choice. However, there are demands it is unable to meet as a universal restorative material. Dental amalgam requires larger tooth preparation, is unaesthetic, and contains mercury, an environmental hazard and patient health concern. It also lacks the ability to bond to tooth structure, making large restorations more likely to fracture. These limitations have continually caused researchers to develop a material that had the durability of amalgam, but could meet the esthetic demands of the patients and providers. This led to the development of dental composite, an inert plastic material that matches tooth color.

Dental composites are synthetic resins made up of inorganic filler particles coated with a silanating agent which are then embedded in a synthetic organic matrix. It took decades of research and development to create a reliable long term composite resin material and viable bonding protocol to become the restorative material of choice that both dentists and patients would demand. In the 1800's silicate cements were the first esthetic materials used in dentistry. However, they were subject to acidic decay and were only useful for four to five years on average.<sup>2</sup> During the ensuing decades the development of epoxy resins were used widely for industrial purposes. The intriguing properties of epoxy resin suggested that they might be useful for dental applications.<sup>2</sup> The liquid epoxy was mixed with a hardening material that would cause it to harden at room temperature and with minimal shrinkage, however the major flaw was that these

materials failed to harden quick enough for dental applications.<sup>2</sup> The synthesis of a new monomer was sought, one that exhibited low shrinkage and a quicker hardening reaction. This led to the development of methyl methacrylate; however, it still exhibited too much polymerization shrinkage, low stiffness and had a high coefficient of thermal expansion which was detrimental for use as a direct restorative material.<sup>2</sup> In 1962, Bowen developed a hybrid monomer, Bisphenol-A-glycidyl dimethacrylate (BIS-GMA).<sup>3</sup> This new material could polymerize rapidly under oral conditions and only shrunk about 1/3 during polymerization when compared to methyl methacrylate.<sup>2</sup> At this point the acrylic was still required to be mixed in office as a base paste and catalyst reaction. Mixing, proper proportions and color errors remained common.<sup>3</sup> By the 1970's composites began to contain filler particles.<sup>3</sup> However, the filler particles were too large, only four shades were available and the resins were difficult to polish.<sup>3</sup> As they aged, they also exhibited "plucking", or a physical loss of the larger filler particles from the resin matrix. To reduce this problem, various sized particles and filler materials have been introduced to improve the quality and durability of the composite. As a result of these advancements, today's composites are much more insoluble, aesthetic, insensitive to dehydration, easy to manipulate and reasonably inexpensive.

One area of recent research in composite technology has focused on the viscosity of the material to improve its adaptability to the internal aspect of the preparation. Composites are "viscous" or "soft" prior to hardening. This allows the material to be intimately adapted to the tooth structure. Dental composites can then be "hardened" or "cured" by various methods: light, auto or dual cured. Light cure composite

consists of a photo-initiator that will harden the composite once it is activated by light in a specific wavelength. Auto cure composite consists of chemicals that when mixed together initiate the curing or hardening of the composite and dual cure is that both activating methods are incorporated into the composite material. This allows the practitioner to have the option of speeding up the process by curing the composite with a light. It also ensures that composite far from the light source will also get cured, such as in a core build-up of an endodontically treated tooth.

Composite resin viscosity varies greatly from material to material. Each dental composite has a proprietary make-up that differs from others, thus the physical properties can differ between brands of composite. A popular subgroup of composite, known as a flowable composite, is less filled and contains a larger amount of organic matrix when compared to composites indicated for larger direct restorations.

Flowable composite is a type of resin that is more viscous and can “flow” easily to fill small class I or class V preparations and can act as an initial layer to decrease internal voids and improve marginal adaptation.<sup>14</sup> Traditionally, flowable composites will wear faster, shrink more and have less fracture resistance since the amount of filler is reduced to decrease its viscosity. This difference in composition affects its physical properties; however it still maintains various clinical uses. Flowable composite can also be used for orthodontic bonding, preventive resin restorations, temporary crown repair and sealants.<sup>12,14</sup> A new type of flowable composite, termed self-adhesive, has come onto the vast market of dental products. This means that the adhesive bonding protocol and composite resin are all combined into one step. This has many potential

benefits which include: decreased storage of materials, decreased chair time and ease of application.

There is no “one size fits all” when it comes to the perfect dental composite. The ideal composite would have: good physical properties, acceptable esthetics, fracture and wear resistance, color stability, be radiopaque, extensive shade range, easy to handle, high viscosity, clinically proven and “be universal,” meaning the doctor can place it for anterior and posterior restorations. Composite can be distinct by any number of variations of ingredients ranging from: filler particle type or size, monomers, silanating agent and type of photo initiator. A brief discussion of each will be addressed.

The resin matrix is the backbone of dental composite. It serves as the matrix that holds the other components together. The matrix is formed by the curing of monomers to form polymers. Most composites are a proprietary mix of a variety of monomers, primarily consisting of the hydrophobic monomers urethane dimethacrylate (UDMA) and bisphenol glycidylmethacrylate (bis-GMA), along with the diluent tetraethyleneglycol dimethacrylate (TEG-DMA) to control viscosity. The degree of polymerization shrinkage will also vary based on monomer type. Varying the percentage and type of monomers in the matrix aids in limiting the polymerization shrinkage as the free flowing monomer converts to the bound, smaller polymers. The degree of shrinkage encountered can affect the integrity of the restoration.

Filler particles contribute greatly to the physical properties of dental composites. Particle type and size can affect many things, such as: polishability, compressive strength, viscosity, degree of shrinkage, translucency, color, fracture and wear resistance. Initially, composites had filler particles that were large, in the 8-12 um diameter range, also known as macrofilled. This contributed to poor compressive strength and poor polishability. Today, composites can be found with particles that have diameters in the range of .0015-.075 um, known as nanofills. Often the composite can contain a few different diameters of filler particles, micro and nano particles for example these are classified as hybrids. The filler particles are composed of various materials, some examples are: previously cured composite, silica, quartz, strontium and zirconia. Today composites are difficult to classify based on filler particle type and size because such a variety exists.

In order to increase handling capability and control curing times, photoinitiators are added to the composite. The most common photoinitiator found in most light cured resins is camphoroquinone. Ausmussen et al found the wavelength at which camphoroquinone begins its reaction to be a range from 370 to 500 nm, with max initiation at 468 nm.<sup>19</sup> Setting of the composite occurs as visible light activates the photopolymerizing agent to create free radicals. These free radicals create a reaction within the resin matrix converting monomers to stiffer polymers and an overall shrinkage of the material.

The most important aspect of a composite restoration is the bonding protocol. Bonding tends to be a vigorous and technique sensitive procedure. Correctly bonding

a composite restoration relies on many factors: good isolation, the proper sequencing and timing of bonding agents, dental restorative materials, incremental light curing and patient cooperation. Research and development has focused over the years at simplifying the adhesive process, making it easier on both dentist and patient.

However, total-etch and rinse systems remain the gold standard in adhesive dentistry.<sup>1</sup>

Advances in the fields of self-etch and self-adhesive systems are creating bond strengths that can meet current clinical restorative standards of practice and that have some benefits over the total etch and rinse system.<sup>1</sup>

Adhesive bonding systems were traditionally classified under a generational system; total-etch (4<sup>th</sup> and 5<sup>th</sup> generations) to self-etch (6<sup>th</sup> and 7<sup>th</sup> generations).<sup>1</sup>

However, due to the complexity and rapid changing field of adhesive dentistry, bonding systems today can be categorized into a few broad categories; total-etch, self-etch and self-adhesive.<sup>1</sup> Each method uses the same general idea for bonding a composite material to enamel and dentin. A typical bonding protocol will include three components: an acid, primer and adhesive. These three steps may be applied separately or combined into two steps or even one.

The discovery of using an acid to alter tooth surface topography was the first step towards creating a dental bonding protocol. Buonocore, in 1955, introduced the idea of using an acid etch to bond acrylic to enamel. Although bond strengths were extremely low compared to today's standards, it laid the foundation for future advancements. Acid etching has two primary purposes: 1) it increases the micro-topography or surface area of the bonding surface and 2) removes or modifies the

smear layer in dentin. Both have the same goal: to increase micro mechanical retention and allow a deeper penetration of the adhesive (SEM) (fig. 1).

Due to histologic differences between enamel and dentin, dentin etching wouldn't gain acceptance until the 1990's.<sup>20</sup> In 1979 Fusayama et al used a 37% phosphoric acid to etch both enamel and dentin. The procedure showed that etching dentin did not increase pulp damage and that it increased retention of the restoration greatly.<sup>20</sup> This opened the door for further studies which by 1982 lead to the discovery that hydrophilic resins could infiltrate a surface layer of collagen fibers in demineralized dentin to form a hybrid layer, consisting of resin-infiltrated dentin.<sup>24</sup> Over etching dentin can affect the outcome of the restoration much more than over etching enamel. Caution must be followed while etching dentin with a strong acid as one can cause the collapse of the remaining collagen if etched too long; etch too short and one can get a decrease in bond strength.

Different acids are used for various purposes in clinical dentistry. A phosphoric acid concentration between 30-40% is standard for total-etch systems in which the acid is applied as a separate and distinct step from the rest of the bonding process.

Phosphoric acid etches enamel very well. It will also remove the smear layer (fig. 2), a layer of debris that covers the dentinal tubules as a result of cutting on tooth structure.

Enamel and dentin vary greatly histologically (fig. 3). Enamel tooth structure is well organized and consistent while dentinal surface topography can vary greatly depending on the presence of caries, previous restoration or proximity to the pulp.



The concentration of dentinal tubules per surface area increases greatly as the dental pulp is approached (fig. 4). Dentin, though mostly mineralized, maintains a moistened surface. Thus, it is difficult to control and predict the effect of the phosphoric acid on the dentinal surface. In a total etch system this commonly leads to over etching of the dentinal tooth structure, episodes of post-op sensitivity and decreased bond strengths. Thus, total-etch systems are technique sensitive.

Self-etch and self-adhesive systems have been developed to alleviate the short-falls of the total-etch technique. Self-etching systems incorporate self-limiting acidic monomers into their bonding protocols.<sup>7</sup> This allows the acid etching of tooth structure to be incorporated into or mixed with one or all the other steps in the bonding process. The pH can vary considerably depending on the proprietary make up the acidic monomers in these systems. Essentially they can contain differing strengths of acids. These products are generally marketed as self-etching systems. The acidic monomers are less acidic than phosphoric acid and are self-limiting. They can produce comparable bond strengths to dentin when compared to total etch systems but provide inferior bond strengths on enamel when compared to total-etch systems.<sup>17</sup> The surface topography is not as well defined on enamel when compared to total-etch systems. This is due to the higher mineralized enamel surface. When etching dentin these acids do not remove the smear layer but modify it, still allowing the penetration of the primer and adhesive molecules.<sup>18</sup> Self-etching systems do have some benefits over total-etch, such as a decrease in episodes of post-operative sensitivity and an increased ease in application of the adhesive process. Over etching and under etching of tooth structure are less a concern with self-etching systems and make the procedure

less technique sensitive for the dentist. Additionally, a selective etch technique has been recommended due to weaker bond strengths that are seen on enamel when comparing total-etch and self-etch systems.<sup>8</sup> A selective etch is when the outer layer of enamel is etched with phosphoric acid and the remaining preparation is etched with the self-limiting acidic monomers. Thus, the best of both techniques can be utilized. The etching of tooth structure is critical to the success of a bonded restoration not only does it increase micro-mechanical retention but also prepares the enamel and dentin surfaces for the rest of the adhesive process.

The next step in the adhesive process is the application of a primer. The goal of the priming process is to bridge the gap between the hydrophilic dentinal tooth structure and the hydrophobic restorative material. To accomplish this, an alcohol or acetone based primer acts as a drying agent to remove moisture and allow the penetration of bi-functional molecules, such as 2-hydroxyethyl methacrylate (HEMA, fig. 5). The acetone or ethanol evaporates the remaining water and allows the bi-functional molecule to penetrate the dentin surface more thoroughly. The primer flows into the exposed dentinal tubules and around the exposed collagen fibers and attaches itself with its hydrophilic component to these organic structures (collagen and calcium), thus acting as a framework to connect the hydrophilic tooth structure and the hydrophobic resin. The free end of the bi-functional molecule is hydrophobic. The surface is now prepared for the final application of resin in the adhesive stage.

The final step is the application of a hydrophobic acrylic resin. This resin is unfilled or lightly filled, meaning there are little or no filler particles in it. The acrylic

resin, much like a composite, also contains a photoinitiator that will initiate the hardening of the resin through a reaction when activated by light in a specific wavelength. The resin flows into the prepared tooth structure and attaches itself to the previously applied bi-functional molecule. This final step creates what is known in the literature as the “hybrid layer” and completes the mechanical interlocking between the hydrophilic tooth structure and the hydrophobic composite. At this point the surface is ready for restorative composite to be added.

The simultaneous development and improvement of composite resins and dental bonding systems is responsible for the vast field of current products on the dental market today. These developments have led researchers to focus on combining the adhesive bonding protocol and the actual composite restorative material into a one-step procedure. This concept has opened up a line of what is termed “self-adhesive flowable composites” that are much less viscous than traditional composites and are able to “flow” and adapt well to the walls and floors of preparations or to the occlusal pits and grooves such as in sealants. Vertise Flow®, the self-adhering flowable composite used in this study, uses glycerophosphate dimethacrylate (GPDM, fig. 6) as the adhesive monomer. The monomer contains a phosphate functional group that acts as an etchant and creates a chemical bond with the calcium ions of the tooth. The GPDM monomer also has two methacrylate functional groups for copolymerization and crosslinking with other methacrylate co-monomers. Thus, this versatile adhesive monomer can be considered a silanating agent due to its ability to create the link between tooth structure and resin through these two functional groups.

Self-adhering flowables contain more organic matrix and less filler particles, thus some of their physical properties are compromised when compared to composite used in larger direct restorations. Though the self-adhering flowable composite isn't indicated for large direct restorations they do maintain many uses clinically. Self-adhesive flowable composites have been indicated for use in: sealants, preventive resin restorations, orthodontic bonding and small class I and class V direct restorations.<sup>13</sup> Flowable composite have also shown to help decrease the formation of internal voids when used as an initial layer under larger direct restorations.<sup>16</sup> Flowable continues to be beneficial in many clinical situations despite their inferior physical properties when compared to composites used in larger direct restorations.

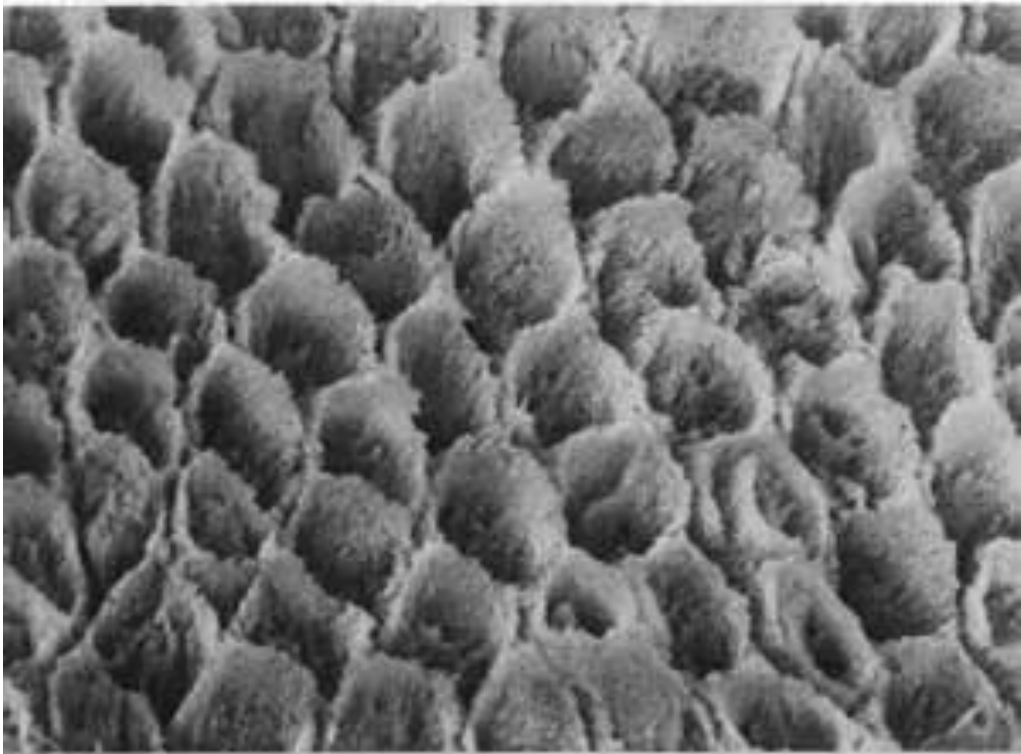
Recent studies have shown promising results for self-adhering composite materials. Research into self-adhering flowable composites have found bond strengths comparable to those of all-in-one bonding systems.<sup>10</sup> When compared to other flowable composites, Vertise Flow® showed comparable bond strengths and decreased micro leakage.<sup>9</sup> When used as an intermediate layer, a flowable composite reduces internal voids. Some studies even show better marginal adaptation when a flowable composite is used, though some research shows it doesn't make a difference.<sup>9</sup>

Though the uses of a self-adhering flowable composite are many, it is not without the same shortcomings/limitations currently noted in literature regarding flowable composites. Their obvious lack of mechanical properties under functional loading continues to limit their use.<sup>4</sup> Goracci et al showed that initial bond strengths of flowables were good but then decreased over time. This gives rise to the question of

bond durability.<sup>6</sup> Miguez et al reminds us of the importance of incremental curing.<sup>15</sup> Though time is money and many practitioners have difficulty gauging how many millimeters have been laid down, it is imperative that adequate depth of cure is reached, especially since initial bonding of composite to tooth substrate is at stake. Sadeghi studied the microleakage of flowable composites in class V restorations and found that greater contraction gaps formed at the restorative/enamel interface than at the restorative/cementum interface.<sup>11</sup> Thus, some advocate the use of a selective etch technique to be able to better penetrate the heavily mineralized enamel.

The success of self-adhesive flowable composites rests on the stability of its pH and thus its ability to adequately etch the enamel and dentinal tooth structure. The importance of acid etching tooth structure for composite restorations is well established.<sup>3</sup> The acidity or pH of the self-limiting acidic monomers needs to remain stable throughout the shelf life of the product. The etching of tooth structure is dependent on this acid and is the key to achieving deep penetration of the adhesive resin into the tooth surface. Thus, if the self-adhesive product cannot maintain its pH over a period of time it cannot be relied upon for clinical success, for the strength and durability of the bond will be in question. The current study was performed for this reason.

Figure 1



**Etched enamel as seen under a scanning electron microscope**

Figure 2

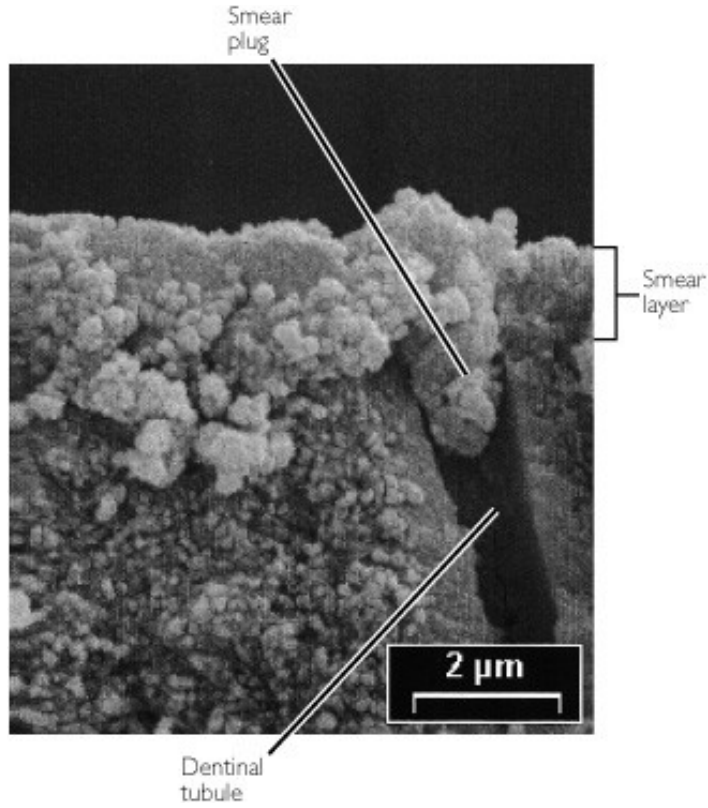
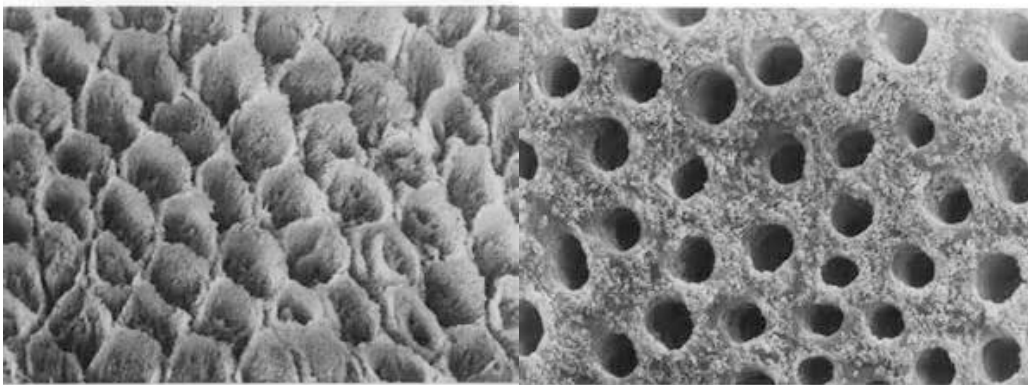
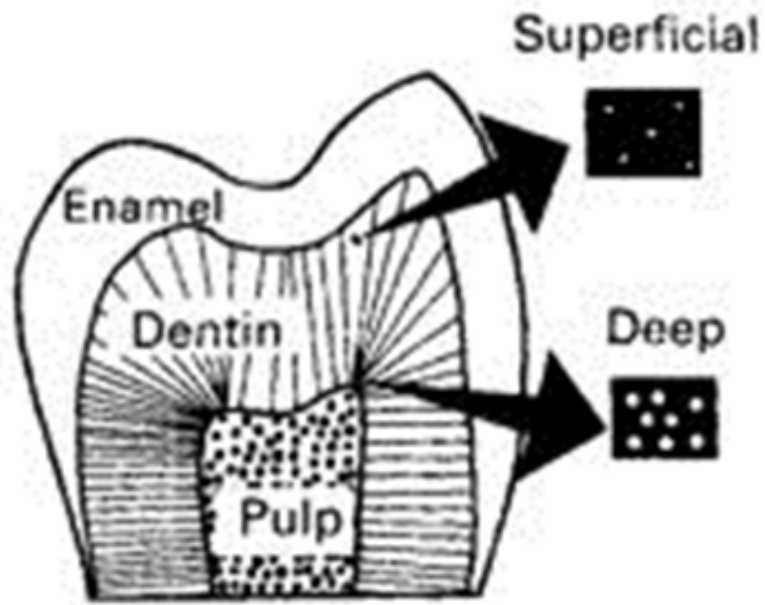


Figure 3



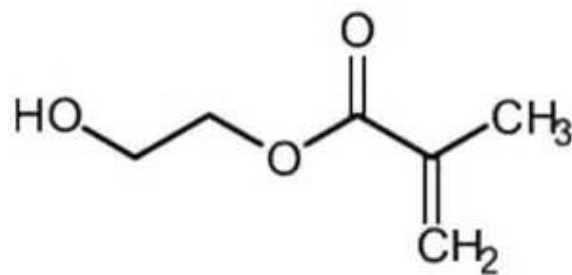
**The microscopic difference between etched enamel (left) and dentin (right) can be appreciated under a scanning electron microscope.**

Figure 4



**Dentin tubules become concentrated as pulp is approached**

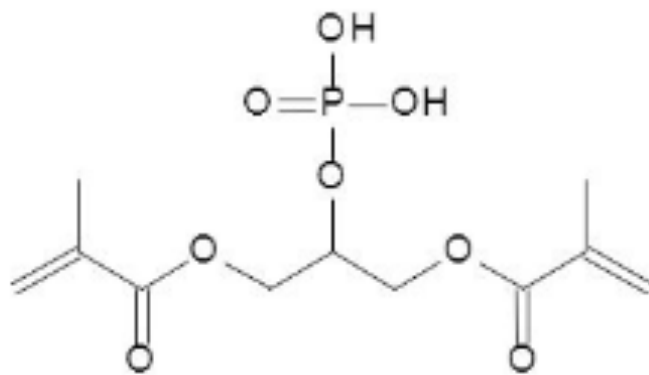
Figure 5



2-hydroxyethyl methacrylate (HEMA)



Figure 6



GPDM

## PURPOSE

The purpose of this study is to evaluate the stability of the pH of a self-adhesive flowable composite under varying storage methods over the course of three months.

## HYPOTHESES

Research question: Will the type of storage affect the pH of a self-adhesive flowable composite?

Null hypothesis: The pH of the proposed self-adhesive flowable composite will not change according to the storage method over the course of three months.

Alternative hypothesis: The pH of the proposed self-adhesive flowable composite will change according to the storage method over the course of three months.

## MATERIALS AND METHODS

This study evaluated Vertise Flow®, a self-adhesive flowable composite, manufactured by KERR. The purpose of this study was to evaluate the stability of the pH and its change over time, under varying storage methods. pH readings were taken of each stored sample at each recording.

Test materials:

Benchtop Meter and Probe – This will be used to assess the pH of the tested product at 0, 1, 2 and 3 months. The probe and meter will be calibrated at every reading using buffer solutions and following instructions from the manufacturer. The probe will be cleaned in between each reading with a 2x2 piece of gauze soaked in a cleaning solution provided by the manufacturer. A special bench top probe with a micro bulb tip design was ordered (fig. 7). The tip design allows for accurate measurement in samples as small as 100 microliters.

Vertise Flow® – The product will be ordered from the same lot and in the same shade, A2. This is to avoid variance due to color and time of manufacture. An adequate amount will be ordered to ensure enough volume for accurate measurements.

Dark Room. A dark room will be set up using a red light bulb. The purpose of this is to establish an environment in which the test product can be dispensed and a proper pH value taken without the chemical state of the material being altered. The photoinitiator, which initiates the chemical reaction, is activated by light in the blue wave length, approximately 440-485 nanometers. However, red light is at the opposite end of the visible light spectrum with a wave length 625-740nm and should provide enough lighting for good

visualization during the data gathering process while not compromising the state of the test material.

The method by which the product arrived was noted (not refrigerated). All samples were from the same lot. They were divided up into three groups and labeled based off of storage method: refrigerated (A), room temperature (B) and incubator (C). Five initial readings were recorded for each storage method, this is marked as month 1.

At 30, 60 and 90 days (month 2, 3 and 4) the samples were gathered from their various storage areas. Their temperatures were allowed to normalize to room temperature, because the pH can be affected by temperature, prior to a pH reading taking place. They were taken to a dark room prior to any material being dispensed. The probe and meter was calibrated prior to each testing period according to manufacturer's recommendations. After proper calibration, readings of each sample took place. While in the dark room an adequate amount of each sample was expressed at each appointed reading time. The readings proceeded according to how the materials were stored and varied at each reading:

At 30 days the reading sequence will be: A,B,C

At 60 days the reading sequence will be: B,C,A

At 90 days the reading sequence will be: C,A,B

Re-calibration during the testing period was done based on need. The number of readings obtained at 0, 30, 60 and 90 days varied slightly. Five readings were taken of each storage method at 0 days. Seven readings were taken of each storage method at 30 days. Seven readings were taken of each storage method at 60 days and eight readings were taken of each storage method at 90 days. The variance of sample readings was necessary to obtain a proper amount of data for statistical analysis.

Data was recorded in the following chart:

Month	pH_Refrigerator	pH Room Temp	pH_Incubator
1	1.0	0.8	0.9
1	1.1	0.8	1.0
1	1.0	0.8	1.0
1	1.0	1.0	1.0
1	1.0	1.0	1.1
2	1.1	1.2	1.3
2	1.1	1.0	1.3
2	1.2	1.2	1.3
2	1.1	1.4	1.3
2	1.0	1.3	1.3
2	1.1	1.3	1.2
2	1.1	1.3	1.2
3	1.2	1.4	1.2
3	1.2	1.2	1.3
3	1.2	1.1	1.3

3	1.3	1.3	1.2
3	1.3	1.3	1.2
3	1.2	1.3	1.2
3	1.2	1.3	1.4
4	1.3	1.2	1.2
4	1.1	1.3	1.1
4	1.3	1.1	1.2
4	1.3	1.2	1.1
4	1.2	1.3	1.1
4	1.1	1.2	1.2
4	1.2	1.1	1.2
4	1.2	1.2	1.2

### **Data analysis**

In this study, the independent variables are storage (refrigerated, room temperature, incubator) and time (0, 1, 2, 3 months). The dependent variable is pH. The appropriate test is a two factor ANOVA (storage, time) with repeated measures on one factor (time) followed by post hoc two-tailed independent sample t-tests corrected for multiple comparisons.

### **Sample size estimate/ power analysis**

A general analysis was performed. An on-line power analysis program was used from the University of British Columbia<sup>21</sup> to estimate the sample size needed for a power of 80% with a level of confidence of 95%. Fifteen comparisons are

appropriate for this study, so a maximum Bonferroni correction of  $p = 0.05 / 10 = 0.005$ . With 27 samples per group (81 total), the investigator will be able to detect a larger 1.0 SD effect size.

### **Additional comments**

Alternatively, if the 27 samples per group are distributed over the four times (0, 1, 2, 3 months) the kinetics of the pH reaction can be calculated from the Arrhenius equation:

$$k = Ae^{-Ea/RT}, \text{ where}$$

k = rate constant,

A = Pre-exponential factor,

Ea = Activation energy,

R = Gas constant and

T = Absolute temperature, K.

The Arrhenius equation<sup>22</sup> can be written as  $\ln(k) = \ln(A) - (Ea/R) (1/T)$ , plotted as  $\ln(k)$  vs.  $1/T$ ,<sup>23</sup> modeled with linear regression analysis and solved for Ea at each of three temperatures (refrigeration, room temperature, incubation).

## RESULTS

### **Two factor ANOVA on pH by storage and time.**

The results of the two factor ANOVA were calculated and plotted in Figure 8. In the box plots, the median is the dark line within the box. The box is defined by the 25<sup>th</sup> and 75<sup>th</sup> percentiles so 50% of the cases have values within the box. The error flags represent the largest and smallest observed values that are not outliers. Outliers (o) are values more than 1.5 box-lengths from the quartile. Extremes (\*) are values more three box lengths from the quartile.

On the ANOVA, there was no statistically significant difference in pH between storage methods ( $p > 0.05$ ). There was a statistically significant difference in pH between times ( $p < 0.001$ ). On the boxplot, the pH measurements did not appear to be normally distributed, so the analysis was repeated with the non-parametric Kruskal-Wallis ANOVA:

#### **Kruskal-Wallis ANOVA on pH by storage:**

There was no statistically significant difference in pH by storage ( $p > 0.05$ ).

#### **Kruskal-Wallis ANOVA on pH by time:**

There was a statistically significant difference in pH by time ( $p < 0.05$ ).



The means and standard deviations of pH as a function of time and temperature and a temperature conversion table are given in Tables 1, 2 and 3. They are graphed in Figures 9, 10 and 11. The graphs suggest that the kinetics fit a limited exponential growth model.

The Solver GRG nonlinear engine was used in Excel to fit the limited exponential growth model to the temperature dependent rate constants. The results are shown in Figures 12, 13 and 14. For refrigerator storage, the model coefficients were:  $k = 0.6$ ,  $a = 1.3$  and  $b = 0.4$ . For room temperature storage, the model coefficients were:  $k = 6.33$ ,  $a = 1.24$  and  $b = 161.25$ . For incubator storage, the model coefficients were:  $k = 6.93$ ,  $a = 1.24$  and  $b = 293.61$ .

The natural logarithms of the rate constants,  $\ln(k)$ , plotted as a function of  $1/T$ , where  $T$  is temperature in degrees Kelvin, is shown in Figure 15. The coefficient of determination ( $r^2$ ) was 0.7168.

Rate constants,  $k$ , plotted as a function of temperature in degrees Kelvin,  $T$ , and fit with the Arrhenius model (solid line) and a general polynomial (broken line) are shown in Figure 16. A general polynomial is an empirical fit that matches the observed trend and is not determined by a theoretical model. The Arrhenius model does not match the empirical distribution.

## **TABLES**

Table 1

Mean	Month	pH_Refrigerator	pH Room Temp	pH_Incubator
	0	1.020	0.880	1.000
	1	1.100	1.243	1.271
	2	1.229	1.271	1.257
	3	1.213	1.200	1.163

Table 2

SD	Month	pH_Refrigerator	pH Room Temp	pH_Incubator
	0	0.045	0.110	0.071
	1	0.058	0.127	0.049
	2	0.049	0.095	0.079
	3	0.083	0.076	0.052

Table 3

<i>Storage</i>	<i>Fahrenheit</i>	<i>Celsius</i>	<i>Kelvin</i>
<i>Refrigerator</i>	36	2	275
<i>Room Temp</i>	73	23	296
<i>Incubator</i>	131	55	328

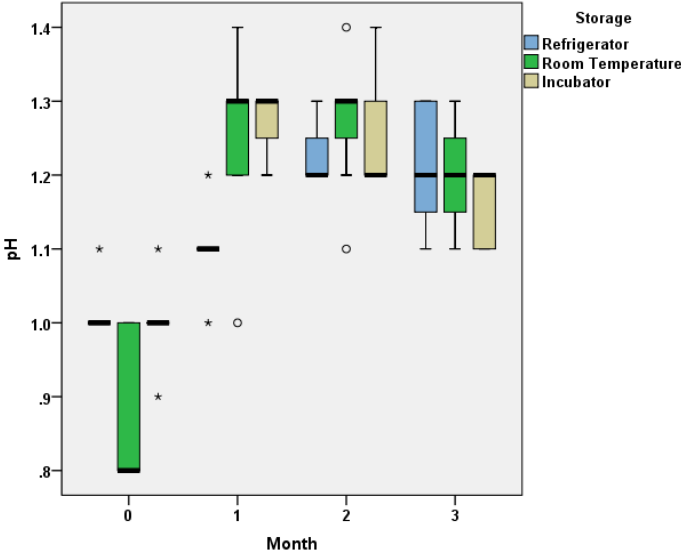
**FIGURES**

Figure 7



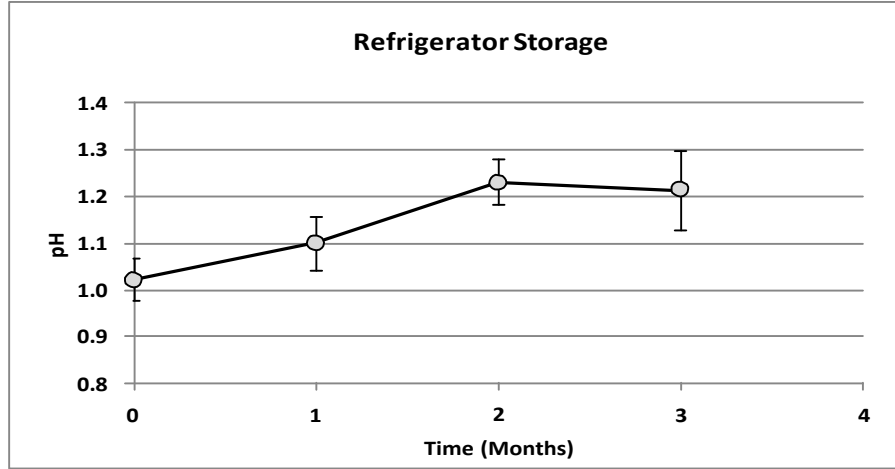
pH probe with micro bulb tip

Figure 8



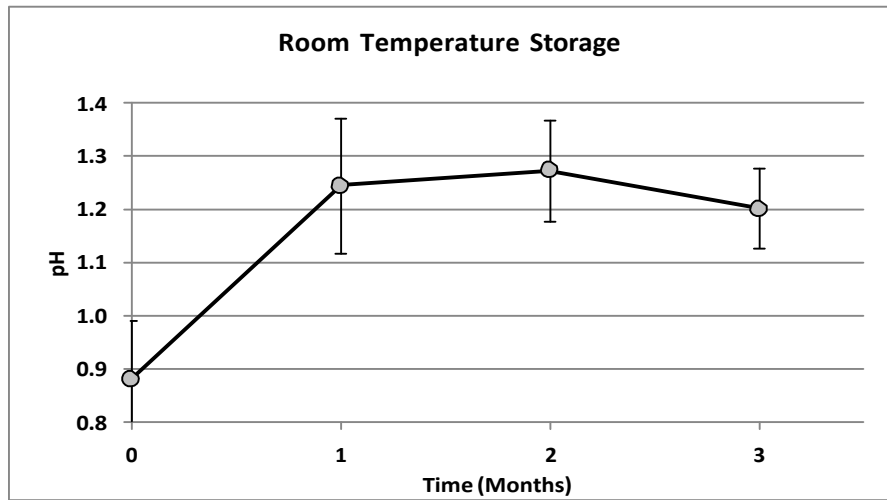
Distribution of pH by storage and month

Figure 9



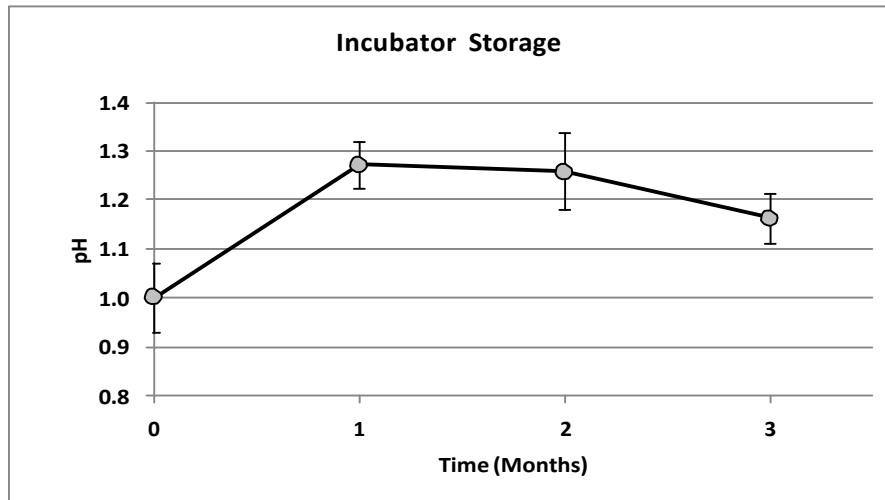
Means and standard deviations of pH as a function of time and temperature, refrigerator storage.

Figure 10



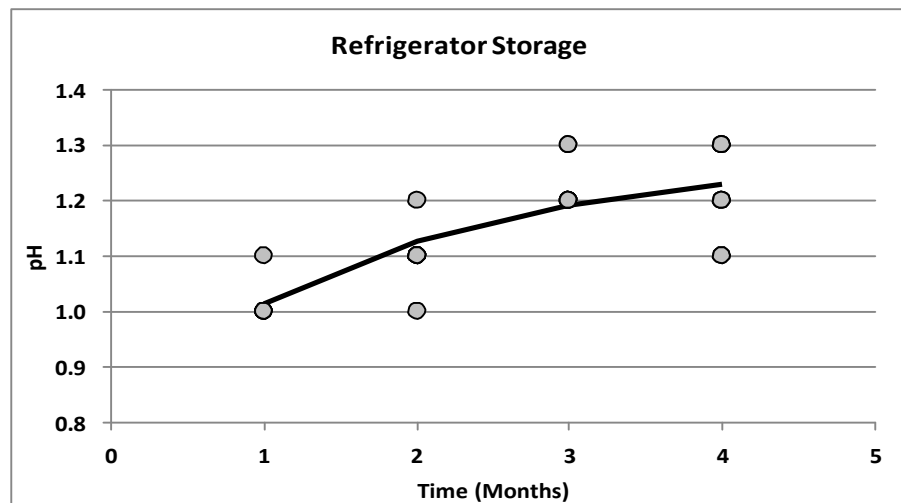
Means and standard deviations of pH as a function of time and temperature, room temperature storage.

Figure 11



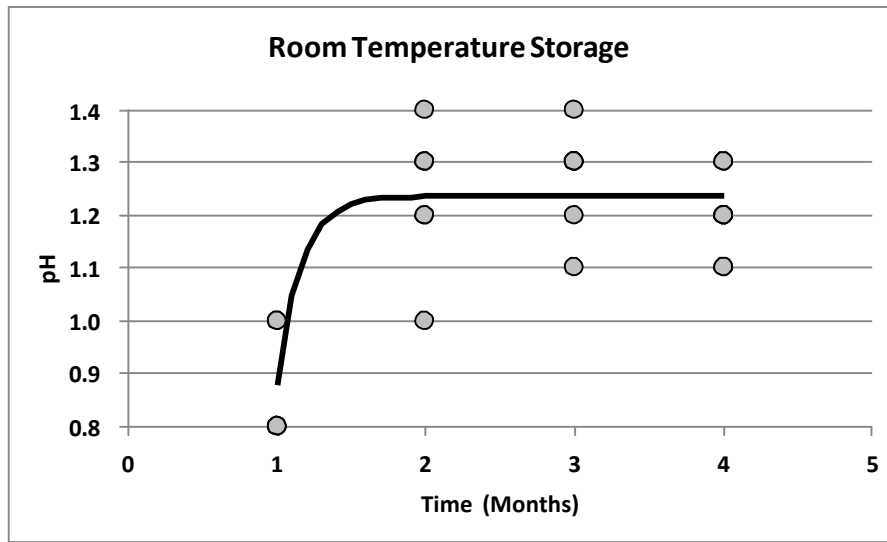
Means and standard deviations of pH as a function of time and temperature, incubator storage.

Figure 12



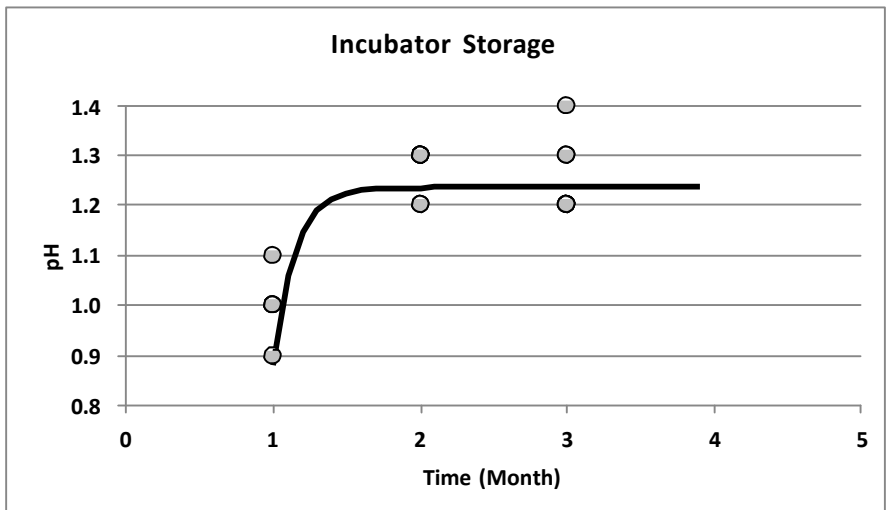
Solver GRG nonlinear engine fit to the limited exponential growth model, refrigerator storage.

Figure 13



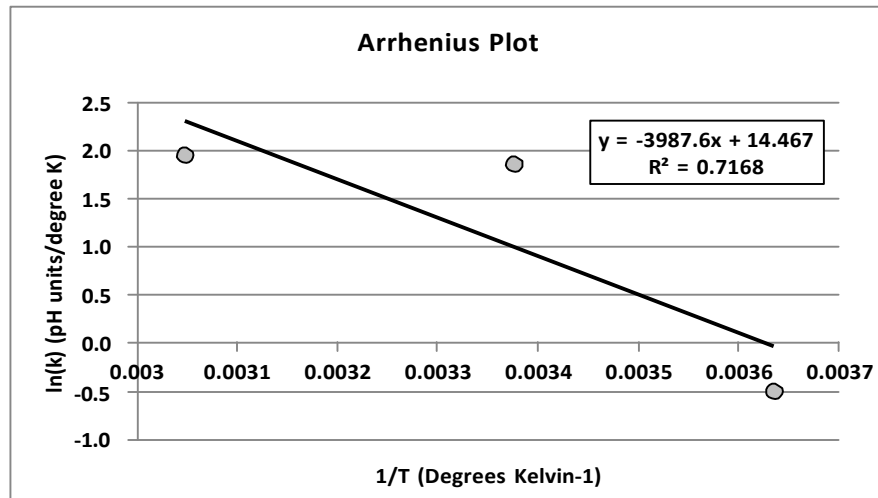
Solver GRG nonlinear engine fit to the limited exponential growth model, room temperature storage.

Figure 14



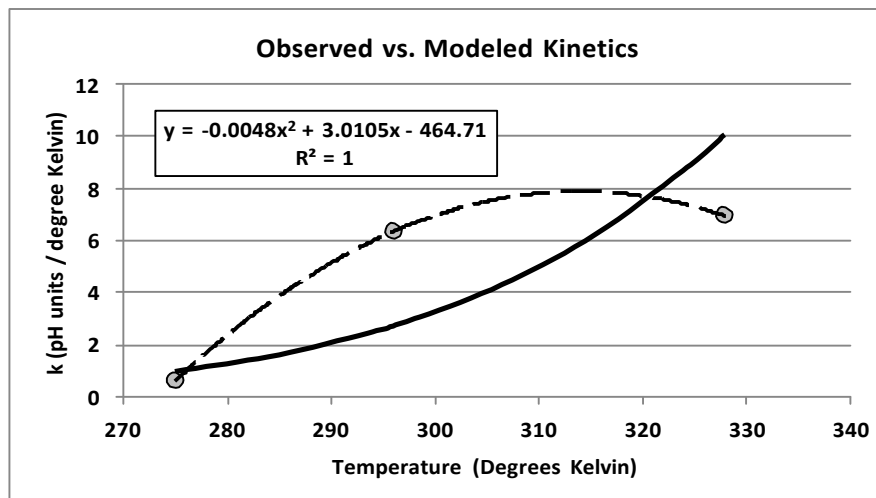
Solver GRG nonlinear engine fit to the limited exponential growth model, incubator storage.

Figure 15



Natural logarithm of rate constants,  $\ln(k)$ , plotted as a function of  $1/T$ .

Figure 16



Rate constant,  $k$ , plotted as a function of temperature in degrees Kelvin,  $T$ , and fit with the Arrhenius model (solid line) and a general polynomial (broken line).

Figure 17



Composite that hardened while stored in the incubator



## DISCUSSION

The continual development of various composites and bonding systems continue to impact current trends in dentistry. Self-adhesive flowable composites are no exception. These new materials are developed in an effort to simplify the bonding process, as demonstrated by the product tested in this study. By simplifying the process, both technical errors and procedure time can be reduced. These benefits increase procedure predictability and profitability. Therefore, the use of a self-adhesive flowable composite can be a valuable adjunct to the practicing clinician. However, simplifying the process by combining steps is not without complications. As discussed earlier, the process of preparing tooth structure for the application of bonding agents and subsequent restoration is a chemically complex procedure that involves multiple structures that vary greatly histologically. Even today, “total-etch and rinse” systems remain the gold standard to which all other systems are measured against. All bonding systems highlight the importance of using an acid to demineralize tooth structure, thus increasing resin infiltration and increasing bond strengths through micro-mechanical means. Self-adhesive systems mimic self-etch systems in that both contain acidic monomers that etch tooth structure. The stability and predictability of the pH dictate the success of the restorations placed using these systems. Thus, it is imperative that the pH remains in a clinically acceptable range that is supported by current literature.

The technical bulletin provided by the manufacturer claimed the product to maintain a pH of 1.9. The current study contradicts that claim and puts the pH of the

provided samples in the range of 1.1 to 1.3. The pH readings taken from this study are closer to that of 37% phosphoric acid (pH of 1), the acid used in total-etch systems. This lower reading may improve its clinical performance through a greater ability to demineralize tooth structure. The long term success of a self-adhering flowable composite relies on its ability to simultaneously demineralize tooth structure (through the use of an acid) and allow adequate resin infiltration. The current study shows that the pH of Vertise Flow® remains stable under varying storage methods. This is supported by statistical analysis.

The analysis showed that in the first 30 days the pH showed the slowest mean increase in the sample stored in the refrigerator. The company recommends that the product be stored under refrigeration despite shipping the product at a temperature dependent upon its mode of transportation. This may or may not have affected the initial readings upon arrival, though it is probably clinically insignificant since the initial pH is near that of other well-known self-etch adhesive systems. The samples stored at room temperature and in the incubator showed sharp mean initial increases in pH during the first 30 days. The greatest increase occurring in the sample stored in the incubator. The two factor ANOVA and Kruskal-Wallis tests did show that there was a significant statistical difference between pH by time ( $p < 0.001$ ). This is supported in figures 6, 7 and 8. This shows that the pH is affected by time but not necessarily by storage method.

The rate of change of the pH for each storage group plateaued by month three. This is shown by the Solver GRG nonlinear engine fitted to the limited exponential

growth model for each sample. It attempted to model the relationship between pH, storage temperature and time with the Arrhenius equation. It was found that the kinetics of the observed pH changes did not fit the trend predicted by the Arrhenius equation. Instead of the reaction rate increasing with storage temperature as predicted by the Arrhenius equation, the average pH tended to increase from a pH of approximately 1 at the baseline measurement to a pH between 1.2 and 1.3 at the end of the first, second and third month of storage, regardless of storage temperature. The observation that the non-activated change in pH does not fit the Arrhenius equation suggests that the self-adhesive composite is relatively stable over three months, regardless of the storage temperature within the range tested. This could be confirmed by measuring the pH of the light-activated reaction; however that was beyond the scope of this study.

It could be hypothesized that the true rate could not be calculated because the actual reaction of the material requires activation by light. This study showed that the material remaining in its viscous state was stable and capable of maintaining its pH within a small range. The rate of change of the pH increased steadily until month two then plateaued by month three for the sample stored under refrigeration. The rate of change of the pH sharply decreased and plateaued by month two for samples stored in room temperature and in the incubator. This shows the effect that refrigeration has on the stored samples. The rate of change of the pH is affected but its benefit is lost after just 30-60 days. So, it can be concluded from this data that refrigeration of the self-adhesive flowable composite can slow the rate of change of pH during the first 30 to 60 days of storage. The importance of this difference in pH is questionable regarding

its clinical application. The mean difference in pH between the samples stored in the refrigerator and those in the incubator was, at its greatest, .171 on the pH scale. At months two and three, the mean difference in pH was .042 and .050 on the pH scale respectively. To put it in perspective, it is the difference between an acid being 1.1 and 1.3, this is unlikely to be clinically significant. The difference also seems insignificant because the range of the pH of self-limiting acidic monomers varies greatly among currently marketed products, ranging anywhere from 1-2 on the pH scale. The pH of Vertise Flow®, even after being stored under different conditions, was able to maintain a pH that is well within the acceptability range for good clinical performance. The results of the two factor ANOVA and Kruskal-Wallis ANOVA further support the idea that there was no statistically significant difference between pH and the various storage methods of the tested self-adhesive flowable composite ( $p>0.05$ ). The pH was found to be stable as long as the sample remained in its viscous state.

All samples maintained some material in a viscous state throughout the data gathering phase. However, it was noted that after the first 30 days that some of the material being stored in the incubator had begun to harden or cure. The curing of the flowable composite continued in the samples stored in the incubator for the duration of the data gathering phase. There was not any amount of detectable material that hardened or cured in the samples being stored in the refrigerator or at room temperature. There remained an adequate amount of viscous sample to get an accurate pH measurement using the special bench top probe with a micro bulb tip design. The tip design allows for accurate measurement in samples less than 100 microliters. The

material that remained uncured was able to maintain a pH similar to the samples stored under refrigeration and room temperature as supported by the statistical analysis.

Based on this study it appears that at a certain temperature, and duration of that temperature, that the self-adhesive flowable composite begins to cure. The temperature and duration at which that occurs was beyond the scope of this research project but could be of value if such a study was undertaken to determine those variables.

## CONCLUSION

Based on the results of this in-vitro study the 1<sup>st</sup> null hypothesis was accepted:

The pH of the proposed self-adhesive flowable composite will not change according to the storage method over the course of three months ( $p>0.05$ ).

Other conclusions that can be drawn as the result of this study include:

1. There was a statistically significant change in pH by time under all three storage methods ( $p<0.001$ ).
2. At some duration and point in time above room temperature the self-adhesive flowable composite begins to harden or cure.

Despite a small initial increase, the pH of Vertise Flow® does remain stable under varying storage temperatures, for at least 90 days. However, this does not mean the product will be useable when stored under any particular conditions. Despite the stability of its pH, when the material is in its viscous state, it is clear that too warm of storage conditions will make the product cure pre-maturely and become unusable. It would be wise for the practitioner to follow recommendations from the manufacturer to store the product in the refrigerator or at least ensure that the product is stored at no more than room temperature to maintain its stability and clinical value.

Though the pH of all samples increased during the first 30 days they eventually plateaued and remained relatively flat. The means of the pH of the three storage methods remained within .042 to .050 of each other during the last two months of data gathering. This small difference in pH is unlikely to affect the ability for the acidic monomers to etch enamel and dentin. Over a 90 day period one can rely on the stability of the pH of this self-adhering flowable composite and its corresponding clinical performance.

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