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## Influencing Factors on the Velocity and Temperature of Propagating Fronts in Acrylate Composites

Samuel Morris Bynum

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# **INFLUENCING FACTORS ON THE VELOCITY AND TEMPERATURE OF PROPAGATING FRONTS IN ACRYLATE COMPOSITES**

A Dissertation

Submitted to the Graduate Faculty of the  
Louisiana State University  
Agricultural and Mechanical College  
in partial fulfillment of the  
requirements for the degree of  
Doctor of Philosophy

in

The Department of Chemistry

by  
Samuel Morris Bynum  
B.S., University of West Florida, 2014  
May 2020

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I would like to dedicate this document to my father, Kenneth Bynum (1/4/54 – 5/10/15).

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## LIST OF ABBREVIATIONS

$\kappa$  – thermal diffusivity

AA – acrylic acid

BDDA – 1,4-butanediol diacrylate

BPO – benzoyl acrylate

DEGDA – di(ethylene glycol) diacrylate

DMSO – dimethyl sulfoxide

DSC – differential scanning calorimetry

DTMPTA - di(trimethylolpropane) tetraacrylate

E – activation energy

FP – frontal polymerization

FS – fumed silica

HA – hexyl acrylate

HDDA – 1,6-hexanediol diacrylate

IFP – isothermal frontal polymerization

IUPAC – International Union of Pure and Applied Chemistry

OcOH – 1-octanol

PC – propylene carbonate

PE – poly(ethylene)

PP – poly(propylene)

PEGDA – poly(ethylene glycol) diacrylate

PETIA – 1:1 pentaerythritol tetraacrylate : pentaerythritol triacrylate

PFP – photo-frontal polymerization

PMMA – poly(methyl methacrylate)

PVC – polyvinyl chloride

$T_f$  – front temperature

TFP – thermal frontal polymerization

TMPTA – trimethylolpropane triacrylate

## ABSTRACT

Thermal frontal polymerization is a type of polymerization in which a localized reaction zone propagates through an unstirred system. It is incumbent upon the production and transport of heat produced as a result of the exothermic reaction associated with free-radical polymerization. First discovered in the 1970s, frontal polymerization has been since utilized to produce a variety of different materials, utilizing a variety of different chemistries. The temperature of the propagating front and the velocity at which it propagates can be influenced via chemical or physical means. We show that through careful selection of monomers and control of the concentration of double bonds in a system, that increasing the functionality of the monomer can increase the velocity of a propagating front. We have also shown that residual water in the monomer can effectively lower the front velocity and temperature via heat loss due to vaporization. It was also shown that secondary functional groups present in certain monomers can act as chain-transfer agents. This slows the propagation of the front.

We have also tested influencing the fronts' velocity and temperature with fillers and conductive elements. The use of powdered fillers with high thermal diffusivity and thermal conductivity can lead to more efficient transport of heat through a system. As heat is transported more efficiently the front can propagate much faster with less heat. Using powdered fillers can become expensive in real world applications so composites were studied that had a continuous conductive element embedded through the length of the composite. In our study copper was used. Copper strips were shown to increase the velocity of the front without changing the front temperature by conducting heat ahead of the propagating front.

# CHAPTER 1. INTRODUCTION

## 1.1. Free Radical Polymerization

The International Union of Pure and Applied Chemistry (IUPAC) defines a polymer as a, “molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass”.<sup>1</sup> The word polymer comes from the Greek “poly” meaning many, and “mer” meaning parts. Polymers make up a significant part of everyday life from bio-polymers in the form of proteins and DNA, to many of the industrial and consumer commodities that are integral in society today.

There are many ways to make polymer be it a radical, anionic, or cationic driven process, but the two main classifications are chain and step-growth polymerizations. Step-growth polymerization, often referred to as condensation polymerization, involves bi- or multi-functional monomers reacting together to first form small dimers and trimers. These small dimers and trimers go on to create larger oligomers and eventually long chains of polymer. Common examples of step-growth polymers are polyurethanes, and polyesters. Chain-growth polymerization, or addition polymerization, is a classification of polymerization that involves the creation of a reactive monomer species and then the subsequent addition of one monomer unit at a time to that reactive site. This reactive site is propagated along the chain as it grows. Common polymers produced via chain-growth are polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC). Chain-growth polymerization will be the focus for the remainder of this document.

The most common mechanism of chain-growth polymerization is free-radical polymerization. There are three main steps in a chain or radical polymerization and those are

initiation, propagation, and termination. In a free-radical polymerization, the initiation step requires the generation of a radical species. This is often achieved using an initiator molecule that decomposes to create the initiating radical. The formation of this initiating radical can occur via heating, redox reactions, irradiation, ultra-violet radiation, and a few other means. The newly formed radical will then react with the monomer that contains, in most cases, a carbon-carbon double bond. This pi-bond is cleaved, and a new radical is formed that can then react with another monomer and so on and so on, growing a long chain polymer. This growth step is known as propagation. Being that the criteria for radical polymerization, in theory, only requires the monomer have a carbon-carbon double bond, there are a vast number of monomers that are suitable for free-radical polymerization. The process through which the growth of the polymer chain is ended is known as termination and can happen in one of two ways; recombination or disproportionation. In recombination two active polymer chains combine to form a stable covalent bond. In disproportionation an active polymer chain transfers a proton to another active polymer chain forming two stable molecules and ending the propagation.

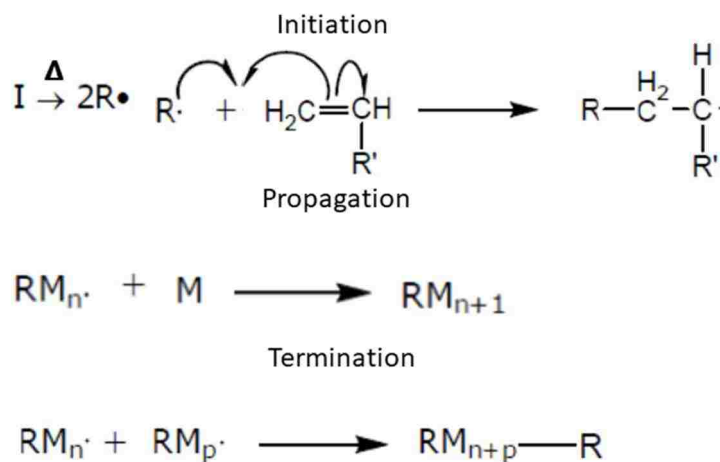


Figure 1. Diagram showing the steps of a free radical polymerization of an "ene"

There is also a process called chain transfer in which an active polymer chain extracts an atom from another molecule, referred to as a chain transfer agent, thus terminating the growth of the original chain and creating a new reactive radical species.

A chain transfer agent can be a molecule added to deliberately facilitate this phenomenon or it can be a side reaction with some part of the polymerization system, such as unreacted monomer or solvent. Chain transfer events effectively lower the average molecular weight of the resulting polymer. Figure 1 shows the general schematic for a free-radical polymerization of an “ene” with termination occurring by combination.

## **1.2. Frontal Polymerization**

One niche form of polymerization is frontal polymerization (FP). Frontal polymerization is defined as a process in which a localized reaction zone propagates through an unstirred system converting monomer to polymer.<sup>2</sup> Figure 2 shows a general schematic of frontal polymerization. There are three modes of frontal polymerization and those are thermal, photo, and isothermal. Each of these forms of FP require unique conditions to allow the phenomenon to occur. In photo-frontal polymerization a continuous flux of radiation is applied to a system containing a photo-active initiator that allows for the reaction zone to propagate through the system.<sup>3,4</sup> In thermal frontal polymerization (TFP) an external heat source, such as a heat gun or soldering iron, is applied to small exposed spot of a system containing monomer and initiator. This causes the decomposition of the initiator molecule, most commonly a peroxide, and the formation of an initiating species such as a radical. The initiating species then goes on to perform the propagation event as described earlier. In the case of an “ene” polymerization, which will be the focus in this document, a  $\pi$ -bond is converted to a  $\sigma$ -bond, and the polymer chain begins to grow. This bond conversion is an exothermic event that releases heat. This heat then diffuses into the surrounding

monomer/initiator and is used to convert more monomer to polymer. The result is a highly reactive zone that propagates through the unstirred system. So, as this reaction zone moves through the system monomer is being converted and polymer is left behind. If the conditions of the system are such that not enough heat is produced or cannot sufficiently diffuse into the surroundings, the front will quench, and the reaction zone will no longer propagate.<sup>5</sup> For this reason, careful consideration must be taken when choosing and designing a TFP system.

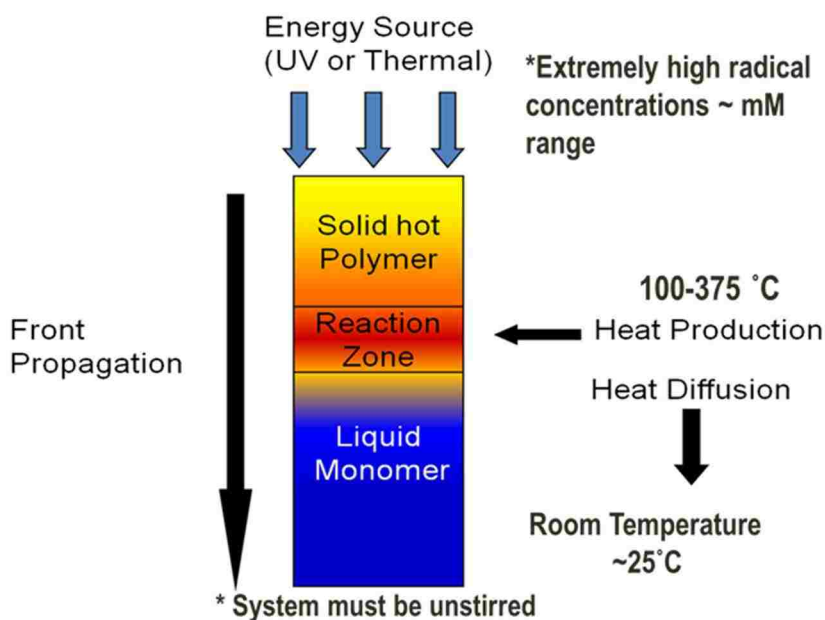


Figure 2. Diagram of a Frontal Polymerization

Chechilo and Enikolopyan first studied the structure and propagation of wave fronts in the Soviet Union in 1972.<sup>6</sup> There were further studies done on initiator type and concentration using methyl methacrylate, as well as the influence of pressure and initial temperature of the system.<sup>7,8</sup> There has been extensive work done by Pojman investigating TFP of acrylates and epoxy resins, copolymerization of urethane-acrylate systems, and thiol-ene systems.<sup>2,9,10</sup> One of



the main aspects of TFP that limit its applications is the high temperatures associated with the propagating fronts, which can reach temperatures greater than 200 °C. They often times also produce undesirable fuming and smoking.<sup>11</sup> However, it is this high temperature that will drastically increase the front velocity. Fronts that propagate faster can be used to create materials with quick cure times. Cure time can dramatically affect the number of applications in which these materials may be used. TFP can be used to make rapid repair materials that can easily conform to unique morphologies and consume much less energy than what is required for traditional bulk curing applications. The faster velocity can also cut down on the amount of fuming and smoking. Fuming and smoking is mostly caused by the decomposition of the initiator. Therefore, if a system can be designed that propagates faster by use of a filler or by carefully selecting a reactive monomer or combination of monomers then less initiator can be used while still supporting a stable front. TFP would also be useful in coatings, but the thin layers required often don't support a front due to the dissipation of heat. However, if a front were robust enough, producing enough heat to support a fast front, then TFP could possibly be used for a multitude of coating applications.

Photo-Frontal Polymerization (PFP) is frontal polymerization in which a continuous input of radiation, usually in the form of ultra-violet (UV) light, is applied to a system containing a photoreactive initiating species that allows a front to propagate. It is very similar to TFP in aspects other than the initiating event. PFP has been used to create a wide variety of materials ranging from gradient optical materials, microfluidic chips, to spatially controlled filaments.<sup>12-15</sup>

Finally, isothermal frontal polymerization (IFP) is a frontal polymerization that occurs at a constant temperature and involves a polymer seed, or solid piece of polymer, that is introduced into a solution of the monomer and initiator.<sup>16</sup> The process of IFP was first discovered by Koike

et al. in a polymethyl methacrylate (PMMA) system and was described as “interfacial gel polymerization”.<sup>17</sup> This solid piece of polymer, usually of high molecular weight, is dissolved by the monomer initiator solution creating a region of high viscosity, or gel. As the initiator decomposed throughout the solution it initiates subsequent polymerization but due to the Norrish-Trommsdorff effect, or gel effect, the polymerization rate is much higher in the more viscous gel region. Experiments conducted by Evstratova et al. confirmed that the process is indeed isothermal and that there is a minimum molecular weight that is required for the “seed” polymer.<sup>18</sup>

While TFP is an effective mode of polymerization there are some issues that can arise. One issue is porosity.<sup>19</sup> Due to the high temperatures created during a typical TFP porosity can be caused by dissolved gases that might be in the monomer used, as well as gases created by volatile by-products created during the decomposition of the initiator molecule. For example a common initiator benzoyl peroxide (BPO) will decompose creating carbon dioxide which will form pores in the polymer created, and because the initiator concentration in typical frontal polymerizations can be quite high large amounts of bubbles or pores can cause problems. These pores can cause convection driven instabilities in the propagating front which can cause deformities that may ultimately quench the front. These pores can also lead to loss in mechanical strength.

The other big issue that can influence the front is buoyancy driven convection.<sup>20</sup> During a frontal polymerization the reaction zone propagating through the system consists of a polymer-monomer interface. The newly formed polymer will be denser and depending on the monomer’s ability to crosslink can be either solid or liquid. As the front propagates convection of the heat produced in the reaction zone can interfere with the propagating front. If a non-crosslinking monomer is used, convection at the fluid-fluid interface can cause irregularity in the front known as “viscous

fingering” which can quench the front or cause faults in the resulting polymer. There are a few methods employed to avoid this problem. One method is to use monomers that will sufficiently crosslink. This creates a solid polymer that does not allow for sufficient fluid motion that may disrupt the front. This allows the front to propagate and avoids any problems. Another, and more applicable, solution is to use nonreactive, or reactive fillers. This modifies the density and viscosity of the monomer system and allows a sustainable front to propagate.<sup>21</sup>

## CHAPTER 2. EFFECTS OF FUNCTIONALITY ON FRONTAL POLYMERIZATION VELOCITY AND TEMPERATURE

### 2.1. Introduction

Frontal polymerization is a method of converting monomer(s) to polymer via a localized reaction zone that propagates from the coupling of thermal diffusion with the Arrhenius kinetics of an exothermic polymerization.

Frontal polymerization was first explored in the 1970s in Chernogolovka, Russia,<sup>6-8, 22-24</sup> with more work in the 1980s.<sup>25-28</sup> Pojman independently “rediscovered” FP in the 1990s while researching methacrylate polymerization.<sup>29-32</sup> Since then, research on FP has expanded significantly to include cure-on-demand materials,<sup>33, 34</sup> synthesis of gels<sup>35-38</sup> and gradient materials,<sup>39, 40</sup> epoxide polymerizations,<sup>9, 41-43</sup> composite materials,<sup>44-48</sup> and self-stiffening materials<sup>49</sup> and deep eutectic solvents.<sup>50, 51</sup> Most of the work on FP has involved free-radical polymerization, although epoxy curing<sup>9, 23, 52-54</sup> has been considered as well as ring-opening metathesis polymerization.<sup>55-58</sup>

Here, we will consider free-radical FP. There are several factors that affect front velocity and front temperature with the relative reactivity of the monomer being paramount. For example, frontal acrylamide polymerization is very rapid,<sup>59</sup> and fronts of acrylate polymerization are more rapid than methacrylate’s due to radical stability.<sup>60</sup> Initiator concentration and stability are also important.<sup>61</sup>

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Although FP is usually performed with neat monomers, it can be performed in high-boiling point solvents such as dimethyl sulfoxide (DMSO),<sup>31, 38, 46, 62</sup> or glycerol.<sup>63</sup>

Young et al.<sup>64</sup> studied the effect of using a dimethacrylate or trimethacrylate on the polymerization rate of octyl methacrylate photopolymerization. The trimethacrylate-containing solution polymerized faster than the dimethacrylate solution. Nason et al. studied 1,6-hexanediol diacrylate (HDDA) and trimethylolpropane triacrylate (TMPTA) polymerization by photo-differential scanning calorimetry (DSC) and found that TMPTA polymerized almost twice as fast as HDDA.<sup>60</sup> Tryson and Schultz studied, by photo-DSC, the polymerization of lauryl acrylate, HDDA, and pentaerythritol tetraacrylate and found that lauryl acrylate polymerized more slowly than the multifunctional acrylates, but also found that the tetraacrylate polymerized slower than the diacrylate.<sup>65</sup> Also, they found that conversion was significantly lower for the multifunctional acrylates due to increased crosslinking. Lauryl acrylate polymerized almost to completion, but HDDA achieved 46% and pentaerythritol tetraacrylate only 22% conversion.

We are particularly interested in the effect of functionality on the front velocity, because the front velocity determines how rapidly the curing can be achieved. Monoacrylates have been known to support slower fronts than multifunctional acrylates.<sup>60</sup> However, front velocity is not only a function of the intrinsic reactivity of the monomer, but also the front temperature.<sup>11</sup> To determine the effect of monomer functionality on the velocity of frontally polymerized systems, the monomers tested need to be chosen carefully. Typically, increasing the functionality of an acrylate decreases the equivalent weight ( $\text{g mol}^{-1}$  of acrylate groups), which increases the acrylate group concentration. Since the front velocity of a system is dependent on the amount of heat released in the polymerization step of the reaction, a higher acrylate group concentration should give a higher front velocity.

To separate the effect of the degree of acrylate functionality from front temperature TMPTA (296.32 g mol<sup>-1</sup>), a trifunctional acrylate, and 1,4-butanediol diacrylate (BDDA) (198.22 g mol<sup>-1</sup>), a diacrylate, were selected for study since both have equivalent weights of 99 g mol<sup>-1</sup> of acrylate groups. Comparing the front velocities obtained for each monomer, and using the same initiator concentration, allowed determination of the effect of monomer functionality on the front velocity and front temperature.

In order to study a variety of multifunctional acrylates, we first determined conditions that would support FP in acrylates with functionalities ranging from mono to tetrafunctional. To compensate for the differences in concentration of acrylate groups that arise from increased functionality, we dissolved the acrylates in DMSO such that the concentration of double bonds was constant. We also studied the effect of low concentrations of alcohol and water on the front velocity.

## 2.2. Materials and methods

BDDA 90%, HDDA 85%, and hexyl acrylate >96% (HA) were obtained from TCI (Portland, Oregon). Di(ethylene glycol) diacrylate 75% (DEGDA), poly(ethylene glycol) diacrylate ( $M_n$  250) (PEGDA), di(trimethylolpropane) tertaacrylate (DTMPTA), and Luperox ® 231 (1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane) 92%, were all obtained from Sigma-Aldrich. Pentaerythritol triacrylate (PETIA) was obtained from Allnex (Frankfurt, Germany). TMPTA was purchased from Sartomer (Exton, Pennsylvania), and 1-octanol 99% (OcOH) was obtained from Acros Organics (Geel, Belgium), fumed silica (FS) (AEROSIL ® M5) was purchased from US Composites (West Palm Beach, Florida). DMSO (99%) and propylene carbonate (PC) were from Aldrich (St. Louis, Missouri). Polygloss 90 was purchased from KaMin performance minerals. All reagents were used as received. Figure 3 shows the structures of the monomers

used. FP samples were prepared by mixing the acrylate or acrylates together with Luperox ® 231. Solvent and fumed silica were then incorporated, when appropriate, and the mixture was stirred thoroughly to ensure homogeneity. The reactant mixture was poured into 16 mm x 150 mm glass test tubes marked at 1 cm intervals, with a typical sample being roughly 20 mL. FP was induced via heat from a soldering iron or butane torch.

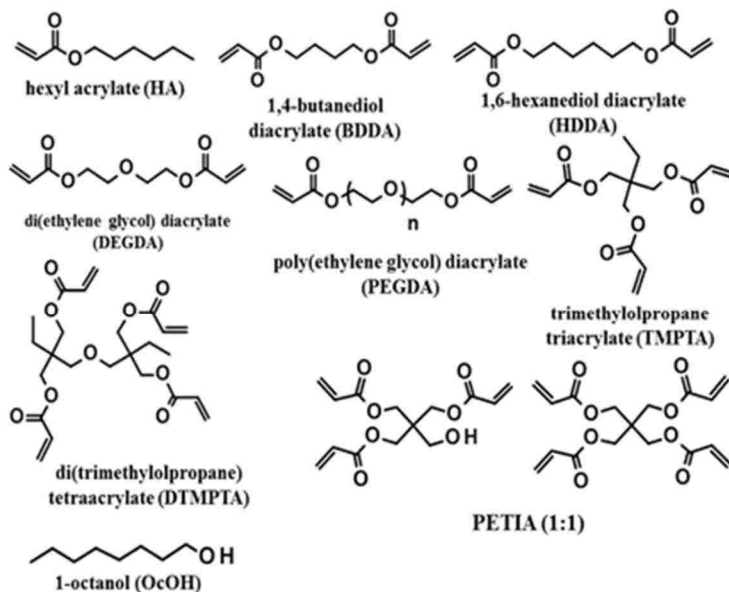


Figure 3. Reagents used

A butane soldering iron was heated and the tip was placed at the top of test tube against the glass. This heating element was held against the glass until the polymerization was initiated. For all intents and purposes, any heat source can be used to initiate the polymerization if the sample amount is great enough to allow the reaction to reach a steady state.

For the neat monomer polymerizations, the required polymerization conditions were 1 part per hundred resin (phr) Luperox ® 231, meaning that for every 100 g of monomer, 1 g of initiator was used. For the remainder of the experiments, a basis was needed to run all acrylates with the same concentration of acrylate groups. First, we determined the conditions to achieve FP with neat HA, which was 5 phr of fumed silica and 3 phr of Luperox ® 231. The

concentration of acrylate groups in pure HA is 5.68 M. To achieve the same for multifunctional acrylates, DMSO was used. All other components stayed the same. For filled systems, a 1 phr Luperox ® 231 and monomer solution was mixed with 50 phr Polygloss ® 90. The resulting putty-like material was then set into a wooden slab mold of dimensions 8 mm x 20 mm x 100 mm.

The propagation of the front was recorded using a camera, and the front temperature was tracked by capturing images periodically using a Seek Thermal infrared camera on an iPhone, see Image 1.

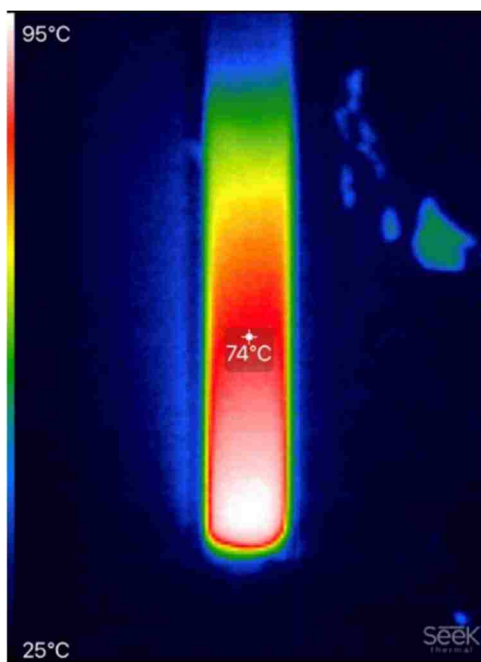


Image 1. Infrared image of descending front in test tube

The values obtained were the temperature of the surface of the glass test tube but were proportional to the internal front temperature. The front velocity was determined by plotting the position of the front versus time and determining the slope of the best fit line. All experiments were run in triplicate, the values averaged, and the standard deviation used for the error bars.



### 2.3. Increased Functionality Effects on Velocity and Temperature

To first establish the front velocity and temperature behavior of acrylic monomers with different functionalities, the concentration of double bonds was not altered. All eight monomers chosen were mixed with 1 phr initiator and polymerized using no diluent. These results are shown in Figure 4. HA, a mono functional acrylate, would not support a front under the chosen conditions. This was overcome in future experiments. There is no clear trend, but it should be noted that TMPTA, a triacrylate, produces the fastest fronts with difunctional acrylates (BDDA, HDDA, DEGDA, PEGDA) being slightly slower. The difunctional acrylates propagate at similar velocities with DEGDA being slightly slower.

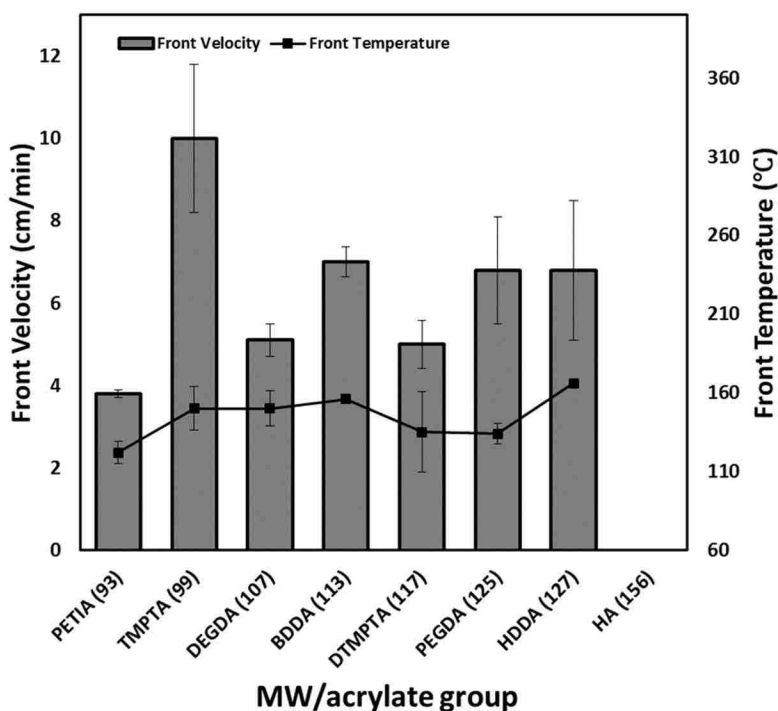


Figure 4. Front velocities and temperatures for acrylates of different functionalities. The initiator (Luperox ® 231) concentration was 1 phr, and no filler or solvent was used. \* indicates that no front would propagate under given conditions

Interestingly, the two tetrafunctional acrylates (DTMPTA and PETIA) produced the slowest fronts. PETIA is a 1:1 ratio of a triacrylate and a tetraacrylate based on pentaerythritol, which in the case of the triacrylate leaves a free hydroxyl group. The possible impact of this free hydroxyl group will be explored later.

Figure 5 shows the comparison of TMPTA, HDDA, and mixtures of the two. As the ratio of TMPTA is increased, the front velocity and temperature both increased. This trend continued with both temperature and velocity increasing as the amount of triacrylate increased. The velocity difference between pure HDDA and TMPTA was more than double, 2.19 times greater. This is in agreement with results reported by Nason et al.<sup>60</sup> TMPTA produces faster fronts than HDDA due to its lower molecular weight per acrylate, 99 and 113 g mol<sup>-1</sup>, respectively, as well as the increased crosslinking due to higher functionality.

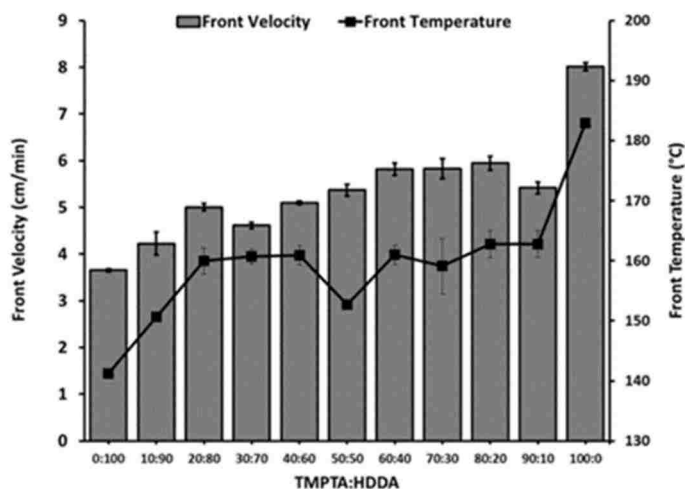


Figure 5. Front velocity and temperature as a function of the ratio of a triacrylate (TMPTA) to diacrylate (HDDA). No solvent or filler was used. The concentration of Luperox ® 231 was 0.1 phr.

## 2.4. Direct Comparison of Monomers with Equivalent Double Bond Concentration

In order to properly compare the intrinsic reactivity of acrylates of different functionalities, it is necessary to control the concentration of acrylate groups. This is difficult given the few monomers that have different functionality, but equal acrylate concentration. One pair of monomers which allows this is BDDA and TMPTA, each having a molecular weight per acrylate of  $99 \text{ g mol}^{-1}$ . Figure 6 shows the comparison of the front velocities and temperatures as a function of the ratio of the two monomers. The data show a similar trend as was observed in the comparison of HDDA and TMPTA. As the fraction of triacrylate was increased, the velocity and temperature increased with pure TMPTA being approximately twice as fast as pure BDDA.

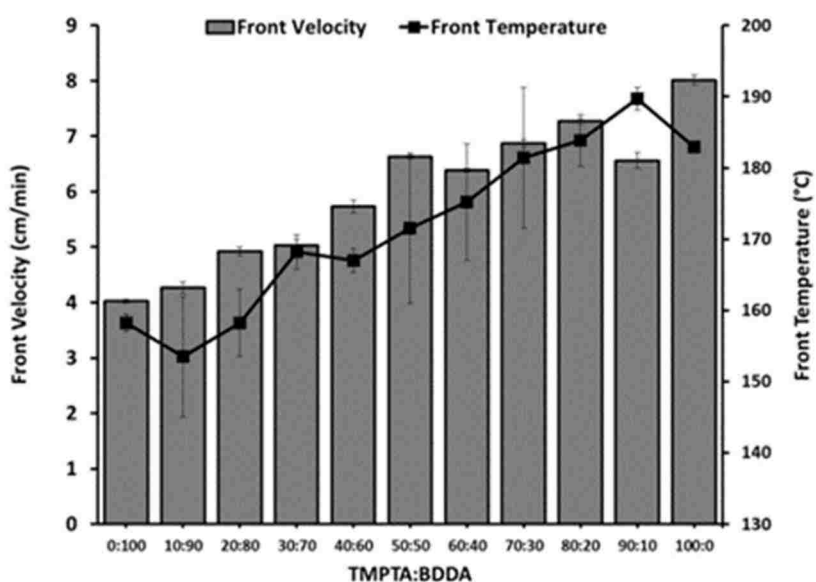


Figure 6. Front velocity and temperature as a function of the ratio of a triacrylate (TMPTA) to diacrylate (BDDA). No solvent or filler was used. The concentration of Luperox ® 231 was 0.1 phr.

## 2.5. Controlling Double Bond Concentration in Multi-functional Monomers

Monofunctional acrylates, or acrylates of higher functionality, are difficult to compare due to the lack of examples with the same equivalent weight; therefore, another method was employed to maintain a constant acrylate group concentration. First conditions to run HA as a front were determined. This monomer served as the standard to which all other acrylates could be compared, if they have an equivalent weight less than  $156 \text{ g mol}^{-1}$  per acrylate groups. It was found that HA required 3 phr of Luperox ® 231 and 5 phr of fumed silica to reliably run as a front. Fumed silica was added to increase the viscosity of the mixture in order to eliminate convection, which can quench fronts.<sup>66</sup> Other acrylates were compared to HA by maintaining constant concentrations of acrylate groups (5.68 M). For acrylates with lower equivalent weights, such as TMPTA ( $99 \text{ g mol}^{-1}$  acrylate groups), DMSO was used as inert diluent to maintain constant acrylate group concentrations. DMSO was chosen because it has a high boiling point ( $\sim 190 \text{ }^\circ\text{C}$ ), was miscible with all the monomers we tested, and has been used in fronts previously.<sup>31, 38, 46, 62</sup>

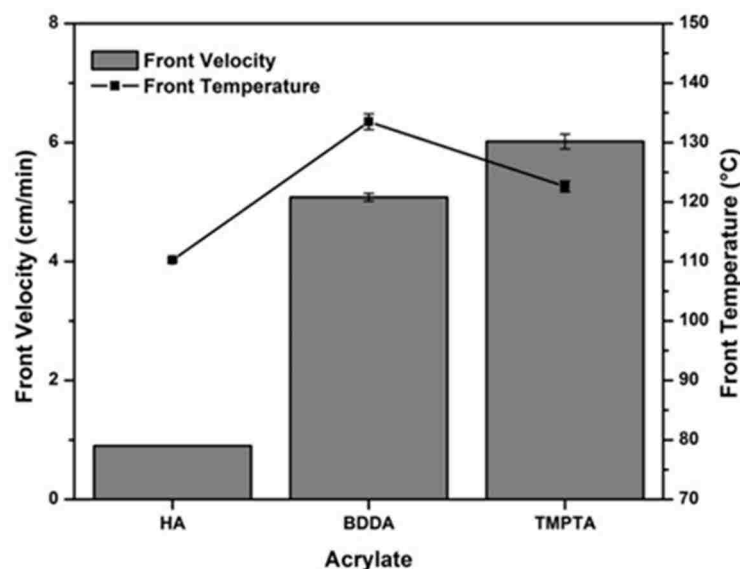


Figure 7. Front velocities and temperatures for HA, BDDA, and TMPTA. Experiments were performed in DMSO with 3 phr initiator, and 5 phr fumed silica.

Figure 7 shows the results for HA, BDDA, and TMPTA using this method. HA, a monoacrylate, has a considerably lower front velocity than either multifunctional acrylate, as well as a corresponding lower front temperature. The increase of front velocity with increasing acrylate functionality, especially from monofunctional to difunctional, is due to autoacceleration. Radical polymerization reactions are known to proceed at increased rates as the local viscosity of the reaction mixture increases.<sup>67, 68</sup> As monomer is converted into polymer, the mobility of large propagating radical chains becomes limited. While relatively small and mobile monomer units can easily diffuse and add to the propagating centers, it becomes harder for two propagating radicals to come together and terminate. This decrease in the rate of termination causes an increase in the rate of polymerization, which is known as autoacceleration.<sup>67, 69</sup> Crosslinking of polymer chains causes this effect to occur at lower conversions, which means that monomers with higher functionality will autoaccelerate at lower conversions. Thoma et al. measured by EPR the concentration of the trapped radicals as high as  $8.7 \times 10^{-3} \text{ mol kg}^{-1}$ .<sup>70</sup> This explains the

large difference in front velocity from monofunctional acrylate, in which there is no crosslinking, to diacrylate, in which there is extensive crosslinking. This also explains the smaller difference between difunctional and trifunctional acrylates.

Figure 8 presents the front velocities and front temperatures for four diacrylates in DMSO. It is curious that HDDA supports slower fronts than the other diacrylates, and a possible explanation for this could be the lower purity.

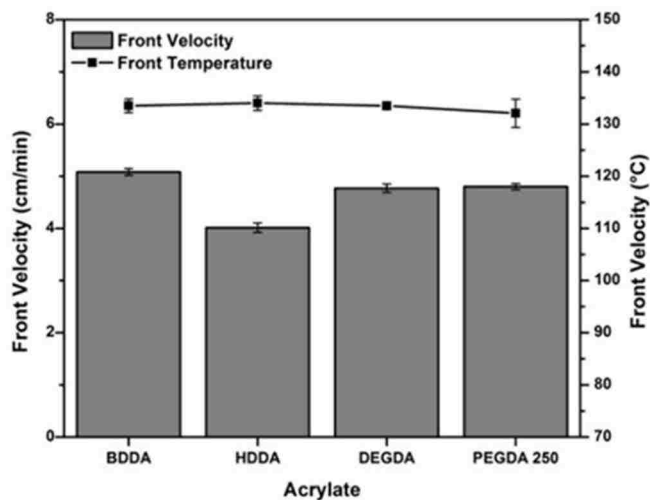


Figure 8. Front velocities and front temperatures of several difunctional monomers. Experiments were performed in DMSO with 3 phr initiator and 5 phr fumed silica.

If the impurity is some sort of monoacrylate, it could be the case that this copolymerization lowers the overall rate of reaction for the system. It has been shown in literature that during some photoinitiated copolymerization of acrylates of increasing side chain lengths, the systems with the highest amount of short chain methacrylate lowered the reaction rate in those systems.<sup>71, 72</sup>

The front velocities and front temperatures for several multifunctional acrylates are shown in Figure 9. The triacrylate, TMPTA, produces the fastest fronts of this group, as well as for all acrylates tested. Although the dimer of TMPTA, DTMPTA, is a tetraacrylate, this additional acrylate group does not increase the velocity of the front. PETIA is a 1:1 mixture of

the tri and tetra acrylate monomers based on pentaerythritol. PETIA produces a slower front than both TMPTA and DTMPTA. As for the differences between the pentaerythritol-based and trimethylolpropane-based monomers, we suspected that the hydroxyl group on the pentaerythritol acted as a chain-transfer agent, which reduced the crosslinking, and lowered the polymerization rate. We tested this hypothesis by adding an equimolar amount of 1-octanol (OcOH) to TMPTA; this indeed lowered the front velocity.

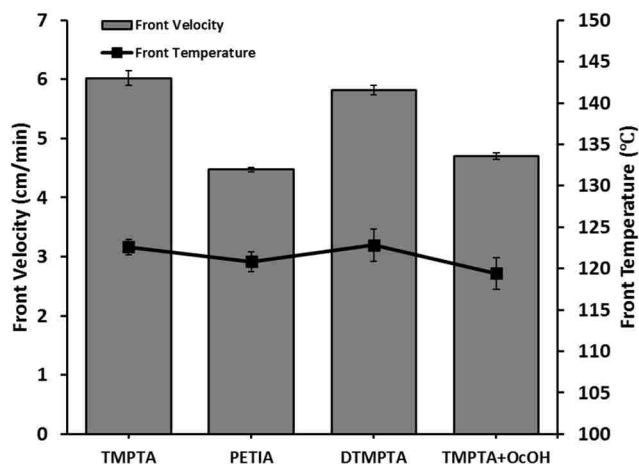


Figure 9. Front velocities and front temperatures of several difunctional monomers BDDA, HDDA, DEGDA, and PEGDA. Experiments were performed in DMSO with 3 phr initiator and 5 phr fumed silica.

## 2.6. Effects of Water and Solvent

We observed in some experiments without solvent that if we dried the monomer, the fronts propagated faster than with the monomer straight from the container. We then tested the effect of water for the BDDA polymerization in DMSO. We added 1.5% by weight water to the diacrylate in DMSO and observed an almost 20% decrease in velocity, this is shown in Figure 10. To test if the components in the DMSO could be acting as inhibitors, we switched to propylene carbonate (PC) as the solvent. The front velocity was decreased, but within experimental uncertainty. We hypothesized that water could cause hydrolysis of the acrylates to produce acrylic acid (AA),

which was observed in the FP of benzyl acrylate.<sup>73</sup> If all of the water hydrolyzed esters, then 13% of the acrylate groups would be converted to AA. We added 13 n/n % of AA to the formulation in PC, which increased the front velocity. Although the system would be less crosslinked, the greater reactivity of AA overcame this effect.<sup>74</sup> However, adding HA also increased the front velocity. In neither case was the front temperature affected.

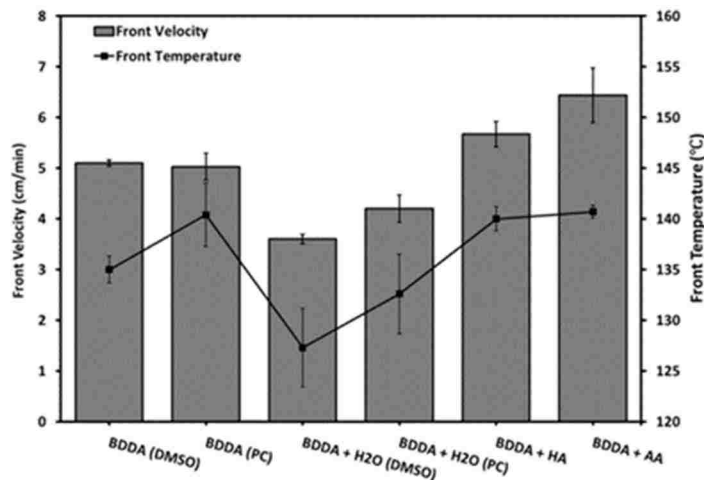


Figure 10. The effect of water, HA, and AA on front velocities. BDDA was polymerized in DMSO or PC. Compositions by mass: BDDA (59.23%), H<sub>2</sub>O (1.52%), Luperox<sup>®</sup> 231 (2.80%), fumed silica (4.65%), and PC (31.80%). HA and AA were substituted in place of water.

We also considered whether water could act as a chain-transfer agent, but this was found not to be the case in previous studies.<sup>75, 76</sup> We calculated the heat absorbed in vaporizing 1.5 g of water in a 100 g sample and using a heat capacity of the acrylate solutions of 2 J g<sup>-1</sup> K<sup>-1</sup>, the result would be a decrease in front temperature of 17 °C. The front temperature was lowered by 8 °C in both DMSO and PC. The front velocity is a strong function of temperature,<sup>77</sup> which suggests that small amounts of water can reduce front velocity by absorbing heat through vaporization.



## 2.6. Conclusions

We studied the effect of acrylate functionality on FP velocity and temperature. BDDA and TMPTA have the same equivalent weight per acrylate. Frontally polymerizing them neat at different ratios revealed that the velocity increases as the ratio of TMPTA was increased with pure TMPTA polymerizing twice as fast as pure BDDA.

To set a baseline, we polymerized several acrylates with different functionalities and molecular weight per acrylate groups. We then studied FP of several acrylates in DMSO such that the concentration of acrylate groups was constant, HA fronts were five times slower than BDDA fronts, and six times slower than TMPTA fronts. Fronts with HDDA propagated 20% slower than BDDA or the two other diacrylates we studied, for which we have no current explanation. We then compared several multifunctional acrylates. TMPTA fronts were the fastest. A 1:1 mixture of tri and tetraacrylate (PETIA), produced slower fronts than those with only tetraacrylate (DTMPTA). PETIA fronts were slower than ones with TMPTA because of chain-transfer from the hydroxyl group, which we confirmed by adding 1-octanol to TMPTA. Finally, we determined that small amounts of water present in the monomers, slowed FP. We first tested to see if this water might be hydrolyzing the ester of the acrylate group. The amount of acrylic acid produced if hydrolysis was 100% efficient was calculated, and this molar amount of AA was added into the polymerization system to simulate the effect of the side reaction. This proved to increase the front velocity which we suspected was from increased double bond concentration, and increased reactivity of AA. It was determined that at the high temperature of the propagating front the water is vaporized. This vaporization pulls heat from the system and this lowers the front temperature and velocity.

## CHAPTER 3. EFFECT OF INORGANIC FILLERS ON THE FRONTAL POLYMERIZATION OF MULTI-FUNCTIONAL ACRYLATES

### 3.1. Introduction

One of the drawbacks of thermal frontal polymerization (TFP) of multifunctional acrylates is that front temperatures can get as high as 250 C.<sup>78</sup> High front temperatures lead to increases in the velocity of the front leading to a faster cure time, but this can also be an issue when considering applications. There have been many different approaches to reducing front temperature such as the addition of thiols,<sup>34</sup> or the use of redox initiators.<sup>79,80</sup> These two solutions, while viable, can drastically lower shelf life and limit the assortment of monomers and initiators that can be used.<sup>81</sup> One way to address the issue of high front temperatures is by using different fillers. Nason et al. showed that using an inorganic filler in conjunction with a trithiol monomer significantly reduced the front temperature, which would necessarily reduce the front velocity.<sup>80</sup> It is herein proposed that by selectively choosing fillers with the certain thermal properties, a filled system could have a lower front temperature while propagating at an increased velocity proportional to filler loading.

To first understand how fillers might influence fronts it is useful to mention first that Novozhilov derived an analytical expression for the dependence of front velocity for a one-step reaction on front temperature, the activation energy of the reaction, and the thermal diffusivity of the system.<sup>77</sup>

This relation is shown in equation [1] where  $E$  is the activation energy of the reaction,  $T_f$  is the front temperature, and  $\kappa$  is the thermal diffusivity.

$$vel \propto \sqrt{\kappa} T_f e^{-2E/RT_f} \quad [1]$$

The equation shows that velocity scales with the square root of thermal diffusivity. From this we hypothesize that creating a system that includes fillers with a high thermal diffusivity should increase the front velocity while keeping the front temperatures relatively stable.

In this study we investigate the effects of different inert fillers on front temperature and velocity. Several fillers including fumed silica, kaolin clay, graphite, aluminum powder, aluminum oxide, and boron nitride were used. Previous studies considered the impact of silica or inorganic fillers on suppressing convection and on front velocity.<sup>62, 82</sup> The problem of adding a filler to reduce the front temperature is that it can greatly reduce the front velocity as well. Viner and Pojman have attempted this by using mixtures of inert phase change materials and kaolin clay but found that substituting kaolin with inert phase change material resulted in lower front temperatures and velocities.<sup>5</sup>

One class of fillers, called refractory materials, are of significant interest. Refractory materials are heat resistant materials that resist decomposition by heat, pressure, or chemical means. For the purpose of these experiments the refractory materials of interest will be compared to kaolin clay. Graphite and boron nitride were of interest due to their thermal properties. Graphite has a slightly lower heat capacity than kaolin clay, but its thermal diffusivity is almost thirty times larger. We hypothesize that the increased thermal diffusivity will lead to an overall increase in the front velocity while maintaining a lower front temperature. Boron nitride has both a higher heat capacity and thermal diffusivity. In this case the heat capacity should hinder the diffusion of heat while the thermal diffusivity should increase it.

Ultra-fine kaolin is used in these composites because of its ability to produce a putty when mixed with monomer. Fumed silica has a greater rheological effect on the monomer than kaolin, so it is used in much smaller amount to obtain the desired viscosity.

### 3.2. Materials and Methods

Technical grade trimethylolpropane triacrylate (TMPTA) was obtained from Sartomer. Benzoyl Peroxide (BPO), 1,1-Bis(tert-butylperoxy)-3,3,5-tricyclohexane (Luperox ® 231), aluminum powder (~20 micron particle size), and graphite (2-12 micron particle size) were obtained from Sigma-Aldrich. Polygloss ® 90 (referred to simply as kaolin for the remainder of the paper) a kaolinite clay (0.4 micron particle size) was obtained from KaMin performance minerals. Fumed silica (Aerosil ® 200 175-225m<sup>2</sup>/g BET surface area) was obtained from Evonik Industries. Hexagonal boron nitride (10 micron) was obtained from Panadyne. Alumina powder was obtained from Huber Engineered Materials (Atlanta, GA). All materials were used as received. Table 1 shows the physical/thermal properties of interest for the various fillers and monomer. Various amounts of 1 phr (parts per hundred resin) initiator in TMPTA and inert filler were manually mixed until a moldable putty was formed. For experiments involving mixed filler systems, the mass fraction of total filler was held constant, but the type of fillers and fractions thereof were changed. Both BPO and Luperox ® 231 were used as initiators.

The putty was formed in wooden molds with dimensions of 3.0 cm wide x 2.5 cm high x 10 cm long. To measure front temperature a type K thermocouple connected to a laptop with Logger Lite ® software was inserted into the middle of the strip of putty at approximately half depth. To initiate the fronts a handheld butane soldering iron was used to heat a small portion of the putty strip at one end. Front velocity data was gathered by filming the reactions with a cm scale in frame in order to track the propagating front. Graphs of front position versus time were plotted in order to obtain the front velocities. All experiments were done in triplicate.

For experiments in which multiple fillers were used, the total filler loading was chosen to be 49% by weight. This filler portion was comprised of various amounts of kaolin and what will

be referred to as “solid additives”. Solid additives include those fillers that have high thermal diffusivity. The amount of solid additive used in a sample will be reported as a fraction of the total filler amount.

Table 1. Thermal properties of selected fillers and monomer

	$\rho$ (g cm <sup>-3</sup> )	$C_p$ (J g <sup>-1</sup> K <sup>-1</sup> )	$\kappa$ (cm <sup>2</sup> s <sup>-1</sup> )
<b>TMPTA</b>	<b>2.00</b>	<b>1.10</b>	<b>1.00 x 10<sup>-3</sup></b>
<b>Polygloss ® 90 (kaolin)</b>	<b>2.60</b>	<b>1.20</b>	<b>3.00 x 10<sup>-3</sup></b>
<b>Matroxid ® TM-3310 (alumina)</b>	<b>2.70</b>	<b>0.88</b>	<b>1.02 x 10<sup>-2</sup></b>
<b>Hexagonal Boron Nitride</b>	<b>2.28</b>	<b>1.61</b>	<b>5.45 x 10<sup>-2</sup></b>
<b>Graphite</b>	<b>2.26</b>	<b>0.70</b>	<b>8.48 x 10<sup>-2</sup></b>
<b>Aluminum</b>	<b>2.70</b>	<b>0.90</b>	<b>6.00 x 10<sup>-1</sup></b>
<b>Aerosil ® 200 (fumed silica)</b>	<b>2.20</b>		

### 3.3. Single Filler System

The first task when working with the selected filler was to establish the upper loading threshold for the system. TMPTA with 1 phr initiator was mixed with the filler of interest until a moldable putty, that would support a front, was formed. This was established as the upper loading limit; the lower limit was established as the amount that would produce a moldable putty. The first filler investigated was kaolin, an ultrafine silicate mineral. It was suspected, based off of thermal data (Table 1), that there would be no increase in velocity or temperature with the addition of kaolin. Figure 11 shows that the upper loading limit for kaolin was 47%, and the lower limit was 27% by mass. For these initial experiments both BPO and Luperox ® 231 were tested. BPO is a common initiator used in free-radical polymerization but has poor solubility in acrylates.

Luperox ® 231 is a liquid and is readily soluble in a variety of monomers, which allows a wider

variety of initiator concentrations. Figures 11 and 12 show that, for both BPO and Luperox<sup>®</sup> 231 respectively, as the fraction of kaolin increases, both the front velocity and temperature decreases.

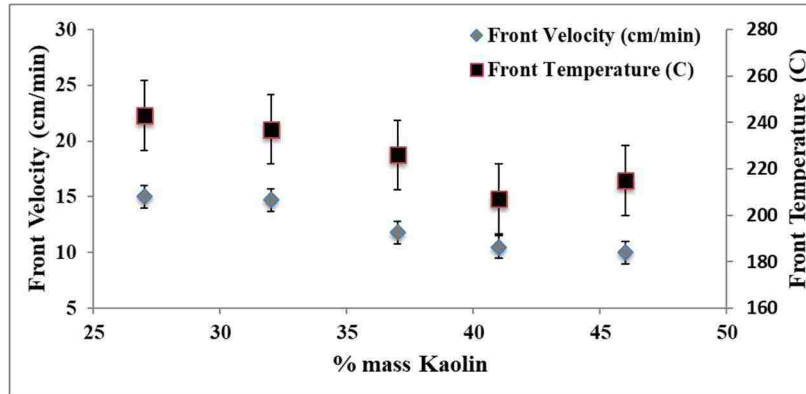


Figure 11. Front temperature and velocity vs. mass fraction of kaolin clay for BPO system

As the amount of kaolin in the system increases the clay acts as a heat sink. The propagating front loses heat to the kaolin reducing the front temperature and thus the front velocity. The other two fillers tested in a single filler system were fumed silica and graphite powder. In the case of fumed silica, extremely low density, and high surface area of the filler only allows for a small amount of filler loading, but the trend was the same as in kaolin systems. As the filler loading increased the velocity and temperature decreased, shown in Figure 13.

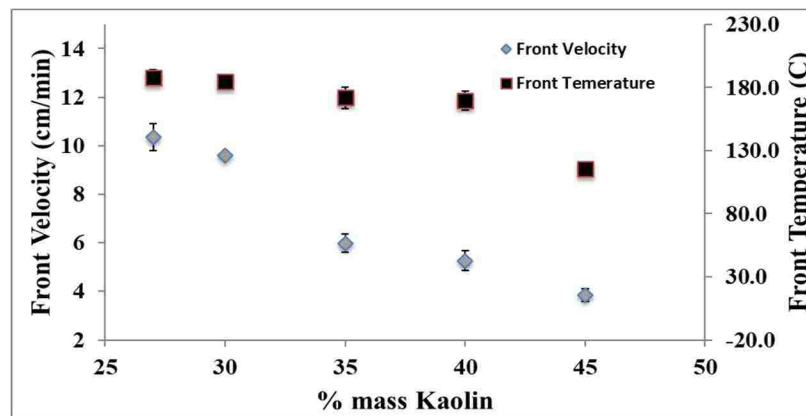


Figure 12. Front temperature and velocity vs mass fraction of kaolin clay for Luperox<sup>®</sup> 231 system

In the case of graphite powder, boron nitride, aluminum, and alumina the amount of filler necessary to form a moldable putty created a composite that would not support a front. There was local polymerization at the site of initiation, but the front soon quenched. This was the case for both initiators, but there was also notable unique behavior in BPO graphite systems

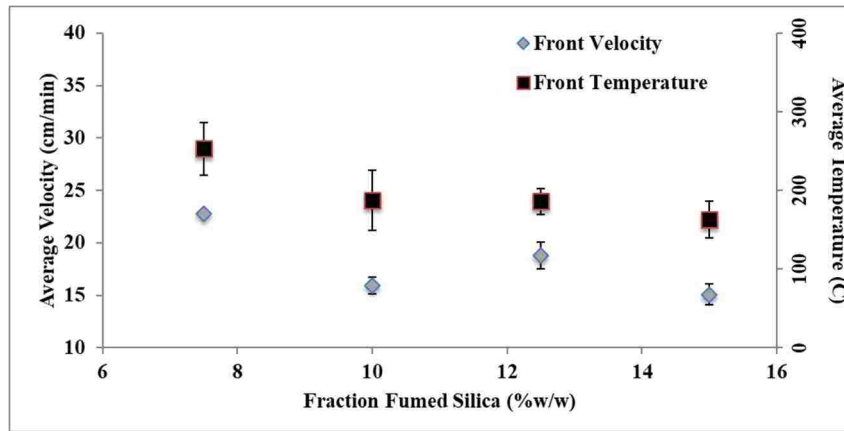


Figure 13. Front temperature and velocity vs. mass fraction of fumed silica in a Luperox ® 231 system

Once the graphite powder was mixed into the monomer/initiator solution a reaction quickly occurred, and the mixture spontaneously polymerized. Lopes et al. studied this phenomenon and found that there is an interaction between graphite and functional groups on the surface of graphite.<sup>83</sup> Image 2 shows this effect, with the left image showing graphite powder, TMPTA, and 1 phr BPO immediately after mixing. The centrifuge tube is tilted to show that the mixture still flows. The right image is the same mixture after ten minutes and is inverted to show that the mixture has hardened indicating spontaneous polymerization.

### 3.4. Multiple Filler Systems

As mentioned in the previous section kaolin and fumed silica were the only two fillers that would form a moldable putty while still supporting a viable front. To work around this dilemma, the fillers that would not support a front, herein referred to as solid additives, would be mixed with

kaolin for the study. The total filler amount would be held constant while the fraction of solid additive would be increased. The total filler amount was based upon the experiments done with kaolin as the single filler. As with the previous experiment both BPO and Luperox ® 231 were tested to see if there were any adverse effects. All velocities were normalized for better comparison.

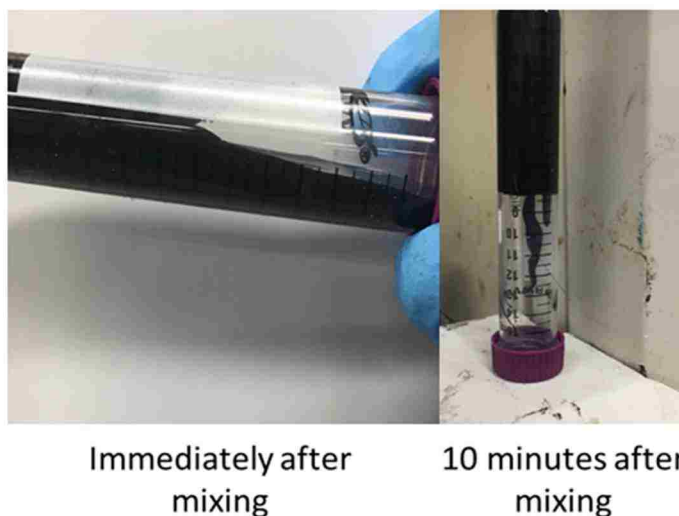


Image 2. The effect of graphite in a BPO/TMPTA system. The image on the left depicts graphite powder, TMPTA, and 1 phr immediately after mixing. The image on the right depicts the same system ten minutes after mixing.

As noted in the Novozhilov equation the front velocity scales directly with the square root of the thermal diffusivity.<sup>77</sup> The thermal diffusivity is proportional to the thermal conductivity, a materials ability to conduct heat, and the density multiplied by the specific heat capacity. The various solid additives have relatively comparable heat capacities and densities. Thus, we expect that highly conductive materials when mixed with kaolin, which has similar heat capacity and density, will increase the diffusion of heat allowing the front to propagate faster with less heat.



Figures 14 and 15 show these results for both BPO, and Luperox ® 231 respectively. For both initiators the most effective filler was hexagonal boron nitride. As the amount of solid additive was increased, the velocity increased as well. The highest solid additive loading of 60%, roughly 30% by weight, increased the front velocity by 30-35%.

In the BPO containing system graphite had a pronounced inhibitory effect, decreasing the velocity by almost 30%. In fact, initially all the additives seemed to lower the velocity. At the highest additive loading of graphite, there seemed to possibly be an increase. The decrease in velocity seen could be some interaction between BPO as in the case of graphite, or it could be radical scavenging. Another reason for the decrease in velocity could be explained by a study conducted by Solomon et al. in which clays were shown to participate in the termination of growing polymer chains.<sup>84</sup> They were able to show that octahedral aluminums at the surface of clays similar to kaolin act as Lewis acids and can react with radicals causing chain terminations. The alumina and aluminum, which would have an oxidized surface, used in these experiments could have some Lewis acidity which would cause them to interfere in the polymerization of TMPTA.

For the systems containing Luperox ® 231 there did not seem to be as much of an inhibitory effect except when alumina was the additive. The graphite and aluminum both had minimal effect on the velocity but were not as inhibitory as in the BPO systems.

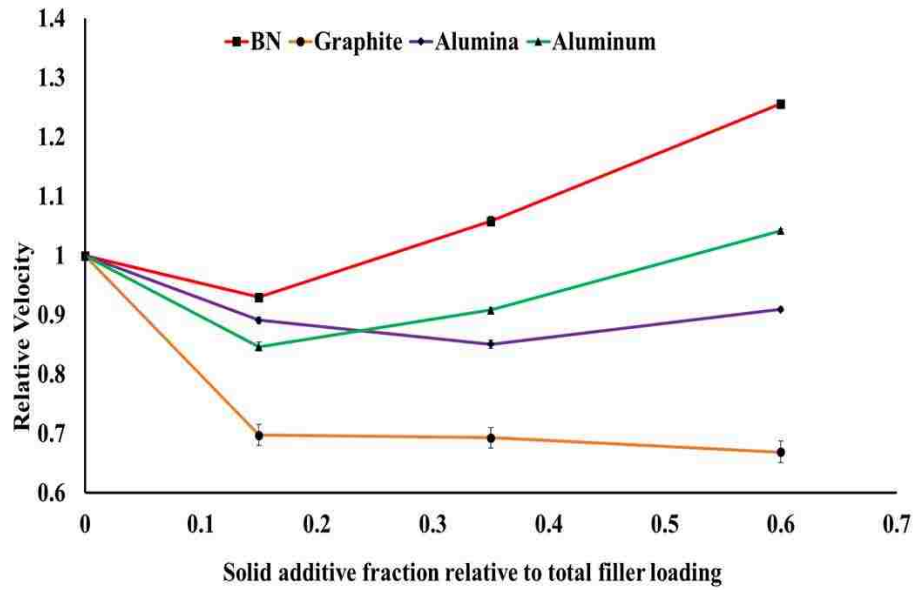


Figure 14. Mixed filler system contains 51% w/w 1 phr BPO in TMPTA and 49% w/w total filler loading. Solid additive loading is reported as fraction of total filler loading

Table 2. Front temperatures for mixed filler systems with BPO as initiator.

Solid additive loading	Front Temperature (°C)			
	Boron Nitride	Graphite	Alumina	Aluminum
0.00	221.3	221.3	221.3	221.3
0.15	222.7	190.0	219.0	216.0
0.35	208.0	176.0	223.7	212.0
0.60	220.3		195.0	216.0

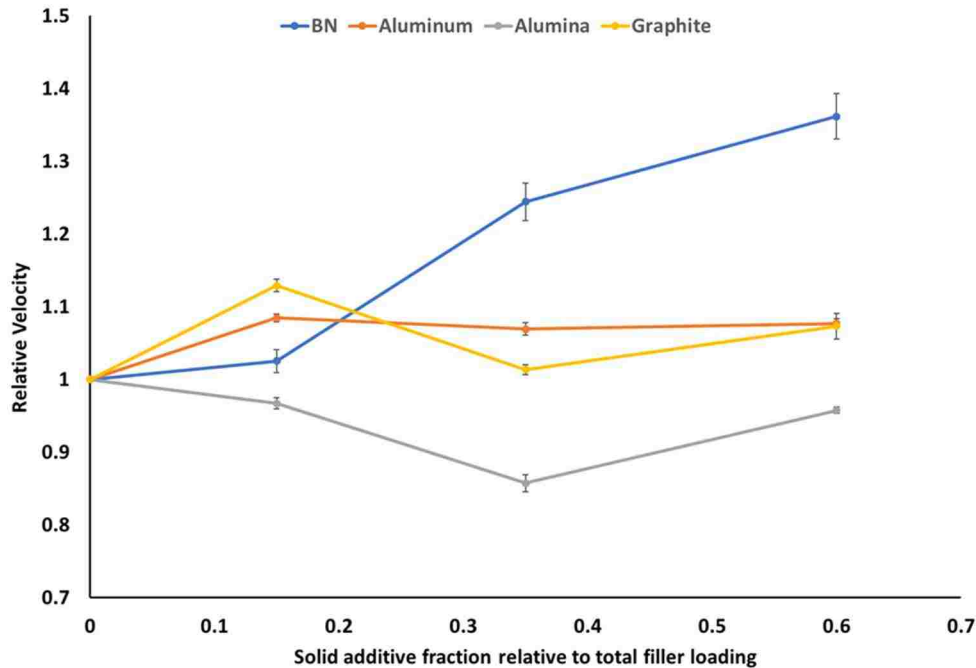


Figure 15. Mixed filler system contains 51% w/w 1 phr Luperox ® 231 in TMTPA and 49% w/w total filler loading. Solid additive loading is reported as fraction relative to total filler loading.

Table 3. Front temperatures for mixed filler systems with Luperox ® 231 as initiator.

Solid additive loading	Front Temperature (°C)			
	Boron Nitride	Graphite	Alumina	Aluminum
0.00	214.5	214.5	214.5	214.5
0.15	222.0	222.3	219.3	208.0
0.35	219.3	173.0	223.7	207.3
0.60	213.7	219.3	201.7	208.7

### 3.5. Effect of Initiator Concentration

It was hypothesized that because the effect of the solid additive was a thermal one, and not an influence on the chemical reaction rate, that the trend seen in the previous mixed filler study would hold constant no matter the initiator concentration. The velocities would still increase with the increased additive loading, but overall the velocities would become higher and higher as the initiator concentration was increased. With this, if the velocities were normalized and plotted on

one graph the individual curves would collapse onto each other. Figure 16 shows this data. While the data fall close to each other there appears to be deviance from the hypothesis for which we have no explanation. In addition to the thermal influence of the solid additive there appears to be some other effects.

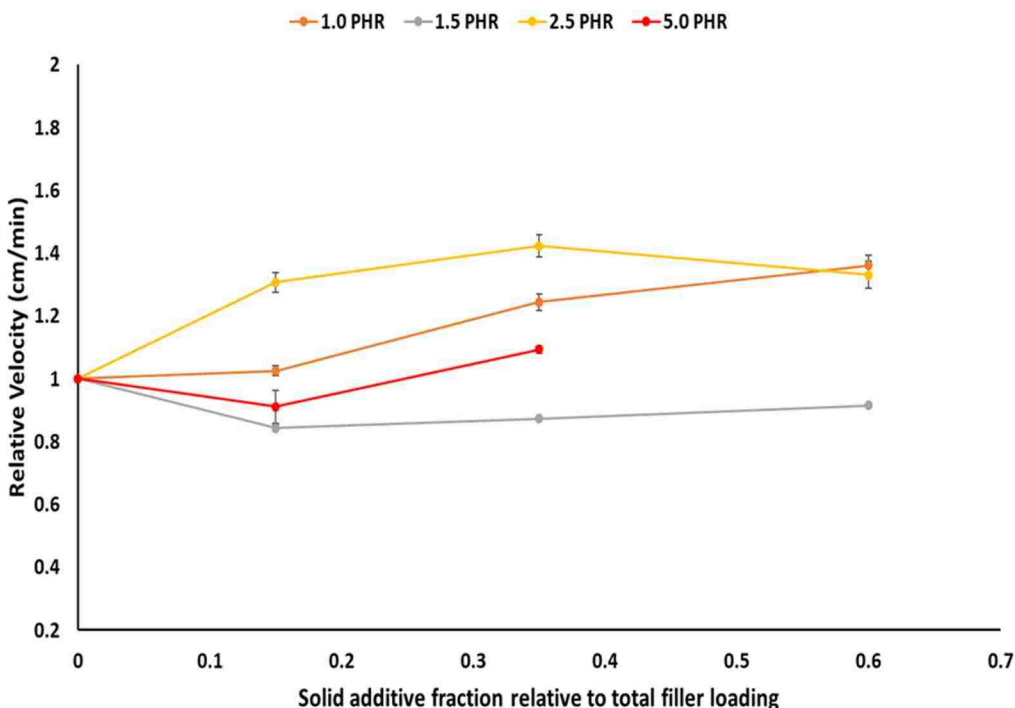


Figure 16. Front velocity vs. solid additive fraction relative to filler loading for 4 different initiator concentrations.

### 3.6. Conclusion

Fillers can be very useful in polymers and can be used to simply add mechanical properties or can be used to influence the polymerization itself. We studied the impact of a variety of fillers on the frontal polymerization of a multifunctional acrylate. We examined how the filler could influence the diffusion of heat through a system which would increase the velocity of the propagating front. Some fillers that do not have sufficiently high thermal diffusivity, and a relatively high heat capacity, can cause the filler to act as a heat sink. Heat is lost to the system

lowering the front temperature and thus the front velocity. To overcome this issue thermally conductive materials were mixed into the clay system in order to allow for greater thermal transport and thus faster moving fronts. The filler that performed the best was hexagonal boron nitride, increasing the front velocity by as much as 30% while not increasing the front temperature. Some fillers seem to act as an inhibitor in the polymerization, significantly lowering the front velocity. These fillers could be interacting with the initiator itself or acting as radical scavengers slowing the propagating front. We also showed that while thermal transport was the dominant influence in increasing the front velocity, the trend does not remain constant over a range of initiator concentrations.

## **CHAPTER 4. INCORPORATION OF CONTINUOUS CONDUCTIVE ELEMENT INTO ACRYLATE COMPOSITES AND THEIR EFFECT ON FRONT VELOCITY**

### **4.1. Introduction**

Thermal frontal polymerization (TFP) is a process that couples thermal transport with the Arrhenius dependent kinetics of an exothermic reaction.<sup>85</sup> As heat is produced by the exothermic reaction it diffuses into the system around it and initiates further polymerization. This creates a reaction zone that propagates through an unstirred system.

Most studies of TFP have dealt with the polymerizations being in homogenous mixtures. However, some experiments have been done to investigate the effect of a continuous conductive element that runs through the length of the entire polymerization system.<sup>86</sup> Choosing an element that efficiently conducts heat could help utilize excess heat produced by the reaction to create faster moving fronts. Normally excess heat produced slowly diffuses into the walls of the reaction vessel, or in this case the mold and the environment. If the conductive element directs excess heat forward the unreacted portion will increase in temperature. It has been shown that FP can increase in reactivity if the initial temperature or the reactants is raised.<sup>87</sup> Copper sheets will be used as the conductive element. The effect of the thickness of the sheets will be tested as well as the spacing between multiple sheets.

### **4.2. Materials**

All materials were used as received with no further processing or purification. The monomer used in these experiments is trimethylolpropane triacrylate (TMPTA) that was purchased from Allnex (Alpharetta, GA, USA). The initiator used was 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane, referred to as Luperox ® 231, that was purchased from Arkema

(Pasadena, TX, USA). The two filler materials used in these experiments were Polygloss 90® and Aerosil 200 purchased from KaMin LLC (Macon, GA) and Aerosil® (Mobile, AL, USA) respectively. Aerosil 200 is a fumed silica with a BET surface area of  $200 \pm 25$  (m<sup>2</sup>/g).

#### **4.3. Preparation of Clay**

To prepare the polymer clays all materials were weighed and mixed together manually until a homogenous even material was obtained. The amounts used of each material has been reported in parts per hundred resin (phr). This is a common mix ratio denotation used in the resin industry with 1 phr being the equivalent of 1 part by weight additive or initiator per 100 parts by weight of resin. The resin in these experiments will always be TMPTA. After testing multiple formulations, the best performing filler loading was determined to be 65 phr kaolin and 5 phr fumed silica in a 1 phr TMPTA/Luperox ® 231 solution. This mixture was used for all experiments reported.

#### **4.4. Method for Copper Setup**

Copper was incorporated into these systems by taking solid copper sheets and cutting them down into strips. The copper sheets were then embedded into the clay slabs. There were multiple thicknesses of copper sheet tested. The length was held constant, but the height and thickness were both varied. There were also experiments done in which multiple copper sheets were embedded into a single system with various spacing tested.

#### **4.5. Method for Collecting Front Data**

For each experiment a constant amount of clay, 100 g, was shaped into a slab using a wooden mold with dimensions of 14 cm x 5 cm x 1 cm. If the experiment called for the use of copper sheeting a precut copper sheet was embedded into the molded clay parallel with the length of the slab. To initiate the polymerization, electric soldering irons were heated, and contact was made

between the hot soldering iron and one edge of the polymer clay. This application of heat caused the decomposition of the initiator and the propagation of a polymer front ensued. To track the velocity of the propagating front a camera was used to film the reaction with a cm scale in frame. Blue phosphorescent powder was dusted over the surface of the polymer clay to aid in tracking the front. This will be evident in photos of the experiments. The videos were then analyzed by tracking front position as a function of time to obtain a velocity in cm/min. Temperatures were recorded for some experiments to compare front temperatures of systems with and without copper. For this a type-K thermocouple embedded in the middle of the clay channel was used in conjunction with LogerLite software and a laptop. As the propagating front passed the thermocouple, a steep increase in heat was registered with the maximum being the front temperature. All experiments were run in triplicate.

## **4.6. Results and Discussion**

### *4.6.1. Establishing baseline data for systems with no copper*

In order to first establish what the baseline front temperature and velocity were, the prepared clay was polymerized without copper. This run was initiated with an electrical soldering iron held on one spot at the end face of the clay slab. The polymer clay with no copper in the system propagated at a velocity of  $8.05 \pm 0.61$  cm/min with a front temperature of 231 °C. The free-radical frontal polymerization of TMPTA with the same initiator concentration, but with no filler, propagates at a velocity of approximately 10 cm/min.<sup>88</sup> When some fillers are added to a system, as the loading is increased the amount of heat absorbed by the filler increases, which reduces the front velocity.<sup>77</sup> For the remainder of the experiments the baseline velocity was established as  $8.05 \pm 0.61$  cm/min, and will be displayed as a reference with all other data.



#### *4.6.2. Velocity and Temperature for Systems with Single Copper Sheet*

To first probe the effects of copper on the propagation of a front a single 0.5 mm thick copper sheet cut to 14 cm x 1 cm was used. The clay was molded into a slab, and then the copper sheet was embedded into the middle of the clay slab parallel to the length of the mold. Upon initiation of the front it was immediately evident that the front was propagating faster along the copper strip where there was direct contact with the clay. Once the front reaches a steady state, the front levels off at a constant angle away from the copper and propagates in a spearhead like fashion. Image 3 shows this phenomenon. The velocity of the front at the polymer copper interface was  $14.2 \pm 0.55$  cm/min which is approximately a two-fold increase in the velocity. There was little change in the front temperature as heat was being transported more efficiently, not being created. For the purposes of this study the focus was on the velocity of the fronts, but the front temperature was recorded for these first two systems for comparison. The front temperature for the system without copper was 231 °C, and the system with copper was 234 °C. Figure 17 shows the plot of temperature vs time for the two systems; there is little difference in the temperature profiles. This supports the hypothesis that heat is being conducted by the copper and that the effect observed is not a result of increased reactivity.

To further investigate the effect of a single copper sheet in these systems the thickness of the copper sheet was increased. The thicknesses tested were 0.5, 1.0, 1.5, and 3.0 mm. The same general front shape and behavior was observed with velocities decreasing as the thickness increased, this is shown in Image 4. This was most likely due to the increased mass of copper absorbing heat as the thickness increased drawing heat away from the polymerizing system. This also translated to slower front velocities as the thickness of the copper was increased. The 3.0

mm copper sheet absorbed so much heat that the front did not reach a steady state within the 14 cm, thus in Image 1 d), the front still has a flat shape.

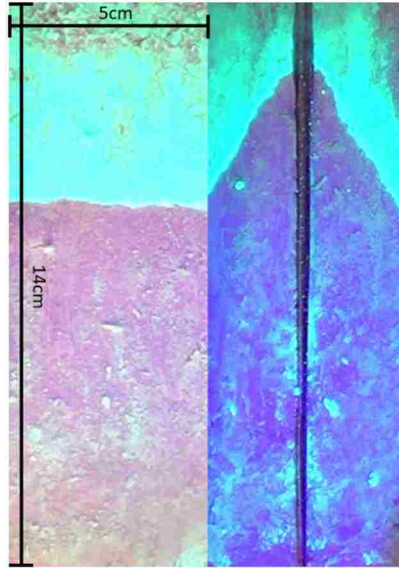


Image 3. Image showing comparison of the front propagation of acrylic composites with and without conductive element

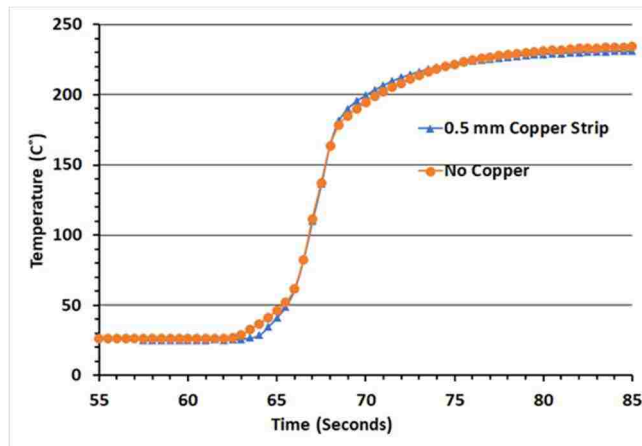


Figure 17. Temperature profile showing frontal polymerization of acrylic composites with and without copper

Figure 18 shows that the addition of a single 0.5 mm copper sheet almost doubles the velocity, but that as the thickness, thus mass, is increased the velocity of the propagating front decreases to almost the same velocity as a front in an acrylate system with no copper.

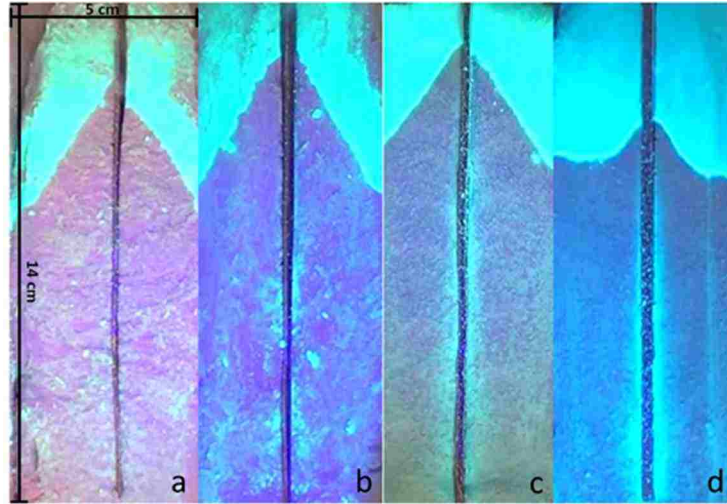


Image 4. Polymerization of acrylate composite with single copper sheet of thicknesses a) 0.5 mm b) 1.0 mm c) 1.5 mm and d) 3.0 mm

#### 4.6.3. Velocity and Temperature for Systems with Two Copper Sheets.

Another system tested was one with two lanes, or strips, of copper. For these experiments the thickness of the copper was held constant at 0.5 mm, with the variable being the space of the gap between the copper strips. The gap widths tested were 0.5, 1.0, and 2.0 cm and produced velocities of  $13.57 \pm 0.45$ ,  $13.19 \pm 0.68$ , and  $12.68 \pm 0.36$  cm/min, respectively. Image 5 shows a snapshot of these systems side by side. It was hypothesized that the polymer in the gap between the copper sheets would polymerize faster than that outside the space, with the difference in velocity becoming less significant as the space increased. However, this was not observed in the experimental data. The front in the middle channel propagated much like a front with no conductive element would. It was concave with the material adjacent to the copper propagating faster.

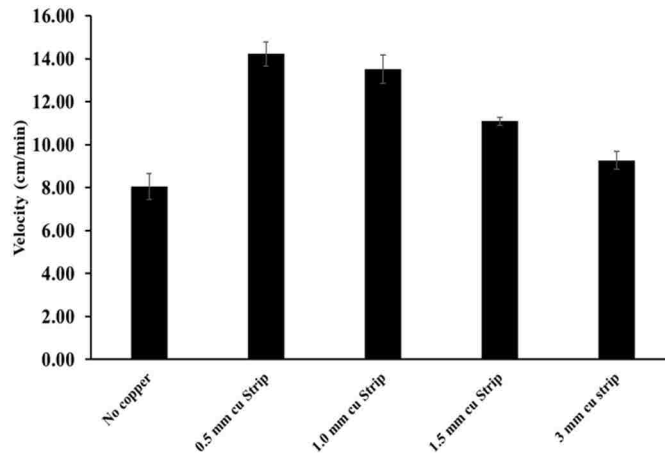


Figure 18. Front velocity for composites with single copper sheets of increasing thickness.

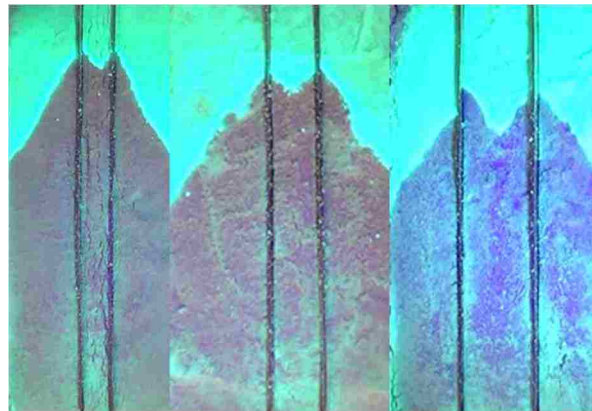


Image 5. Two sheets of copper placed 0.5, 1.0, and 2.0 cm apart

#### 4.7. Conclusions

We were able to investigate the effect of a continuous conductive element embedded in an acrylate composite containing Luperox<sup>®</sup> 231, TMPTA, and kaolin clay. Copper strips of varying thicknesses were tested, as well as two copper strips of constant thickness with varying gap width between the two strips. It was shown that the high thermal conductivity of the copper increased heat transport and caused the propagating polymer front to travel faster along its

length. As the walls of the mold absorb heat the front propagated at an angle with the polymer closest to the copper propagating fastest. The copper transfers the excess heat produced by the front forward to the unreacted monomer instead of having it diffuse to the environment. The experiments showed that a system containing two parallel strips of copper produced similar results with the polymer between the two strips propagating as a more even front than the polymer on the outside. This effect was less noticeable as the gap between the two strips increased.

## CHAPTER 5. SUMMARY AND CONCLUSION

Thermal frontal polymerization utilizes the production and transport of heat produced during the exothermic reaction of a free-radical polymerization. The velocity of the propagating front is directly related to temperature of the propagating front. We have demonstrated different ways to influence the propagation of this front through chemical and physical means. We first demonstrated how the functionality of the monomer used can influence the velocity and temperature. It was shown that as the concentration of double bonds in a system increased the velocity and temperature of the propagating front increased as well. After controlling the concentration of double bonds in multiple different multifunctional monomers by use solvent, we found that increased crosslinking was the main influence on the polymerization due to decreased termination leading to autoacceleration. Residual water in unpurified monomers lowered the velocity and temperature of the front by absorbing heat through vaporization. Secondary functional groups present in some monomers acted as chain transfer agents and also slowed the propagating front.

Another way to influence a propagating front is through the use of fillers. Specific fillers were chosen to not only give proper consistency to the material in order to collect good data, but thermally conductive fillers were chosen in order to increase the velocity of the propagating front. We showed that some fillers will slow a front by absorbing heat and causing the temperature of the front to lower, thus causing the velocity to lower. By selecting fillers that have higher thermal conductivity, such as boron nitride, heat is more easily able to diffuse through the system, and thus increase the velocity of the propagating front. Some of the fillers, such as graphite and alumina, showed inhibitory effect This was most likely due to interaction with the radicals in the system and the surface of the additive.

Finally, it was shown that a continuous conductive element can increase and direct the propagation of a front. Copper sheets embedded into a multifunctional acrylate composite showed that they could effectively direct heat produced by the polymerization, and allow the front to propagate faster along the length of the conductive element. The thickness of the copper strip was also varied and showed that at a certain thickness the copper absorbs more heat and has less influence of the velocity of the front.

Overall, we have shown that thermal fronts can be influenced, and made to propagate at higher velocities, in multiple ways. Chemically, the monomer chosen can influence the propagating front via its molecular weight relative the number of reactive groups and its ability to undergo crosslinking. This can allow for use of less initiator which cuts down on the amount of fume and smoke produced. Physically a front can be influenced by using different fillers which may cause an increase or decrease in the conduction of heat. Using fillers with high thermal conductivity can effectively increase the front temperature and thus the velocity. This could allow for front to be run in systems with high surface area relative to volume in applications such as coatings. A continuous conductive element can be used to help transport and direct heat as well. These techniques can be used to help increase the cure time of these materials which could make bulk curing less energy costly.

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## **VITA**

Samuel Morris Bynum, born and raised in Gulf Breeze, Florida, received his bachelor's degree in Biochemistry from the University of West Florida. He began work in the lab of Dr. John Pojman in 2015, focusing on frontal polymerization. During his tenure at LSU Samuel served one term as president of the chemistry graduate student council and participated as a mentor with the upward bounds program during the summers. He also mentored a number of undergraduate students conducting independent research. In the summer of 2017 Samuel participated in the NSF's iCorps program through LSU. Samuel is interested in pursuing a career in science policy.