

INTRODUCTION

The demand for esthetic restorations has greatly increased in the past decade. More patients are seeking to have old amalgams replaced with resin composites. A continuing concern is whether these restorations are a long-lasting and predictable treatment alternative. Modern and advanced technology allows companies to continue to improve and develop resin composites. An identified concern surrounding the use of composite resin restorations continues to be the polymerization stress generated during setting. Upon setting, stress is created between the tooth structure and the restoration. Based on the type of composite resin used, these shrinkage stresses can exceed the tensile strength of the dental adhesive interface. The interfacial bond strength between the resin and the tooth becomes compromised, leading to the formation of a small gap. The resultant gap formation could lead to microleakage, sensitivity, secondary decay, and possible loss or fracture of the restoration.^{1,2} Multiple companies have continued to change the formulation of resin composites in pursuit of the ultimate product, one that has ease of handling and is quick, strong, durable, cheap, and esthetic. Making decisions regarding which resin to use in practice has become more difficult. This question is facing private-practice dentists on a daily basis.

STATEMENT OF PROBLEM

Resin composites continue to experience rapid development. Recently, a new resin was formulated incorporating a novel photoinitiator system, which enhances light-curing efficiency: rapid amplified photopolymerization (RAP) is proprietary technology

that increases the free radicals associated with each activated camphorquinone molecule. Some preliminary testing from another laboratory (Tokuyama Dental Corp. internal testing data) compared the flexural strength and modulus of two resins with and without this new technology. In order to fully understand the characteristics of this activation system, more tests need to be completed. Determining the degree of conversion and the amount of polymerization stress created will allow a more complete understanding of the properties of this new system. With these data, comparisons can be made about the advantages of this technology.

REVIEW OF LITERATURE

RESIN SYSTEMS

Resin composites have become very popular restorative materials for today's esthetically demanding world. Since primary development in the 1960s, composites have continued to evolve into the improved materials we have today. Four primary components make up a resin composite: organic polymer matrix, inorganic filler particles, coupling agent, and the initiator-accelerator system.³ All these components continue to be modified in many different ways. Many companies continue to work to create the ultimate resin with the best mechanical properties and esthetics.

Many of the resin composites today contain either Bis-GMA (2,2-bis[4(2-hydroxy-3-methacryloxy-propyloxy)-phenyl]propane or urethane dimethacrylate (UDMA)³ (Figure 1). These two oligomers contain the reactive carbon-carbon double bond needed for free-radical addition polymerization.³ Due to the viscous nature of most composites, triethylene glycol dimethacrylate (TEGMA) is added to allow for better clinical handling.³ One area that has drastically changed composite resins deals with the filler material. Today, resins are classified according to the type of filler particles, microhybrid and microfilled.³ These fillers vary in size, shape and distribution, but commonly tend to be glass, quartz, or silica.³ These filler particles are treated by the manufacturer with a coupling agent to allow better bonding between the filler and the oligomer.³

Different initiators and accelerators are used depending on the type of resin. In dentistry today, there are two common ways in which polymerization begins in direct

restorative materials: light activation or chemical activation. Camphorquinone (CQ) is typically added to light-activated resins as a photo-initiator along with an amine as an accelerator (Figure 2). Visible light (~ 470 nm) plus aliphatic amines in combination with CQ leads to the production of free radicals (Figure 3). With the production of sufficient free radicals, reaction with monomer molecules results in the propagation of a polymer chain in a process called free radical polymerization. With chemically activated resins, the mixing of an organic amine (catalyst) and an organic peroxide (base) starts the polymerization process by the production of free radicals.³ In comparison, both systems have their advantages and disadvantages. In the light-activated system, the advantages include; no mixing, longer working times and on-demand polymerization. The major disadvantage with chemically activated resins is the working time. Once these two pastes are mixed clinically, the reaction has begun and will continue quickly, not allowing much time for placement. There are different inhibitors that can be added to help slow down the process and minimize spontaneous polymerization in storage. BHT is commonly added as an inhibitor in these chemically cured resins.³

POLYMERIZATION PROCESS

Regardless of the type of activation, all composite resin restorative materials undergo a polymerization reaction to form a solid structure. Most dental resins specifically undergo a process called free radical addition polymerization. In this type of reaction, multiple small monomer units become chemically linked into a large macromolecule during the polymerization reaction.³ In order to better understand the advantages and disadvantages of these restorative materials, a good understanding of the

polymerization process is required.

In free radical polymerization there are three stages: initiation, propagation, and termination.³ In order to start this reaction, an initiator is activated causing the production of free radicals.³ Visible light (~ 470 nm) activates CQ to accept electrons from an electron donor such as an amine. A photo-excited complex called the “exciplex” is formed momentarily.⁴ This complex breaks down forming free radicals (Figure 3). The free radicals then initiate the reaction by attacking the C=C of the monomer (Figure 3). This attack leaves an unpaired electron on the center carbon.³ Therefore, this monomer itself then becomes a free radical, and the polymerization reaction is initiated.

In the second stage, propagation, the newly formed monomer radical becomes the active component. This radical now attacks and joins to another C=C bond containing monomer, leading to a new radical. Ideally, this process would continue until all the monomers have been used, but due to multiple constraints, this is not the case. Finally, in the third and final stage of polymerization, the growing chain is stopped in a process called termination. There are multiple ways in which this process can occur. A common termination reaction occurs when two active chains interact.⁵ This can either lead to the formation of one long chain or to disproportionation, which is the exchange of a hydrogen atom resulting in two dead chains.^{3,5} Secondly, termination can take place by the transfer of a hydrogen or other atom to the polymer from another compound in the system.⁶ This is called a chain-transfer reaction. This chain transfer terminates the growth of that specific polymer molecule and then reinitiates polymerization of a new radical.⁶ Finally, an impurity or inhibitor can interact with the growing chain and lead to

termination.^{3,5,6} Due to the variety of termination processes, a great variety of chain lengths exist in the final composite resin.

CONTRACTION STRESS

With any dimethacrylate-based resin composite comes an inherent shrinkage upon setting. The intertwining of the polymer network associated with a decrease in volume and intermolecular distance has been reported to be 1.5 percent to 5 percent leading to these internal stresses.⁷⁻¹¹ The contraction of resin composites has received much attention in the dental materials literature. Many different attempts have been made to formulate a resin with minimal shrinkage resulting in a more predictable restorative material.

Dental composites are viscous materials available as light and/or chemical cured systems. During the polymerization process, the material develops rigidity by passing through a visco-elastic solid phase into a rigid elastic phase.¹⁰ At this point, the ability of the resin to flow decreases. This is considered the gel point.¹⁰ Davidson describes the gel point as “the moment at which the material can no longer provide viscous flow to keep up with the curing contraction.”¹⁰ It has been estimated that this gel point is about 1 percent of conversion and therefore occurs early in the polymerization process.¹² The ability of the material to flow is greatly decreased after this point and is obviously time-dependant. Once beyond this gel point, the deformation of the resin produces stresses according to Hooke’s Law.⁷ This law describes stress and strain in an elastic solid.⁷ With stress being the product of the elastic modulus and strain, any resin with high volumetric shrinkage and high elastic modulus will have high polymerization stresses.⁷

There have been many studies done concerning the ability of a resin to flow prior to the gel point and the correlation with contraction stress.

The effect of contraction stress on the bond between tooth and resin has been documented *in vitro* and *in vivo*. It has been shown that the stress created is transferred to the tooth/resin interface as tensile and shear forces.^{7,10} These forces, if greater than the adhesive bond, may cause microleakage leading to secondary caries, sensitivity, and fracture.¹³ This is a major problem in restorative dentistry because secondary caries is the leading cause of replacement of resin restorations.¹⁴ For this reason, many studies have been done to minimize this problem. Stansbury et al. divided the quest into two sets of phenomena for evaluation: 1) changes in monomer structure or chemistry, and 2) changes in fillers or use of additives.¹² These different avenues will be discussed, but first, the concept of configuration factor (C-factor) will be addressed.

In early studies by Davidson and DeGee, it was reported that there was a difference in contraction stresses between a two-dimensional and three-dimensional cavity model.^{11,13} This led to research by Feilzer, DeGee, and Davidson in 1987, correlating cavity configuration and the development of polymerization stresses.¹⁵ The use of a term, the configuration factor (C-factor), was then adopted. This factor takes into account the amount of bonded-to-unbonded surface area.^{15,16}

$$C = \frac{\text{bonded surfaces}}{\text{unbonded surfaces}}$$

With a greater amount of bonded surface area comes a decrease in the ability of the resin to flow. With that, there will be a decrease in the resin's ability to compensate for the

volumetric shrinkage, leading to higher amounts of stress.¹⁵⁻¹⁷ Therefore, the higher the C-factor, the higher the resulting stresses.¹⁷

Another area of interest in contraction stress comes when chemical-cured and light-cured composites are compared. Feilzer et al., in 1993 compared light-cured composites to chemically initiated composites using a tensometer.¹⁸ The polymerization rate with a chemically cured composite (CC) tends to be slower than the rate seen with a light-cured composite (LC).¹⁸ Therefore, there is more opportunity for the CC to flow during the extended setting time. This ability to flow for a longer period of time was related to a decrease in setting stress in the CC as compared to the LC.¹⁸ Furthermore, the effect of internal porosities on the release of polymerization stresses was also investigated.¹⁸ In CC composites, inherent porosities are mixed in with the addition of the two pastes. There was a belief that these internal porosities would allow for some relief of the internal stresses. Since these porosities tended to be in CC rather than LC, Feilzer et al. produced porosities in the LC and tested them.¹⁸ The results showed that by the induction of porosities, there was a decrease in the polymerization stress.¹⁸ Some caution should be used in interpreting these results because the introduction of porosities may lead to poorer mechanical properties.¹⁹

Kinomoto et al. performed a similar study investigating differences in internal stresses with light-cured vs. chemical-cured composite restorations.¹⁹ Using class 1 cavity preparations and photoelastic analysis, this group determined that the most important factor in creating internal stress was the velocity of polymerization.¹⁹ To try to reduce the chance that the internal porosities of the chemical-cured resin allowed for

greater stress distribution and flow, this group used a bubbleless mixing technique.¹⁹ This allowed them to determine that indeed the velocity of polymerization was a significant factor. Therefore, a potential pathway to better the next generation of light-cured composites would be to control the velocity of polymerization without losing mechanical properties.

Many groups have looked into different curing methods in order to find ways to decrease the internal stress. For example, in a study evaluating a pulse-delay method of curing, it was shown that the stress decreased 19 percent to 30 percent, compared with a continuous high-intensity cure.²⁰ However, the question arose regarding the mechanical properties of these composites that were being cured at different rates. Were they as strong as the conventional high intensity light-cured composites? Witzel et al.²¹ performed a study to try to answer this question. This group used two different composites with three different photoactivation modes, but similar power densities. Different mechanical properties including degree of conversion, flexural strength, and contraction stress were evaluated. They concluded that the degree of conversion was unchanged by the different photoactivation methods. As in the Kinomoto study, they found a reduction (28 percent) in the contraction stresses created using the low-intensity or pulse-delay method.²¹

Even though these results looked promising, Asmussen and Peutzfeldt²² determined that these different curing modes made these resin composites more susceptible to degradation in ethanol. They determined that once placed in ethanol, there was softening of the resin. In the study above by Witzel, ethanol submersion was also

performed, but it was deemed statistically insignificant, possibly due to the low submersion times. Inconsistencies in results in this area are greatly influenced by the type of resin used and the energy densities applied to the resins.²¹ The importance of ethanol storage relates to the degradation of the resin composite in the mouth. Slower light-curing methods may be associated with softening of these resins over time in the oral environment. More research is needed to fully understand how each light-curing method affects different types of resins.

DEGREE OF CONVERSION

Degree of conversion is another important factor in resin composites. Many articles have been published focusing on this property and its relation to polymerization contraction stress. Degree of conversion describes the percentage of double bonds that react and convert to single bonds during the polymerization reaction.³ Infrared spectroscopy is commonly used to determine the degree of conversion. The interaction of infrared light with matter produces an infrared spectrum. Structural fragments within the molecule, called functional groups, are sensitive to the infrared light.²³ With the knowledge of common functional groups within a material, this technique is commonly used to identify unknowns.

The FTIR (Fourier Transform Infrared Spectrometer) is the most commonly used machine to determine the degree of conversion. The advantages of this technique include its being a universal technique (solids, liquids, gasses, and semi-solids can be tested); its information (much can be gained from one spectrum); its speed and sensitivity (only small specimens need to be fabricated), and its relatively low cost.²³ The disadvantages

include that the amount of an element cannot be measured, just its presence and that complex mixtures are hard to analyze.²³

In multiple studies by Braga and Ferracane⁸ and others, it has been shown that as the degree of conversion increases, so does the contraction stress.²⁴ After looking at differences in energy density, they found a non-linear relation between degree of conversion and contraction stress.⁸ This was due to the inability of the resin to flow after a certain point in polymerization. If the resin is unable to flow, then the material is not able to compensate for the shrinkage forces. Therefore, one would see large increases in stress with small increases in conversion.⁸ Thus, the question was, at what point should degree of conversion be compromised to allow for a decrease in shrinkage stress? The amount of conversion that can be compromised to allow for decreased shrinkage stress is not well understood. The level of degree of conversion that will not compromise the physical properties of the resin requires further understanding.

This method can be used because of the inclusion of benzene rings in the oligomeric structures of the matrix of composites. When analyzing the mid-IR range spectra of resin composites, the Bis-GMA benzene ring (Figure 1) shows up in the 1608 wavenumber.²⁵ This is considered peak 2 (Figure 4). The unreacted vinyl C=C double bond shows up around 1638 wavenumbers. This is considered peak 1 (Figure 4). When comparing a cured specimen with an uncured specimen, the height of peak 1 changes. This is due to the change in the amount of C=C double bonds present. In the polymerization process, the amount of double bonds decreases due to the conversion to

C-C single bonds as the reaction proceeds (Figure 3). By analyzing the area under the curves, the degree of conversion can be calculated.

FLEXURAL STRENGTH

Flexural strength is important in dentistry due to the amount of forces applied to posterior restorations in the mouth. The amount of force required to break a beam of material describes its flexural strength.⁵ This property is usually measured when a load is applied to the middle of a beam supported at each end. This is called a three-point bending test.⁵ As stated above, the most optimum resin would be able to withstand adequate occlusal forces, but also withstand the oral environment.

Many questions remain concerning restorative resin composites, but only with further research can some be answered. Research is being done as fast as the formulations are changing in these materials. With the high demand for these esthetic restorations, improvements are needed. Marginal adaptation, microleakage, polymerization shrinkage, and contraction stress are all still major issues. It has been shown in many different studies that amalgam has a better survival rate than composite restorations.^{26,27} Marginal leakage and secondary decay are still leading reasons given for replacement.²⁷ Until some of the answers to the above questions are resolved, replacement of restorations will continue to be frequent procedures in the dental office.

PURPOSE OF STUDY

The objectives of the present study were:

1. To measure the flexural strength of two types of light-cured composites (flowable and microfilled), each formulated with one of two different initiator systems, RAP + CQ or CQ only.
2. To measure the contraction stresses of the two formulations of the two types of composites described in #1.
3. To measure the degree of conversion of the two formulations of the two types of composites described in #1.

HYPOTHESES

The hypotheses tested were:

1. Null Hypothesis: There will be no significant difference in contraction stress in the resin formulations with the RAP initiator system compared with the CQ resins.

Alternative Hypothesis: There will be a significant difference in contraction stress in the resin formulations with the RAP initiator system compared with the CQ resins.

2. Null Hypothesis: There will be no significant difference in the flexural strength in the resin formulations with the RAP initiator system compared with the CQ resins.

Alternative Hypothesis: There will be a significant difference in contraction stress in the resin formulations with the RAP initiator system compared with the CQ resins.

3. Null Hypothesis: There will be no significant difference in the degree of

conversion in the resin formulations with the RAP initiator system compared with the CQ resins.

Alternative Hypothesis: There will be a significant difference in the degree of conversion in the resin formulations with the RAP initiator system compared with the CQ resins.

MATERIALS AND METHODS

This study was conducted in a laboratory setting to compare and contrast a new photoinitiator system in composite resins. The results from the new photoinitiation system were compared with the traditional system to evaluate the effects on flexural strength, contraction stress, and degree of conversion of these composite resins.

SPECIMENS

Light-cured resin composites were prepared and supplied by Tokuyama Dental and used in this experiment. Four experimental composites were evaluated. These composites were either flowable or microfilled and were formulated either with or without the RAP photoinitiator system (RAP + CQ or CQ only). The experimental groups were as follows:

1. Microfilled composite resin with RAP + CQ (ESQ w/ RAP).
2. Flowable composite resin with RAP + CQ (EFQ w/ RAP).
3. Microfilled composite resin with only CQ (ESQ w/o RAP).
4. Flowable composite resin with only CQ (EFQ w/o RAP).

FLEXURAL STRENGTH TEST

Flexural strength was determined with a three-point bending test. Specimens were prepared using a stainless steel split mold (Figure 5). PTFE Release Agent Dry Lubricant (Miller-Stephenson) was used to allow for easier separation of the specimen from the mold. The split mold was placed on a Mylar sheet on top of a glass slab. The mold was filled with the experimental composite and Mylar placed on top prior to light

curing. Each specimen (25x2x2mm) was light cured in three overlapping 20-second cycles. (L.E. Demetron I curing unit, Kerr Corporation, Danbury, CT). A #11 scalpel blade was used to trim away the flash from the mold and the specimen was removed. The specimens' non-testing surfaces (surfaces not against the Mylar strips) were then wet-polished using SiC paper (600 grit). Throughout the entire specimen fabrication, the power of the curing light was monitored with the Cure Rite Radiometer (Model: #644726 Dentsply Caulk, Milford, DE) and was greater than $600\text{mW}/\text{cm}^2$. All specimens were then stored in deionized water at 37°C for 24 hrs before testing.

Specimens were removed from the deionized water, dried, and edges finished and polished. Each specimen was labeled and measured (length and width) using the Digimatic Caliper (Mitutoyo). All measurements corresponding to the specimen number were entered into the computer prior to testing. A universal testing machine (Sintech Renew 1123, Instron Engineering Corp., Canton, MA) attached to a three-point bending apparatus was used for testing (Figure 6). Data collection was obtained through a computer connected to the machine utilizing software designed specifically for this machine (Test Works 4.0 MTS Systems Co., Eden Prairie, MN). Each test was conducted with a crosshead speed of 1 mm/min and a span length of 20 mm. Ten different specimens for each group were tested. The following equation was used by the software to calculate flexural strength:

$$FS = \frac{3WI}{2bd^2}$$

Where:

W = maximum load at break (N);

I = supporting span (20mm)

b = specimen width (mm)

d = specimen thickness (mm)

CONTRACTION STRESS TEST

The experimental set-up was originally described by Feilzer et al. in 1987.¹⁵ Modifications have been made to the original set-up to coincide with materials used in this lab. A tensometer (American Dental Association Health Foundation, NIST, Gaithersburg, MD) was used to measure contraction stress (Figure 7). A linear variable differential transformer (LVDT) measured the tensile force generated by the shrinking composite.⁵ Contraction stress was then calculated by dividing the tensile force by the cross-sectional area of the composite sample.⁵ Two quartz rods (6-mm diameter) were positioned vertically in the tensometer; the upper was attached to a stainless steel beam, and the lower attached to complete the assembly. The lower quartz rod was attached to the light-curing unit (The LVDT (model: 050-HR-000, Component Distributors Incorporation, Ft. Lauderdale, FL) guiding the light to the specimen.

Prior to obtaining stress measurements, the quartz rods were initially cut using the Isomet Saw (Isomet 1000 Precision Saw, Buehler) to create the needed flat surfaces. They were then polished with 600-grit wet silicon carbide paper, washed, and dried. The flattened end of the quartz rod was silane-treated two times prior to insertion into the

machine. The distance between these quartz rods was standardized to 2.25 mm in height and 6 mm in diameter for each specimen. These measurements correspond to a C-factor of 1.33 ($\text{diameter}/(2)\text{height}$). A polytetrafluoroethylene (PTFE) sleeve was used to form the composite specimens to the exact diameter of the quartz rods. Two holes were placed opposite each other in the sleeve, one for sample injection and the other for air and excess material release. Each sample composite was injected through the PTFE onto the silanized quartz rods. Once placed, the composite resin was light cured for 60 sec through the bottom quartz rod (Demetron A.1, courtesy of SDS Kerr). The light intensity was monitored at the end of the quartz rod throughout the experiment using a Cure Rite radiometer (Dentsply Caulk, Milford, DE) and was greater than $600 \text{ mW}/\text{cm}^2$. The polymerization contraction stress was measured for 30 minutes from the start of the photoinitiation. The data was collected every second. Five different specimens from each of the four experimental groups were tested.

DEGREE OF CONVERSION TEST

The degree of conversion was determined using near-infrared spectroscopy. The spectra were collected using the Jasco FT-IR spectrometer (Model: 4100, Jasco Corp., Tokyo, Japan) in attenuated total reflection (ATR) mode (Figure 8). The uncured specimens were placed directly on the 5-mm glass opening of the spectrometer. The scan was run three times per specimen ($n = 5$). The spectrum obtained for each run was used for analysis. The glass opening was then cleaned with acetone on a cotton ball in order to completely remove the uncured resin. The cured specimens were not paired with the uncured specimens due to the difficulty in removing the uncured specimen from the

machine. The cured specimens were fabricated in the following way. Resin composite was placed between two glass slides (Mylar between) and compressed to an even, thin thickness. The resin was then cured for 60 sec (Optilux curing unit, Model: 401, Demetron Research Corp., Danbury, CT). The specimen was then removed from the Mylar strips using a # 11 blade scalpel and placed directly on the spectrometer. As above, the scan was run three times per specimen ($n = 5$) producing a spectrum for each run. Each spectrum obtained was then used for analysis ($n = 5 \times 3 = 15$ spectra analyzed). The IR spectra were obtained in absorbance mode from 64 coadded scans at 4 wavenumber resolution. To avoid any internal reflectance patterns from the empty mold, a background spectrum was run prior to the running of the samples.⁵

In this type of spectroscopy, the degree of conversion comes from the peaks between 1600 cm^{-1} and 1640 cm^{-1} (Figure 4), which is considered mid-IR range. The peak showing the unreacted vinyl C=C groups appears at 1638 cm^{-1} (Peak 1) while the peak showing the aromatic ring C=C appears at 1608 cm^{-1} (Peak 2).²⁵ The analysis of the peaks was done using the area under the peaks to determine the P1/P2 ratio for both cured and uncured specimens. The change in the area under the peaks between cured and uncured was calculated using the following equation:

$$DC = \left(1 - \left(\frac{\text{Cured} \left(\frac{P1}{P2} \right)}{\text{Uncured} \left(\frac{P1}{P2} \right)} \right) \right) \times 100\%$$

(P1= Peak 1 area under peak at 1638 cm^{-1})

(P2 = Peak 2 area under peak at 1608 cm^{-1})

STATISTICAL METHODS

The effects of composite resin type (microfilled or flowable) and RAP (presence or absence) on flexural strength, contraction stress, and degree of conversion were analyzed using two-way analysis of variance (ANOVA). The interaction between composite resin type and RAP was significant, so that RAP comparisons therefore were presented within microfilled and flowable composites and resin type comparison were presented with and without RAP. If the interaction effect was not significant, the main effects were examined for significance.

SAMPLE SIZE JUSTIFICATION

Based on the data collected in previous *in vitro* studies using the same testing methods, the flexural strength measurements were expected to range between 80 MPa and 100 MPa with a standard deviation in the 10-MPa to 15-MPa range.²⁸ With a sample size of nine specimens in each of the four groups, the study had 80-percent power to detect a difference of 15 MPa in flexural strength between composite resin types and between specimens with and without RAP, assuming a two-sided test at a 5-percent significance level with a non-significant interaction between composite resin type and RAP. Previous data for shrinkage stress indicated a within-group standard deviation of approximately 0.25 MPa. With a sample size of five samples per group for shrinkage stress, the study had 80-percent power to detect a difference of 0.5 MPa. Previous data for degree of conversion indicated a within-group standard deviation of approximately 0.9. With a sample size of 5 samples per group for degree of conversion, the study had 80-percent power to detect a difference of 1.2.

RESULTS

After evaluation of the results using two-way ANOVA, it appears that the addition of RAP has significantly changed some of the physical properties of these experimental composite resins. The peak stress and flexural modulus are given in Tables I and II. The interaction between resin type and RAP was significant. With the addition of RAP to the EFQ, there was a significant increase in the peak stress ($p = 0.0001$) as depicted in Figure 9. There was not a significant increase in the ESQ ($p = 0.28$). The flexural modulus increased significantly in both EFQ and ESQ. These results appear in Table II and are graphically depicted in Figure 10. The interaction between resin type and RAP was not significant when associated with the flexural modulus.

The maximum stress and maximum stress rate were calculated from stress curves generated using the tensometer (Figure 11). The slope of the line between the gel point and the end of the elastic portion of the stress strain curve was used to determine the rate. After analysis using two-way ANOVA, the interaction between resin type and RAP was significant ($p = 0.0019$). When looking at the EFQ group, the addition of RAP significantly increased the maximum stress rate (Table III). This was consistent with the polymerization stress increasing with the addition of RAP. This was not significant in the ESQ group ($p = 0.64$), but is still evident in the graphic depiction of the data (Figure 12). The experimental formulations with RAP appeared in general to have a higher polymerization stress than those with camphorquinone only (w/o RAP). For the maximum stress generated, the interaction between resin type and RAP was also significant ($p = 0.0006$). When looking at the EFQ group, the addition of RAP

significantly increased the maximum stress (Table IV). This was not statistically significant in the ESQ group ($p = 0.14$). In general again, there was an increase in the amount of stress created with the addition of RAP to both EFQ and ESQ (Figure 13).

Finally, after using two-way ANOVA, there was not a significant difference between resin type and RAP in the degree of conversion ($p = 0.12$). However, there was a significant difference in the materials that contained RAP compared with those that did not (Table V). As depicted in Figure 14, with both ESQ and EFQ, those with RAP had a higher degree of conversion than those without. There was also a significant increase in the degree of conversion with the EFQ as compared with the ESQ (Figure 14).

TABLES AND FIGURES

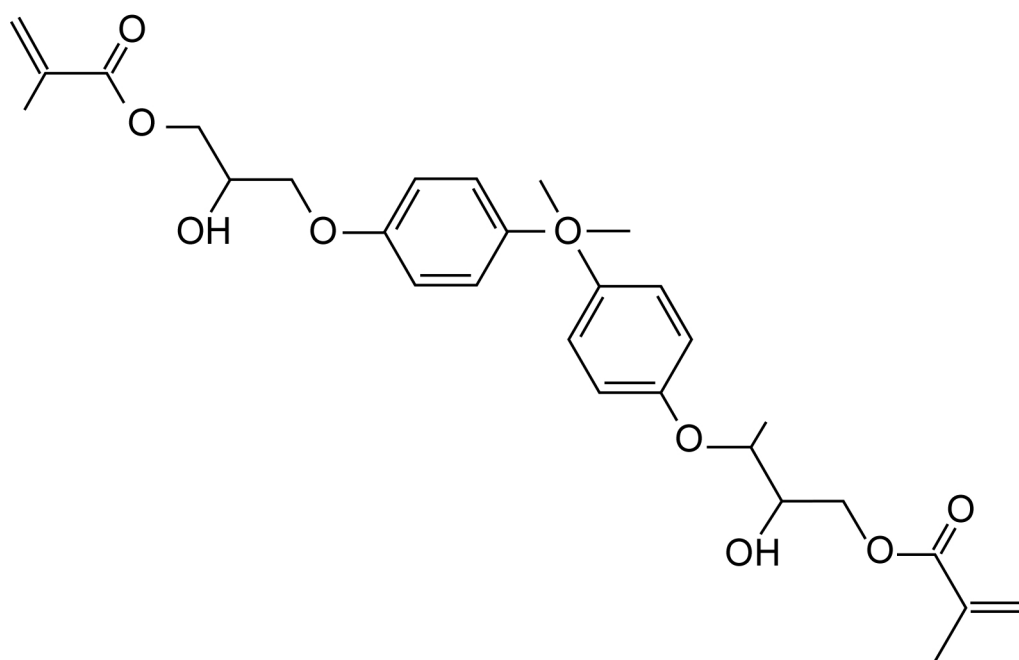


FIGURE 1. Bis-GMA (2,2-*bis*[4(2-hydroxy-3-methacryloxypropoxy)-phenyl]propane).

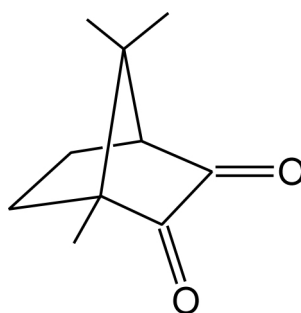


FIGURE 2. Camphoroquinone molecular structure.

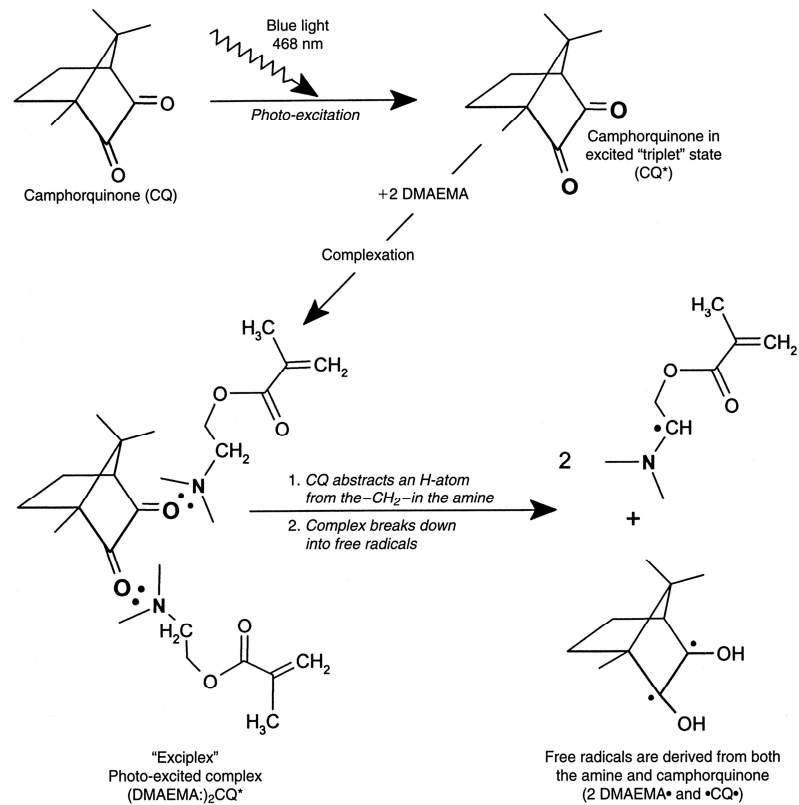


FIGURE 3. Free radical addition polymerization activation. Production of free radicals (denoted by \cdot) with activation by CQ and blue light. Exciplex is formed after donation of an electron from an electron donor such as an amine (DMAEMA). It is thought that this amine is altered to produce the RAP photoinitiation system. (Figure from *Anusavice's Phillips Science of Dental Materials*.)

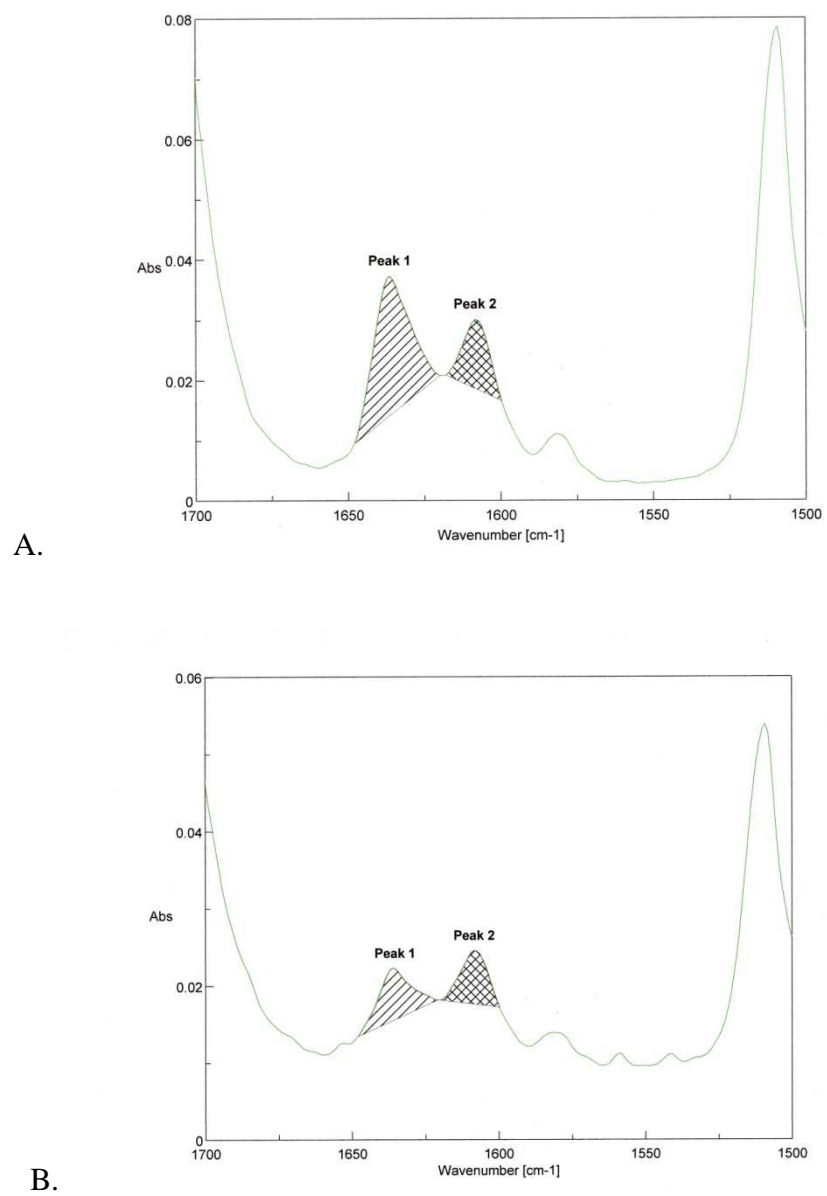


FIGURE 4. Sample of FTIR spectra uncured (A) and cured (B).

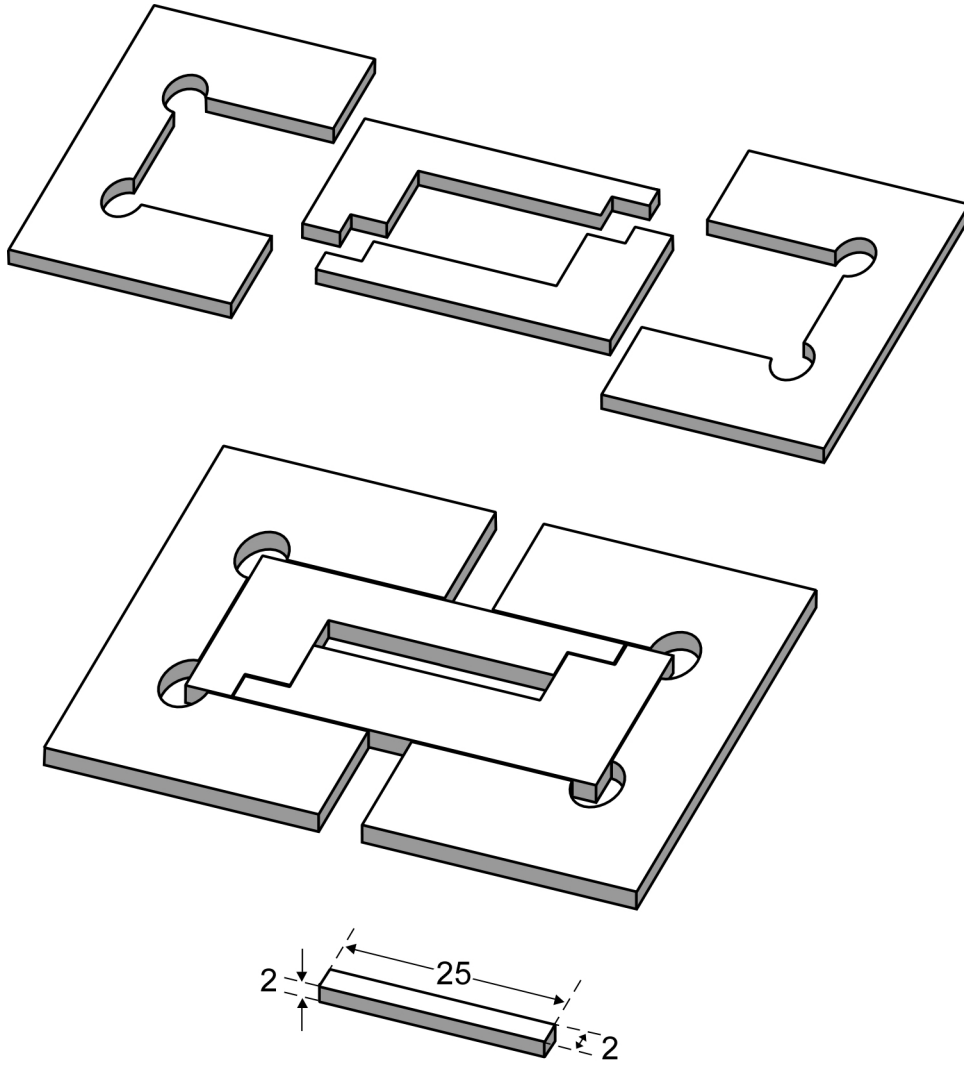


FIGURE 5. Stainless steel split mold.



FIGURE 6. Three-point bending apparatus.

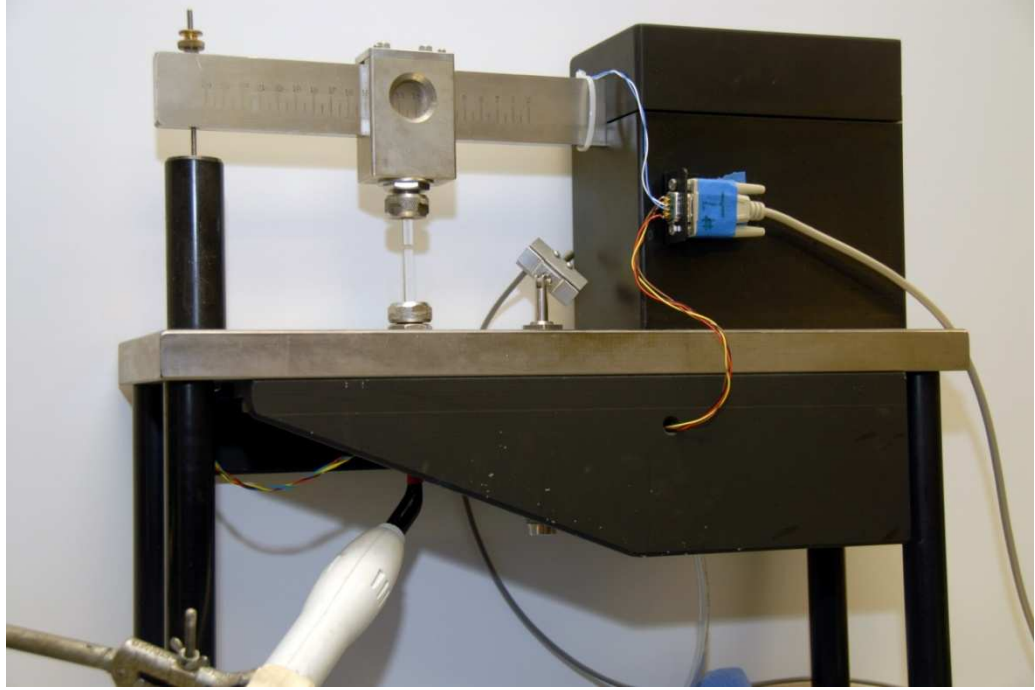


FIGURE 7. Tensometer.



FIGURE 8. FTIR.

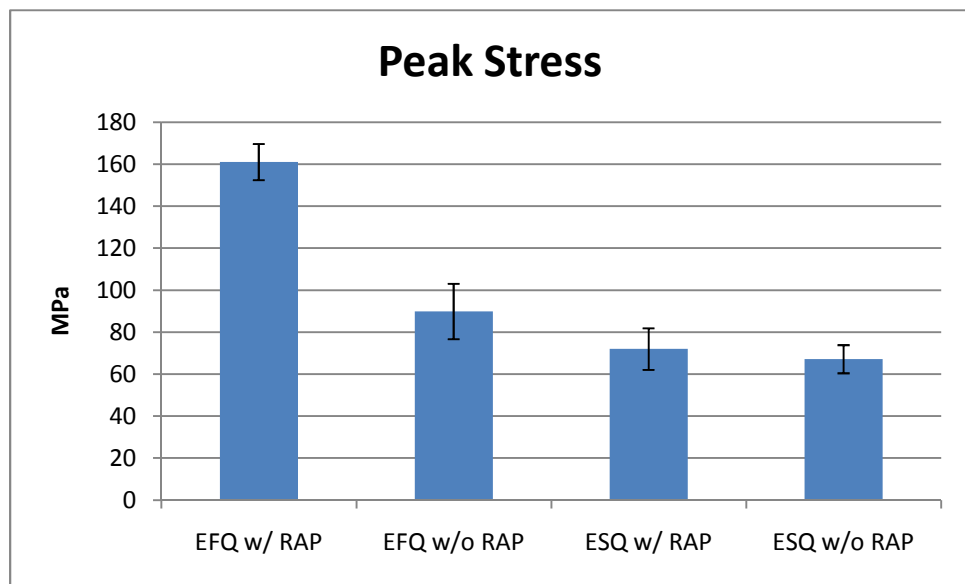


FIGURE 9. Peak stress.

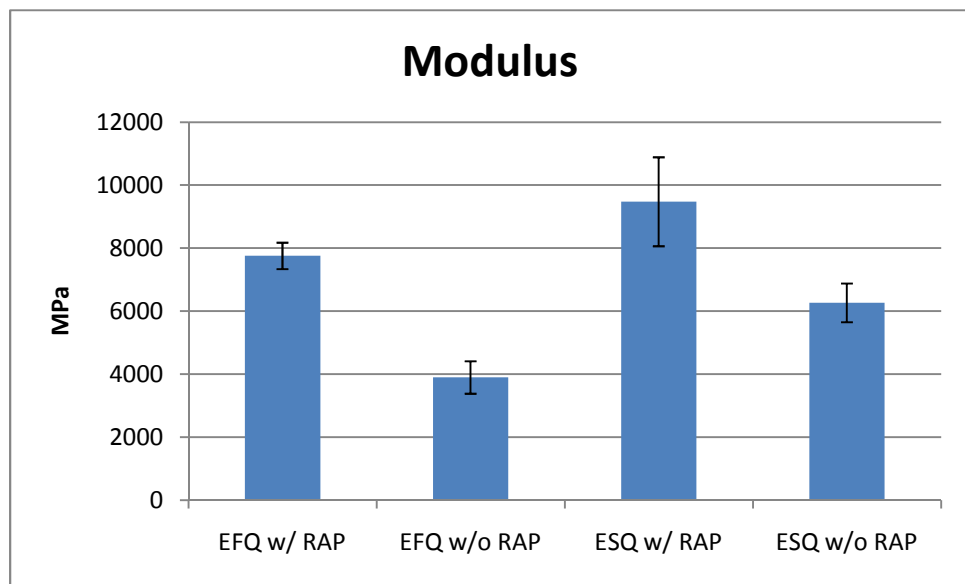


FIGURE 10. Flexural modulus.

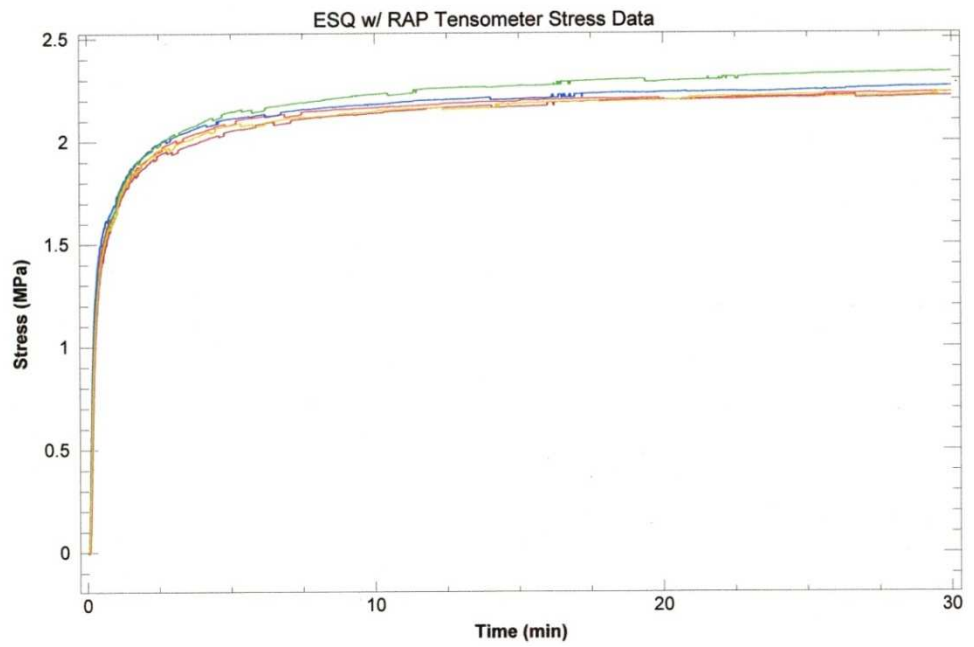
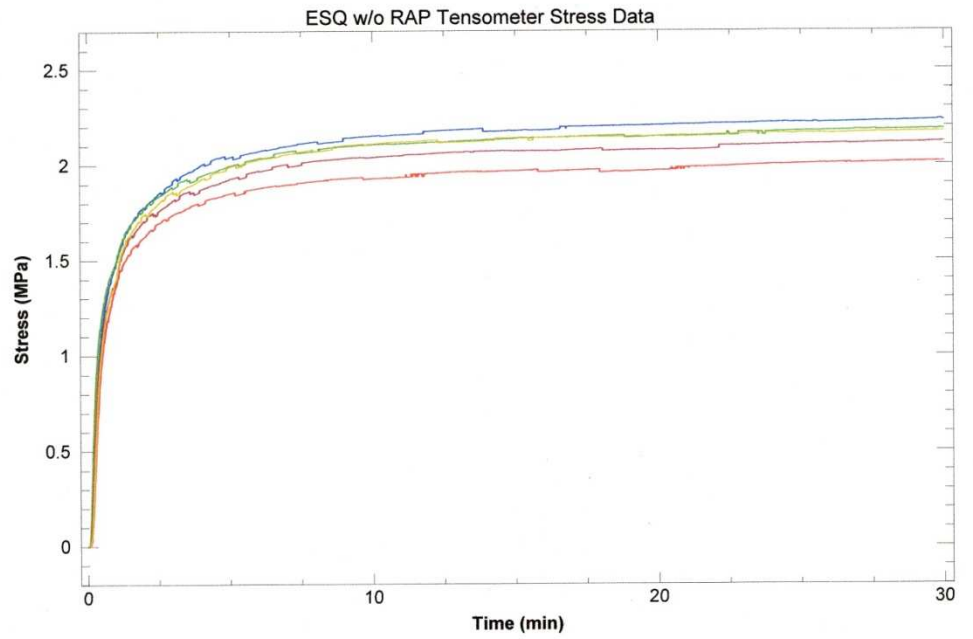


FIGURE 11. Example of tensometer curves.

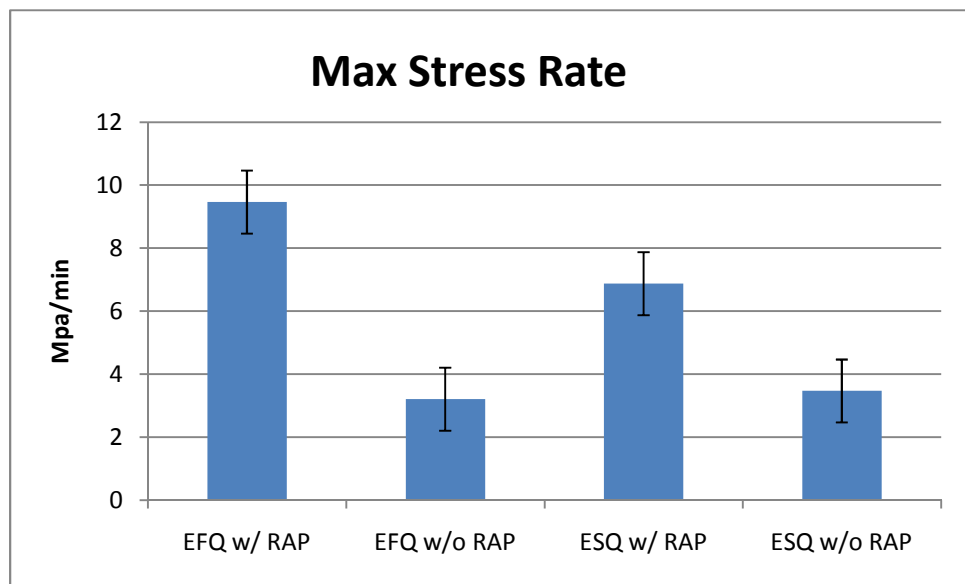


FIGURE 12. Maximum stress rate.

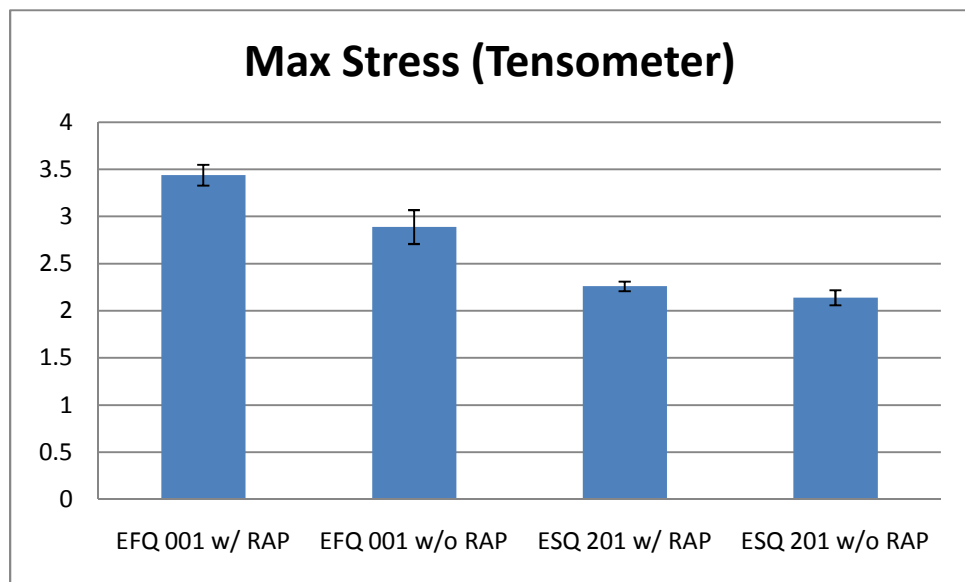


FIGURE 13. Maximum stress (tensometer).

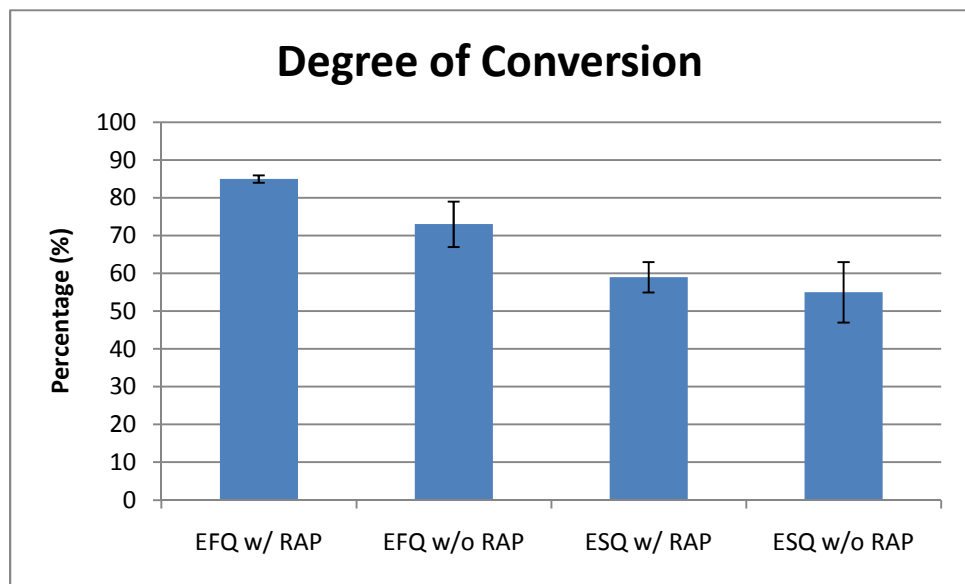


FIGURE 14. Degree of conversion.

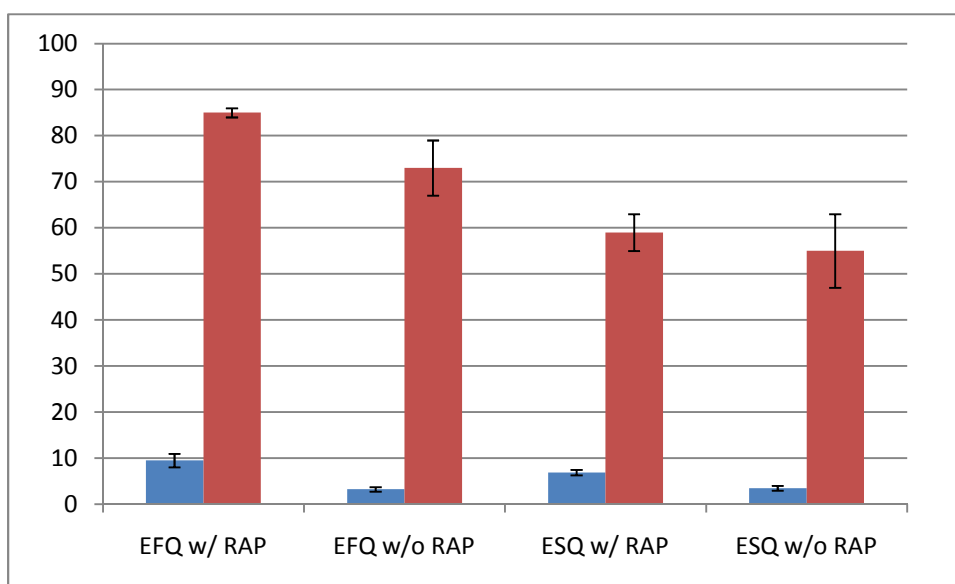


FIGURE 15. Degree of conversion vs. polymerization stress.

TABLE I

Peak stress data collected from flexural strength testing

Group	N	Mean (SD)
EFQ 001 w RAP	11	161.1 (8.6) ^a
EFQ 001 w/o RAP	11	89.9 (13.2)
ESQ 201 w RAP	11	72.0 (9.9) ^b
ESQ 201 w/o RAP	10	67.2 (6.7)

^a indicating $p < 0.05$.

^b indicating $p > 0.05$ in comparison to w/ RAP and w/o RAP.

TABLE II

Flexural modulus data from flexural strength testing

Group	N	Mean (SD)
EFQ 001 w RAP	11	7760 (419) ^a
EFQ 001 w/o RAP	11	3897 (514)
ESQ 201 w RAP	11	9478 (1412) ^a
ESQ 201 w/o RAP	10	6265 (615)

^a indicating $p < 0.05$ when comparing w/ RAP and w/o RAP.

TABLE III

Maximum stress rate data from tensometer testing

Group	N	Mean (SD)
EFQ 001 w RAP	5	9.47 (1.44) ^a
EFQ 001 w/o RAP	5	3.21 (0.50)
ESQ 201 w RAP	5	6.88 (0.59) ^b
ESQ 201 w/o RAP	5	3.47 (0.51)

^a indicating $p < 0.05$.

^b indicating $p > 0.05$ in comparison to w/ RAP and w/o RAP.

TABLE IV

Maximum stress data from tensometer testing

Group	N	Mean (SD)
EFQ 001 w RAP	5	3.44 (0.11) ^a
EFQ 001 w/o RAP	5	2.89 (0.18)
ESQ 201 w RAP	5	2.26 (0.05) ^b
ESQ 201 w/o RAP	5	2.14 (0.08)

^a indicating $p < 0.05$.

^b indicating $p > 0.05$ in comparison to w/ RAP and w/o RAP.

TABLE V
Degree of conversion data from FTIR testing

Group	N	Mean (SD)
EFQ 001 w RAP	5	85 (1) ^a
EFQ 001 w/o RAP	5	73 (6)
ESQ 201 w RAP	5	59 (4) ^a
ESQ 201 w/o RAP	5	55 (8)

^a indicating $p < 0.05$ in comparison to w/ RAP and w/o RAP.

DISCUSSION

In this study, a novel photoinitiator system (RAP) was evaluated in comparison with a more studied photoinitiator, camphorquinone (CQ). The intent of the study was to determine the effects of RAP on the physical properties of two composite resins, flowable (EFQ) and microfilled (ESQ). RAP has been shown to cause an increase in free radicals produced in the polymerization process, which thereby allows for a faster curing time. Curing time was not evaluated in this study, but should be evaluated in future studies.

Overall, the results showed that with the addition of RAP to both flowable and microfilled composite, the values of all tests increased. Not all are considered beneficial. It has been shown that with an increase in degree of conversion, there is also an increase in the polymerization stress.^{8,24} In this study, there appears to be the same relation between the degree of conversion and polymerization stress as depicted in Figure 15. With the addition of RAP to both EFQ and ESQ, both of these properties increased. As stated above, there appears to be a significant problem with polymerization shrinkage and the leakage of resin composites at the tooth-restoration interface. With the addition of RAP, both EFQ and ESQ showed a higher polymerization stress. Kinomoto et al. showed that with an increase in the velocity of polymerization comes an increase in the polymerization stress.¹⁹ RAP has been shown to cause an increase in the free radicals formed to allow a faster curing time. This increase in velocity has been shown to cause an increase in the polymerization stress compared with the resin systems using camphorquinone.

What is not fully understood is how much shrinkage is considered clinically acceptable. Obviously, concern is valid about this experimental resin, considering the presence of a problem with leakage using resins with CQ. More studies will need to be done to determine if the percentage of RAP can be modified to allow a decrease in the polymerization stress, yet still keep the increase in the other physical properties.

An evaluation of the degree of conversion showed an increase in the degree of conversion in the materials that contained RAP. This result appeared to be more significant in the flowable (EFQ) resin as compared with the microfilled (ESQ). This correlates with the information released about the benefits of this novel photoinitiator system. The production of more free radicals allows for a faster curing time and a higher degree of conversion.

Flexural strength and the flexural modulus were both enhanced by the addition of RAP. In general, microfilled composites tend to have a slightly lower flexural strength than flowable composites.³ Conversely, flowable resin appears to have a significantly lower flexural modulus than microfilled.³ These general statements appear to stand true in this experiment as well. There was a slight increase in the flexural strength of EFQ when compared with ESQ. The significant jump was when RAP was added as compared with CQ. Both EFQ and ESQ showed a significantly higher flexural strength with RAP than w/o RAP. As the degree of conversion increases, so does the amount of cross-linking of the polymer chains, which enhances the formation of a polymer network. As the polymer network becomes greater, the molecular weight increases, leading to higher mechanical properties. As for flexural modulus, it was expected that EFQ would be

slightly lower than ESQ. Again, there was a significant increase with the addition of RAP to both composites. With the increase in the polymer network, and accordingly the molecular weight, comes an increase in both the flexural strength and flexural modulus.

In restorative resins, the photoinitiation process can be modified in many different ways in order to change the properties of the material. The amines used as an electron donor in the light activation pathway have been modified many times. After evaluating this material, it is believed that the donating amine is the material changed in some way to produce the restorative resin with RAP. As CQ is activated by the blue light, amines are used to donate electrons to CQ to form the “exciplex,” which is a photo-excited complex. This exciplex is momentary and breaks down into two free radicals, which allow the process of free radical addition polymerization to proceed.⁴ With the understanding that this material causes an increase in the amount of free radicals produced, it is evident that this part of the process is the area in which RAP is involved. Changing the chemistry of the donating amine may allow more free radicals to be produced, allowing for a faster curing time and a higher degree of conversion. Not knowing the exact chemistry of this material makes this an assumption only.

Understanding the clinical relevance of the present study is very difficult. Determining if the amount of polymerization stress presented here is too much is yet to be determined. Incremental placement techniques have been introduced along with different light-curing modes in order to decrease the amount of polymerization shrinkage. The question still is, what amount of polymerization stress is considered too much *in vivo*? This new technology may be well worth the risk clinically due to the increase in

the physical properties seen with RAP. Placing a restoration with a large C-factor incrementally or using a pulse-delay light curing regimen may compensate for the amount of polymerization stress increase when using RAP versus the conventional CQ resin composite. Until a randomized, controlled clinical trial can be completed to determine the amount of clinically acceptable polymerization stress, the choice of material will continue to be at the discretion of the clinician.

SUMMARY AND CONCLUSIONS

The purpose of this study was to evaluate the effect of a novel photoinitiator (RAP) on the physical properties of resin composites. Tokuyama Dental fabricated experimental resin composite systems that contained RAP + CQ and CQ only. Flexural strength, polymerization stress, and degree of conversion were all evaluated. Small beams (25x2x2) were fabricated, polished, measured and tested in the universal three-point bending apparatus. Maximum stress rate and flexural modulus data were obtained using software specifically made for use with this machine. The polymerization stress was calculated through the use of a tensometer. Specimens were injected into a PTFE tube and bonded to two quartz rods to which the light source was attached. The polymerization stress was measured for 30 minutes (recording every second) beginning at the start of photoinitiation. The FTIR instrument was used to record the degree of conversion. Uncured specimens were placed directly on the 5-mm glass opening of the spectrometer. Cured specimens were fabricated in a thin sheet using Mylar strips and a glass slab. All specimens were run three times, each of which was used in the analysis.

With these experimental resin systems, it appears that there was a significant increase in some of the physical properties. There was a statistically significant increase in the peak stress with the addition of RAP to the flowable (EFQ) composite. This was not seen with the microfilled composite. Flexural modulus increased significantly with the addition of RAP in both the microfilled (ESQ) and the flowable. Overall, the addition of RAP to both experimental composites increased the polymerization stress. The maximum stress rate was significantly higher for the EFQ and ESQ with RAP compared

with those without. The EFQ with RAP also showed a significantly higher degree of conversion compared with the EFQ with CQ. This was not as evident in the ESQ group. As to what extent these will benefit the clinician has yet to be determined.

In general, RAP did enhance physical properties. Some conclusions can be drawn from this study. First, with the addition of RAP, both EFQ and ESQ did appear to have a higher flexural strength, modulus, and degree of conversion that could be beneficial to the clinician. Creating a composite resin that is more durable in the posterior quadrants of the mouth may be beneficial. Secondly, the increase in the polymerization stress with the addition of RAP may be detrimental to this experimental composite. Creating a composite resin with a small amount of polymerization stress, yet a high degree of conversion, flexural strength would be ideal. More studies need to be done to evaluate different percentages of RAP in these systems and how they affect the physical properties. Understanding how the polymerization shrinkage stress reacts to a change in formulation is also important to know. Overall, the addition of RAP to resin composites has been positive. The only setback comes with the amount of polymerization stress created. Once this is controlled, RAP may become a very commonly used photoinitiator system.

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ABSTRACT

THE EFFECT OF A NOVEL PHOTOINITIATOR SYSTEM (RAP) ON DENTAL
RESIN COMPOSITES' FLEXURAL STRENGTH, POLYMERIZATION
STRESS, AND DEGREE OF CONVERSION

by

Kellie Schaub

Indiana University School of Dentistry
Indianapolis, Indiana

Objectives: A new technology has been introduced into the field of dental resin composites that professes to enhance light-curing efficiency. Rapid amplified photopolymerization (RAP) initiator technology has not yet been fully compared with resin composites with conventional initiators such as camphorquinone (CQ). The purpose of this study was to compare and contrast the effects of this novel technology

(RAP) on properties of two light-cured resin composites. Flowable (EFQ) and microfilled (ESQ) experimental composites were fabricated and supplied from Tokuyama Dental with (w/RAP) and without RAP (w/o RAP). The flexural strength (MPa) and flexural modulus (MPa) were obtained using a three-point bending apparatus (Sintech Renew 1123, Instron Engineering Corp., Canton, MA). Polymerization stress curves were created using a tensometer (American Dental Association Health Foundation, NIST, Gaithersburg, MD) which were then used to calculate the maximum stress rate. Finally, the degree of conversion was measured using infrared spectroscopy (Jasco FT-IR spectrometer, Model: 4100, Jasco Corporation, Tokyo, Japan). When evaluating the flexural strength, the peak stress for EFQ w/RAP was significantly higher than EFQ w/o RAP ($p = 0.0001$). This was statistically not significant for the ESQ group, even though ESQ w/RAP did have a higher peak stress than ESQ w/o RAP ($p = 0.28$). The interaction between resin type and RAP was not significant when evaluating the flexural modulus ($p = 0.21$). Formulations with RAP had a significantly higher flexural modulus than w/o RAP ($p = 0.0001$). Experimental resins with RAP had significantly higher maximum stress rates than those w/o RAP when evaluating polymerization stress ($p = 0.0001$). Finally, groups w/ RAP appeared to have a higher degree of conversion than groups without ($p = 0.0057$). This study showed that the experimental composites with RAP had greater mechanical properties than those without. Unfortunately, the increase in polymerization stress causes concern clinically due to the chance of leakage at the restoration/tooth interface. One of the main potential disadvantages of this new RAP

technology is an increase in the polymerization stress. Deciding if this amount of polymerization stress is clinically acceptable is yet to be accomplished.