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Cure-on demand wood adhesives using frontal polymerization of acrylates

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CURE-ON DEMAND WOOD
ADHESIVES USING FRONTAL
POLYMERIZATION OF ACRYLATES

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ABSTRACT

Frontal polymerization (FP) is when the monomer is polymerized by a zone of reaction propagating through the monomer. The reaction zone is fueled by the heat given off by the polymerization of the monomer. FP is a promisig method for curing adhesives because it allows for cure-on-demand and fast cure times. The monomers selected for the adhesive is the main factor in determining the adhesive's properties. Trimethylolpropane triacrylate (TMPTA), pentaerythritol tetraacrylate (PETA), and other multifunctional monomers make the polymer formed more brittle. The brittleness can be reduced by using trimethylolpropane ethoxylate triacrylates (TMPEOTA) in the place of the other multifunctional acrylates. The ethoxylation makes for a more elastic polymer, but it also reduces the reactivity. Acrylic acid (AA) is highly reactive and can be coupled with less reactive monomers, like the TMPEOTAs, to make them polymerize. Fillers can also impact the mechanical properties of the polymers. Kaolin clay and alumina trihydrate make the polymer stronger, whereas styrene-ethylene/butylene-styrene (SEBS) and styrene-butadiene-styrene (SBS) can make the polymer more elastic. The strength of the adhesive was tested by using it to bind two piece of wood and then using ASTMD 143 Hardness and Compression Method testing with an Instron.

INTRODUCTION

The purpose of this research was to make an acrylate-based wood adhesive with high shear strength using free-radical frontal polymerization. A secondary purpose was to give the adhesive a degree of water resistance and flexibility. In order to do this, the polymer needed a high elastic modulus. As we will see, all of the goals were-met by changing the types and ratios of the monomers used, changing the types and ratios of the fillers used, and by changing the concentration of the initiator.

Frontal Polymerization Overview

Frontal polymerization (FP) is a localized reaction zone that propagates through the reactants. As the front moves through the mixture, everything that is behind the front is polymer and filler while everything ahead of it is unreacted monomer (Pojman, 1991). The three types of FP are frontal photopolymerization, isothermal frontal polymerization and thermal frontal polymerization. Frontal photopolymerization (FPP) requires a photoinitiator. Ideally FPP requires a sample that has a high absorbance, an initiator that photobleaches, and no convection. When the photo-initiator is exposed to UV light, it decomposes and forms free radicals that initiate the reaction. The decomposed initiator undergoes photoinduced bleaching that allows UV light to penetrate deeper into the sample (Decker 1998). This enables more of the sample to be polymerized.

In isothermal frontal polymerization (IFP), a polymer seed is introduced to a solution containing the monomer and initiator. The polymer seed is a small amount of the resulting polymer that will be formed and must be soluble in the monomer (Lewis 2005). The temperature is held constant throughout the polymerization. The polymer seed being able to be dissolved in

the monomer leads to parts of the solution being more viscous than others. When the

polymerization starts, the Norrish-Trommsdorff effect (gel effect) causes the more viscous

regions to have a higher rate of polymerization (Lewis 2005). The gel effect is a reduction in the

rate of termination caused by high viscosity, which hinders the reactive end groups' ability to

undergo termination by keeping them away from one another (Odian 2005). As the

polymerization continues the monomer dissolves the polymer that is formed, which keeps a

viscous region in the solution. The last type is thermal frontal polymerization (TFP). In TFP the

heat generated by the polymerization is the energy required to continue polymerization (Caria

2009).

Thermal Frontal Polymerization

Thermal frontal polymerization was first observed in Russia by Chechilo and

Enikolopyan (Chechilo 1972). Many different types of polymerization can make use of FP such

as free-radical polymerization (Chechilo 1972, Pojman 1991and Pojman 2004), anionic

polymerization (Begishev 1985), ring-opening metathesis polymerization (Mariani 2001), and

atom transfer radical polymerization (Bidoli 2003). Free-radical FP is the one most commonly

studied (Pojman, et al, 2010).

Free-radical polymerization is polymerization that uses radicals to grow polymer chains.

This is a type of chain growth polymerization. There are three steps involved in a chain growth

polymerization: initiation, propagation, and termination. Initiation involves using an initiator to

generate a radical that attaches to the monomer and creates a monomer radical. Propagation is

the process of continuing to grow the polymer chain by having the radical on the chain react with

more monomers. Termination occurs when two radicals meet and form a stable bond.

In TFP the initiator used is a thermal initiator. An external energy source or heat from other reaction for example, is used to decompose the initiator to form radicals. If UV light is used as the energy source then a photoinitiator is required as well. The decomposition of the initiator is a significant step in determining the rate of polymerization, and its high activation energy allows for a front (Pojman 1996)(Pojman, Ilyashenko et al. 1996). The initiator's radical then reacts with the monomer, and the chain grows as more monomer units are incorporated. The reactivity of the initiator is determined by how fast the initiator decomposes (Pojman 1996, Odian 2004 and Hiemenz 2007). More unstable initiators decompose faster. By increasing the initiator concentration, the reaction's front temperature also increases (Hu 2006). Peroxides are a good choice of initiators for TFP because their decomposition is exothermic. However, a problem with the use of peroxides is that they give off gaseous side products. These gases can give the polymers formed by TFP a porous morphology. The gaseous side products can be reduced by using persulfates (Masere 2000) or ionic liquids like tricaprylmethylammonium (Aliquat) persulfate (APSO) (Mariani 2008) in the place of the peroxide. The APSO is the product of a reaction between tricaprylmethylammonium chloride and ammonium persulfate. The ammonium persulfate does not produce any volatile gases when it decomposes (Masere 2000 and Mariani 2008). It does produce inorganic salts that are insoluble with organic materials (Mariani 2008). The salts can be made soluble my modifying the ammonium group like in the case of APSO (Mariani 2008).

The front velocity is how fast the front propagates through the monomer and can be affected in many ways. The stability of the initiator affects the front velocity. The more stable the initiator the lower the front velocity, and the more unstable the initiator the higher is the front

velocity (Pojman 1995). An increase in initiator concentration also leads to an increase in the front velocity (Pojman 1995 and Hu 2006).

Front temperature is the temperature the front has while it propagates through the monomer. The front temperature must stay above the temperature require for the monomers to reacts or a front will not be supported (Pojman 1996). The conversion of monomer to polymer is proportional to change in the temperature (Pojman 1996). The higher the front temperature the faster the initiator will decompose. If the front temperature is too high, the initiator will be fully decomposed before the reaction has finished in a process called initiator burn out (Pojman 1996). The initiator burn out can lead to decreases in monomer-to-polymer conversion and front velocity. The use of fillers and more stable initiator are used to prevent the problem (Viner 2010).

The more reactive the monomer the higher the front velocity will be. The reactivity of the monomer is determined by steric factors, how easily the initiator radical can add to the monomer, and by the stability of the monomer radical. Inductive effect from functional groups can also stabilize monomers such as the methyl group on methyacrylates. The less sterically hindered the ene group is on a monomer the more reactive the monomer, so methacrylates are less reactive than acrylates because the methacrylates will form a more stable tertiary radicals. These are the reason why acrylates are more reactive than methacrylates. The more ene groups present in the monomer the faster the front velocity. This increase in the front velocity comes from the cross-linking that multifunctional monomers achieve. The cross-linked networks allow the gel effect to take place (Pojman 1995). The gel effect, or Trommsdorff effect, is decrease in the rate of termination of a polymerization due to an increase in the viscosity (Hiemenz 2007 and Odian 2004)

1.) Initiation

$$I \longrightarrow I*$$

2.) Propagation

$$I* + M \xrightarrow{\ M\ } IMM* = P*$$

3.) Termination

$$P_i* + P_j* \longrightarrow P_{i+j}$$
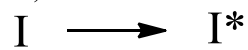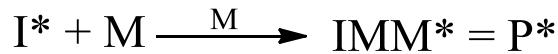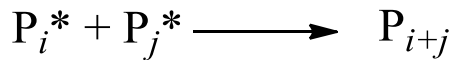
Figure 1 (Hiemenz 2007)

Monomer Properties

The purpose of this investigation is to create an adhesive that allows for cure-on demand that has a high strength. Trimethylolpropane triacrylate (TMPTA) was the monomer chosen as the basis of the adhesive for its low toxicity and ability to form a strong bond when polymerized. TMPTA highly crosslinks when it polymerizes, which gives the polymer a high glass transition T_g. When a material is below its T_g it is a glassy solid. The high T_g corresponds to a more rigid polymer. The cross-linking contributes to the high strength of the polymer. Trimethylolpropane ethoxylate triacrylates (TMPEOTA) were also used because they add flexibility to the polymer. The more ethoxylated the TMPEOTA the more flexible the resulting polymer becomes. The disadvantage of the TMPEOTAs is that the more ethoxylated the monomer becomes, it also becomes less reactive because the more flexible chains lead to an increased rate of termination. This is caused by the longer more flexible chains are able to move around more in the mixture and find other free-radicals to terminate. The higher the Mw per ene also means that the heat release density is lower. This problem can be addressed by coupling the monomer with one that is more reactive, like acrylic acid (AA) (Pojman 2004).

TMPTA and TMPEOTA form what are known as thermosets. Thermosets are polymers that remain in their solid form after being polymerized. Thermosets are cross-linked polymers that are stable at high temperatures (Odian 2004). The cross-linking in the thermosets is referred to as chemical crosslinking because the cross-linking is made through chemical bonds (Odian 2004). The cross-linking gives them a rigid network that gives the polymer its mechanical properties. Polymers whose viscosity deceases when heated are known as thermoplastics. All thermoplastics are not cross-linked except for thermoplastic elastomers. The cross-linking that takes place in the thermoplastic elastomers is physical cross-linking (Odian 2004). Block copolymers are thermoplastic elastomers. Physical cross-linking involves the aggregation of copolymers (Odian 2004). The process does not involve the formation of chemical bonds so at higher temperatures the copolymers can soften (Odian 2004). An example of a thermoplastic polymer would be poly(styrene ethylene-butylene styrene) elastomer(SEBS). Using SEBS as an additive for a polymer would make it tougher. Toughness refers to how strong of an impact a material can take without fracturing.

Thiols were also chosen for this study because of the ability to make use of thiol-ene chemistry. Acrylates contain ene groups, and the thiol chosen was trimethylolpropane tris(3-mercaptopropionate) (TT1) because is structurally similar to TMPTA. Thiol-ene chemistry involves making polymers by free-radical step-growth polymerization (Cramer 2003, Cramer 2003, and Pojman 2004). This chemistry is advantageous for TFP because it follows a different mechanism and does not need heat to start the reaction (Rissing 2008). This allows the thiol-acrylate reaction to act as a fail-safe reaction because it is not always possible to tell visually if the front went through the entire mixture. The disadvantage to this approach is that the pot life is short since the thiol is believed to react with the peroxide initiator (Antonucci 1983, Giovando

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1994, and Viner paper to be published). Multifunctional thiols at as accelerators in the decomposition of organic initiators like peroxide (Antonucci 1983 and Giovando 1994)

Acrylic acid (AA) was chosen to copolymerize with the less reactive ethoxylated triacrylates. Tredici et al. showed that AA increase the front velocity when used with methacrylic acid (Tredici 1998 and Pojman 2004). AA has a high rate of polymerization for photopolymerization with a rate of 28 ± 1 % conversion/s for a light intensity of 18.7 mW/cm^2 and using 2.0 wt % of the photoinitiator Darocur 1173 (Jiménez 2007). That was more the more than seven times higher than the next closest monomer, (2-acrylate) ethyl dimethylammonium isobutyrate at 3.6 ± 0.1 % conversion/s, and butyl acrylate had a rate of 2.4 ± 0.1 % conversion/s This would enable the polymer to take more of the elastic properties from the ethoxylated acrylates because AA is monofunctional it does not cross link so the resulting polymer with not be as brittle as a polymer using TMPTA as the copolymer. The problem that may arise with using AA as a copolymer is that since it is a monoacrylate the structure may not be as strong as using a triacrylate such as TMPTA.

Fillers

Fillers can also be added to the polymers to enhance their mechanical properties. A filler is anything other than the monomer or initiator that is added to the mixture. They can be added to enhance the mechanical properties or to lower the cost of the polymer (Rothon 2001). They can also be used to increase the viscosity of the monomer mixture (Nowak 2010). The viscosity is important for the acrylate adhesives. If the mixture is not viscous enough, it flows too readily and will be hard to apply to a material's surface. When the monomer polymerizes, it expands through thermal expansion as the polymer forms and pushes the monomer ahead of the front.

This causes the less viscous mixtures to spread and increase the surface area and rate of heat loss to the surroundings, which can extinguish the front.

Another way the front can lose heat is through buoyancy-driven convection (Bowden 1997). Heat loss due to buoyancy-driven convection occurs when the convection formed during the polymerization of monomers draws the colder monomer into the reaction zone (Bowden 1997). Fumed silica can be used to reduce convection (Pojman 2010).

Fumed silica is used to thicken the mixture. It takes a small percentage, around 5-6 %, to increase the viscosity of the mixture from "soupy" to a gel. This takes place because of the silica's ability to form a network via hydrogen bonding when it is exposed to a liquid (Nowak 2010). The network can be broken, and the mixture will lose its viscosity if agitated. The property is known as thixotropy. Thixotropy is the ability of a substance to be viscous when it is left static, but while it is sheared the viscosity decreases (Nowak 2010, Blair 2004). Thixotropy differs slightly from shear thinning because with shear thinning the viscosity decreases with increasing shear rate while a thixotropic system decreases in viscosity with a constant shear rate (Blair 2004).

Adhesive Characteristics and Mechanical Properties

An interesting feature of FP is the speed of the reaction. Frontally polymerizing a 4 x 4 cm area can be done in a few seconds depending on the composition. This feature has led to FP being used as alternative method of producing some polymers. FP is being used to make some hydrogels instead of free-radical batch polymerization because it is faster and require less energy (Feng 2010). Hydrogels are used in drug delivery which gives FP a medical application (Gavini 2009 and Feng 2010). FP can be used to make thermochromic composites. FP is a better choice

than the previous batch polymerization because batch polymerization is slow and the mixture may separate before the composite is formed (Nagy 1995).

Another area where FP's speed gives an advantage is in adhesives. Adhesives are substances that are applied to join two or more objects together (Petrie, 2007). The idea of using adhesives to join materials in the place of nuts and bolts has gained popularity because adhesives reduce the weight, improve the stress distribution, and are more visually pleasing due to no visible sign of bonding (Pizzi, 2003). Curing is the process of the adhesives "drying." This occurs by having the adhesive's solvent evaporate and bind whatever is connected to the adhesive or by having the adhesive react chemically with the object that it contacts, with the adhesive itself, or both. By using FP as the method of curing an adhesive, it allows for quick curing once the heat source is applied. This gives adhesives using FP as the method of curing an advantage over most of the other types. The advantages are that it does not take overnight to cure, and it only cures when heat is applied. Because curing only happens after heat is applied, time can be taken to position objects carefully. Having this cure-on demand property would be advantageous for an adhesive.

For an adhesive to be useful, it must strongly adhere to surface of the adherents, the objects that are being bound. There are many different parameters that determine the strength of the material. Toughness refers to the amount of energy an object can absorb before it fails. Stress is the amount of force applied over the area of the material. This is expressed by the equation where σ is stress, F is the force, and A is the area on which the force is acting.

$$\sigma = \frac{F}{A}$$

(Equation 1)

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Another parameter used determines the strength of a material is its shear strength. Shear strength refers to the amount of force required to shear two objects apart. This is done by applying force parallel to the object. The strain is another quantity that is used to determine the strength of a material. Strain is the measure of how the material is deforming. The equation for strain ε is shown below with change in length ΔL over length L.

$$\gamma = \frac{\Delta L}{L}$$

(Equation 2)

By combining equation 1 and 2, it gives the equation for the shear modulus G.

$$G = \frac{\sigma}{\gamma}$$

(Equation 3)

The shear modulus gives the elasticity of the polymer.

The Instron machine tests the mechanical properties of material. The ASTM D143 hardness and compression method was the program used to test the samples. The test starts with placing the sample material in a metal apparatus that allows force to be applied on one side of the adhesive bond, and then applies a shearing force to break the material. The shear stress is given as the total load along with the extension (or change in length). The strain and modulus can be solved by using the equations above. The Instron used is pictured below.

Figure 2 The Instron with the ASTM D143 attachment with a sample loaded.
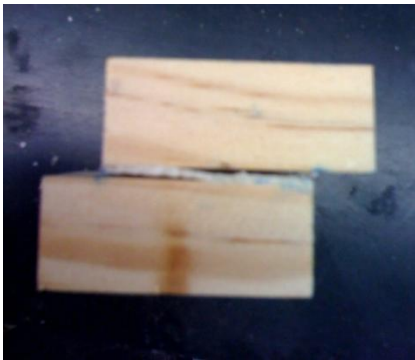
Figure 3 A sample that has undergone Instron testing.
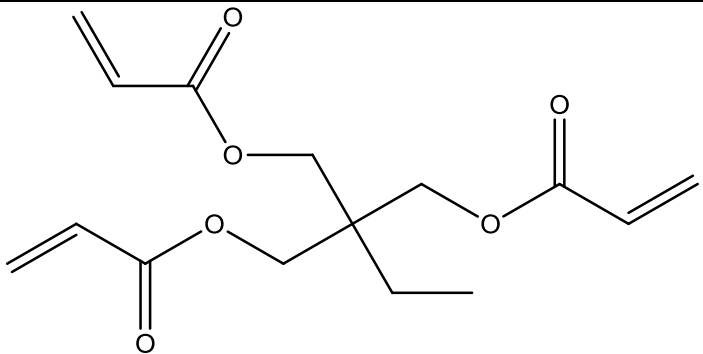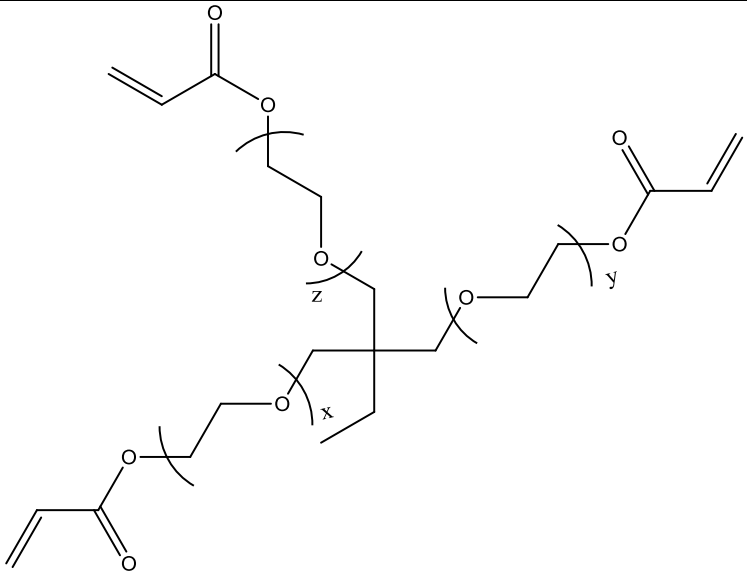
Many different factors play a role in determining how strongly the adhesive adheres to the adherent. In the case of the acrylate adhesive and wood, the wood's surface is a factor. The denser the wood the harder it is for an adhesive to bind. The growth period of the wood determines its density. The earlywood, which grows during the spring months, has a lighter color and is low density (Keating 1982). Latewood grows during the summer months and has a darker color and a higher density (Keating 1982). Adhesives bind easier to earlywood because it
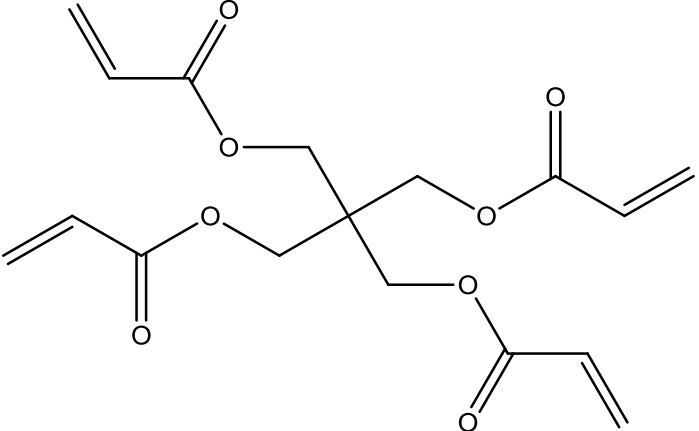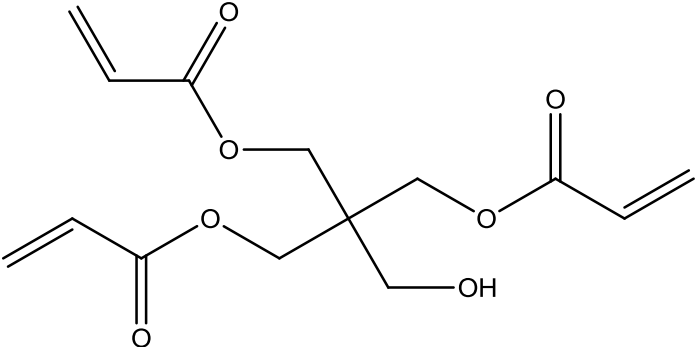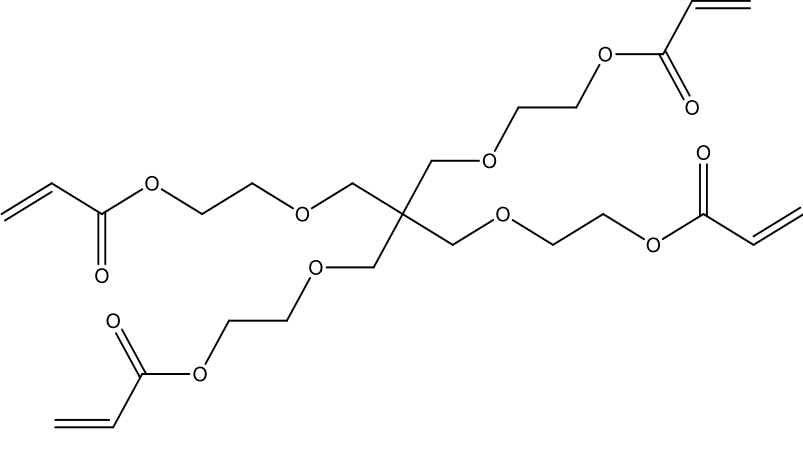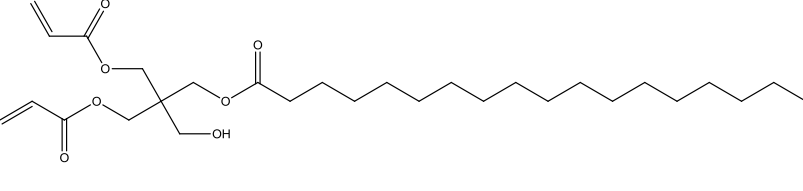
can be absorbed into the pores of the wood. Increasing the binding to the wood would be beneficial because that would lead to a cohesive failure. A cohesive failure occurs when the structure fails at the adhesive where the adhesive is coming apart (Petrie 2007). The opposite of that would be an adhesive failure. That type of failure occurs when the adhesive separates from the adherent. If the adhesive is stronger than the adherend, a different type of failure will occur (Petrie 2007). This type of failure happens when the adherend fails while leaving the adherent intact. It is referred to as a cohesive failure of the adherend (Petrie 2007). The last type would be the most beneficial for permanent repair because the material would fail before the adhesive.
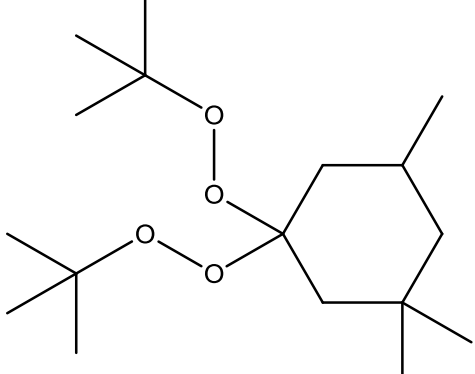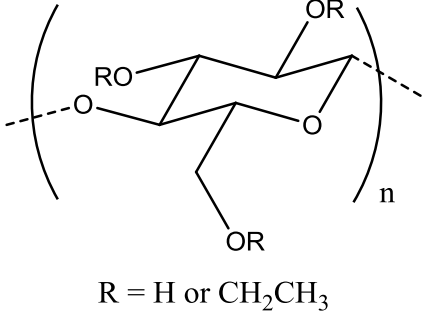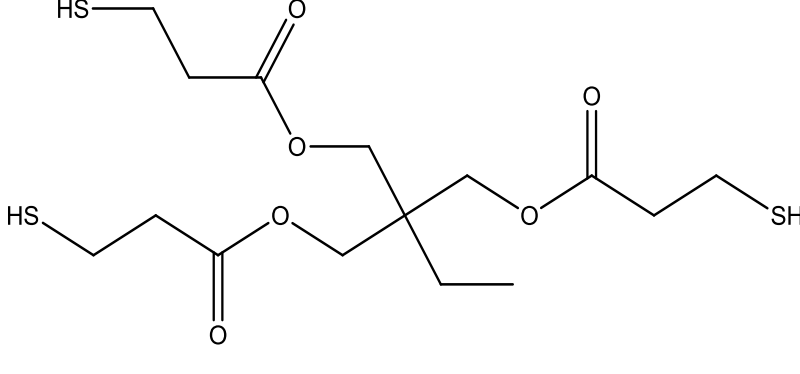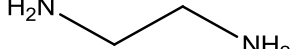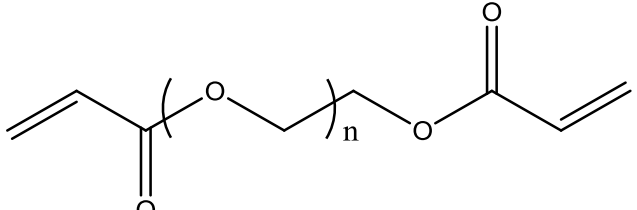
Another factor that impacts how effectively the adhesive binds to the wood using FP is the thermal conductivity. Thermal conductivity is the ability of material to conduct heat. This is important when binding wood because the thermal conductivity can vary greatly over a small distance on the wood. This happens because the lighter less dense parts of the wood have a lower thermal conductivity than the darker more dense regions (Forest Products Laboratory 1999 and Keating 1982). TFP relies on the transfer of heat for propagation. The darker regions of the wood remove heat faster, and as a result, it is harder to achieve adequate curing in those regions.

MATERIALS AND METHODS

Materials and Their Structures

Chemical name	Name used	Structure
Trimethylolpropane triacylate	TMPTA	
Trimethylolpropane ethoxylate (1/1 EO/OH) triacylate	1/1 TMPEOTA	The 1/1 means there is 1 ethoxylate group each at x, y, and z. Mn = 428
Trimethylolpropane ethoxylate (7/3 EO/OH) triacylate	7/3 TMPEOTA	Refer to trimethylolpropane ethoxylate (1/1 EO/OH) triacylate The 7/3 means there are 7 ethoxylate groups between the x, y, and z positions. Mn = 604
Trimethylolpropane ethoxylate (14/3 EO/OH) triacylate	14/3 TMPEOTA	Refer to trimethylolpropane ethoxylate (1/1 EO/OH) triacylate The 14/3 means there are 14 ethoxylate groups between the x, y, and z positions. Mn = 912

Pentaerythritol tetraacrylate	PETA	
Pentaerythritol triacrylate	PETriA	
pentaerythritol alkoxylated tetraacylate	PEAOTA	
Pentaerythritol diacrylate monostearate	PEDAS	

1,1-Bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane	Luperox® 231	
Ethyl cellulose	EC	 $R = H$ or CH_2CH_3
Trimethylolpropane tris(3-mercaptopropionate)	TT1	
Urethane acrylate oligomer	UA	The structure information was propriety.
Urethane acrylate; acrylic ester	UA-AE	The structure information was propriety.
ethylenediamine	EDA	
poly(ethylene glycol) diacrylate	PEGDA	

poly(ethylene glycol) dimethacrylate	PEGDMA	
Acrylic acid	AA	
Bispheonl A ethoxylate (1.5 EO/phenol) dimethacrylate	BPAEODA	

The TMPTA, 14/3 TMPEOTA, 7/3 TMPEOTA, PEGDA, PEGDMA, EDA, TT1, EC, Luperox 23, PETriA, PETA, and 1 mm borosilicate solid-glass beads were obtained through Sigma-Aldrich. The 1/1 TMPEOTA was provided by both Sigma-Aldrich and Sartomer. The Toluene, ethanol, hexane, and AA were supplied by Fisher-Scientific. The UA and UA-AE was provided by Sartomer. The styrene-butadiene-styrene (SBS) and styrene-ethylene/butylene-styrene (SEBS) were provided by Kraton. The BYK-070 organic deformer was acquired from BYK USA Incorporated. Expancel 461was provided by Expancel Incorporated. Polygloss® 90 was obtained from KaMin and Huber. The Aerosil 200 (fumed silica) was supplied by Fiberglass & Composite Materials. The talc, alumina trihydrate (ATH), and milled fibers were provided by US Composites. The three coathylenes (TB 3580, HX 1681, and HA 1681) were supplied by Clariant.

Methods

The samples consisted of monomer, filler and initiator. The total mass of the monomer was always 10 g per sample. The concentrations of the other components were calculated in

parts per hundred resin (phr). The adhesive was applied on the face of two wooden (pine) blocks that were marked off so each block had an area that is 3.8 cm X 3.8 cm. One gram of the monomer mixture was applied to each block. A few glass beads were placed on one side. The two blocks were then pressed together so that the adhesive sample overlapped. A soldering iron or heat gun was used to initiate the front. Once the reaction finished, the sample was taken to the Instron to test the mechanical properties. The ASTM D143 hardness and compression method was used to measure the shear strength and elongation. The rate of compression was set at 0.60 cm/min.

Fillers like SEBS, SBS, and ethyl cellulose needed to have their particle size reduced. This was initially accomplished by grinding them through the use of a mortar and pestal or by using a blender or food processor. Those methods still left filler sizes that were too large to be dispersed in the monomer mixture. Solvent dispersion was used to make the filler small enough to be dispersed in the monomer mixture. The first step was to dissolve the filler in a solvent. Toluene was the solvent used to dissolve SEBS and SBS, and ethanol was the solvent used to dissolve ethyl cellulose. The solution remained covered to prevent evaporation of the solvent. Next, the monomers were added to the solution except AA because it would evaporate. A stir bar was placed in the mixture. The mixture was left uncovered as it was stirred to allow the solvent to evaporate. This step would take at least 6 hours. If AA was used it would be added along with the other fillers and the initiator after the solvent evaporated.

Surface modification was attempted to increase the binding of the polymer to the wood surface. An attempt at esterification was used to change the change the wood's surface. A 5:1 volume mixture of 18 M sulfuric acid to acrylic acid was applied to the area of the wood where the adhesive is applied. The sulfuric acid/AA mixture gave the wood a green color. A Chicago

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Electric® Power Tools heat gun was used to start the esterification. The heat source was passed

back and forth in a sweeping motion. An Omega® OS423-LS non-contact infrared thermometer

was used to determine the temperature of the heat gun. The low setting produce a temperature of

~150 - 160°C, and the high setting produced temperatures greater than 200°C. The color would

change from green to black after heated. The adhesive was applied after the heating was

complete.
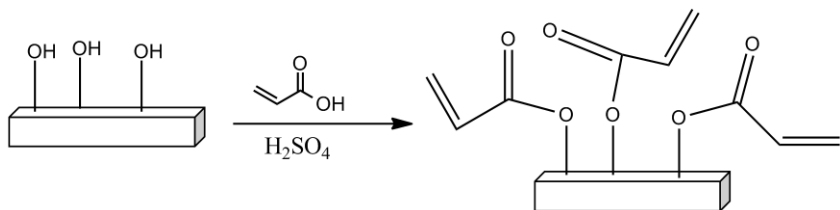
Figure 4 An illustration showing how the bonding the acrylic acid to the wood surface was attempted.

RESULTS AND DISCUSSION

TMPTA and TMPTA Combinations Results

Trimethylolpropane triacrylate /poly(ethylene glycol) dimethacrylate (TMPTA/PEGDMA) was the first combination tried. The TMPTA, which was more reactive than PEGDMA, was coupled with the PEGDMA to increase the reactivity while keeping some of the flexibility from the PEGDMA. The first TMPTA/PEGDMA combination was 5 g/5 g ratio with 40 phr of kaolin using 12 phr Luperox. The mixture did not sustain a front. It would only react where the soldering iron was in contact. The ratio was then changed to 7.5 g TMPTA/2.5g PEGDMA. The 7.5 g/2.5 g mixture had 40 phr of kaolin for the filler, and the concentration of Luperox for each sample was 7, 8, 9, 10 phr. The 10 phr Luperox mixture had shear strength of 0.69 ± 0.6 MPa (100 psi). The 9 phr Luperox mixture had shear strength of 1.1 ± 0.2 MPa (159 psi). The 7 and 8 phr Luperox concentrations samples did not always completely react. The reason for this is that heat lost to the 40 phr of kaolin was occurring faster than the heat generated by the reaction with 7 or 8 phr of Luperox. A ratio of 6.0 g TMPTA/4.0 g PEGDMA was tried using 40 phr of kaolin as the filler and 9 phr Luperox as the initiator. Three samples were tried using 40 phr of kaolin and 15 phr of Luperox with the monomer ratios for each run of 6.0 g/ 4.0 g, 7.0 g/3.0 g, and 5.0 g/5.0 g TMPTA/PEGDMA. All of these samples did not completely polymerize.

Poly(ethylene glycol) diacrylate (PEGDA) was tried next using 10 g PEDGA, 40 phr kaolin, and 10 phr Luperox. The sample did not react. The reason was that PEDGA was less reactive than TMPTA because it was a diacrylate. After that the PEDGA was combined with TMPTA to increase the sample's reactivity.

Table 1 Composition and Shear Strenght of Samples Using TMPTA and PEDGA as monomers

	TMPTA (g)	PEGDA (g)	Kaolin (phr)	fumed silica (phr)	Luperox (phr)	SS (MPa) ((psi))	STDEV (MPa)
TH 1.9.8	7.5	2.5	40	0	10	0.94 (136)	49
TH 1.9.9	7.5	2.5	0	6	10	0.77 (112)	31
TH 1.9.10	7.5	2.5	0	6	7	0.70 (102)	52

Since it was a diacrylate it should have been more reactive than the dimethacrylate PEGDMA because secondary radicals are more reactive than tertiary radicals. When the samples polymerized they had a plastic-like appearance. The first sample that was tried was a 50/50 TMPTA/PEGDA mixture with 30 phr kaolin and 10 phr Luperox. The adhesive, once reacted, did not bind well to the wood. The next sample consisted of 6 g TMPTA, 4 g PEDGA, 6 phr fumed silica, and 5 phr Luperox. It also did not sustain a front. The next sample was the 50/50 mixture of TMPTA and PEDGA with 6 phr fumed silica, and 5 phr Luperox. The front did not propagate completely through this mixture between two wood blocks. The last sample used 7 g TMPTA, 3 g PEDGA, 6 phr fumed silica, and 5 phr Luperox. The results did not different much from those of PEGDMA. The effect that the PEGDA or PEGDMA had on the adhesive was negligible when in the presence of that much TMPTA.

The next runs were done using trimethylolpropane triacrylate/pentaerythritol diacrylate monostearate (TMPTA/PEDAS) blends. The ratios used were 5.0 g/5.0 g and 7.5 g/ 2.5 g. Both of the combinations had 40 phr kaolin and 10 phr Luperox 231 added as the filler and initiator, respectively. Another 7.5 g TMPTA/2.5 g PEDAS mixture was made using 40 phr kaolin and 15 phr of Luperox 231. All of the mixtures that used PEDAS did not completely react. The PEDAS is very viscous, so it had to be heated to make it mix readily with the TMPTA. PEDAS

has a long carbon chain. That carbon chain acted like a diluent that absorbed heat and reduced

the front temperature.

Lauryl acrylate (dodecyl acrylate) was the next monomer to be mixed with the TMPTA.

All of the combinations used 40 phr of kaolin. The 50/50 ratio used l0 phr of Luperox, and there

was no reaction. Three 7.5g TMPTA/2.5 lauryl acrylate mixtures tested, and they used 10 phr, 8

phr, and 6 phr Luperox 231. The results are shown in Figure 5. Two mixtures of 6.0 g

TMPTA/4.0 g lauryl acrylate were made using 10 phr and 8 phr of Luperox 231, and both of

them produced no reaction. Lauryl acrylate, like PEDAS, has a large carbon chain. This could

act like filler in removing the heat from the reaction zone causing early termination of the FP.

The lauryl acrylate is monofunctional, which would also make the adhesive less reactive.
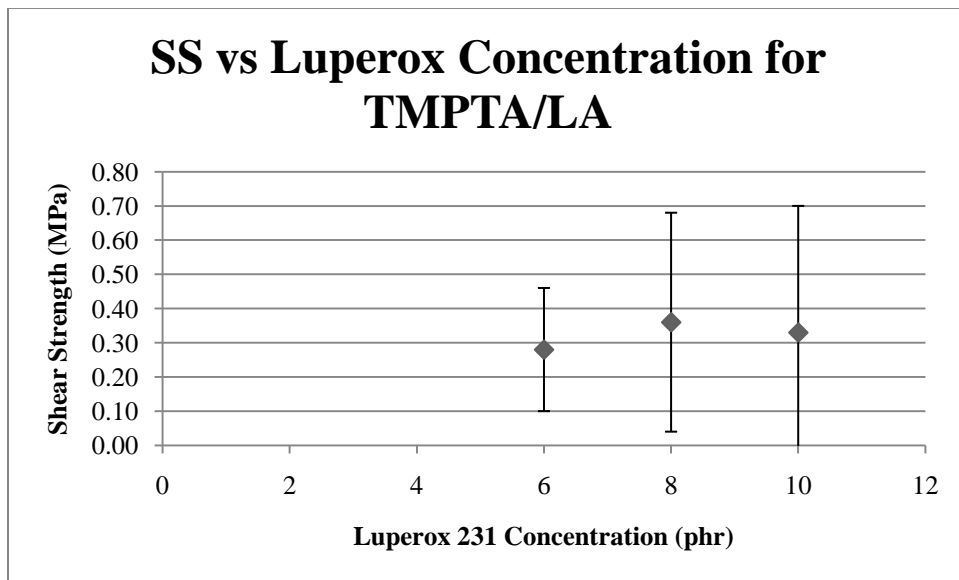
Figure 5 Shear Strength vs. Luperox 231concentration using 7.5 g TMPTA, 2.5 g LA, and 40
phr kaolin.

Four mixtures of 7.5 g TMPTA/2.5 g PEGDMA were used to test the properties of

Expancel on the bond. All the mixtures were 7.5 g TMPTA/ 2.5 g PEGDMA blends and

contained 40 phr of kaolin and 15 phr of Luperox 231. The Expancel concentrations used were

6.8 phr, 3.4 phr, 1.7 phr and 9 phr. None of them reacted all the way through, and the

polymerized material was powder-like and weak.

Adding ethoxylated triacrylates to the mixtures was the next experiment performed. The

first objective was to determine which type of ethoxylated triacrylate to TMPEOTA to use. This

was conducted by using 10 g of both 14/3 TMPEOTA and 7/3 TMPEOTA. It consisted of

mixtures by using both 4 phr fumed silica and 10 phr Luperox 231 for each. These reactions

were tested in open air and not between two blocks of wood. The 14/3 TMPEOTA mixture

would not support a front. The 7/3 TMPEOTA mixture showed reactivity, but it did not

propagate. The 7/3 TMPEOTA was selected to be coupled with the TMPTA. The first sample

was a 50/50 mixture of TMPTA and the 7/3 TMPEOTA along with 40 phr of kaolin and 10 phr

Luperox 231. That mixture did not react. The mixture composed of 40 phr kaolin had more

filler to absorb the heat which slowed down the polymerization, causing early termination of the

front. Fumed silica was used to replace kaolin since it can achieve the same viscosity as kaolin

but at lower concentrations, reducing the heat loss. The next sample was 50/50

TMPTA/TMPEOTA mixture with 6 phr fumed silica and 10 phr of Luperox. It had a shear

strength of 1.13 MPa (164 psi).   The next 50/50 mixture was 6 phr fumed silica and 8 phr

Luperox, and its shear strength was 0.67 MPa (97 psi).

The ratio was changed to 7.5 g of TMPTA/2.5 g of 7/3 TMPEOTA. The 75/25 ratio was

first used in a sample that consisted of 4 phr fumed silica with 10 phr Luperox. The results are

shown in Figure 6. The mixture had a very low viscosity. During the reaction, the mixture

would run down the sides of the wood, and after the reaction was complete, the adhesive bond

was very brittle and easily broken by hand. The polymer was easily removed by simply rubbing

a finger across it, which caused the polymer to crumble. Because of the runniness of the 4 phr

fumed silica mixture, the next set of samples contains 6 phr fumed silica so the adhesive would be a gel when it was applied. Although the adhesive no longer ran down the sides of the wood, the polymer formed was still brittle, soft and crumbled easily.

SS vs Luperox Concentration for 75/25 TMPTA/ (7/3) TMPEOTA
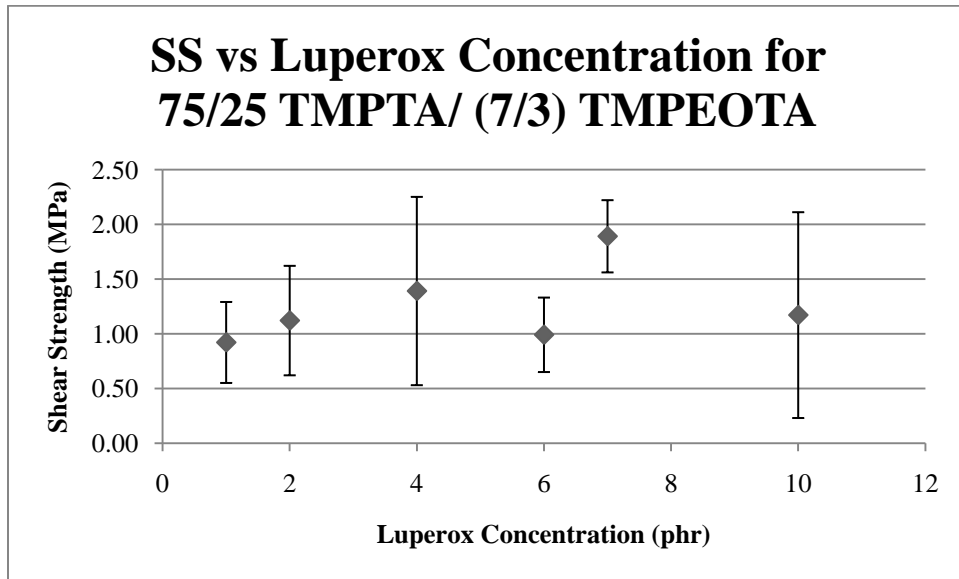
Figure 6 Shear Strength vs. Luperox 231 concentration for 7.5g TMPTA, 2.5 g TMPEOTA, 6 phr fumed silica monomer mixture with 6 phr fumed silica as the filler.

The TMPEOTA mixtures were visited again. The 7.5 g TMPTA and 2.5 g 7/3 TMPEOTA combinations was used with 6 phr fumed silica and 5 phr Luperox. It produced shear strength of 0.99 MPa (144 psi). Next a 2.5 g TMPTA and a 7.5g 7/3 TMPEOTA combination was used with 6 phr fumed silica and 10 phr Luperox. That mixture did not react because the 7/3 TMPEOTA is too unreactive for that monomer ratio to support a front. The 75/25 TMPTA/TMPEOTA mixture with 6 phr fumed silica and 4 phr Luperox was used to measure the effect of time delay on the strength of the adhesive. There were no conclusive results that showed a time delay had an effect on the shear strength. Different adhesive samples were tried with varying time delays. The results for the time delayed curing were not consistent, and no trend could be obtained.

Trimethylolpropane triacrylate/trimethylolpropane tris(3-mercaptopropionate) (TMPTA/TT1) mixtures were also tested. The first sample was made from a 50/50 TMPTA/TT1 combination with 4 phr fumed silica and 10 phr Luperox, but the mixture did not react. The formula was change to 7.5 g TMPTA, 2.5 g TT1 and 6 phr fumed silica.

The next adhesive was the TMPTA/TT1 combination with kaolin used instead of fumed silica. The results are shown in Figure 7. The mixture consisted of 75/25 TMPTA/TT1 monomer combination with 40 phr of kaolin and 10 phr Luperox. The adhesive did not react. (The TT1 could undergo a redox reaction with the Luperox as well as copolymerizing with the acrylate. (Viner paper to be published) It took mixtures that contained 10 phr Luperox 231 about 40 min to gel, or begin to harden. If the Luperox 231 concentration was reduced to 2 phr, gelation did not occurred overnight. . Instead of forming a rigid polymer, it formed a polymer that was like wax.
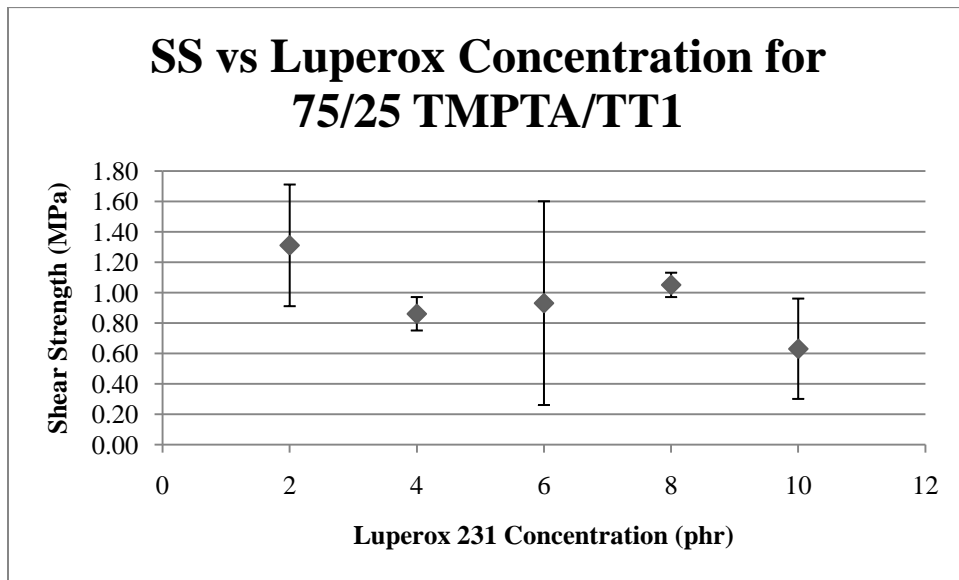
Figure 7 Shear strength vs. Luperox 231 concentration for 7.5 g TMPTA, 2.5 g TT1, and 6 phr fumed silica.

The combination of kaolin and fumed silica was then used as the filler of the TMPTA/ Trimethylolpropane ethoxylate triacrylate (TMPEOTA) mixtures. The monomers used were 7.5 g TMPTA and 2.5 g Trimethylolpropane ethoxylate (7/3 EO/OH) triacrylate (7/3 TMPEOTA). The filler composition was 20 phr kaolin and 3 phr fumed silica. The fumed silica/kaolin combination is beneficial because it adds the strength of the kaolin with only using 20 phr. It would take 40 phr of kaolin alone to make the adhesive viscous enough to be applied to the wood. The shear strength results are shown in Figure 8.

SS vs Luperox Concentration for 75/25 TMPTA/ (7/3) TMPEOTA
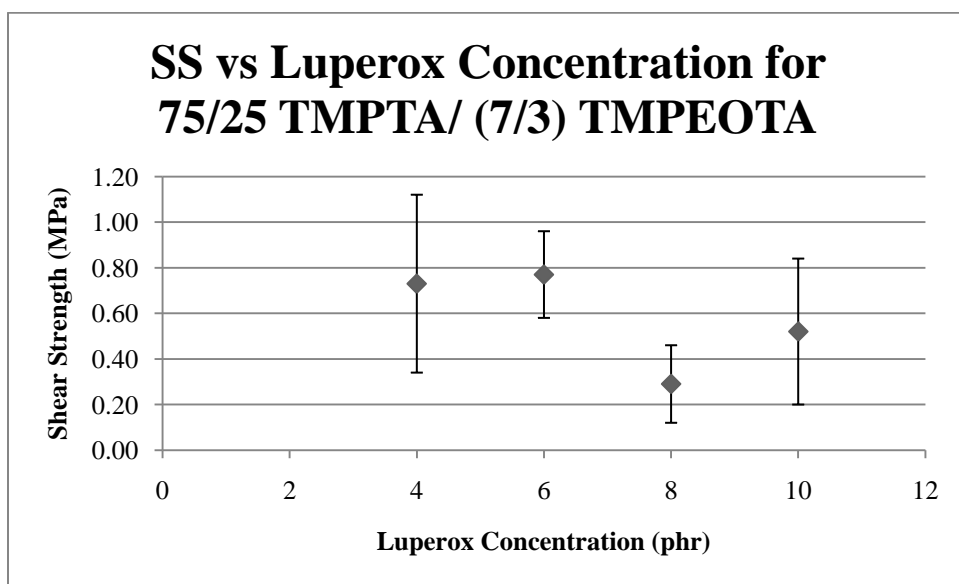
Figure 8 Shear Strength vs. Luperox 231 for a mixture containing 7.5 g TMPTA, 2.5 g 7/3 TMPEOTA, 20 phr kaolin and 3 phr fumed silica.

Different types of urethane acrylates were tried to make a more flexible adhesive. The first urethane acrylate to be tested was the acrylic ester that was difunctional. It was used in combination with the TMPTA. A 50/50 monomer mixture of TMPTA and urethane acrylate, acrylic ester (UAAE), was tried using 3 phr fumed silica and 20 phr kaolin as filler and 7 phr Luperox for the initiator. Because of the UAAE, the adhesive was hard to spread. The reason for this was the UAAE was not miscible with the TMPTA. The mixture reacted on top of a

tongue depressor and produced a tough polymer. It was not hard, but it did not crumble under pressure like the TMPTA adhesive.. The 50/50 monomer mixture was then tried with 2 phr fumed silica, 10 phr kaolin, and 6 phr Luperox. The UAAE was heated first to decrease its viscosity and then the other reagents were added to it. The UAAE separated from the TMPTA.

Another urethane acrylate (UA) used was a 9 functional acrylate. This UA was miscible with the TMPTA, and it was also very reactive. A 50/50 TMPTA and UA mixture with 5 phr Luperox was tried first. The initial filler amounts were 4 phr fumed silica and 20 phr kaolin. Adding filler to the adhesive made it thicker, but it took much more filler than was normally used to achieve the necessary viscosity to prevent it from flowing. This problem was still present when using 6 g TMPTA 4 g UA mixtures but at 7 g TMPTA to 3 g UA ratio the problem was solved. The closer to 50/50 that the TMPTA/UA ratio got the more filler was required to make the solution sufficiently viscous. At a concentration of 12 phr fumed silica, the mixture stilled flowed easily when thoroughly mixed. No more fumed silica was used because it was too difficult to stir. This characteristic was not observed in the TMPTA/ UAAE samples.

The next monomer tried was bisphenol A ethoxylate (1.5 EO/phenol) dimethacrylate (BPAEODA). BPAEODA, as with the other diacrylates, was added to TMPTA in order to make the resulting polymer elastic. There were no significant results to show that the BPAEODA was having an effect. The effects that BPAEODA concentration has on the shear strength is shown in Figure 9.
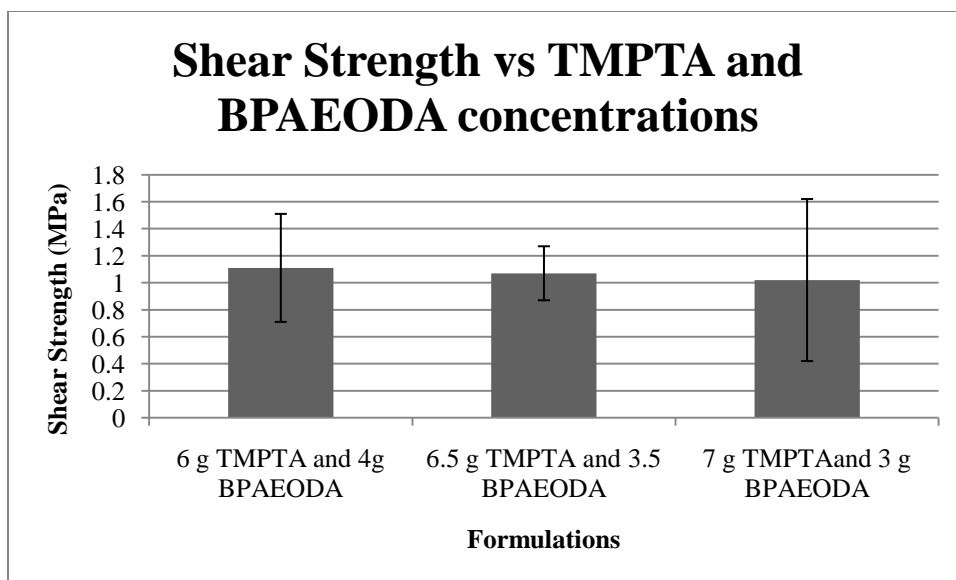
Figure 9 The Shear strength for various concentrations of the monomers TMPTA and BPAEODA. The filler was 6 phr fumed silica, and the initiator was 5 phr Luperox 231.

The 1/1 TMPEOTA (or the TMPEOTA with the lowest MW) was used next. Only one sample was tried. That sample was made from 7.5 g TMPTA, 2.5 g 1/1 TMPEOTA, 6 phr fumed silica, and 5 phr Luperox. After that 7/3 TMPEOTA was used again along with PVS. The combination of reagents were 7.5 g TMPTA, 2.5 g 7/3 TMPEOTA, 6 phr fumed silica, 5 phr PVS, and 7 phr Luperox. There was a noticeable decrease in the brittleness from the addition of the PVS, but it also had a noticeable decrease in shear strength, with an average of 0.47 MPa (68 psi).

The Effects of Fillers Results

Ground rubber tires were used as filler. All samples used 30 phr of rubber. The first four samples all used 10 phr of Luperox and used fumed silica in the amounts of 4, 3.5, 3, and 2 phr. Only the mixture that had the 4 phr fumed silica reacted all the way through, and it had an average shear strength of 1.49 ± 0.13 MPa (216 psi). The next sample used 10 phr Luperox and 25 phr kaolin, and it would not support front propagation. The last sample contained 4 phr

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fumed silica with 8 phr Luperox. The sample appeared to react all the way, but after it was

tested there were still some unreacted areas between the two wood blocks. The average shear

strength for that sample was 0.95 ± 0.37 MPa (138 psi). The results are summarized in Table 2.

The reaction left the rubber particles trapped in the polymer and prevented the rubber particles

from contributing to improving the strength of the adhesive. The rubber also did not improve the

toughness. This was observed by submerging the cured sample in water. As the wood swelled,

the adhesive bond failed.

Table 2 Rubber's effects on the Shear Strength

	TMPTA (g)	fumed silica(phr)	Rubber (phr)	Luperox(phr)	SS (MPa) ((psi))	STDEV (MPa)
TH 1.5.1	10	4	30	10	1.49 (216)	0.13
TH 1.5.2	10	2	30	10	N/R	
TH 1.5.3	10	3	30	10	N/R	
TH 1.5.5	10	3.5	30	10	N/R	
TH 1.5.6	10	4	30	8	0.95 (138)	0.37
	TMPTA (g)	Kaolin (phr)	Rubber (phr)	Luperox (phr)	SS	STDEV
TH 1.5.4	10	25	30	10	N/R	

The next compound that was tried was BYK-070, an organic defoamer. The first mixture

was made of 10 g TMPTA, 4 phr fumed silica, 1 phr BYK-070 and 10 phr of Luperox. The

shear strength was 0.47 MPa (68 psi). The second mixture was comprised of 10 g TMPTA, 6

phr fumed silica, 1 phr BYK-070, and 10 phr Luperox. It had shear strength of 1.00 MPa (145

psi). The third sample contained 10 g TMPTA, 6 phr fumed silica, 0.5 phr BYK-070, and 10 phr

Luperox with its shear strength being 0.57 MPa (82 psi). Only one sample from each

formulation was tested because the properties shown were undesirable. The 4 phr fumed silica

was soupy and did not form a gel. All of these samples had the adhesive spill out from the side

while reacting. The polymer adhesive was flaky and powder like.

The next additive tried was styrene-ethylene/butylene-styrene (SEBS) as a filler. The SEBS is very elastic, so it was used in hopes of increasing the adhesive's ability to absorb shocks. The results for the shear strength are shown in Table 3. The first sample contained 10 g TMPTA, and the amount of fumed silica added was 6 phr. Only one trial was run, and the shear strength was 1.37 MPa (198 psi). The sample consisting of 10 g TMPTA, 35 phr kaolin, 10 phr SEBS, and 10 phr Luperox did not react between the wood blocks. The high kaolin concentration and the used on SEBS made covering the top of the two wood blocks with 2 g of adhesive difficult. The SEBS was not well dispersed in the mixture, and gaps formed when the adhesive was applied in the 2 g amounts. The sample made of 10 g TMPTA, 4 phr fumed silica, 13.5 phr kaolin, 23.8 phr SEBS and 5 phr Luperox 231 did not fail when submerged in water. The higher SEBS concentration enabled the adhesive to expand with the swelling wood. The next sample had its kaolin and SEBS concentrations reduced to 6.7 phr and 1.12 phr, respectively. Its shear strength was 1.10±0.4 MPa (159 psi), and it failed when submerged in water. The sample had its SEBS concentration reduced to 5.6 phr and kept the kaolin concentration at 6.7 phr. The shear strength was 0.81 ± .2 MPa (117 psi). It also failed in water. The 23.8 phr SEBS mixture was the only sample to withstand the swelling on the wood.

Table 3 Effects of SEBS on the Shear Strength of TMPTA based adhesives

	TMPTA (g)	kaolin (phr)	SEBS (phr)	Luperox (phr)	SS (MPa) ((psi))	STDEV (MPa)
TH 1.11.1	10	35	7	10	1.25 (181)	0.33
	TMPTA (g)	fumed silica (phr)	SEBS (phr)	Luperox (phr)	SS (MPa) ((psi))	STDEV (MPa)

(Table 3 con'd.)

	TMTPA (g)	fumed silica (phr)	Kaolin (phr)	SEBS (phr)	SS (MPa) ((psi))	STDEV (MPa)
TH 1.11.2	10	4	10	10	1.08 (157)	0.36
TH 1.13.2	10	6	10	10	1.37 (198)	
TH 1.13.4	10	4	13.5	23.8	1.62 (235)	0.81
TH 1.13.5	10	4	6.7	11.2	1.10 (159)	0.38
TH 1.13.6	10	4	6.7	5.6	0.81 (118)	0.15

The SEBS was dissolved in toluene to reduce the size of the particles. The SEBS was then dispersed in the TMPTA. The first sample contained 10 g TMPTA, 2 phr fumed silica, 20 phr, kaolin, 7.1 phr SEBS, and 6 phr Luperox. The sample's shear strength was 2.05 MPa (298. psi). The following samples used 5.8 phr SEBS. This is close to 5 % weight and was the amount suggested by Lei et al. in another paper (Lei 2008). The results are shown in Table 4.

Table 4 Effects of Dispersed SEBS on the Shear Strength of TMPTA-based adhesives

	TMPTA (g)	fumed silica (phr)	kaolin (phr)	SEBS (phr)	Luperox 231(phr)	SS (MPa) (psi)	STDEV (MPa)
TH 1.53.1	10	2	20	7.1	6	2.05 (298)	1.12
TH 1.53.2	10	0	20	5.8	5	2.99 (434)	0.44
TH 1.53.3	10	0	20	5.8	8	2.53 (367)	0.68
TH 1.53.5	10	2	20	5.8	8	2.70 (392)	0.40

The dispersion technique only worked for a certain amount of SEBS. The higher the concentration of SEBS used the more toluene is required to dissolve it. This lead to using a larger beaker for larger concentrations of SEBS in order to accommodate the amount of toluene that was needed, and it also took more time for the toluene to evaporate off once the TMPTA was added. In higher concentrations, the SEBS made the mixture very viscous and made it more difficult to stir. The stirring being hindered also prevented dispersion and lead to agglomeration. An overhead stirrer could be used to make it easier to stir mixtures containing a higher

concentration of SEBS, but they were not practical for the small sample sizes used for these experiments.

Various low density polyethylenes (LDPE) and an ethylene/acrylic ester/maleic anhydride terpolymers (EEAMA) were tried as additives. The first LDPE to be tried was high gloss polyethylene, which is used in paints. The first sample tested contained 10g TMPTA, 5 phr fumed silica, 12 phr kaolin, 24.6 phr LDPE, and 5 phr Luperox. The sample did not react. The next formulation tested was 10 g TMPTA, 6 phr fumed silica, 8 phr kaolin, 12 phr LDPE, and 5 phr Luperox . That solution's sample had a shear strength of 0.73 MPa (106 psi). The following sample was made from 10 g TMPTA, 6 phr fumed silica, 10 phr kaolin, 18 phr LDPE, and 5 phr Luperox. The solution's sample had a shear strength was 1.48 MPa (215 psi), but the insides were still wet. The next sample contained an LDPE loading to 22 phr and increased the Luperox concentration to 6 phr, but not all of those runs went through completely. The next two solutions used only the LDPE as the filler. The first one contained 6 g TMPTA, 66.7 phr LDPE, and 5 phr Luperox. The second one contained 6 g TMPTA, 41.7 phr LDPE, and 5 phr Luperox. Both of the samples did not react. The two samples were left out overnight, and the next day they had dried out. The 66.7 phr LDPE sample was completely solid while the 41.7 phr LDPE sample was only solid on top. The LDPE absorbed the TMPTA and Luperox 231. Neither one had a propagated front, but did react when heat was applied. The 66.7 phr LDPE formulation reacted only after the solid had melted. When a heat source was applied to the solidified mixture, it melted the area it is applied to. If the heat source was left in the same area after the mixture melted it started to react. If front velocity of melted area was high enough, the front would be sustained long enough to polymerize the solid region.

The next LDPEs and EEAMA tested were pure and did not have any unknown additives. All of the following samples were not run between two wood blocks because they reacted slowly. The samples were run on the top of one block of wood. There were no strength tests conducted because the sample was not used to bind two blocks of wood. However, he visible characteristics of the polymer created were noted. The first one tested was the EEAMA labeled as TB3580. The sample was made of 6 g TMPTA, 33.3 phr TB3580, 6.7 phr fumed silica, and 3 phr Luperox. The next sample had 6 g TMPTA, 33.3 phr TB3580, 5 phr fumed silica, 4.2 phr SEBS, and 5 phr of Luperox. After those two samples, a sample was made from 6 g TMPTA, 33.3 phr HX1681, 5.8 phr fumed silica, and 5 phr Luperox. The next sample had 6 g TMPTA, 37.5 phr TB3580, 6.7 phr fumed silica, 10 phr kaolin, and 7 phr Luperox. The following sample contained 6 g TMPTA, 33.3 phr TB3580, 3.3 phr fumed silica, 20 phr kaolin, and 10 phr Luperox. Two samples were made for HX1681 and HA1681 varying only in which LDPE was used as filler. The first one consisted of 6 g TMPTA, 33.3 phr HX1681 or HA1681, 5 phr of fumed silica, 10 phr kaolin, and 5 phr Luperox. The second sample was made of 6 g TMPTA, 33.3 phr HX1681 or HA1681, 3.3 phr of fumed silica, 20 phr kaolin, and 5 phr Luperox. Another two samples were made with TB3580 as the LDPE filler. One of the adhesives prepared used 4.2 phr SEBS, and the other contained none. The one that had SEBS also contained 6 g TMPTA, 2.5 phr fumed silica, 20 phr kaolin, and 5 phr Luperox. The other contained 6 g TMPTA, 2.5 phr fumed silica, 23.3 phr kaolin, and 5 phr Luperox. All of these adhesives that contained, TB3580, HX1681, or HA1681 did not bind well to wood. These fillers are of no use in making wood adhesives because of that trait. All the polymeric materials formed were tough, rigid polymers that were white in color.

Next the hot melt adhesive (HMA)200F was used as one of the components. Three samples were run using three different amounts of the HMA200F. It was hypothesized that when the front propagated, the increase in temperature would allow the HMA 200F to flow. After the adhesive returned to ambient temperature, the HMA 200F would solidify making the adhesive tougher by giving it some mechanical characteristics of the HMA 200F. The other components were 7.5 g TMPTA, 2.5 7/3 TMPEOTA, 6 phr fumed silica, and 7 phr Luperox. The three concentrations of HMA200F were 6 phr, 20 phr, and 10 phr. The 20 phr concentration sample did not support complete frontal polymerization. The 6 phr HMA200F had a shear strength of 0.52 MPa (75 psi), and the 10 phr HMA200F adhesive had a shear strength of 0.54 MPa (78 psi). The addition of the HMA200F made the adhesive release more smoke, and it foamed more when it reacted.

The effect that kaolin had on the adhesive was studied. All of the samples used 7.5 g TMPTA, 2.5 g 7/3 TMPEOTA, 6 phr fumed silica, and 9 phr Luperox. The effect that the kaolin concentration had on shear strength is shown in Figure 10. The general trend was that as the kaolin loading was increased the adhesive expanded less. Kaolin also made the adhesive harder than fumed silica. The higher the kaolin loading the more heat was absorbed by the filler. That would slow down the polymerization or prevent the mixture from supporting a front. A mixture containing the 20 phr kaolin was applied to the surface on a block of wood in a thin layer. After the reaction was initiated, the front only propagated in the regions of the less dense wood. The front moved through the parts of the mixture that were above the lighter portions of the wood and avoided the denser regions. If the front did cross into the denser regions, it would only continue to propagate if it can quickly extend into another lighter region. The

thermoconductivity being higher in the denser parts of the wood causes this (Forest Products

Laboratory 1999 and Keating 1982).
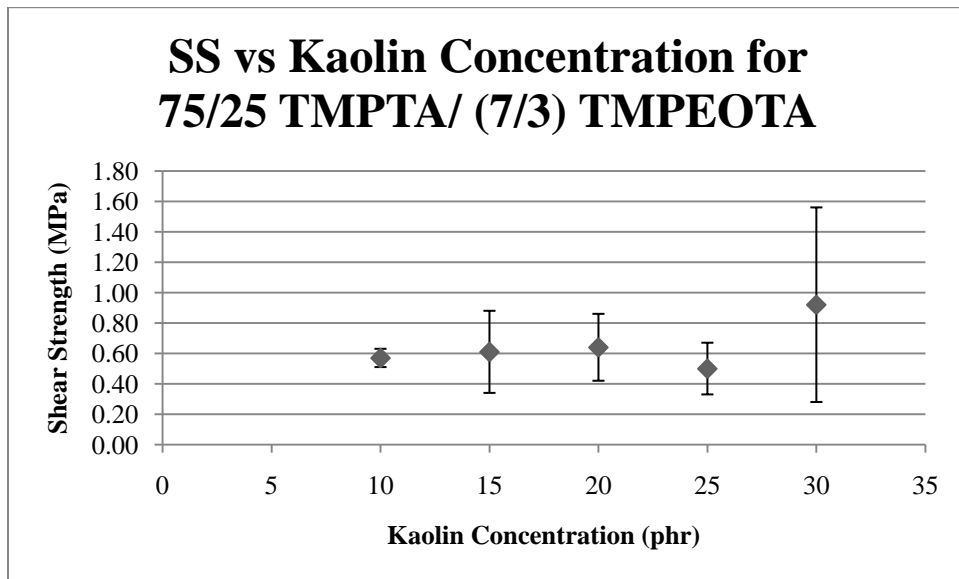
Figure 10 Shear Strength vs. kaolin concentration. The mixture was made of 7.5 g TMPTA, 2.5 g 7/3 TMPEOTA, 6 phr fumed silica, and 9 phr Luperox 231.

The next substance that was tried was ethyl cellulose (EC). The idea behind using this

was that the ethyl cellulose might be able to hydrogen bind to the wood and increase the shear

strength. Figures 11-14 show the shear strength with respect to Luperox 231 concentrations with

increasing EC concentrations. The set that contained 30 phr kaolin did not have data for less

than 6 phr of Luperox because the reaction would stop before it had propagated through the

whole adhesive. This happened because the amount of filler was too high for that amount of

initiator to sustain the reaction. The EC came in powder with particles about the same size as a

grain of sand, so they would not disperse in TMPTA because the particle size was too large. The

undispersed EC lead to an adhesive that wa more difficult to spread. The next experiment was to

disperse the EC in the mixture. The results are shown in Table 5.

Figure 11 Shear strength vs. Luperox 231 concentration for mixtures containing 10 g TMPTA, 5 phr EC, 25 phr kaolin, and 3 phr fumed silica.

Figure 12 Shear strength vs. Luperox 231 concentration for mixtures containing 10 g TMPTA, 10 phr EC, 25 phr kaolin, 3 phr fumed silica.
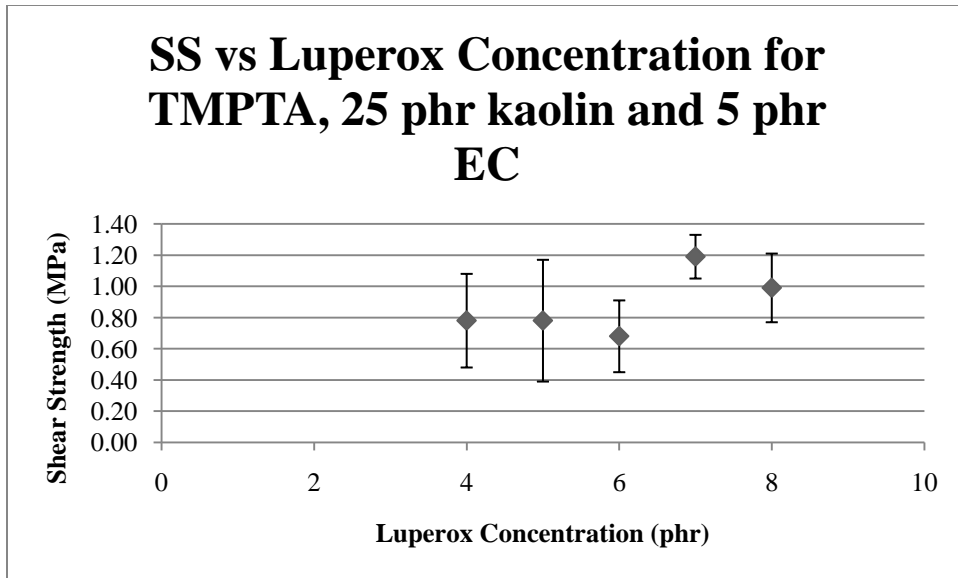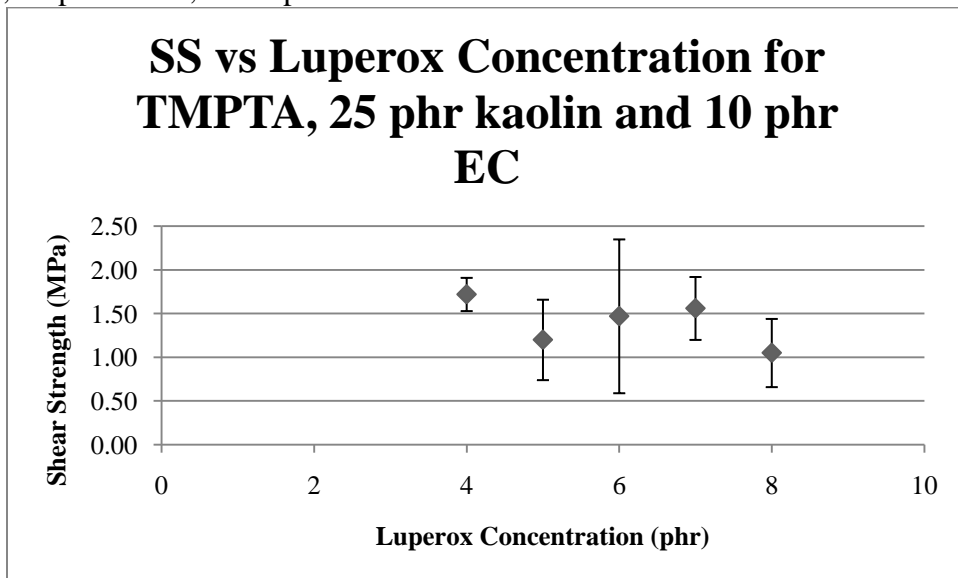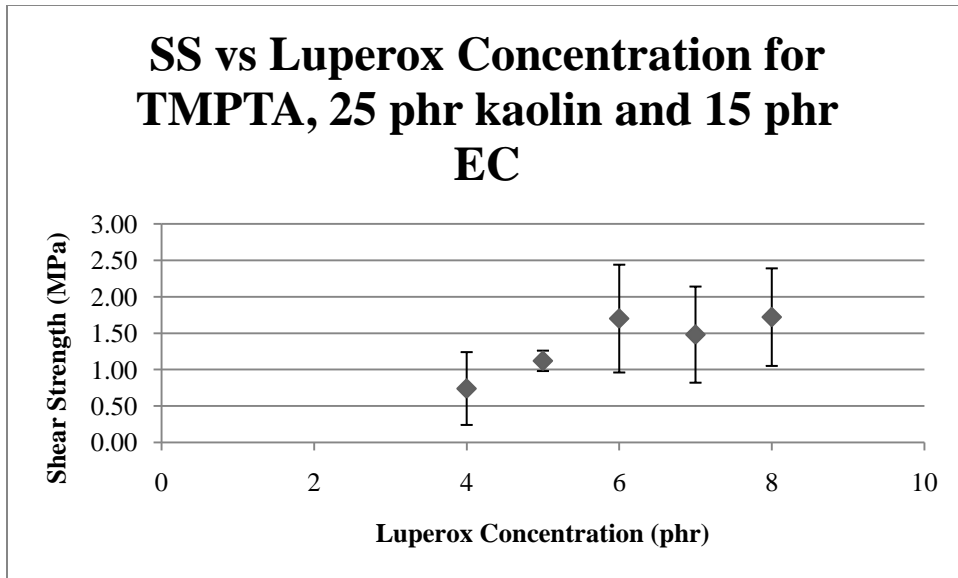
Figure 13 Shear strength vs. Luperox 231 concentration for mixtures containing 10 g TMPTA, 15 phr EC, 25 phr kaolin, 3 phr fumed silica.
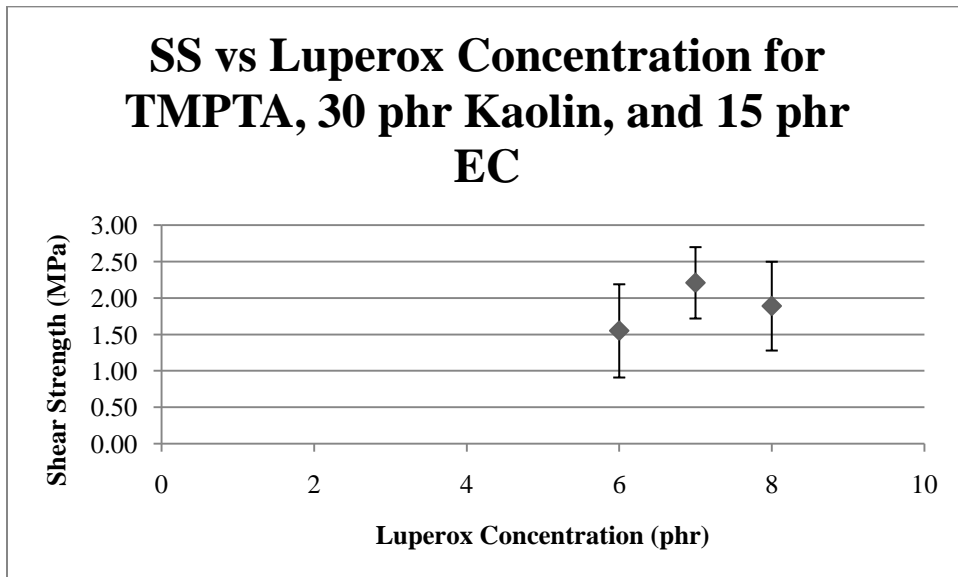

Figure 14 Shear strength vs. Luperox 231 concentration from mixtures with 10 g TMPTA, 15 phr EC, 30 kaolin, and 3 phr fumed silica.

Table 5 Effects of Dispersed EC on the Shear Strength of TMPTA-based adhesives

	TMPTA (g)	fumed silica (phr)	kaolin (phr)	Ethyl Cellulose	Luperox (phr)	SS (MPa) ((psi))	STDEV (MPa)
TH 1.53.6	10	4	15	7.5	10	1.90 (275)	0.28
TH 1.53.7	10	4	15	7.5	6	No front	
TH 1.53.9	10	4	15	4.5	8	1.68 (243)	0.62
TH 1.53.10	10	4	15	4.5	5	1.04 (151)	0.17
TH 1.53.11	10	4	15	7.5	7	1.65 (239)	0.24

Pine sawdust was used as the next filler. It was chosen because sawdust is made from wood, and it contains cellulose. It was also cheaper to obtain sawdust with a small particle size than ethyl cellulose. The first experiment done with sawdust used 10 g TMPTA, 6 phr fumed silica, 5 phr Luperox and 10 phr sawdust. The shear strength from this experiment was found to be 1.39 MPa (201 psi). Kaolin was added to the adhesive to increase its strength. The first experiment used 10. g TMPTA, 3 phr fumed silica, 20 phr kaolin, 10 phr sawdust, and 5 phr Luperox 231. This sample did not support complete propagation. This was because the 3 phr fumed silica did not make the adhesive viscous enough to undergo frontal polymerization. The rest of the samples had 5 phr of fumed silica added to the mixture to ensure it formed a gel. The results of the shear strength with respect to Luperox 231 concentration for 10 phr sawdust and 15 phr kaolin is shown in Figure 15, and the results for 5 phr sawdust and 20 phr kaolin is shown in Figure 16. Figures 17-19 show the results for samples using 7.5 phr sawdust with increasing kaolin concentrations.
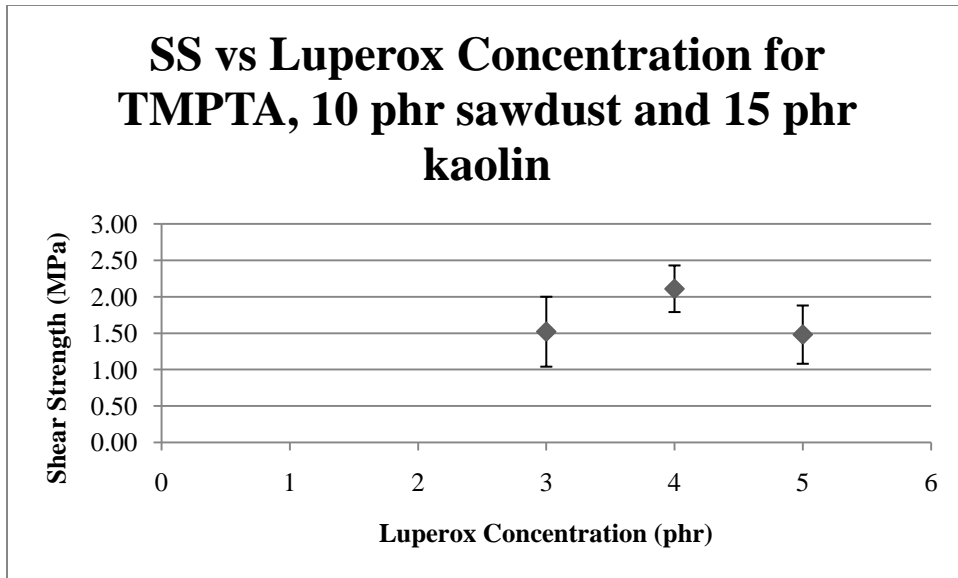
Figure 15 Shear Strength vs. Luperox 231 concentration for 10 g TMPTA, 10 phr sawdust and 15 phr kaolin.
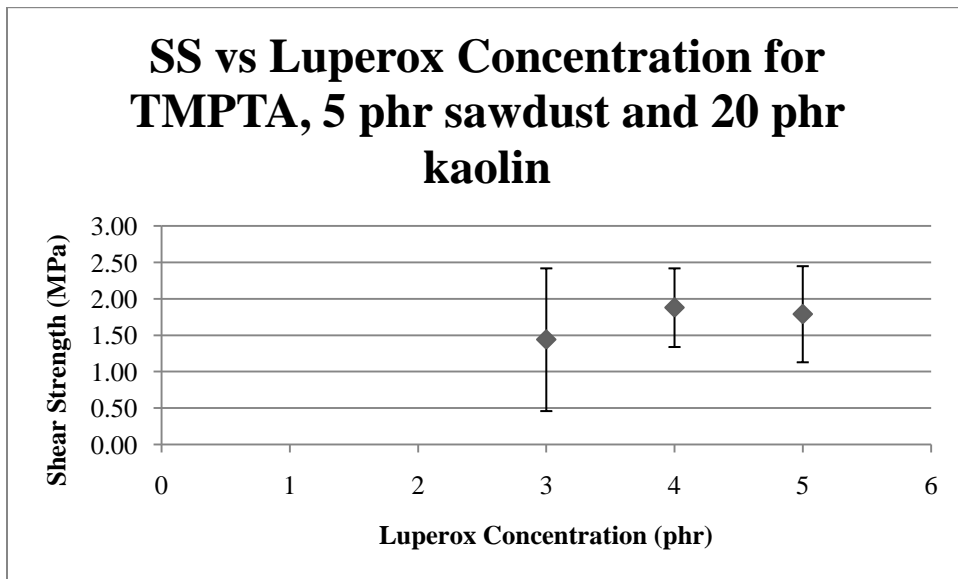
Figure 16. Shear Strength vs. Luperox 231 concentration for 10 g TMPTA, 5 phr sawdust and 20 phr kaolin.
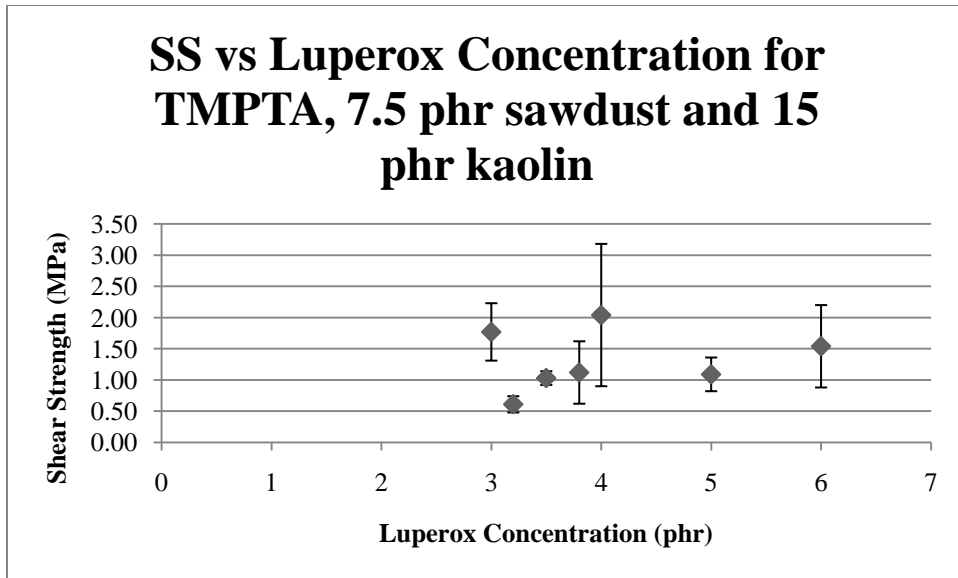
Figure 17. Shear strength vs. Luperox 231 concentration for 10 g TMPTA, 7.5 phr sawdust, and 15 phr kaolin.
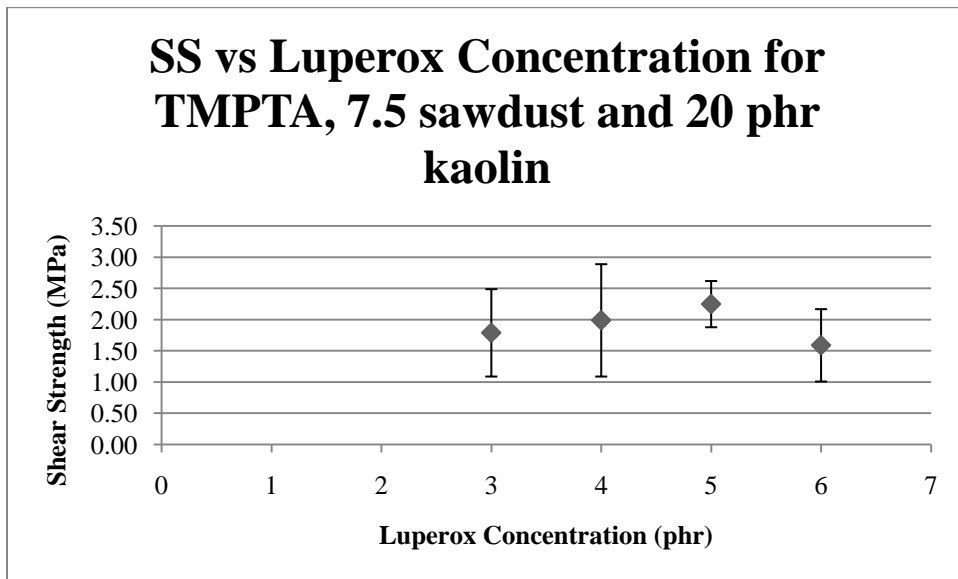
Figure 18. Shear strength vs. Luperox 231 concentration for 10 g TMPTA, 7.5 phr sawdust, and 20 phr kaolin.

SS vs Luperox Concentration for TMPTA, 7.5 sawdust and 25 phr kaolin
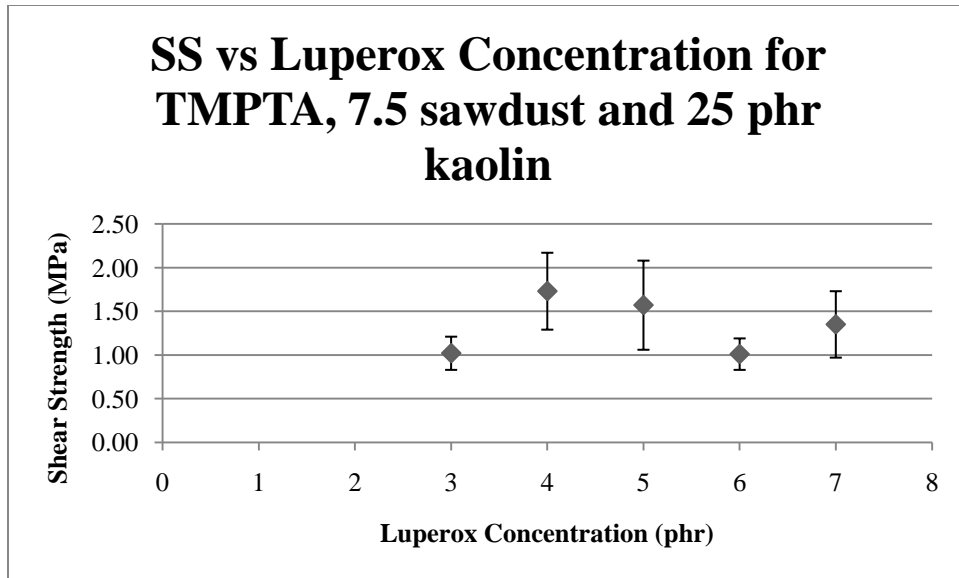
Figure 19. Shear strength vs. Luperox 231 concentration for 10 g TMPTA, 7.5 phr sawdust, and 25 phr kaolin.

The pine sawdust was place in a 75 μm sieve to reduce the particle size. The reduced particle size of the sawdust was used to determine if the smaller particle size impacted the mechanical properties that the sawdust gives the polymer. All the samples used TMPTA as the monomer. The first sample contained 5 phr fumed silica, 20 phr kaolin, 7.5 phr sawdust, and 5 phr Luperox. The sample had a shear strength of 2.32±0.3 MPa (336 psi). The next set of experiments used 7.5 g TMPTA and 2.5 g 7/3 TMPEOTA as the monomer. Figure 20 shows the effects that 5 phr sawdust and varying kaolin concentrations had on the shear strength at two Luperox 231 concentrations. Figure 21 shows the shear strength with 7.5 phr sawdust and various kaolin concentrations at three Luperox 231 concentrations.
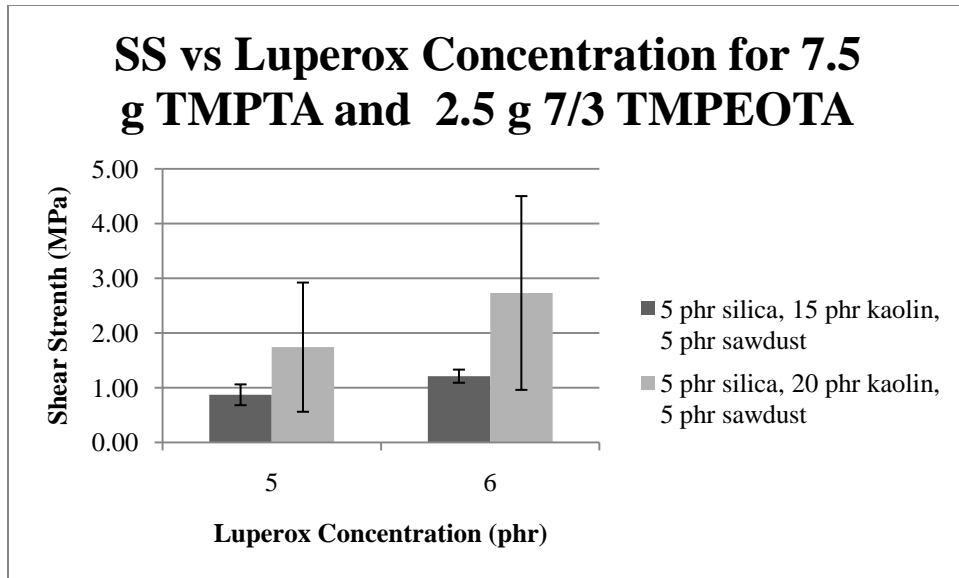
Figure 20. A comparison of shear strength vs. Luperox 231 concentration for two samples with two kaolin loadings.
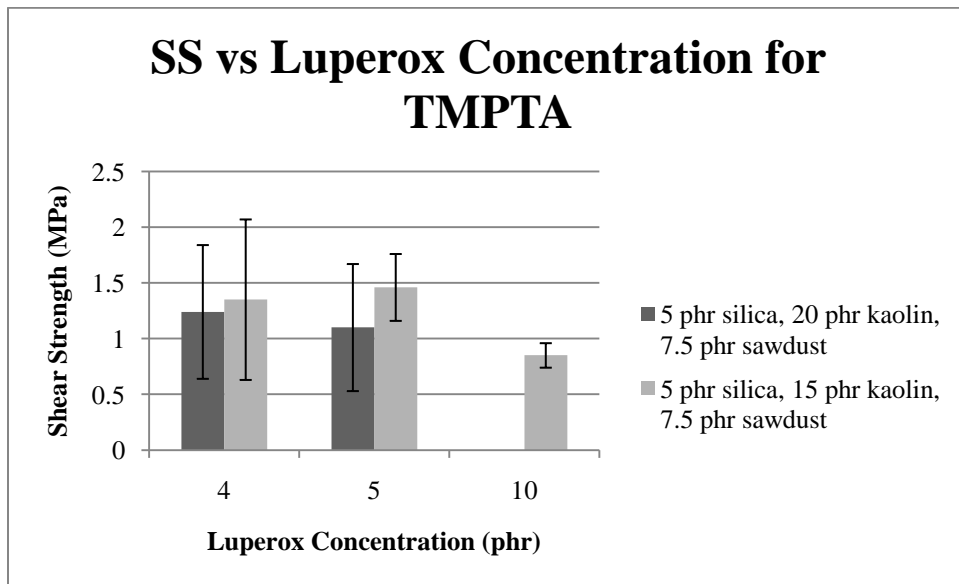
Figure 21. A comparison of shear strength vs. Luperox 231 concentration for two samples with two different kaolin loadings.

The BPAEODA was tried again also using the sawdust. The first sample did not contain

any sawdust. It contained 7.5 g TMPTA, 2.5 g BPAEODA, 20 phr kaolin, 5 phr fumed silica,

and 5 phr Luperox. The shear strength of this sample was 1.88 MPa (273 psi). The next 2

samples used the same formulation as the previous one but contained different amounts of

sawdust. One sample had 7.5 phr of sawdust and second one had 5 phr of sawdust. The 7.5 phr

sawdust adhesive would not react, and the 5 phr sawdust-containing sample did not also react

completely. The last sample used the 7.5 g TMPTA, 2.5 g BPAEODA, and 20 phr kaolin like in

the previous sample, but used 3 phr fumed silica and 5 phr of sawdust. This sample also did not

sustain a front.

The next experiment involved using a 75/25 TMPTA to 14/3 TMPEOTA mixture as the

monomer. The first mixture included the 75/25 monomer mixture, 6 phr fumed silica, and 8 phr

Luperox. The results are shown in Table 6.

Table 6 Shear Strength of Adhesives made from TMPTA and 14/3 TMPEOTA

	TMPTA (g)	14/3 TMPEOTA (g)	kaolin (phr)	fumed silica (phr)	sawdust (phr)	Luperox (phr)	SS (MPa) ((psi))	STDEV (MPa)
TH 1.35.1	7.5	2.5	0	6	0	8	1.34 (195)	0.41
TH 1.35.2	7.5	2.5	0	6	5	8.5	0.70 (102)	0.39
TH 1.35.3	7.5	2.5	20	5	5	8	1.19 (172)	0.46

The next formulations contained chitosan as a filler. The initial sample consisted of 10 g

TMPTA, 6 phr fumed silica, 10 phr chitosan, and 8 phr Luperox. The results are shown in

Figure 22. After the sample was tested, it was noted that the chitosan separated from the silica

during the polymerization. The chitosan congregated in the center of the block while the silica

was around the chitosan.
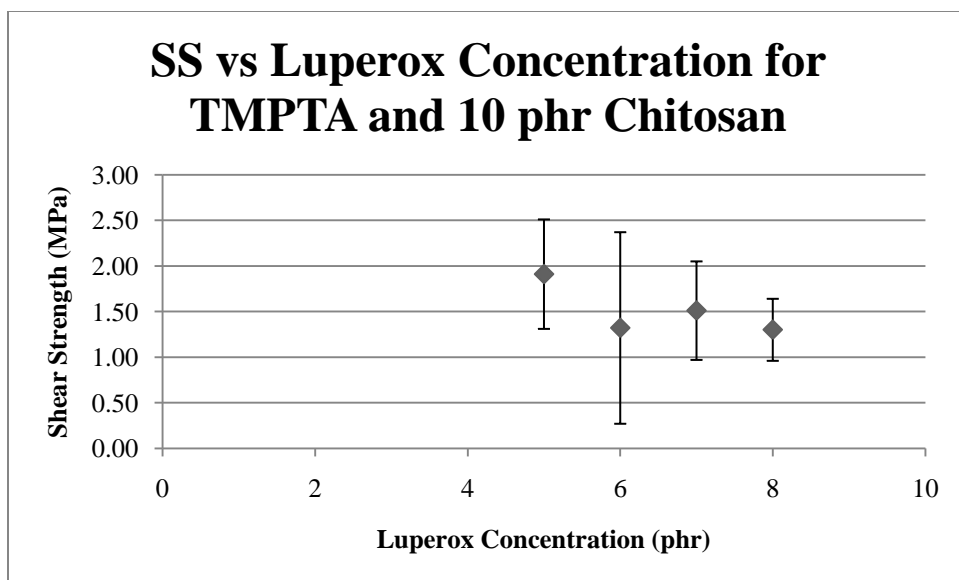
Figure 22 Shear Strength vs, Luperox 231 concentration using 10 g TMPTA as the monomer with 10 phr Chitosan, 4 phr fumed silica, and 20 phr kaolin as the filler.

Elmer's glue was used in combination with TMPTA. Four different mixtures were utilized. The first combination was 7.5 g TMPTA, 2.5 g Elmer's glue, 4 phr fumed silica, and 5 phr Luperox. The second combination was 9 g TMPTA, 1 g Elmer's glue, 6 phr fumed silica, and 5 phr Luperox. The third combination was 9 g TMPTA, 1 g Elmer's glue, 6 phr fumed silica, and 10 phr Luperox. The fourth combination was 9.5 g TMPTA, 0.5 g Elmer's glue, 6 phr fumed silica, and 10 phr Luperox. The first combination did not react. The second, third, and fourth reacted, but did not completely go through. The reason why most of the formulations did not react is because the Elmer's glue is made of a polyvinyl acetate (PVA) emulsion, which is an emulsion with water. The water quenched the front.

Friendly Plastic was the next compound tried as filler. Friendly Plastic is a trademarked name for polycaprolactone (PCL). The PCL was used because when heated above 60°C it melts, which enables the PCL to be molded. We hypothesized that if the particles would be small enough then when they would be heated by FP, they could flow together though out the polymer. After the polymer cools, it would have a rigid support structure. Since Friendly Plastic comes in

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5 mm diameter spheres, it had to be broken down to a smaller size in order for it to be dispersed

in the monomer. First, the Friendly Plastic was heated. The idea was that the Friendly Plastic

would become a liquid when heated. The Friendly Plastic was placed in a beaker containing

water. The water and Friendly Plastic mixture was stirred and heated. A surfactant, Triton X,

was added to disperse the particles. When the heat source was removed the Friendly Plastic

should have solidified and formed small particles. This did not work because the Friendly

Plastic never became a liquid.

The next filler tested was styrene-butadiene-styrene (SBS). The reason behind using SBS

is the same one for using SEBS. The goal was to use the SBS to increase the toughness of the

adhesive. The increase in toughness was observed by submerging the samples in water and

seeing if the polymer could handle the swelling wood. The results are given in Figure 23.
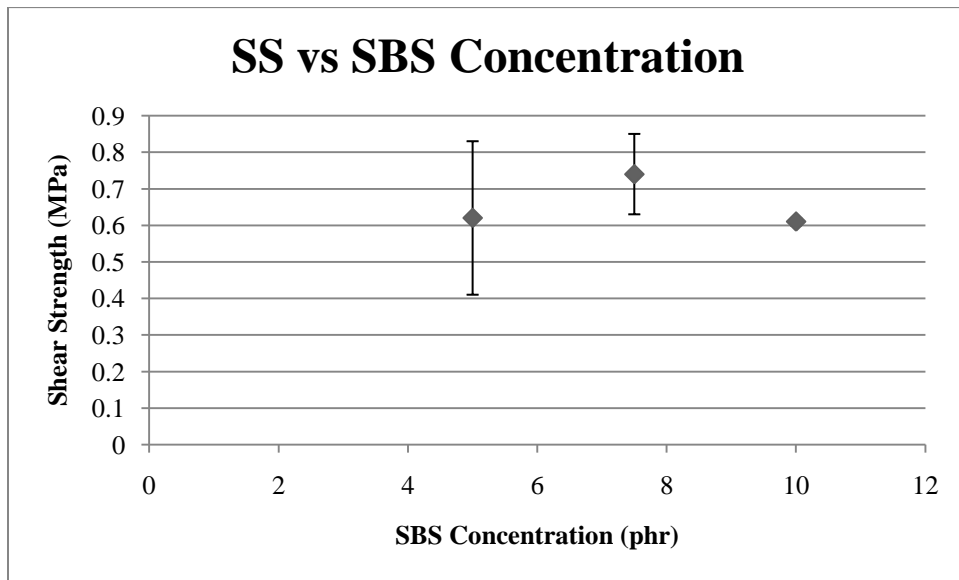
Figure 23 Shear strength vs SBS concentration, for 10 g TMPTA, 10 phr kaolin, 5 phr fumed silica, and 5 phr Luperox 231.
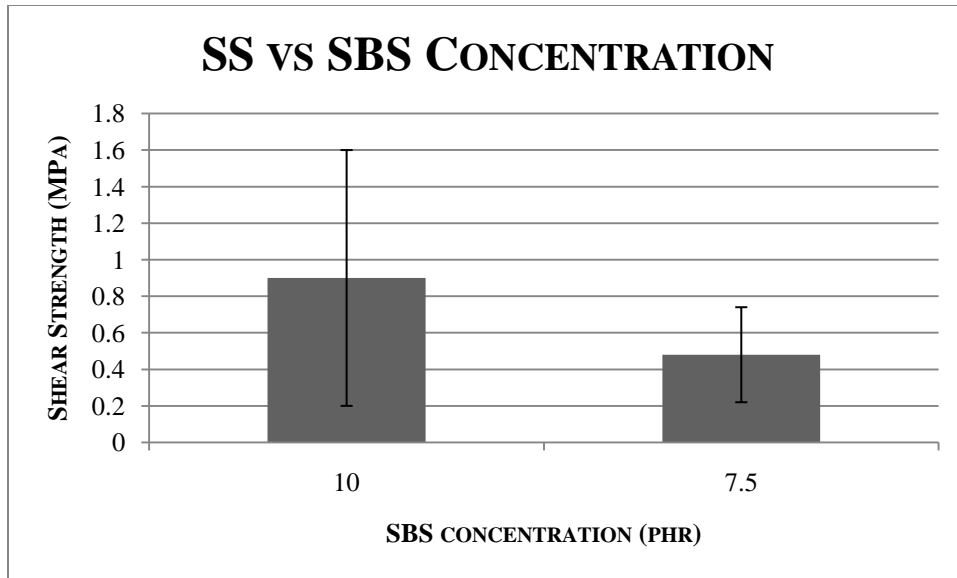
Figure 24. Shear strength vs, SBS concentration for 10 g TMPTA, 7.5 phr sawdust, 10 phr kaolin, 5 phr fumed silica, and 5 phr Luperox 231.

The two mixtures from Figure 24 did not support a front. After testing using the Instron, the 10 phr SBS mixture had two samples that were unreacted in the center. The 7.5 phr SBS mixture had one sample where the front stopped. These two mixtures contained a high filler loading. This caused more heat loss to filler, which hindered the mixture's ability to sustain a front. Table 7 has more samples that had this problem. Mixtures TH 1.47.13, TH1.47.14 and TH 1.51.2 exhibited the same problem with some samples being unreacted due to the high filler concentration.

Table 7 Effect SBS has on the Shear Strength of TMPTA adhesives

	TMPTA (g)	fumed silica (phr)	kaolin (phr)	sawdust (phr)	SBS (phr)	Luperox (phr)	SS (MPa) ((psi))	STDEV (MPa)
TH 1.47.13	10	6	0	0	25	10	0.94 (137)	0.57
TH 1.47.14	10	6	0	7.5	15	10	1.24 (180)	0.23
TH 1.51.1	10	5	10	5	10	8	1.01 (146)	0.18

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(Table 7 con'd.)

TH 1.51.2	10	5.5	0	5	20	8	1.92 (279)	0.69
TH 1.51.3	10	0	15	0	7.5	5	1.39 (201)	0.21

The next experiment was to disperse the SEBS, SBS, and EC in the monomer. This was first tried with 1 g of SBS following the steps described in the Materials and Methods section. The SBS was added to 10 g of TMPTA and 1 g of Luperox. The mixture was stirred to allow the toluene to evaporate off. The contents of the beaker were transferred to a weigh boat. The amount transferred was close to 8.30 g. The mixture was not viscous enough so 0.5 g of fumed silica was added. This experiment was tried two times. The first time the shear strength came to be 0.72 MPa (105 psi), and the second time it was 1.56 MPa (226 psi). After the samples were tested in the Instron, it was observed that the parts of the adhesive were still unreacted, and some formed a film of rubber. The film may have come from allowing the SBS/TMPTA mixture to remain static too long before using it. If the mixture was left static while the toluene was evaporating off the SBS film would form instead dispersed small particles. Instead of having fully dispersed SBS in the monomer, some of the SBS will be dispersed and some will have formed a film. The SBS film prevented the adhesive from being applied evenly. This occurred with SEBS or EC. Other reason is that there was not enough toluene to completely dissolve the SBS. This procedure was also tried for dispersing rubber cement. The problem with rubber cement was that the rubber latex particle agglomerated as the solvent evaporated.

AA/TMPEOTA Combinations Results

The next part of the research deals with adding acrylic acid (AA) to TMPEOTA to make a tougher adhesive. AA was used with the TMPEOTAs because AA was more reactive than TMPTA. Another reason was that AA is a monofunctional acrylate so the polymer it forms

would not be as brittle as one formed using the trifunctional TMPTA. The first experiment used 7.5 g of 7/3 TMPEOTA and 2.5 g of AA as the monomers. The fillers were made of 5 phr fumed silica, 20 phr kaolin, and 5 phr sawdust. The Luperox concentration was 6 phr. This mixture did not finish reacting when used between two wood blocks. It did completely react when it was applied on one side of the block, but the front velocity was slower than when using higher AA ratio.   When the monomer mixture was 5 g 7/3 TMPEOTA and 5 g AA, the reaction took less time to complete than the 7.5.g 7/3 TMPEOTA and 5 g AA.

The next experiment used 5 g of AA with the other 5 g being one of the three types of TMPEOTA. The first of the ethoxylated acrylates used was the 7/3 TMPEOTA. The results are shown in Figure 20 below. The 10 phr sawdust mixtures did not react because the concentration of sawdust was too high and removed heat from the front. The mixtures that just used silica were more elastic. The samples with the others fillers were more rigid. This trend is shown in the graph for the relative modulus of the samples (Figure 26). The higher the modulus the stiffer the adhesive bond. Stiffness is the resistance to deformation. Generally the higher the shear strength the higher the shear modulus except in the case of SBS and SEBS. Since both SEBS and SBS are elastomers, they increase the shear strength along with increasing the elongation, which decreases the modulus. The initiator does not appear to have an effect on the modulus as the samples using the same filler concentration but initiator concentrations of 5 phr and 8 phr Luperox 231 had the same modulus. More tests would be required to confirm this.
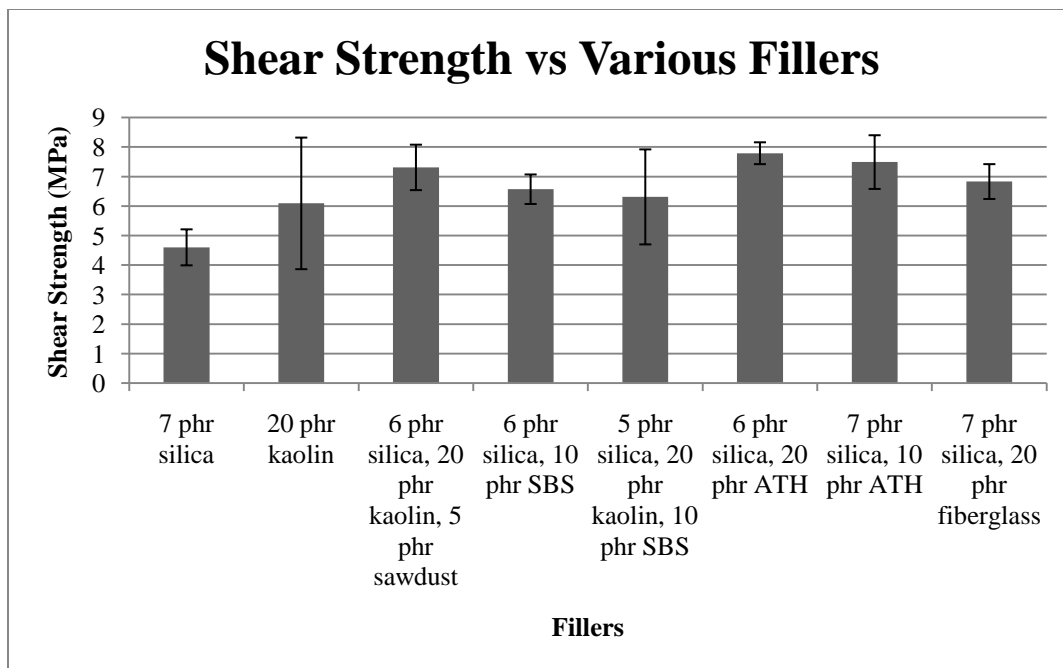
Figure 25. The shear strengths of adhesives made from 5 g AA/5 g 7/3 TMPEOTA, 8 phr Luperox, and various filler concentrations.
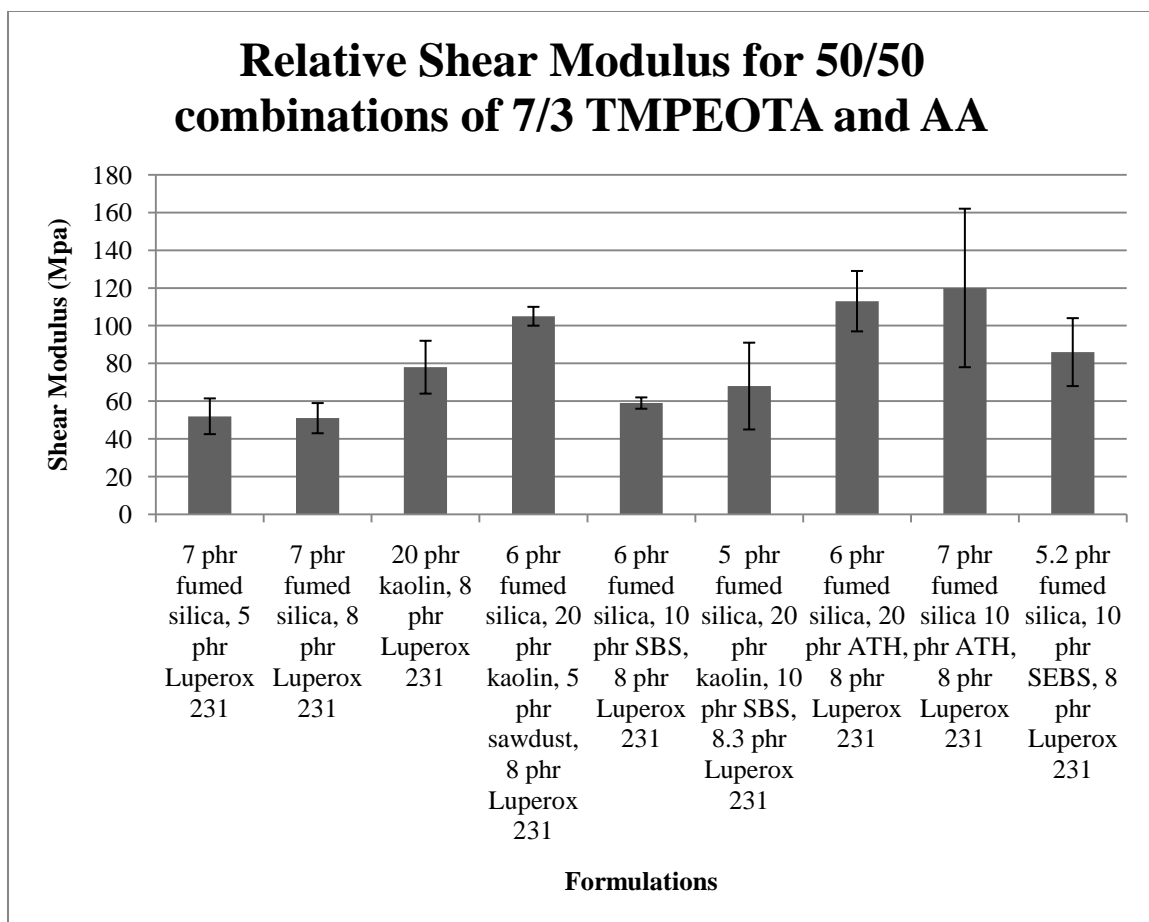
Figure 26 The relative shear modulus of adhesives made from 5 g AA/5 g 7/3 TMPEOTA and various filler and Luperox 231 concentrations.

The next type of TMEOTA tested was the 14/3 TMPEOTA. The first sample used 50/50 14/3 TMPEOTA/AA combination with 7 phr fumed silica and 8 phr Luperox. The second sample used 5 phr fumed silica and 20 phr kaolin as the filler. The third sample used 6 phr fumed silica and 10 phr of sawdust. The shear strength of first was 258 psi. The second and third samples did not react between two pieces of wood. The shear strength results are shown in Table 8. Each of the three samples was placed on a tongue depressor to examine the differences in appearance and by pressing down on them to determine a general trend of toughness and hardness. By just touching each sample, they were more elastic than previous samples. The mixture with only fumed silica was the most elastic followed by the sawdust mixture.

Table 8 Shear Strengths of Adhesives Using 14/3 TMPEOTA and AA as the Monomers

	14/3 TMPEOTA (g)	Acrylic Acid (g)	fumed silica (phr)	kaolin (phr)	sawdust (phr)	Luperox (phr)	SS (MPa) ((psi))	STDEV (MPa)
TH 1.57.5	5	5	7	0	0	8	1.78 (258)	0.33
TH 1.57.6	5	5	5	20	0	8	3.01 (436)	0.79
TH 1.61.1	5	5	5	20	0	10	3.18 (461)	0.21

The next experiment was pairing AA with 1/1 TMPEOTA. The monomer ratio used for these experiments was 50/50 1/1 TMPEOTA/AA. The Luperox concentration for these experiments was 8 phr. The first sample had 7 phr fumed silica as the filler. The 1/1 TMPEOTA/AA mixture produced adhesives with strongest shear strength. The higher the ethoxylation the yellower the resulting polymer is. The 1/1 TMPEOTA has less ethoxylation than the 7/3 TMPEOTA so it makes more rigid polymer. Because of this, these samples had the highest shear strength and relative shear modulus as shown in Figures 27 and 28 respectively.
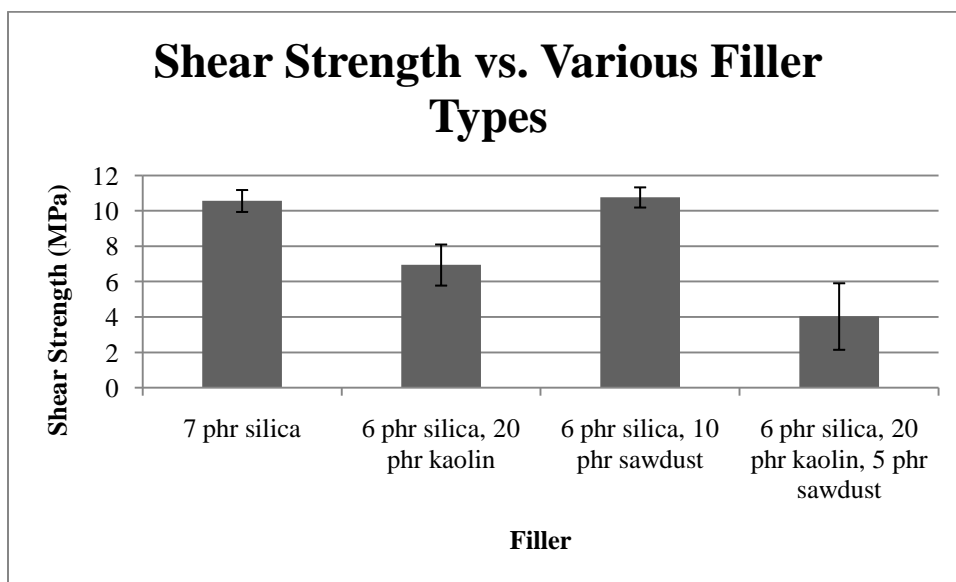
Figure 27. Shear strength vs. different combinations of fillers using 5 g 1/1 TMPEOTA and 5 g AA as the monomers.
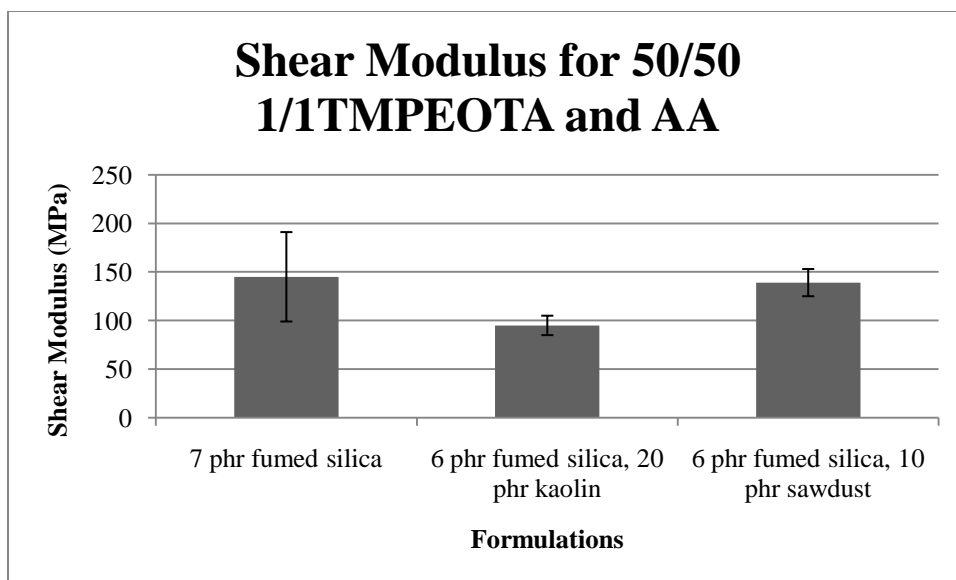
Figure 28 Relative shear modulus vs. different combinations of fillers using 5 g 1/1 TMPEOTA and 5 g AA as the monomers and 8 phr Luperox 231 as the initiator.

Most samples resulted in an adhesive failure. Therefore, the next idea tried was increasing the adhesive binding to the wood by modifying the surface of the wood. The method chosen for modifying the wood's surface was esterification. The esterification was tried on samples using both 1/1 TMPEOTA/AA and 7/3 TMPEOTA/AA as the monomers. A 1 g sulfuric acid/9 g AA solution was used to esterify the wood's surface. The 7/3 TMPEOTA/AA adhesives were tested. The first sample contained 7 phr fumed silica and 8 phr Luperox. No heat was applied to the wood after the acid was applied to the wood. The second sample contained 20 phr kaolin, and 8 phr Luperox. No heat was applied to this sample either. The second sample was tested again. The wood treated with the acid was left overnight before having the sample applied to it. The second sample was tested once more by using a heat gun to heat the wood at more than 200°C after it was treated with the acid. The results are shown in Figure 29. The 1/1 TMPEOTA/AA adhesives were tested next. The sample contained 7 phr fumed silica and 8 phr Luperox. The wood was heated at more than 200°C after it was treated with the acid. The sample was tested for a second time. This time the wood blocks were heated

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before and after they were pretreated with acid. The sample was tested again with a different

pretreat process. The wood blocks treated with the acid were heated at a lower temperature of

around 150-160°C. The results are shown in Figure 30. The esterification process did not

increase the mechanical properties of the adhesive. This is shown by comparing Figures 29 and

30 to Figures 25 and 27. The overall shear strength decreases as a result of the esterification

process.
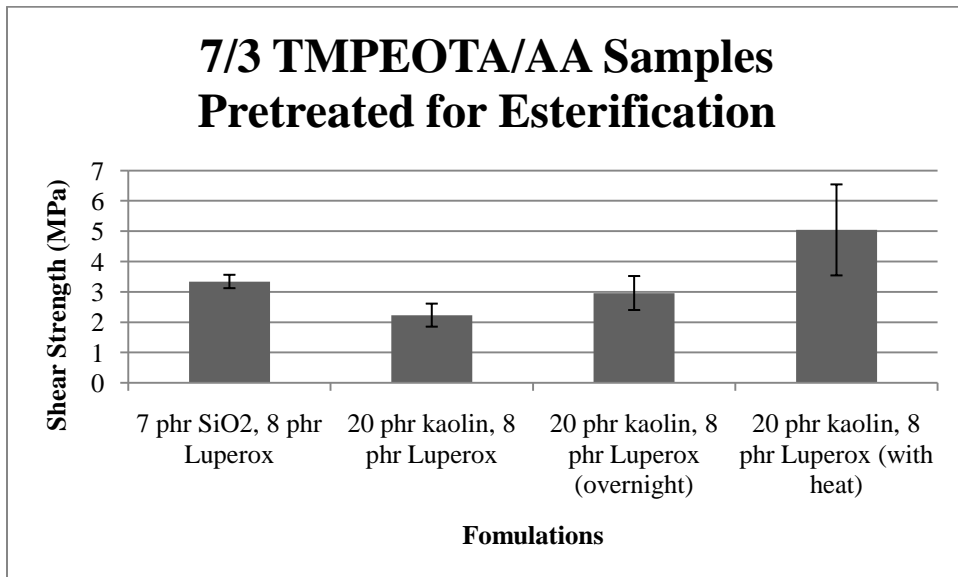
Figure 29. The shear strength results for 7/3 TMPEOTA based on various methods of using
sulfuric acid and AA to esterify the surface of the wood.
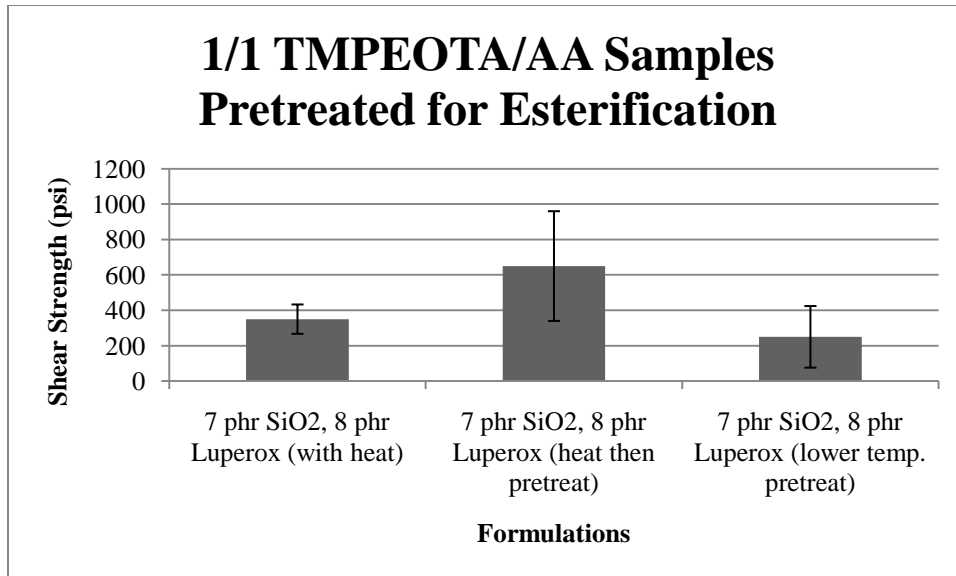
Figure 30 The shear strength results for 1/1 TMPEOTA based on various methods of using sulfuric acid and AA to esterify the surface of the wood.

Persulfate Initiator Results

New initiators were tried in place of the Luperox 231. When Luperox reacts it produces gas. The gas makes voids in the polymer. Those voids are locked in place since the front passes soon after the gas is released in that area. This makes the polymer very porous. These new initiators were used because they were described as gas-free initiators (Masere 2000 and Mariani 2008). The initiators tried for this were three persulfates, tricaprylmethylammonium (Aliquat) persulfate (APSO), tetrabutylphosphonium persulfate (TBPPS), and trihexyltetradecylphosphonium persulfate (TETDPPS). The TETDPPS and the APSO are liquids and made the adhesive less viscous. The TETDPPS and the APSO still produced many pores. Both TETDPPS and APSO contain the 10 g of TMPTA, 15 phr of kaolin, 7.5 phr of sawdust and 5 phr of fumed silica. 4 phr of TETDPPS was used in the adhesive and yielded a shear strength of 1.47 MPa (213 psi). The concentration of APSO in the other mixture was 5 phr, and the shear strength of the polymerized adhesive was 0.77 MPa (111 psi). Only one trial

was run of each. The TBPPS was a solid and reacted slower than the others, but it also reduced

the number of visible pores. The TBPPS results are shown in Figure 31.
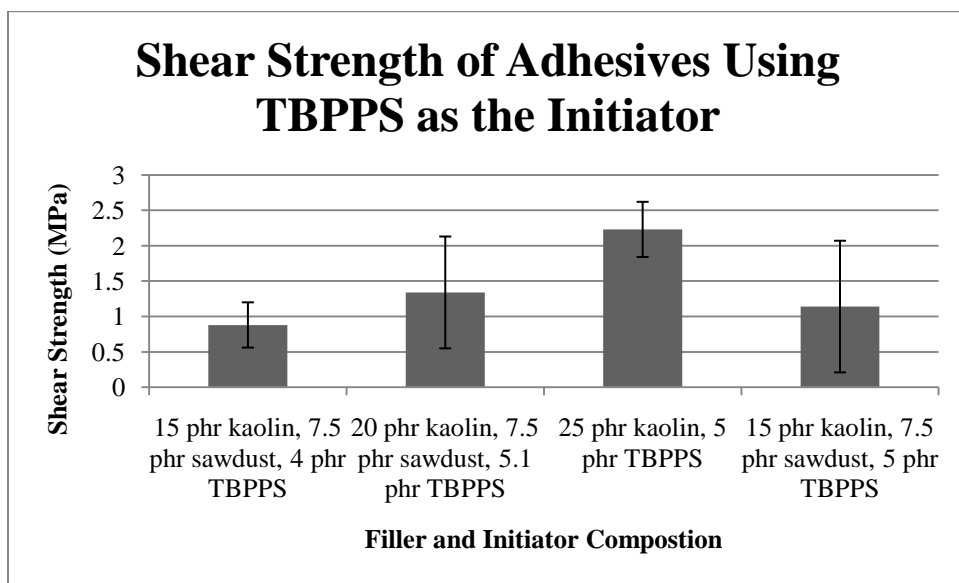
Figure 31. The graph depicts the shear strength of mixtures containing different filler
concentrations using TBPPS as the initiator.

Other Monomers, Additives, and Other Results

TMPTMA with 40 phr kaolin as filler was the first monomer tested. The Luperox 231

concentrations that were used for the different samples were 1, 2, 3, 4, 5, and 10 phr. PEGDMA

was the next monomer used. It was also used in samples containing 40 phr kaolin, and the

Luperox concentrations were 1, 2, 3, 4, and 5 phr. None of the TMPTMA or the PEGDMA

samples were reactive.

Zinc acrylate was the next component to be added into the adhesive. Ammonium

persulfate was used as the initiator. Both the acrylate and the initiator were dissolved in water.

All of the samples tested were too unreactive to support between two pieces of wood. They were

tested on the top of one piece of wood to see if they would react. The first sample used 3 g of

zinc acrylate along with 7 g of water, 0.3 phr fumed silica and 3 phr ammonium persulfate. The

sample would not react. The next also used 3 g zinc acrylate and 7 g of water, but this sample used 0.2 phr of fumed silica and 4 phr of ammonium persulfate. It also produced no reaction. The sample used 10 g of the zinc acrylate and 4.7 g of water with 2.04 phr fumed silica and 11.16 phr ammonium persulfate. The adhesive reacted very slowly. The next sample also used 10 g zinc acrylate, 4.7 g of water, and 11.16 ammonium persulfate, but used 3.06 phr fumed silica. It also reacted but only in a thick layer. All of the zinc acrylate-based adhesives had a very short pot life. They would self-initiate in 20 minutes.

The two monomers PETA and BPAEODA were tried in conjunction with one another. PETA was used with the BPAEODA because it is a tetraacrylate so it should be more reactive than the triacrylate. After that 7/3 TMPEOTA was coupled with the PETA to reduce the brittleness of the resulting polymer. PETA was then combined with TMPTA to make an adhesive stronger than TMPTA but not as brittle as PETA.

Table 9 Shear Strengths of Adhesives Using PETA and BPAEODA as the Monomers

	PETA	BPAEODA (g)	Kaolin (phr)	fumed silica (phr)	sawdust (phr)	Luperox (phr)	SS (MPa) ((psi))	STDEV (MPa)
TH 1.31.5	7.5	2.5	20	4	5	8.3	1.65 (239)	0.23
TH 1.31.6	7.5	2.5	20	4	5	5	1.25 (181)	1.16
Some samples were unreacted on the inside								
TH 1.31.7	7.5	2.5	20	4	5	6	1.43 (207)	0.28
Some samples were unreacted on the inside								
TH 1.31.8	10	0	20	4	5	5	0.77 (112)	0.27

Table 10 Shear Strengths of Adhesives Using PETA and 7/3 TMPEOTA as the Monomers

	PETA (g)	7/3 TMPEOTA (g)	kaolin (phr)	Cabosil (phr)	sawdust (phr)	Luperox (phr)	SS (MPa) (psi)	STDEV (MPa)

(Table 10 con'd.)

	PETA (g)	14/3 TMPEOTA (g)	kaolin (phr)	Cabosil (phr)	sawdust (phr)	Luperox (phr)	SS (psi)	STDEV (MPa)
TH 1.31.9	7.5	2.5	20	4	5	5	1.26 (183)	0.30
TH 1.31.11	7.5	2.5	20	4	7.5	5	1.12 (162)	0.19
TH 1.31.10	7.5	2.5	20	4	5	5	1.58 (229)	0.72

Table 11 Shear Strengths of Adhesives Using TMPTA and PETA as the Monomers

	TMPTA (g)	PETA (g)	Cabosil (phr)	kaolin (phr)	sawdust (phr)	Luperox (phr)	SS (psi)	STDEV (MPa)
TH 1.39.11*	7.5	2.5	5	15	5	5	105.41	26.16
TH 1.39.12	7.5	2.5	5	15	7.5	5	134.85	43.51
TH 1.39.13	7.5	2.5	5	20	5	5	95.53	9.73
TH 1.39.14	7.5	2.5	0	45	0	7	246.31	149.04

PEAOTA was then used as the monomer. The first sample used 10 g PEAOTA, 20 phr kaolin, 5 phr fumed silica, 7.5 phr sawdust, and 5 phr Luperox. The next sample used 10 g PEAOTA, 6 phr fumed silica, and 5 phr Luperox. The first sample did not react between wood and was slow to react in the open air. The second sample did not always completely react between wood. PEAOTA was then used in conjunction with TMPTA. Three samples were tried using PEAOTA. All samples contained 7.5 g TMPTA, 2.5 g PEAOTA, 5 phr fumed silica, 15 phr kaolin, and 7.5 phr of sawdust. The Luperox was varied between the samples with one having a Luperox concentration of 5 phr, another one having a concentration 6 phr, and another one having a concentration of 10 phr. The results for the PEAOTA and TMPTA samples are shown in Figure 31. PEAOTA made the polymer crack as it was formed. The product was a translucent polymer that was smooth and rigid.

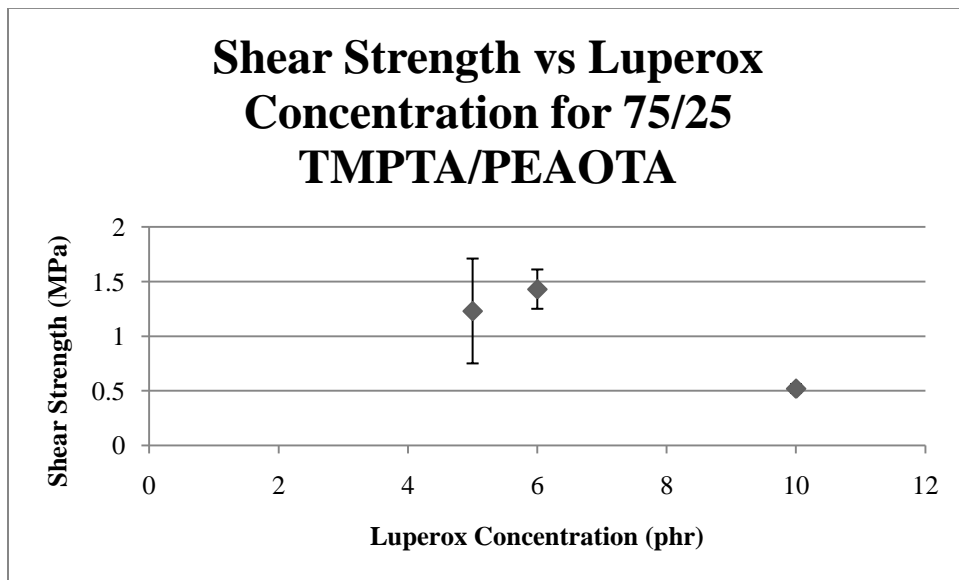**Figure 32**. Shear strength vs. Luperox 231 concentration using 7.5 g TMPTA, 2.5 g PEAOTA, 7.5 phr sawdust, 15 phr kaolin, and 5 phr fumed silica.

PETA was then used as the sole monomer in the adhesive. All of the samples contain 10 g of PETA, 20 phr kaolin, 5 phr fumed silica, and 7.5 phr pine sawdust. The samples were varied by the amount of Luperox added. The concentrations were 5, 4.5, 4, 3, 2, and 1 phr

Luperox. The results are shown in Figure 33. The 1 phr Luperox mixture did not completely react.
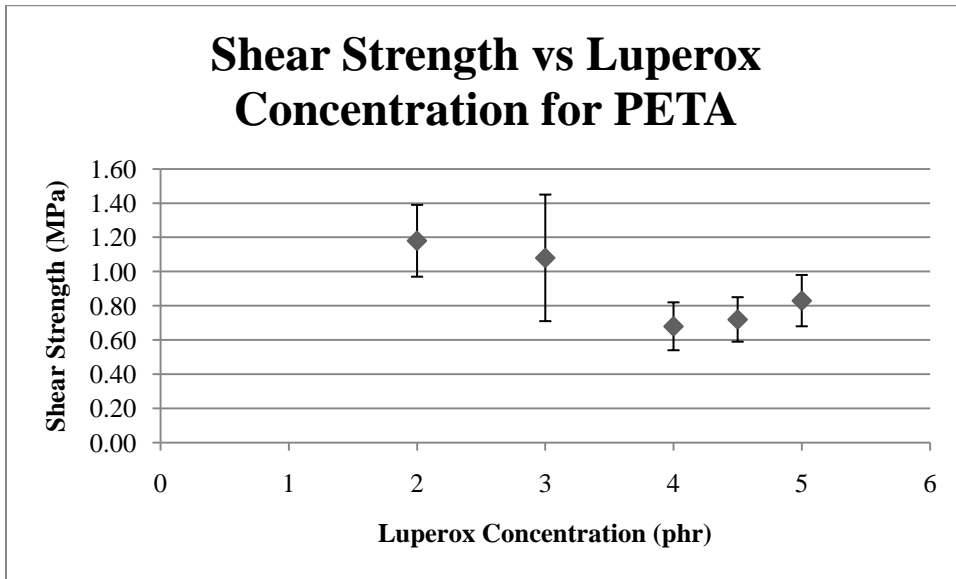
Figure 33 Shear Strength vs. Luperox concentration using PETA as the monomer and sawdust and fumed silica as the filler.

Ethylenediamine (EDA) was added to the monomer mixture as an accelerator. The objective was to speed up the reaction and enable a secondary polymerization to occur if FP did not complete cure the adhesive. In the initial trial 5 phr EDA was added to a 10 g TMPTA, 5 phr fumed silica, 15 phr kaolin, 7.5 phr sawdust, and 5 phr Luperox mixture. The mixture's polymerization started as soon as the EDA was added. Next the sample's Luperox 231 concentration was changed to 8.1 phr and the EDA concentration to 0.5 phr. The shear strength was measured at 1.66 MPa (241 psi). The Luperox 231 concentration was held constant at 5 phr for the next three samples. The amount of EDA used decreased for each sample. The sample with a concentration of 1 phr EDA had a shear strength of 2.16 MPa (313 psi). The sample with an EDA concentration of 0.7 phr had a shear strength of 1.03 MPa (150 psi). The 0.6 phr EDA concentration sample's shear strength was 2.36 MPa (343 psi).

A sample made from 10 g TMPTA, 6 phr fumed silica, 10 phr kaolin, and 5 phr Luperox was applied in a thin layer on the top of a piece of wood. The reaction was initiated by a soldering iron like other experiments. The front would only propagate through the light regions of the wood. It would not propagate in the darker regions, but if the dark region was narrow, it would polymerize over to the lighter region of the other side. Figure 34 shows this problem. This comes from the differences in the thermal conductivity between the lighter (earlywood) regions and the darker (latewood) regions of the wood. The denser wood had a higher thermal conductivity. This is a binding problem for the adhesive.

Figure 34 The wood that was used in a thin layer test. The lighter areas were able to support a front while the darker areas were not. The layer of adhesive applied was thin enough to make out the different regions in the wood.

SUMMARY AND CONCLUSIONS

The frontally-cured adhesives created strong bonds with wood. The adhesive composed of a 50/50 blend of 1/1 TMPEOTA and AA yielded the greatest shear strength. Both samples, one containing only fumed silica and one containing fumed silica and sawdust, produced shear strengths of over 10.3 MPa (1500 psi). This was about 3.5 times stronger than the best TMPTA formulation. By changing the 1/1 TMPEOTA with either the 7/3 TMPEOTA or the 14/3 TMPEOTA, the toughness of the polymer increased but the shear strength decreased. These adhesives also contained samples that broke the adherend. TMPEOTA/AA can be used as a cure-on demand adhesive with high shear strength and a high toughness. The TMPTA combinations were too brittle. Even with the addition of diacrylates added to the TMPTA, the resulting polymer had no significant change in its toughness.

Fillers affect the properties of the cured adhesive. Fumed silica was used to thicken the monomer mixture because of its ability to form a network via hydrogen bonding with the monomer. The kaolin, sawdust and alumina trihydrate (ATH) made the resulting polymer stronger. SEBS and SBS made the resulting polymer tougher. 14/3 TMPEOTA and the high concentrations of SEBS enabled the polymer to be tough enough to withstand the deformation that occurs when the wood swells in water. However, if too much filler was added to the monomer mixture, it would not sustain a front.

The darker regions of the pine wood would not support a front. The trend was also observed in other dense woods like oak. In a thin layer, it is easy to observe this trend. The reason is that the denser wood has a higher thermal conductivity. This is one of the problems that are inhibiting better adhesive binding. In future works it may be able to overcome this by adding an exothermic reaction in conjunction with the FP. This could possibly heat up the

darker regions of the wood, and allow the FP to take place in that region. The reaction could also be used to improve the adhesive bonding to the wood.

The thermal conductivity problems lead to adhesion problem. Surface modifications was tried to correct this problem. Esterification, using and combination of sulfuric acid and acrylic acid, was used to pretreat the wood. The esterification did not increase the wood binding to the adhesive. Instead, the process used cause the adhesive to be weaker and to bind weakly to the wood. The process also discolored the wood. The use of a different surface modification technique or a better esterification technique may yield better results.

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