Polymers in Restorative Dentistry

Tooth Fairy

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I. Abstract

Tooth decay affects roughly 2 billion people world wide making it the most common oral disease. Severely damaged teeth typically require root canal treatment or tooth extraction, but both solutions could lead to weakened long-term performance of teeth with increased risk of infection. Tooth Fairy's objective is to develop a polymeric dental filling that supports dentin pulp stem cell (DPSC) regeneration as an alternative method to treating severely damaged teeth. Current resin-based materials do not consider regenerative properties of teeth and can negatively impact the dentin layer of teeth by disrupting proper stem cell functionality. Our formula consists of Trimethylolpropane triacrylate (TMPTA), pentaerythritol triacrylate (PETA), trithiol, and photoinitiator. TMPTA and PETA were chosen as they exhibit strong supportiveness for DPSC growth. The concentrations were varied to tune the material properties with molar triacrylate-thiol ratios of 1.3, 1.4, and 1.5. Shear bond tests were conducted to determine the degree of adherence between the polymer and the dentin surface. Rheology and tensile tests were used to calculate the curing time and Young's modulus of the polymer. Shear bond tests revealed that the 1.3:1 sample performed the best with a bond strength of 36.7 MPa, greater than that of the industry gold standard, Clearfil SE Bond. Tensile tests have resulted in yield stresses of ~20 MPa and Young's modulus of ~600-900 MPa. The yield stress is comparable to that of dentin (44.4 MPa), which shows that these materials are compatible with dentin. Furthermore, the curing time was measured to be ~10 seconds. All results have shown that Tooth Fairy's polymer material is a promising upgrade to current treatment materials and potentially suitable for clinical use.

II. Project Objectives

2.1-2 Introduction & Value Proposition

Tooth decay is a highly prevalent issue affecting 2B people globally.[1] Tooth decay involves acid producing bacteria that causes the tooth to lose its minerals.[2] Regular tooth caries (decay) are treated by removing the decayed tooth tissue and then restore the tooth by filling it with a filling material. However, a severely damaged tooth with a deep cavity that reaches the dentin layer may require root canal or tooth extraction.

Over 15 million teeth are treated with the root canal,[3] which costs between $600 and $1,600 in the United States without insurance.[4] During the root canal, the endodontist removes the infected pulp and nerve in the root of the tooth, cleans and shapes the inside of the root canal, then fills and seals the space.[4] Afterwards, a crown is placed to protect and restore the tooth to its original function, and a crown ranges from $500 to $3,000.[5] Tooth extraction and implant can also cost up to $3,000.[6] Both methods are costly and can lead to a weakened tooth in the long-term.

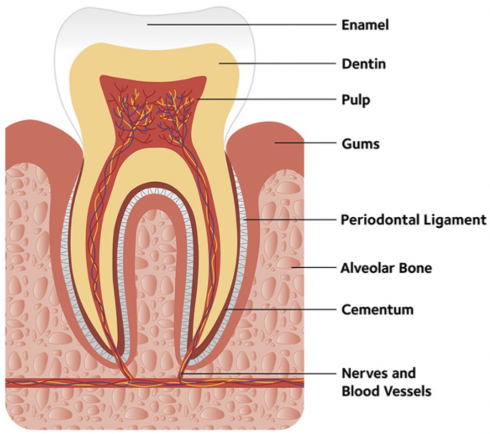


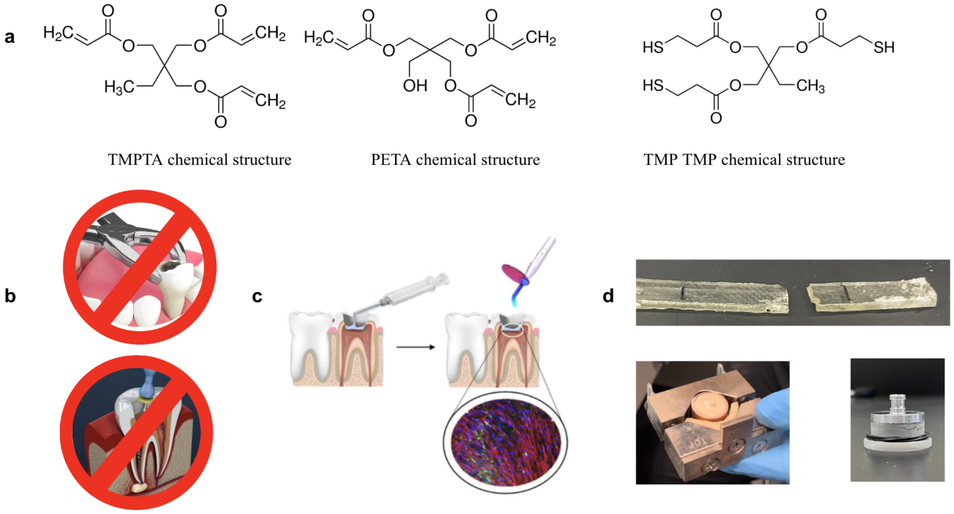
Figure 1. Tooth anatomy.[3]

As shown in **Figure 1**, teeth consist of four tissues: enamel, dentin, cementum, and pulp. Enamel, dentin, and cementum are hard tissues while pulp is a soft tissue. Tooth decay starts at the enamel surface and can spread to dentin. Dentin is one of the most important layers as it is located right before the pulp cavity level that contains important nerves and blood vessels. Dentin is formed by odontoblasts cells, which are produced by DPSCs in dental pulp, present only in limited quantities.[7] Stem cells are special human cells which can be used to produce many different types of cells,[8] and DPSCs specifically are a heterogeneous population of stem cells in the pulp layer.[9] DPSCs are used to treat tissues of an infected tissue by forming a reparative dentin layer.[10]

Current solutions mainly consist of synthetic polymer-based chemistries. The existing synthetic polymer-based chemistries in dental materials cannot be used to restore stem cells as they contain residual methacrylate monomers, such as bisphenol A glycidyl methacrylate (BisGMA), which negatively impact cells, preventing the regeneration of dentin.[11]

Tooth Fairy aims to deliver a dental filling product that can repair severe damages from dental caries, saving a tooth that would otherwise need to be removed, by adopting a new chemistry that can support DSPCs growth and regenerate dentin.

Tooth Fairy's light-curable, triacrylate-trithiol mixture uses monomers that have proven successful in supporting stem-cell adhesion in past research,[11] and Tooth Fairy fine tunes the molar ratio of the different components to maximize product performance in 3 properties: stiffness, adhesion strength, and curing time. The vision figure (**Figure 2)** shows the chemical structures of components that are used in Tooth Fairy's restorative polymer product and how it could be applied in a dental procedure to restore dental tissue.



TMPTA chemical structure PETA chemical structure TMP TMP chemical structure

Figure 2. Vision Figure (a) Chemical structures of the two triacrylates (TMPTA, PETA), and TMPTMP. (b) Traditional tooth extraction and root canal procedures. (c) Proposed procedure utilizing triacrylate polymers to restore dental tissue and support dental pulp stem cell adhesion. (d) Samples for tensile test, shear bond test, and rheology test.

Additionally, the innovative monomer mixture, when cured, should exhibit comparable mechanical properties to existing dental fillings, display similar adherence to dentin to existing dental fillings, and allow for DSPCs to differentiate in their presence. When the monomer mixture is cured onto dentin, the interface should have a maximum tensile strength of 25-30 GPa and a shear strength of 13-20 MPa.[10, 11] Curing times should be relatively quick, around 20 seconds,[12] so that the mixture could be practically applied in dental practices.

III. Industry Dynamics

3.1 Market Size & Growth

The global overall dentistry market size was valued at $371.4B in 2020, and within that market, the restorative dentistry category was valued at $16.3B.[14] Even though the restorative dentistry market currently takes up a small portion, it is expanding fast and is expected to grow at a CAGR of 8.8% from 2020 to 2027 (faster than that of the overall dentistry market at 6.4%), with regular dental checkups anticipated to boost the growth of the market.[14] In 2020, the restorative materials segment accounted for the largest share within the restorative dentistry market, contributing to over 40% share with $4.1B in sales.[15] The restorative materials market is large and it is fast-growing capturing more market share annually. In addition to the traditional restorative materials market, the global root canal market was $1.0B in 2021 (4.5% 2021-2028 CAGR)[16] and the global dental crowns and bridges market was $2.6B in 2021 (7.8% 2018-2026 CAGR).[17] In total, Tooth Fairy's product addresses an over $9B target market, with restorative materials being the core growth driver and the largest segment.

3.2 Customer Segments

The main customer segments for the dental restorative materials market consists of dental hospitals and clinics, representing over 50% of the market share in 2020.[18] Therefore, it is critical to focus on the customer needs of dental hospitals and clinics to tailor the technology and the properties of the final product to those needs. The key considerations when choosing the dental filling products are the cost, ease-of-use, and accessibility. Firstly, with the competitive advantage of being a stem-cell-supportive product, Tooth Fairy can justify its higher retail price compared to regular filling products. Secondly, Tooth Fairy's light-curable, direct restorative material applies the same as traditional products in clinical practices (with curing time under 20 seconds), which implies minimal switchover cost other than the cost of the material itself. Lastly, Tooth Fairy can leverage its connections at Penn Dental as sources for first-hand data and improve product accessibility.

3.3 Competition

Tooth Fairy competes with both the regular filling products and the regenerative bioactive resins. The current competitive landscape for regular restorative materials in the dental industry remains moderately fragmented. There are five large companies - 3M ESPE, Dentsply Sirona, Danaher, Ivoclar Vivadent, and Mitsui Chemicals - accounting for 51% market share of the total restorative market.[18] The remaining market consists of other small players, indicating the potential for new players to enter the space. Bioactive composites are a type of dental composite material that can stimulate the formation of new bone and/or promote the regeneration of dental tissues, where the elastic modulus usually ranges from 5-25 GPa and shear bond strength ranges from 5-20 MPa.[19, 20] Tooth Fairy stands in between the two product categories in terms of functionality and the respective mechanical properties.

Table 1. Competitive Landscape - Product Comparison

Current Solutions	**Product Category**	**Elastic Modulus**	**Adhesion Strength**	**Curing Time**	**Stem Cell Supportive**	**Depth of Cure**
3M ESPE Filtek[21]	Regular	10 GPa	62 MPa	20s	No	2mm
Dentsply Sirona Surefil One[22]	Regular	7.2 GPa	19 MPa	20s	No	4mm
Ultradent[23, 24]	Regular	8.0 GPa	71 MPa	20s	No	2mm
Ivoclar Vivadent[25]	Regular	10 GPa	15 MPa	20s	No	4mm
Tooth Fairy	—	472 MPa	36.7 MPa	10-20s	Yes	2mm
Pulpdent Activa[26]	Bioactive	—	13 MPa	20s	Yes	0.011mm
Bioactive glass-modified hybrid composite[27]	Bioactive	—	—	—	Yes	—
Modified Mineral Trioxide Aggregate[28]	Bioactive	—	9 MPa	—	Yes	—

IV. Business

4.1 Revenue & Cost Model

Due to Tooth Fairy's current early stage of research and the product's unique positioning in the market as regenerative fillings for severely damaged teeth, it is difficult to price the end-product. However, Tooth Fairy anticipates that the dental mixture will be a premium product that exceeds the current pricing of existing dental fillings and a more cost-effective solution compared to root canal and tooth extraction, which could cost up to $3,000.

As a reference, two of the biggest current players, 3M ESPE and Dentsply Sirona currently price their leading dental filling at $17.17/mL and $21.66/mL.[29] The cost of technical grade raw material includes the cost of photoinitiator at $0.04/mL,[30] the trimethylolpropane tris(3-mercaptopropionate) (TMPTMP) at $0.36/mL,[31] and the pentaerythritol triacrylate (PETA) and trimethylolpropane triacrylate (TMPTA) mixture at \$1.73/mL.[32] The mixture of the three components would lead to a raw material cost of \$2.13/mL.

Preclinical studies involve *in vitro* testing to evaluate the safety and efficacy of the dental materials before proceeding to clinical trials, and the cost can go up to several hundred thousand dollars.[33, 34] Clinical phase 1 trials involve testing the safety and tolerability of the dental material in a small group of healthy volunteers, and the cost can go up to several million dollars.[35] Additionally, in the long-term horizon and further down the research process, Tooth Fairy would have to patent the stem-cell-supportive chemistry, which could take up to 20 years for the application to be granted.

4.2 Stakeholders

Relevant stakeholders include dental clinics and hospitals, treated patients, competitors, and the investors. Customers are the most important stakeholders for medical devices, where dental clinics and hospitals are the direct customers who would purchase products from Tooth Fairy, and patients would be the ones ultimately using the new materials. Hence, product quality and performance is crucial, and Tooth Fairy strives to deliver the best products to its customers. Additionally, competitors' products will be an important benchmark, whether regarding the mechanical properties or the price. Therefore, Tooth Fairy's research team will do active competitor research to stay on top of the industry news and make sure the offerings stay competitive. The regenerative solution would also require the approval of the United States Food and Drug Administration (FDA), which could take 10 to 15 years or more to complete all phases of clinical trials prior to the licensing stage.

V. Experimental

5.1 Context

In prior research, Dr. Kyle Vining of Penn Dental identified two monomers that provide a supportive niche for DPSC growth: TMPTA and PETA. These monomers were selected out of a group of 119 monomers that consisted of mono- and multifunctional acrylates, methacrylates, acrylamides, and meth acrylamides.[7] Triacrylates provide better interaction with cells due to their higher reactivity and stability of triacrylate free-radicals which enhance bulk polymerization.[11]

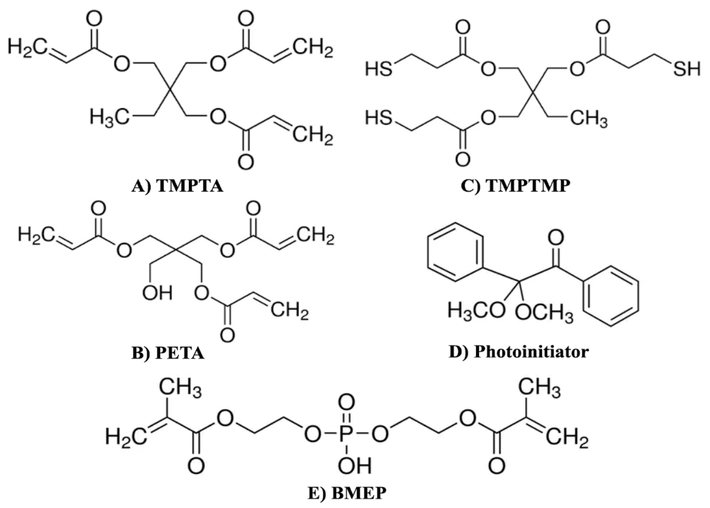


Figure 3. TMPTA (A), PETA (B), TMPTMP (C), 2,2- dimethoxy-2 phenyl acetophenone (D), and BMEP (E) chemical structures[25]

5.2 Material Selection

The monomer samples created for materials research consisted of three components: the triacrylate base, tri-thiol monomer, and photoinitiator powder. The triacrylate base was a mixture of pentaerythritol tetraacrylate (50-70% concentration), PETA (20-30%), and TMPTA (20-30%) as the individual triacrylates were not available for individual purchase.[43] Trimethylolpropane tris(3-mercaptopropionate) (TMPTMP) (≥95.0% purity)[44] served as the cross-linking reagent to achieve rapid light-curing while minimizing residual monomer. TMPTMP was also chosen as the tri-thiol due to its structural similarities to TMPTA. 2,2-dimethoxy- 2-phenylaceto- phenone (99% purity)[45] was selected to be the photoinitiator due to its structural similarities to the triacrylates and its reactivity to UV light.

5.3 Parameters

To adjust the stiffness, dentin adhesiveness, and curing time, two parameters were changed: the triacrylate-trithiol molar ratio and the photoinitiator concentration. The triacrylate-trithiol molar ratios included 1.3:1, 1.4:1, and 1.5:1 and the photoinitiator amount was varied from 0.5 weight % to 1 weight %. A relatively greater trithiol concentration (smaller molar ratio) was expected to result in greater crosslinking density as trithiol is the crosslinking reagent. Greater crosslinking density would result in greater stiffness and less shrinkage which increases the adhesion to dentin. The photoinitiator concentration was varied to control the curing time. The 1.4:1 ratio with 1 weight percent photoinitiator was chosen as the starting point as this composition has demonstrated good stem cell adhesion.[7]

5.4 Sample Fabrications

Samples were initially made by sequentially adding photoinitiator, triacrylate, and trithiol to 2-ml amber vials using micropipettes rated at 50 and 1000 μL. **Table 1** lists the quantities of each material used for each formulation. Sample preparation was performed in a red-light environment to prevent premature polymerization. Each amber vial was then placed in thermo scientific 15 ml conical centrifuge tubes and centrifuged for 5 minutes at 2000 rpm to mix all contents. This method proved problematic as the high viscosity of triacrylate and trithiol made it difficult to measure exact amounts. Also, in the time span of a week the trithiol would separate from the triacrylate and solidify.

Table 1. Initial Sample Formulations

	Photoinitiator	Triacrylate	Trithiol
Density (g/ml)	1.132	1.18	1.21
Molar mass (g/mol)	-	888.51	398.56
Formula A (1.4:1)	24.1 mg	1532 μl	479 μl
Formula B (1.3:1)	24.1 mg	1557 μl	454 μl
Formula C (1.5:1)	24.1 mg	1504 μl	506 μl

To resolve these problems a bulk sample fabrication method was used where 5ml samples were produced. In this method, the triacrylate and trithiol monomers were weighed according to **Table 2** to create better consistency and precision between samples. Once weighed, the triacrylate and trithiol were deposited into larger amber vials. Separate 2-ml amber vials were prepared with the same amount of photoinitiator. Immediately before any test was performed, approximately 2 ml of the bulk solution was transferred to the small amber vials and centrifuged. This method led to more accurate sample formulations and prevented premature curing.

Table 2. Bulk Sample Formulations

	Photoinitiator	Triacrylate	Trithiol
Formula A (1.4:1)	24.1 mg	4.4482 g	1.4253 g
Formula B (1.3:1)	24.1 mg	4.3682 g	1.5073 g
Formula C (1.5:1)	24.1 mg	4.5200 g	1.3517 g

5.5 Tensile Testing

Once mixed, samples were deposited into a rubber mold with dimensions of 0.2 x 0.635 x 8.0 cm. The rubber mold was sandwiched between two glass plates to create flat surfaces and immediately cured. Initially monomer mixtures were transferred to the mold via pipetting. A scoopula was used for future samples to reduce the amount of bubbles formed.

Tensile tests were run on the Instron model 4206 150 kN and model 5564. The load was set at 0.1 kn/V, the crosshead displacement was set at 0.5 mm/V, the displacement rate was 1 mm/min and the clamp pressure was ~40 lb/in^2. Tensile testing was used to determine the relative stiffness of each sample. Measurements were taken using an iGaging OriginCal micrometer. All micropipettes came from Accumax and Finnpipette. Amber vials used for storage of monomer mixtures were purchased from Supelco. The centrifuge used to mix the solution is a Thermo Electron Corporation Centra CL3R centrifuge. UV curing was done using a Mineralight Lamp Model UVGL-25 at 365 nm wavelength.

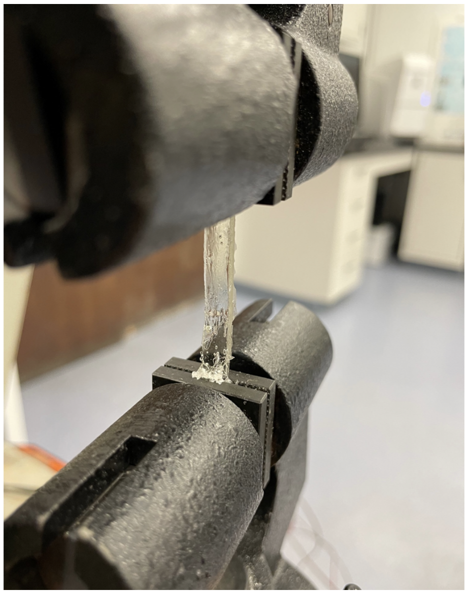


Figure 4. Cured polymer sample undergoing tensile testing

5.6 Rheology

Rheology testing was performed to measure material characteristics of the solidified monomer mixture as well as to tune the curing time. The Discovery HR 30 with the UV Curing Accessory was used to conduct testing. The UV light used had a wavelength of 365 nm and an intensity of 20 mW/cm^2. Furthermore, the Peltier standard disposable parallel plate (49586) with 20 mm diameter was used. The gap was set at 1000.0 µm.

The photoinitiator concentration was varied with initial samples having 1% weight photoinitiator and later samples having 0.5%. This was done to reduce the curing time. The strain was also changed from 1% to 0.1% strain to record more accurate data and prevent the sample from slipping.

Samples for rheology testing were prepared directly before testing using the same centrifuge method described above. Then approximately 0.4 mL of the solution was pipetted onto the aluminum surface of the Peltier plate. Strong sources of light such as sunlight were avoided during this process to prevent premature curing. Lastly, a metallic casing was placed around the plate to prevent interaction with light.

5.7 Adhesion Testing

To measure the adhesive shear bond strength of the cured monomer solution to dentin, the Bisco Shear Bond Test instrument was used. Dentin samples were obtained by the Ozer group at the Penn Dental School. The dentin samples were polished using 400 then 600 grit sandpaper then cleaned and dried. For samples that utilized primer, a thin layer of primer was deposited onto the exposed dentin surface then dried. Then a thin layer of a freshly mixed monomer mixture was applied to the surface then cured using the Mineralight Lamp UV light for 40 seconds. Then the GrandIso liquid composite was applied through a plastic mold and cured using the SmartLite

Focus blue light for 40 seconds. The composite formed a cylindrical shape onto which the test instrument applied a shear force.

Testing consisted of 5 groups: the 1.3, 1.4, 1.5 samples with primer, 1.3 with no primer, and Clearfil SE Bond 2 composite. Clearfil SE Bond 2 composite was used as the control group as it is the industry gold standard. Clearfil SE Bond 2 primer was used for all samples that used a primer. The primer is amphiphilic to aid in the interaction between hydrophobic monomers and hydrophilic dentin. Specifically, it contains an acidic phosphate monomer that penetrates the dental tissue and dissolves the smear layer - a zone of tooth preparation debris found on the surface after tooth preparation.[46] The primer contains the acidic phosphate monomer MDP (10-Methacryloyloxydecyl dihydrogen phosphate) that chemically bonds with the calcium in teeth and mechanically by diffusing and polymerizing throughout the tooth structure.[47] It also contains hydrophilic aliphatic dimethacrylate, dl-Camphorquinone, accelerators, water, and dyes.[48]

VI. Results and Discussions

6.1. Progress

During the first semester, around 20 monomer mixtures were created. However, due to various complications with preparations such as spillage and premature solidification, only 7 samples could be cured. Of the 7 cured samples, only 5 demolded successfully. Of the two samples that did not demold well, one sample fractured in the mold during curing, and another fractured as it was removed from the mold. Potential reason for the fracture was that the glass slide on top was not being pressed hard enough so that the monomer mix was pulled up towards the glass slide, creating extra stress.

Last semester, of the 5 samples, 3 samples of 1.4:1 triacrylate-trithiol ratio and 2 samples of 1.3:1 ratio were used to perform tensile tests. These tensile tests were run to determine yield stress and Young's modulus. Despite good progress with sample-making and running tensile tests, consistent results were needed to be obtained for each formulation, where the stress-strain curve had to be confirmed by multiple trials. This past semester, tensile tests were run once again on 1.3:1 and 1.4:1 triacrylate-trithiol ratios. Additionally, tensile tests were run on samples with 1.5:1 triacrylate-trithiol ratio just as planned. These tests were used to determine more accurate yield stress and Young's modulus results. Additionally, new tensile strength tests were tested with the newly designed 3D-printed mold that was thinner. A thinner mold required less material, and the cured samples resulted in fewer bubbles, which was more favorable for tensile tests.

This past semester, adhesion to dentin and the curing time were tested as well using shear bond and rheology tests. 21 monomer mixtures of various samples of 1.3, 1.4, 1.5 triacrylate-trithiol ratios were tested for dentin adhesion testing. These monomer mixtures both with primer and without primer. Additionally, multiple rheology tests have been conducted for all three triacrylate-trithiol ratios under different conditions to figure out average curing time.

6.2. Rationale

Yield stress and Young's modulus are key information obtained from tensile tests. Yield stress indicates the limit of elastic behavior and refers to the minimum stress at which a material will deform without significant increase in load. This is one of the most important properties because the filling material should have a comparable value as the dentin for it to be a compatible and long-lasting solution. Young's modulus is also an important trait for the filling and the tooth to function properly together. It measures the longitudinal stress divided by the strain and indicates the ability of the teeth to resist elastic deformation. A study that tested the mechanical properties of the dentin structure obtained 44.4 MPa as the median yield stress of the inner dentin.[26] Another experiment measured the elastic modulus of dentin to be 1653.7 MPa.[27] These values are being compared to the values obtained from Formula A and Formula B for material selection.

Adhesion to dentin is also a critical factor in the success of dental filling products. The ability of the filling material to adhere to dentin is crucial to ensure the longevity and stability of the restoration. Inadequate adhesion may lead to microleakage, marginal gaps, and eventually, failure of the restoration. Curing time is also a crucial factor in the setting and polymerization of the filling material. The proper curing time is essential to ensure that the material has fully hardened and achieved its optimal mechanical properties. Insufficient curing may result in an inadequate hardness, which can lead to premature wear and eventual failure of the restoration. Additionally, the curing time of a dental product should occur within seconds so that it can be realistically applied in dental practices.

6.3. Data & Analysis

6.3.1 Tensile Test Data

All cured samples contained bubbles, which were produced when the solution was transferred from the amber vial to the mold. The solutions did not contain obvious bubbles in the vial prior to the transfer as they were properly centrifuged. **Figure 5** shows the fracture locations of the 5 samples. A1 and B6 have fractures at bubbles (defects), with B6 having relatively more bubbles. Their fracture locations should result in underperforming mechanical properties. A2 has visible signs of incomplete curing, indicated by the slightly wet surface and the liquid streaks at the center of the sample. A5 has a fracture at the desired location, in between the Instron grips (marked by the black line) and free of bubbles, so its mechanical property analysis should generate the most credible results. Lastly, B7 fails at the upper grip area, outside of gauge length.

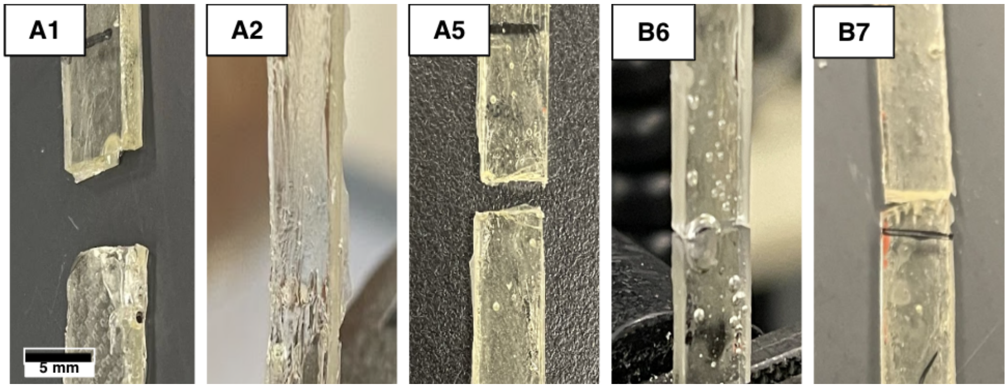


Figure 5. Fracture Locations: fracture at bubble (A1), fracture with incomplete curing (A2), fracture at desired location (A5), fracture at bubble (B6), fracture at grips (B7)

Both engineering and true stress-strain values are derived to calculate yield stress and Young's modulus. Engineering stress is calculated from Equation (1), where F is the load (kN) and A_0 (mm^2) is the initial rectangular cross sectional area. Engineering strain is calculated from Equation (2), where ΔL (mm) is the total elongation and L_0 is the initial gauge length (mm).

$$\sigma_{engineering} = \frac{F}{A_0} \tag{1}$$

$$\varepsilon_{engineering} = \frac{\Delta L}{L_0} \tag{2}$$

Figure 6 shows the engineering stress-strain curve for mechanical property analysis.

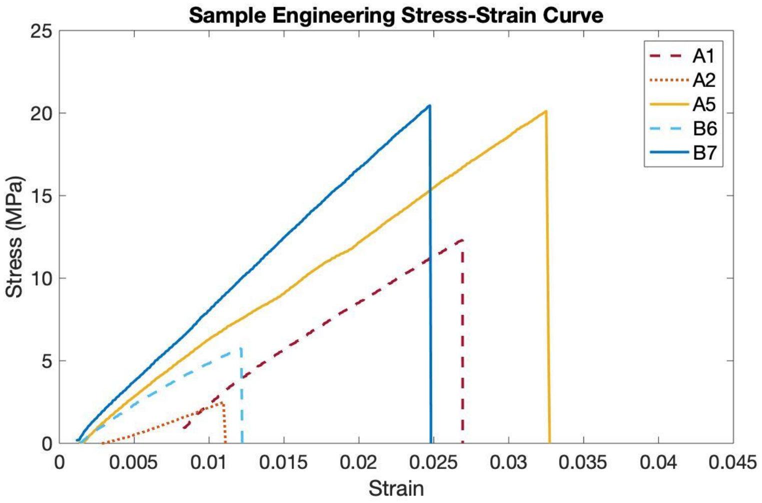


Figure 6. Engineering Stress-Strain Curve of Samples with Triacrylate-Trithiol Ratios of 1.4:1 (Formula A) and 1.3:1 (Formula B)

The value for yield stress is taken as the highest point of the engineering stress-strain curve. All samples from this experiment deform elastically upon brittle fracture. Young's modulus is calculated from Equation (3), and it is the slope of the best-fitted linear plot from the true stress-strain curves.

$$\sigma_{true} = \sigma_{engineering} * (1 + \varepsilon_{engineering}) \tag{3}$$

$$\varepsilon_{true} = ln(1 + \varepsilon_{engineering}) \tag{4}$$

$$E = \frac{\sigma_{true}}{\varepsilon_{true}} \tag{5}$$

Table 2 shows the calculated mechanical properties. Given that samples A1 and B6 fail at bubbles, their low yield stress values are expected, and they cannot be used for fair analysis of the material properties. Defects lower the material elasticity as confirmed by the data.

Table 2. Mechanical Properties Calculated from Stress-Strain Curves

Sample	Triacrylate-trithiol ratio	Yield stress (MPa)	Young's modulus (MPa)
Dentin	-	44.4	1653.7
A1	1.4:1	12.31	592.05
A2	1.4:1	2.50	265.24
A5	1.4:1	20.11	634.64
B6	1.3:1	5.74	556.12
B7	1.3:1	20.46	894.85

A2 is the worst-performing sample. While all samples were cured for 3 minutes, A2 did not cure completely due to its lack of photoinitiators caused by human error in preparation. It was noted after the tensile test that there was spillage of photoinitiators for A2, and the spillage was unnoticeable in the red-light sample preparation environment. To prevent similar mistakes in the future, more careful examination of the sample preparation environment will be conducted.

A5 has a fracture point within the gauge length and free of bubbles. The sample has the second highest yield stress of 20.11 MPa (~45% of the dentin value) and second highest Young's modulus of 634.64 MPa (~38% of the dentin value). B7 has similar mechanical properties as A5 but is outperforming in both aspects, with yield stress of 20.46 MPa (~46% of the dentin value) and Young's modulus of 894.85 MPa (~54% of the dentin value). Additionally, since the fracture point of B7 is at the upper grip, the sample can most likely withstand even more stress upon fracture. More tests need to be done for both Formula A and B to generate repeated results that can confirm these values, but based on existing data, Formula B outperforms Formula A. A smaller triacrylate-trithiol ratio proves to result in a greater degree of crosslinking, leading to both higher strength and modulus. It is expected that Formula C will perform worse than both Formula A and B.

This semester, further tensile testing was conducted to determine the ideal triacrylate-trithiol ratio and validate the hypothesis on crosslinking and strength. These samples were created using the more accurate bulk preparation method. **Figure 7** shows the engineering stress-strain curve for analysis of mixtures with three different triacrylate-thiol ratios, 1.3:1, 1.4:1, and 1.5:1.

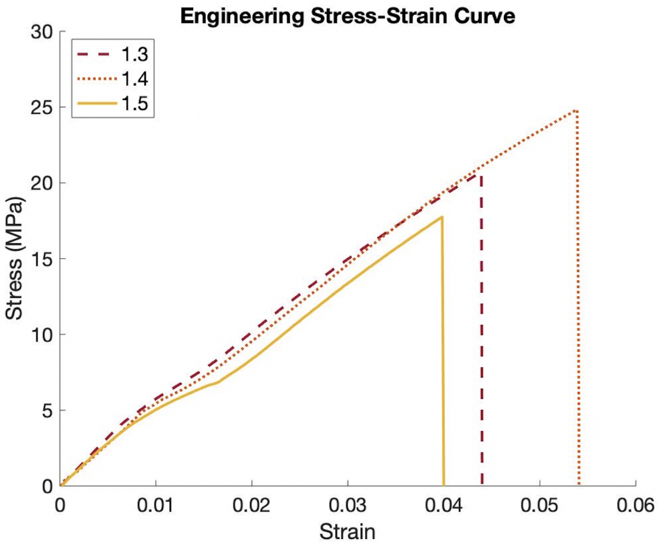


Figure 7. Engineering Stress-Strain Curve of Samples with Triacrylate-Trithiol Ratios of 1.3:1, 1.4:1, and 1.5:1.

These values were found using the same setup as the tensile testing in the previous semester. Three samples were tested for each ratio. Using the stress-strain curves, the Young's Modulus was calculated for each ratio. **Table 3** summarizes the calculated values.

Table 3. Young's Modulus of Different Ratio Samples

Triacrylate/Trithiol Ratio		
1.3	1.4	1.5
472 MPa	461 MPa	446 MPa

A general trend in this data is that as the trithiol ratio increases, the Young's Modulus measured of the material also increases. This data confirms that due to greater trithiol concentration present in the mixture, there is an increase in crosslinking density of the polymer, which creates a stronger dental product.

6.3.1 Adhesion Data

Table 4. Dentin Adhesion Data of Different Ratio Samples with Primer

Triacrylate/Trithiol Ratio			Clearfil SE Bond 2
1.3*	1.4*	1.5*	Control Group
36.67 MPa	11.24 MPa	25.43 MPa	29.4 ±8.5 MPa

*Did not have time to obtain sufficient data due to delays in obtaining dentin samples

The adhesion data for the three molar ratios were compared to the industry gold standard, Clearfil SE Bond 2, which was used as the control group. **Table 4** demonstrates the data collected throughout the dentin adhesion tests where a primer was used, and it is clear that 1.3 molar ratio performed the best out of all three prepared monomer samples. 1.3 MR samples contain a higher trithiol concentration and a smaller triacrylate concentration which results in a higher cross-linking compared to the other MR samples. Higher cross-linking leads to a higher adhesion between Tooth Fairy's monomer mixture and the flowable composite.[49] Additionally, higher cross-linking leads to less shrinkage of the synthesized monomer mixture which in return also leads to improved adhesion.[50] When the monomer mixture is applied, the mixture seeps into the collagen fibers as seen in **Figure 8**. Lower volumetric shrinkage would mean that cured polymers are better able to stay in place between those fibers and mechanically lock with dentin. Additionally, it is the only sample that performed better compared to the industry gold standard.

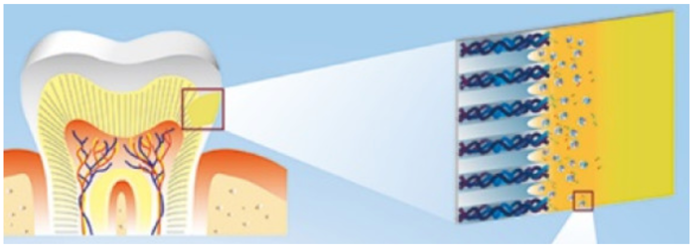


Figure 8. Dentin - Resin interface

Table 5. Dentin Adhesion Data of Different Ratio Samples without Primer

1.3 Triacrylate/Trithiol Ratio with Primer*	1.3 Triacrylate/Trithiol Ratio without Primer
36.67 MPa	8.71 ±2.93 MPa

*Did not have time to obtain sufficient data due to delays in obtaining dentin samples

Table 5 shows data for the 1.3 mixtures which were tested for adhesion both with a primer and without primer. Although the sample performed better with primer (which was expected), the tests revealed that there is a bond between the polymer and the dentin surface. This shows that there is potential for Tooth Fairy's product to not require a primer.

Figure 8 shows the storage and loss moduli obtained from rheological tests run on a 1.3 molar ratio sample in order to test for the curing time. The storage and loss moduli are two important mechanical properties used to describe the viscoelastic behavior of materials, including polymers and other soft materials. The storage modulus is a measure of a material's ability to store energy elastically when it is subjected to an external force. The storage modulus is related to the stiffness of the material and is typically measured as the ratio of the applied stress to the resulting strain. The loss modulus is a measure of a material's ability to dissipate energy when it is subjected to an external force. The loss modulus is related to the material's ability to absorb energy, and it is measured as the ratio of the applied stress to the resulting strain rate.

In the context of dental filling products, the storage modulus is closely related to the curing time of the material, which is the time it takes for the filling to harden and reach its full strength. The rheometer test conducted on the 1.3 molar ratio sample shows that its storage modulus peaked at around 10 seconds, indicating a quick curing time. This means that the filling material begins to harden and reach its maximum stiffness after only 10 seconds of curing. As mentioned previously, rheology testing involved 1% and 0.5% weight photoinitiator concentration. The 1% weight caused the mixture to cure too quickly making it difficult to collect data. Therefore, the concentration was reduced for following samples such as the one in **Figure 9.**

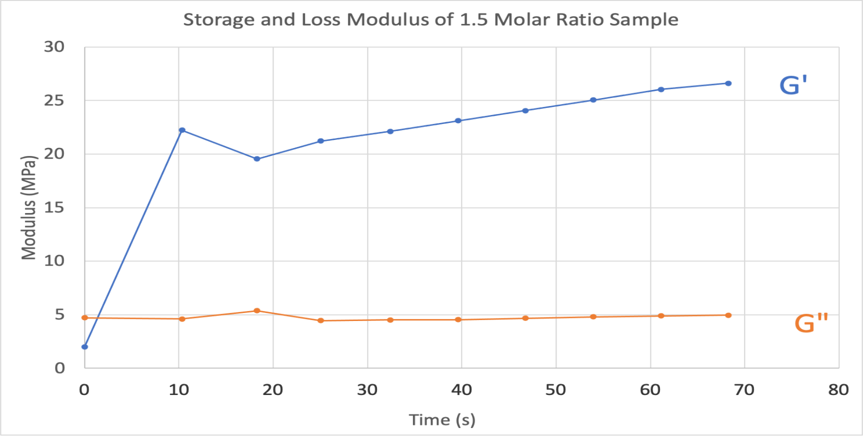


Figure 9. Storage and loss moduli obtained from a rheometer for the 1.3 molar ratio sample. G' represents the storage modulus, and G'' represents the loss modulus.

In the context of dental fillings, the storage modulus is closely related to the stiffness and solid-like behavior of the filling material. The data shown conducted on the 1.3 molar ratio sample have shown that its storage modulus had a relatively constant slope after it cured. This confirms that the material has solid behavior, meaning that it is able to maintain its shape and stiffness over time, and is less likely to deform or flow under stress.

6.4. Challenges & Improvements

Experimental challenges arose with dentin adhesion tests as some samples could not adhere to the composite layer that is typically attached on top of the monomer mixture. Originally, a solid composite was used, but all the tests failed. Hence, a new flowable composite was used. However, after more dentin adhesion tests were conducted, all three triacrylate-trithiol ratio monomers were not able to adhere to the flowable composite. A potential reason may be that the samples were too old. Future experiments will always be conducted with freshly made samples.

6.5. Future Plans

In the future, the Tooth Fairy product will need to undergo further R&D efforts to validate the viability of the dental filling. It is essential to conduct volumetric shrinkage tests, longevity tests, fracture toughness tests, and secondary stem cell tests. The volumetric shrinkage tests can have implications for the durability of the filling. Longevity tests will simulate the wear and tear that a filling undergoes over time. Fracture toughness tests will assess the filling material's ability to withstand external forces. Secondary stem cell tests will confirm whether the adjustments made to the initial formula will change its biocompatibility.

Future research might also investigate how the formula may be changed such that a primer is not needed. Potential avenues include the use of Bis[2-(methacryloyloxy)ethyl]phosphate which is a hydrophilic monomer that can improve triacrylate-trithiol and dentin interaction.

VII. Social and Ethical Issues

Economic, environmental, global, and societal contexts were not relevant to this project, but were considered. The most relevant would be societal contexts, specifically preserving the health of people in our society. Tooth Fairy's goal in working on this project was to better the health of those suffering from tooth decay.

As with any product in the healthcare industry, the primary ethical concern is how the patient will be affected. In the case of this project, the final product must undergo rigorous testing to ensure that the selected monomers will not have any undesirable side effects on the patient. Additionally, there is also the concern of cost in the healthcare industry. Ultimately, Tooth Fairy's final product will reduce the amount of times patients must have their fillings replaced and/or help patients avoid costly surgeries. Given that the dental industry is very conservative, they would be opposed to this new product especially since it might detract from their revenue. This ethical dilemma between doing what's best for the patient and generating revenue can also become an issue.

VIII. Conclusions

Over the past semester, significant progress has been made. The polymer formulations have been refined such that adhesiveness to dentin can be controlled through varying crosslinking density, and it has been shown that the 1.3:1 triacrylate to thiol mixture adheres best to dentin. The sample fabrication process has also been refined to create samples more efficiently with less bubble defects and more consistent dimensions. Sufficient curing time has been investigated using a rheometer to confirm a curing time of around 10 seconds. Additionally, further tensile tests have been conducted to confirm that these samples have yield stresses around 20 MPa and young's modulus of 600-900 MPa. This yield stress is on a similar magnitude of the yield stress of dentin (44.4 MPa).[26] Furthermore, the 1.3:1 sample had a greater modulus than the 1.4:1 sample (894.85 vs 634.64 MPa). This confirms that the lower ratio leads to a greater crosslinking density and therefore greater strength. These results show that these polymers have appropriate properties for dental restorative materials and efforts into controlling crosslinking density are on the right track.

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