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Development Of A High Strength Laminate Repair System

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DEVELOPMENT OF A HIGH STRENGTH LAMINATE REPAIR SYSTEM

by

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Bachelor of Science in Chemical Engineering
University of Minnesota Duluth, 2009

A Thesis

Submitted to the Graduate Faculty

of the

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in partial fulfillment of the requirements

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Master of Science

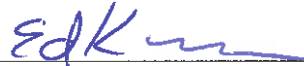Grand Forks, North Dakota
August
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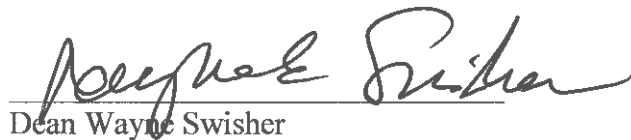
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This thesis meets the standards for appearance, conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

Dean Wayne Swisher

August 1, 2012

Date

Title   Development of a High Strength Laminate Repair System

Department   Chemical Engineering

Degree   Master of Science

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Andrew Onken

July 26, 2012

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ABSTRACT

Composite manufacturing often requires repairs at some point during the life of the part. Working with LM Wind Power, the Chemical and Mechanical Engineering Departments at the University of North Dakota worked to develop a new laminate repair system to be used in composite repairs. Both chemical and mechanical test methods were explored to analyze various resins in an attempt to increase the interface toughness between the parent laminate and repair laminate. A total of six resins from four suppliers were tested. Differential scanning calorimetry and dynamic mechanical rheological testing were performed to analyze the curing kinetics of each resin tested. Static double cantilever beam and tension-tension fatigue tests were performed to measure the mechanical performance of each resin. All specimens were prepared to mimic that of a large-scale wind turbine blade. Each resin tested was compared to the current repair resin system to determine which choice was best to meet the requirements set for by LM Wind Power for repair laminate improvement. The results indicated that toughened resin performance is superior to that of the current resin system.

Along with the analysis of new repair resins, an initiator study was performed. The initiator study was done on the blade resin used for vacuum assisted resin transfer molding (VARTM). Four initiators were tested and compared to the current initiator. Methods included differential scanning calorimetry and rheology. The goal with testing these initiators was to see if changing the initiator would increase the working time while

decreasing the overall curing time. To achieve this, the initial viscosity of the resin needed to remain low to ensure a full wet out of the part and once wet out was complete a sharp increase in viscosity would indicate a fast cure. Of the initiators tested, Pulcat from Syrgis Performance Initiators performed better than the others. However, without testing it in production, it is unclear whether or not it is superior to the current initiator MCP-75.

CHAPTER I

INTRODUCTION

The work performed for this thesis was the result of a new relationship between the University of North Dakota and LM Wind Power. In an effort to bring academic excellence and industrial practicality together, UND and LM Wind Power joined efforts to improve repair methods for composite wind turbine blades. Specifically, LM wanted to research and implement methods to reduce the cost of performing repairs while maintaining the integrity of their blades. Cost reduction can be achieved by reducing the labor involved to make a repair to a blade. In other words, reducing the amount of time it takes for a repair to be applied and cured reduces costs. Other ways to reduce costs are material selection and reduction of material usage. Choosing materials that perform better than others may mean that less material is needed to meet the same design specifications. Note that choosing a better material may cost more for the material per unit, but may also be more economical than using more of a cheaper material. Together, LM Wind Power and the University of North Dakota researched materials that could be suitable to improve repair methods on composite wind turbine blades.

LM Wind Power is the leading supplier of blades for wind turbines. The only supplier that operates on a global basis, LM has produced over 140,000 blades since 1978. LM not only does research with universities, but also internally and with their material suppliers. A collaborative research effort with these groups has allowed LM to

gain extensive knowledge about composites and turbine blade manufacturing resulting in technologies that build more efficient and longer lasting wind turbines [1]. To improve their knowledge base and remain one of the leading manufacturers of wind turbine blades, LM decided to work with the University of North Dakota on a research project to develop and implement a new repair resin for use in blade production.

LM Wind Power needs to make repairs to their blades for a variety of reasons. Some of these reasons include design flaws that create weak spots in blades that require repairs before shipment of the blades. Other reasons repairs are needed can be due to environmental impurities during manufacturing. For example, if particles such as dust or debris contaminate the blade prior to infusion, resin may not bond well or flow evenly, creating areas of the composite that are referred to as either fiber-rich or resin-rich areas. During composites manufacturing, it is desirable to achieve a fiber-to-resin ratio called the fiber weight fraction that is set by the mechanics and design of composites. These fiber-rich areas are often referred to as dry glass. During the infusion process, the resin flow across glass reinforcement is called wetting. Thus the term dry glass comes from the glass fiber-rich regions not getting wetted out to the desired ratio. LM has explained that they have issues during infusion and they will get areas of dry glass that require repairs. LM uses nondestructive thermal imaging to detect areas requiring repairs.

Per LM's requirements, both the Chemical Engineering and Mechanical Engineering Departments at the University of North Dakota were charged with the task of developing a resin system for laminate repairs in order to complete three tasks: 1) improve the interface toughness between fully cured repair laminates and blade laminates; 2) decrease the curing time of repair laminates; and 3) reduce the scarf ratio

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required for laminate repair. The projected outcomes included reduced cost of poor quality as defined by LM Wind Power by 25%, reduced scarf ratio resulting in reduced labor, and overall increased integrity of each blade. This means that wind turbine blades produced by LM Wind Power will require fewer in field repairs and any costs associated with other repairs will require less time and money. In order to reach the goals as defined by LM Wind Power, it was required that baseline testing of the current repair resin be conducted and followed by a study to determine a system that would increase the interface toughness, or the amount of energy required to crack the bond between the repair laminate and main blade, by three times.

Although the current method works for LM, in attempt to reduce costs and improve quality, two hypotheses were developed to reach the goals defined by LM. The first was the use of high styrene resin would soften the cured blade laminate during repairs and result in increased interface toughness between the blade and repair laminates. The theory with this hypothesis was that a higher concentration of solvent used for the polymer would increase absorption of the repair resin into the parent laminate. This hypothesis was chosen because styrene is the solvent used that keeps the polyester or vinyl ester resin in solution until the polymerization reaction is initiated. The second method was the use of toughened resins for repair methods will increase the interface toughness between the laminates. Using said hypotheses, various resins were explored and tested for the discovery of a new repair resin system for LM Wind Power. After a brief overview of the background of composites, geared towards fiber reinforced plastics, the methods used for characterizing and analyzing materials for improving repair laminate technology are discussed. These methods include differential scanning

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calorimetry, rheology, and mechanical testing. As the reader continues, data and analysis are presented for various resins tested for the LM Wind Power repair resin project. Using these methods, resins were either accepted or rejected for the hypotheses and use by LM for a new repair system.

Along with the exploration of repair systems, a side project was performed exploring the effects of different initiators on the blade resin. This project was a spin-off of the repair resin project. The hypothesis was that choosing a better initiator for the blade resin will improve the infusion process of blade production and reduce the amount of repairs required during manufacturing. This study used the same techniques as the repair resin project other than mechanical testing. Using differential scanning calorimetry and rheology, various initiators including methyl ethyl ketone peroxide, cumyl hydroperoxide, acetyl acetone peroxide, and blends of these were explored to help improve blade infusion. The end goal of exploring both the new repair resins and initiators for blades was to improve LM's repair methods and increase cost savings.

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CHAPTER II

BACKGROUND

Composites are two or more materials that together provide superior properties for desired applications. Composites have been used dating back to biblical times in ancient Egypt where straw reinforced clay bricks were used [2]. During this early stage in history these composites were primitive compared to the technology used presently. As technology progressed through history, fiberglass composites and steel reinforced structure became more and more common. During the 19th century masons used iron rods as reinforcements which lead to steel reinforced concrete commonly used in road construction. In 1935 Owens Corning invented fiber reinforced plastics using glass fibers and polymer matrix commonly referred as fiberglass [3]. The use of this technology lead to the applications of composites to industries including marine, aerospace, automotive, sporting goods, biomedical and many other applications.

Common composites include concrete and fiber reinforced plastics (FRP). FRPs have a wide variety of uses, and have been used for products such as window frames, boats, snowboards, and airplanes. Composites have even been used in the sporting goods industry. For example, most hockey sticks used are either one piece graphite composite sticks or a two part graphite composite shaft and blade. The aerospace industry has been able to utilize composite materials for the manufacturing of airplanes. Cirrus Design

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based out of Duluth, Minnesota manufactures complete airplanes using carbon fiber and glass fiber reinforced polymer matrix composites. These are some of the most advanced personal aircraft built today. Other uses have included government aircraft including the B-2 Stealth Bomber [4] and automotive uses. Generally composites have been used and can be used for just about anything the mind desires. The wind industry has been able to utilize the benefits of composites for the manufacturing of blades with the large benefit coming from the strength to weight ratio that can be achieved using composite materials. Due to the properties of composites, they can be built to sustain forces equal to a part made out of metal, but have far less mass. This superior property comes from reinforcement, and matrix material selection.

Often times composites manufacturers are looking for the best materials to give the highest strengths with the lowest weights. This is especially true in the aerospace industry for the manufacturing of airplanes and airplane parts. To obtain this high strength to weight ratio, the aerospace industry typically uses carbon reinforcement fibers with an epoxy matrix in what is called a prepreg. A prepreg is a composite material that is pre-impregnated with semi-cured epoxy resin. Prepregs are great for producing very consistent parts but require a heating cycle at elevated temperatures to fully cure the part. These materials and methods would be considered the top end of composites manufacturing. Other common reinforcement materials include glass fibers and aramid fibers while matrix materials include epoxies, vinyl esters, acrylics, and unsaturated polyesters. The matrix material is the glue that holds the composite together. Beginning in a liquid form and then going to solid form, the matrix binds the reinforcement together and maintains the shape of the composite part. The cheapest of these materials are glass

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fiber reinforcements and unsaturated polyester resins. Occasionally a metal matrix composite may be used but this is uncommon and not applicable to the wind industry. Metal matrix composites are usually seen in industrial electrical transmission and use aluminum as the matrix material.

LM Wind Power uses composites technology to manufacture wind turbine blades. Like all composites manufacturers, LM uses this technology to achieve high strength to weight ratios. Since wind turbine blades are exposed to the elements, these blades need to withstand average wind speeds of about 10 miles per hour over a 20 year period [5]. At these continuously high wind speeds, tremendous amounts of force are applied to the blades. Thus, LM requires high strength but wishes for low weight since each blade is suspended approximately 300 feet up. Another reason low weight is desirable is that any friction created during the rotation of the turbine is generally lost energy in the form of heat. Lower blade weight results in lower amounts of energy lost due to friction and thus create a more efficient wind turbine.

Like most materials, composites break or degrade and require repairs eventually. Fiber reinforced plastic composites are built using a polymer matrix. Because wind turbine blades are exposed to the elements continuously, degradation to polymer composites usually is from exposure to sunlight and/or moisture. To prevent degradation, wind turbine blades are manufactured with a gel coat, or a protective layer, encasing the main structure of the composite. The purpose of this gel coat is to protect the composite from elements that cause degradation.   The gel coat is another polymer made of acrylic. It will usually contain polymer additives such as TiO_2 to prevent ultraviolet penetration to the main composite blade. The gel coat is also non-porous for reduction of the diffusion

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of nature's elements that can potentially cause damage to the main composite blade. Composite wind turbine blades also degrade over time due to prolonged fatigue stresses.

The wind applies force to each turbine blade which creates spinning motion of the turbine. This applied force is semi-continuous and thus blades experience fatigue stresses that, with time, reduce the strength of a turbine blade. Since wind turbine blades are exposed to various methods of degradation, they often times require repairs to reinforce the strength of the each blade. Because these repairs are performed in the field, it was essential to explore thixotropic resin systems, resins that have high viscosities that reduce flow unless a shear stress is applied, thus allowing for vertical application of repairs. Other reasons blades may need repairs can include other exposure to the elements. For example they may have hail damage or wind damage that resulted from a severe storm. They may also need repairs before departure from manufacturing. These repairs result from human error, design flaws, and environmental contaminates during production.

Resins

Thermoset resins are plastics that once cured cannot be melted and/or recycled. For the case of composite wind turbine blades, crosslinked thermosetting resins are used in the manufacturing of fiber reinforced plastic composites. Orthophthalic unsaturated polyester resins are commonly used during blade production. Composite repairs are necessary for various reasons. Some of these reasons include inherent flaws from blade design, stress concentrations, ply delamination, and other flaws.

Currently, LM Wind Power uses an orthophthalic unsaturated polyester resin, similar to that of their blade resin, for repair methods. This resin (GT80) is described by the supplier as being designed for hand layup applications with improved toughness

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relative to that of other general purpose polyester resins [6]. In general, orthophthalic

UPE resins are formed through the condensation reaction of maleic anhydride (MA),

phthalic anhydride (PA), and propylene glycol (PG). These monomers begin in solution

using styrene monomer as the solvent. Once initiated using organic peroxide, usually

MEKP, the styrene monomer becomes the crosslinking agent resulting in a three

dimensional crosslinked polymer network. Figure 1 shows the chemical structure of each

of these monomers. The product of this condensation reaction is an unsaturated polyester

alkyd, a generic chemical structure of which is shown in Figure 2
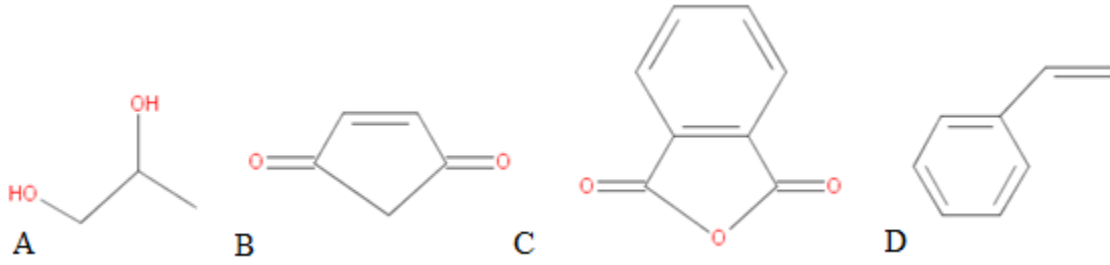
Figure 1: Monomeric components of an unsaturated polyester resin: a) propylene glycol (PG), b) maleic anhydride (MA), c) phthalic anhydride (PA), and d) styrene. [7]
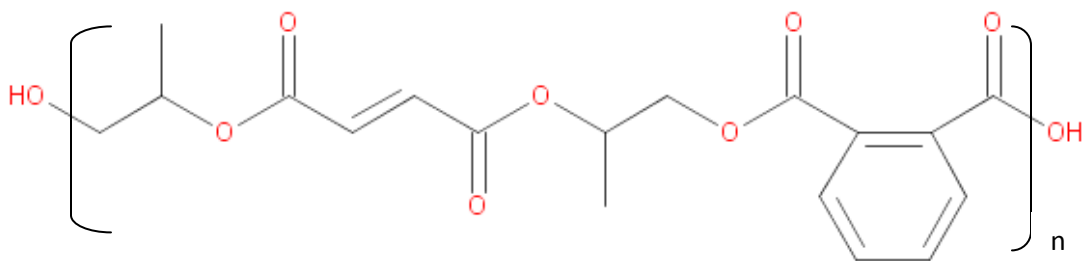
Figure 2: Generic chemical structure of the alkyd backbone of an orthophthalic unsaturated polyester resin. [7]

Typically, a large fraction of the MA isomerizes during the polymerization to form a fumerate unit, which has a "trans" configuration. This is normally advantageous, as the fumerate unit is much more reactive than the maleate, or "cis", isomer. The unsaturated polyester alkyd is then diluted with styrene and other additives (promoters, thixotropic agents, tougheners, etc.) to produce the final resin. Curing of the resin takes place through the reaction of the unsaturated double bonds of the MA units and styrene. During this reaction, the addition of MEKP and cobalt ions along with styrene monomer produces a styrene radical. The styrene radical then attacks the carbon – carbon double bonds present in the unsaturated polyester alkyd. As diffusion of radicals progress, a crosslinked polyester network is formed resulting in a cured thermoset plastic. Figure 3 shows the mechanism during the cure of unsaturated polyester resin.
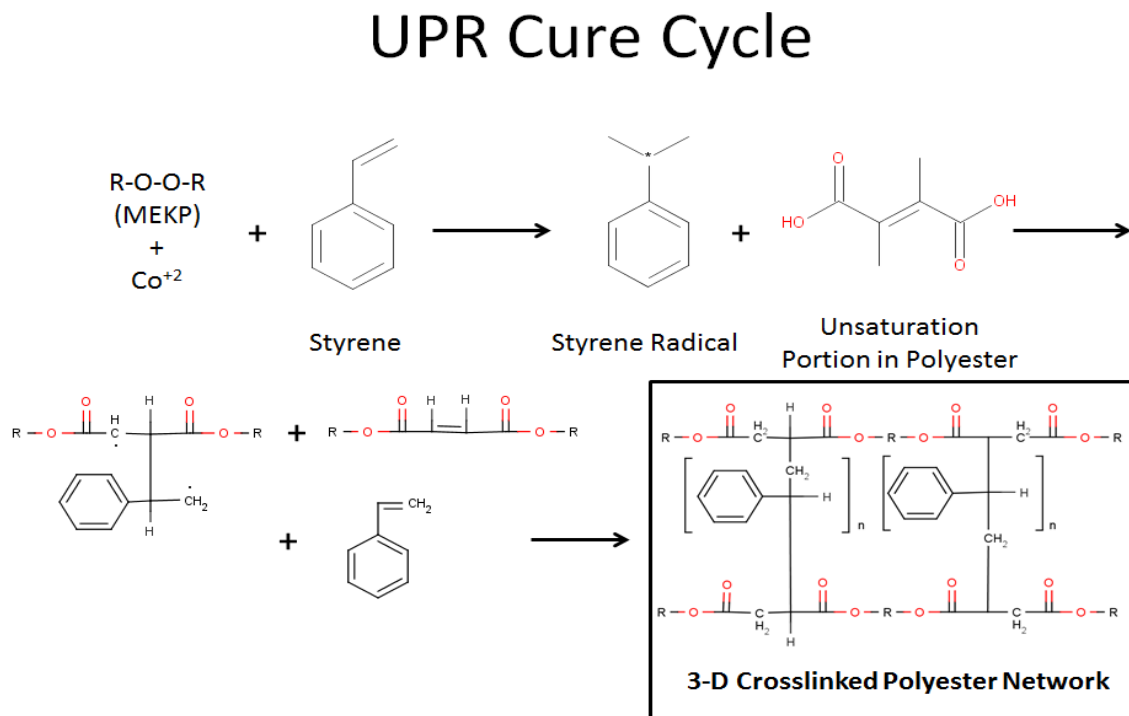
Figure 3: Reaction mechanism for an unsaturated polyester resin cure. [8]

Per LM's requirement, resin selection was done assuming that each resin was available globally and meets the health, environmental, and safety regulations for which LM manufactures blades. The new resins tested were selected based on this requirement and included low styrene vinyl esters, high styrene vinyl ester, and three rubber modified toughened vinyl esters. In general, vinyl ester and toughened resins display superior properties relative to unsaturated polyester resins. This is due to the epoxy backbone that makes up the vinyl ester structure. Vinyl esters are commonly produced by esterifying a diepoxide with methacrylic acid forming an unsaturated terminal bond. The presence of the unsaturated bond allows vinyl ester resins to be highly reactive and allows for a crosslinked polymer network. Fewer ester linkages mean that vinyl esters are less susceptible to degradation. The double bond of an ester linkage is less stable than single bonds and therefore is more likely to react undesirably or degrade [7]. Figure 7 shows a general reaction mechanism for producing vinyl ester resin. Similar to Figure 6, the carbon-carbon double bonds are attacked by styrene radicals creating a crosslinked polymer network.

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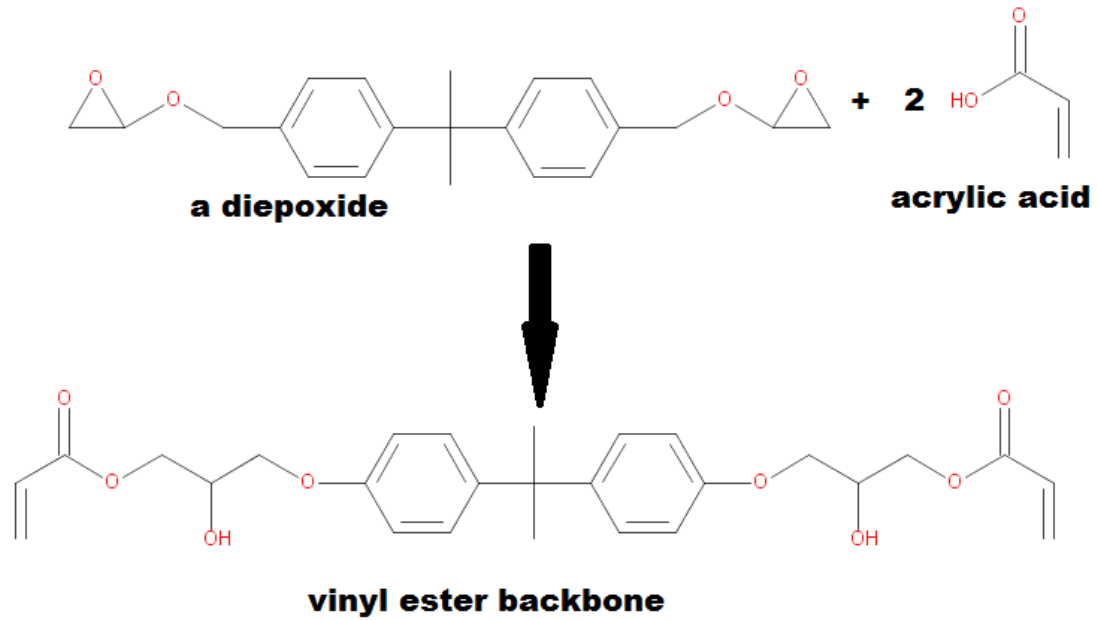
Figure 4: Reaction scheme for vinyl ester production [9]

Toughened resins are also viable selections for improving fracture toughness of repair laminates. Toughened resins are typically vinyl esters with toughening additives. The additive is generally a material that retains its shape after force is applied, or an elastomer. Since fracture occurs in the path of least resistance, toughening agents absorb fracture energy and divert fracture along various pathways. Thus, the amount of energy required to fracture a toughened resin increases. Using this type of resin can improve performance without affecting the cure of the resin. Figure 5 depicts how the flow of energy should propagate with a CSR resin matrix compared to an unobstructed flow in a normal resin as shown in Figure 6. As can be shown from the illustrations, the core shell particles deflect the energy flow thus increasing the amount of energy required for crack propagation through the resin. Whereas in Figure 6, the energy flow is a straight line meaning less energy is required for crack propagation. Another possible mechanism that

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CSR particles could use to increase fracture energy could be energy conversion from potential to thermal energy, where the CSR particles absorb any crack energy rather than deflecting it.
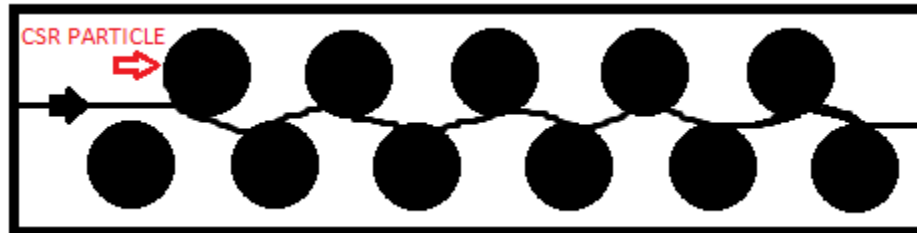
Figure 5: Energy flow through resin with core shell rubber additive
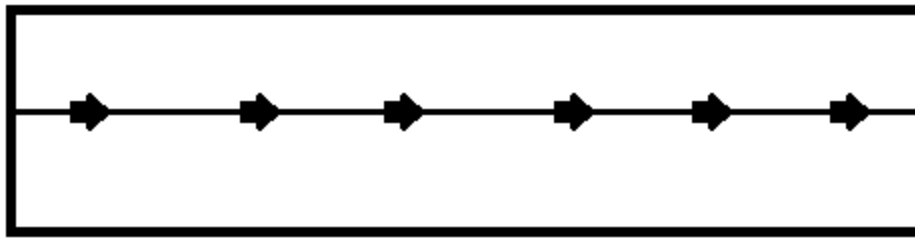
Figure 6: Energy flow through resin without core shell rubber additive

Understanding of the chemical characteristics of each resin type allow for better decision making when choosing resins for testing. Knowing that vinyl esters are inherently tougher than polyester suggests that vinyl ester alone will meet the requirements set for improvements on repair laminates. However, for this study both vinyl ester and toughened vinyl esters were tested to broaden the spectrum of results.

<div align="center">

Reinforcements

</div>

There are several commonly used reinforcements used in composite materials. Concrete, for example, is inherently a composite. The reinforcement is present in the form of pebbles and stones dispersed throughout the mixture before it hardens. Once

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concrete hardens, the pebbles and stones are distributed throughout the matrix as reinforcement. It is also common for concrete roadways to use steel rods as reinforcement. These rods, called rebar, are positioned through the concrete matrix to help carry the load of traffic. Thus reinforcement adds strength and increases the lifetime of the road while decreasing the amount of cracks and potholes that occur. In the case of fiber reinforced polymer composites, a variety of materials, and their orientation can be used to design the composite part. Depending on the use of the part, including the cost, the reinforcements can be more or less ridged Table 1 lists some of these materials and their advantages and disadvantages.

Table 1: Advantages and disadvantages of reinforcing fibers [4]

Fiber	Advantages	Disadvantages
E-glass, S-glass	High Strength Low cost	Low Stiffness Short fatigue life High temperature sensitivity
Aramid	High tensile strength Low density	Low compressive strength High moisture absorption
Boron	High stiffness High compressive strength	High cost
Carbon	High strength High stiffness	Moderately high cost
Graphite	Very high stiffness	Low strength High cost
Ceramic	High stiffness High use temperature	Low strength High cost

Along with the various types of materials available, fibers may be arranged in different orientations. These orientations include chopped fibers, chopped strand mats, woven fibers, continuous fibers, semi-continuous fibers, and many other orientations. For the purposes of manufacturing wind turbine blades, a combination of continuous

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unidirectional fibers, chopped strand mats, and biaxial mats are used. For the case of LM, the continuous fibers are backed with chopped strands and are called "combi." Continuous unidirectional fibers run the length of the part without any breaks and all the fibers are oriented in the same direction. Chopped strand mats are shorter fibers that are dispersed evenly in random directions through the part. Biaxial mats have fibers that are woven and oriented perpendicular to each other. LM uses this combination of glass fibers because through the design of their blades, these fiber orientations and materials meet the needs of the design and are cost effective. Each orientation is used to give the manufactured blade the required strength in both the latitudinal and longitudinal directions. Figure 7 below shows some of the various fiber orientations used in composites manufacturing.

Fiber Orientations for Fiber Reinforced Composites

Discontinuous Alligned

Chopped Strand Mat

Continuous Alligned
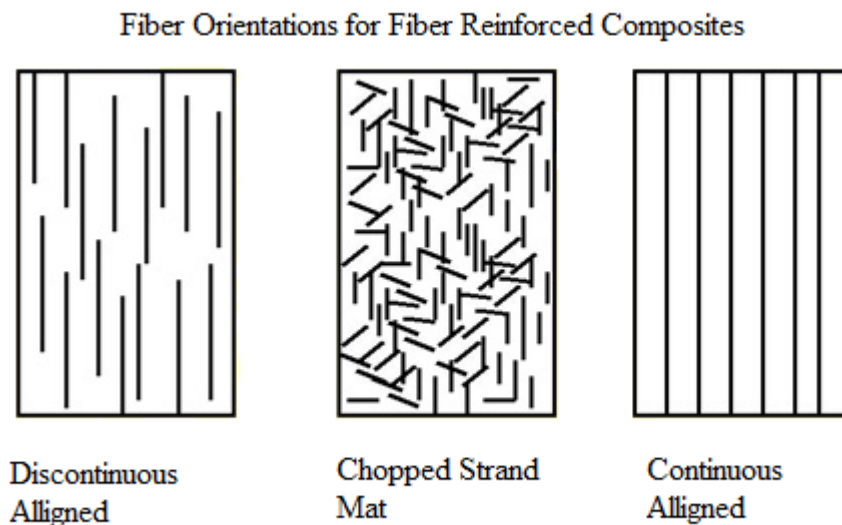
Figure 7: Examples of various fiber orientations [10]

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There are various types of repair methods commonly used in industry and include patch, scarf, and step repairs. Each of these methods has advantages and disadvantages. Table 1 describes the common methods and their advantages and disadvantages.

Table 2: Advantages and Disadvantages of repair methods [11]

Repair Method	Advantages	Disadvantages
Patch	-Quick and simple -Requires minimum preparation	-Adds thickness and weight -Especially good surface treatment required
Scarf	-Marginally thickness added -Each repair ply overlaps the ply that it is repairing giving straighter, stronger load paths -Goods bonds achieved from freshly exposed surfaces	-Time consuming -High skill needed
Step	-Same as scarf	-Extremely and most difficult to perform

Patch repairs are easy to do, but add mass to the part when repaired. Step repairs are often challenging because it takes a highly skilled individual to prepare the main laminate for repair application [11]. Scarf repairs are beneficial because they don't add much weight, each ply overlaps the ply it is repairing giving straighter, stronger load paths, and freshly exposed material allows for greater adhesion between the repair and main laminates. Like the step repair, scarf repairs are difficult and require high levels of skill, but not to the extremes as in a step repair. Figures 8, 9, and 10 show these methods respectively [11].

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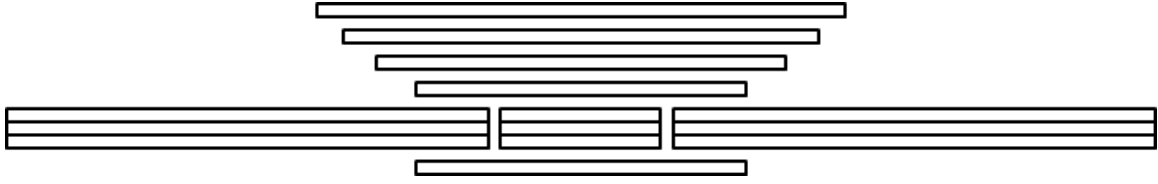
Figure 8: Composite Patch Repair [11]
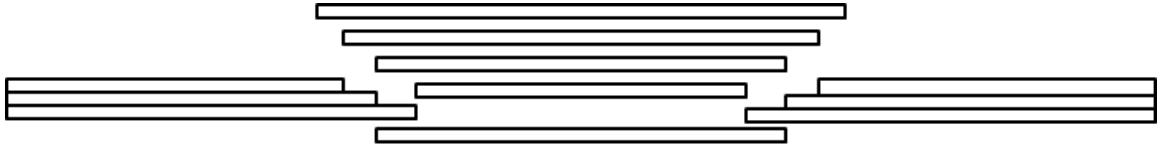
Figure 9: Composite Step Repair [11]
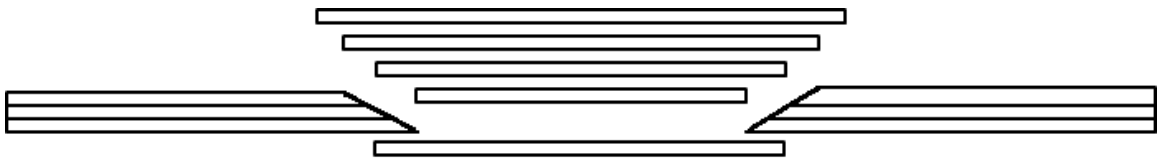
Figure 10: Composite Scarf Repair [11]

LM Wind Power uses the scarf method for structural repairs on wind turbine blades. Because the step repair is extremely difficult to perform, the scarf repair is often the choice of composite manufacturers. Using the scarf method exposes fresh material for boding between the main laminate and the repair laminate. Since the quality of the repair is directly related to how well bonded it is to the parent laminate, resin selection can be an important factor when performing repairs. The type of resin used can help to increase the bond strength of a repair. Increasing the bond strength between the repair and the parent laminate allows for steeper scarf ratios, or the degree of taper, to be used. Reducing the scarf ratio greatly reduces the amount of labor required for repairs and

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results in cost savings. It was hypothesized that using the method of grinding that exposed fibers would increase the interface toughness between the parent laminate and the repair laminate. Because of this both methods were tested using the resin only bond as a baseline test to compare the half ground method to.

Analytical Techniques

The methods used for analyzing new repair resins utilized two primary polymer science analytical tools; differential scanning calorimetry and rheology. Differential scanning calorimetry (DSC) is a thermal analysis tool that measures the heat flow of a sample compared to a control sample. When using thermoset resins, the polymerization undergoes an exothermic reaction releasing heat energy. DSC measures the amount of heat that is given off during this reaction over a given time period during an isothermal DSC scan. Similarly, DSC machines can add known amounts of heat to measure any heat flow from chemical reactions during dynamic DSC scans. Using isothermal scans along with dynamic scans allows for measuring the degree of cure of a thermoset resin.

Rheology is another tool for measuring the properties of thermoset resins. For the case of thermoset resins, dynamic oscillatory time sweep tests measure the viscoelastic behavior of the polymer as it cures. All polymers experience both visco, meaning fluid like, and elastic, meaning solid like behavior. Viscoelastic behavior of polymers can be broken into two sections, the storage modulus, and loss modulus. The storage modulus, G', is the measurement of how well the sample stores heat energy and in phase response. This parameter indicates how solid like a polymer is. The loss modulus, G'', is the measurement of how well the sample dissipates heat energy and out of phase response, or

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how liquid like the polymer is. Figure 11 depicts the behavior of an arbitrary thermoset

during a rheological test.
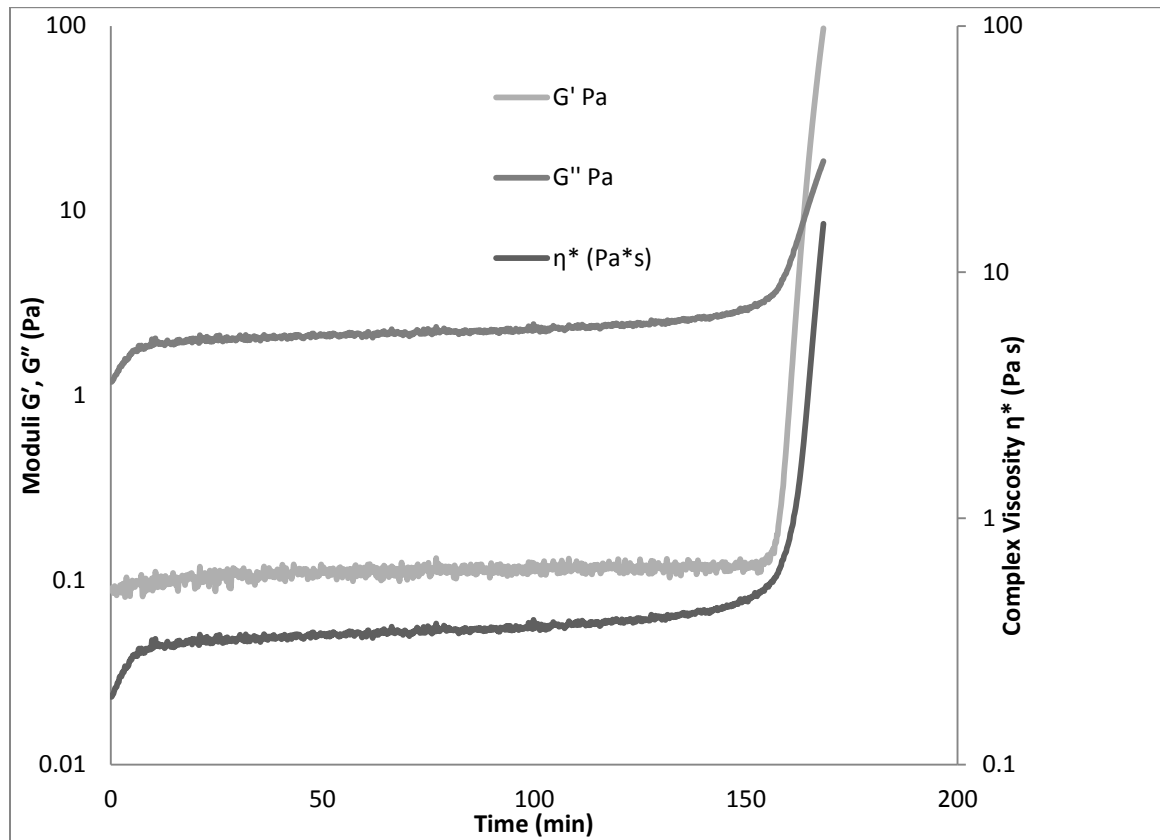
Figure 11: Example of Storage and Loss Modulus for a thermoset plastic

During the cure of a thermoset resin, these two parameters can be measured to

approximate a gel time. During the initial stages of curing, resins display liquid like

properties and G″ is a dominating parameter. Over time the resin becomes highly

crosslinked from styrene radicals reacting with unsaturated carbon-carbon double bonds

and growth of polymer chains. Thus, the storage modulus (G′) increases and eventually

crosses the loss modulus (G″) indicating that the polymer has become more solid like.

The crossover point of G′ and G″ indicate an approximate gel point of the resin [12].

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Once a resin has reached its gel point, the polymer has reached essentially infinite molecular weight and no longer flows with fluidity.

Resins can be characterized by coupling the data from both DSC and rheology. During composite manufacturing the working time, or the amount of time needed to complete the part layup, is an essential parameter needed to optimize the time need to manufacture a part. Large composites manufacturers such as LM Wind Power want to minimize the time it takes to make a part. Understanding of the rheology of the resin during the cure allows them better judgment of the cost of manufacturing. Without the DSC data however, only the working time can be evaluated. In other words, the amount of time a manufacturer has for production is related to the rheological behavior of the resin system. In order to maximize production, a blade mold needs to be infused with resin quickly without reaching the gel point of the resin prior to wet-out. Using rheology, a viscosity profile can be generated to define the resins working time. Using information from DSC with rheology allows for an even more detailed picture of cost of manufacturing. Knowing how long it takes for a resin to reach a certain degree of cure means the composites manufacturer knows how long they need before they can ship the part. In general, using a resin that meets the required properties with rheology doesn't mean it is a good resin choice if DSC shows that this particular resin will not reach a 95% degree of cure within a day's time.

Mechanics

Not only are the chemical characteristics important, but ultimately the mechanical properties of cured laminates dominate resin selection. Mechanical properties, in both static and fatigue modes, when coupled with the chemical characteristics of the resin

selection, provide valuable information. All this information together gives a clear picture of what can be expected when a transition is made from one repair resin system to another repair resin system. Various ASTM standards were examined prior to testing to find the most applicable test methods available. Since the interface toughness between the parent laminate and the repair laminate is the data required, a double cantilever beam test was performed following ASTM D 5528. This standard tests Mode I interlaminar fracture toughness of unidirectional fiber reinforced plastics. Since blades are mainly unidirectional fiber orientation, this test was fitting for the analysis. Using this test, the ultimate strength of the composite repair for each resin was determined. Although this is important information, wind turbines experience prolonged amounts of stress from wind gusts. Most wind turbine blades are designed to last 20 years or more. Therefore, the fatigue strength is also very important. The fatigue testing was performed by LM Wind Power. Although fatigue testing followed a tension-tension fatigue method, the actual test is specialized for LM and thus is proprietary information.

Surface Treatment

The most important part of a repair laminate is the bond strength at the interface between the repair and the main laminate. There are three main theories that describe how adhesion between a parent laminate and a repair laminate occur. These three theories are the adsorption theory, diffusion theory, and the chemical reaction theory. Adsorption theory states that intimate contact between the parent laminate and the repair laminate will result in a permanent bond with secondary molecular forces, or Van der Waals forces. Diffusion theory states that at the molecular level, molecules from both the parent and repair laminates will diffuse together to form a bond. The third theory,

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chemical reaction theory, is the result of primary chemical bonds such as covalent bonds forming between the parent and repair laminates to create a permanent bond interface. [13]. Primary chemical bonding between the repair laminate and parent laminate would result in the strongest repair laminate. However since composite wind turbine blades are manufactured with thermoset resins, it is extremely difficult to break the existing bonds of the cured parent laminate to bond with the repair laminate. Because chemical bonding is nearly impossible between cured laminates, adsorption theory is accepted as the dominating form of bonding between laminates. This means that for a repair to bond adequately with the parent laminate, there needs to be enough space between the polymer molecules for the repair resin to form contact resulting in a strong bond. Because thermoset resins are essentially infinite in molecular weight, it is difficult for new resins to bond well solely on adsorption theory. However, when applying a repair laminate, surface treatment aids in the adsorption of new repair resin into the main laminate that is already cured.

Surface treatment can be crucial for improving this bond. Due to the nature of scarf repairs the surface of the laminate is prepared by grinding. This exposes fresh material for bonding as well as roughens up the surface to create bonding sites. These bonding sites are exposed microscopic area of the laminate that comes in contact with fresh resin during a repair. The more area available the better the bond should be.

Various methods were discussed with LM Wind Power on how to prepare the surface for repairs. One mentioned was to use excimer lasers. Using lasers would act the same as grinding but result in larger surface area for bonding sites. Another suggestion

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was to look at silane primers. However, in the past LM tried using polyurethane primers. Polyurethane primers use diisocyanate as a primary monomer with toluene solvent.
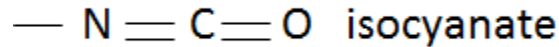
$$— N = C = O \quad \text{isocyanate}$$

Figure 12: Isocyante monomer used in polyurethanes

Toluene diisocyanate has been deemed a poisonous chemical by the Environmental Protection Agency [14] and thus LM ceased use of polyurethane primers. Because of the issues that arose from LM Wind Power's previous usage of primers, the use of primers for improvements on repair resin methods was declared out of the scope of the project. Because primers were out of scope, only discussions of them were brought to the table and no primers or other surface treatment options were experimented with during the development of the new repair resin system. For the purposes of this thesis, grinding of the parent laminate was the only form of surface treatment prior to the application of the new repair resin system.

Although the only surface treatment used prior to repairs was grinding there are various ways to enhance bonding between the repair laminate and the main laminate based on the grinding method. LM Wind Power has used a grinding method that removes enough material to leave one complete ply intact for bonding. This method of grinding reveals no glass reinforcements of the composite allowing for a resin to resin bond. Another approach is to grind the main laminate so that there is half of a ply exposed. The half ground method exposes both glass reinforcement and polymer for

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bonding.   It was later decided by LM Wind Power to include the half grind and full grind of the parent laminates for testing.

CHAPTER III

EXPERIMENTAL METHODS

A total of six resins were tested and compared to the current repair resin both mechanically and chemically. Baseline testing was performed on the current repair resin prior to testing the new repair resin candidates. All six resins were tested using AkzoNobel Cadox M-50A MEKP initiator except for resins HA and HB. HA was initiated with Norox 925H from Syrgis Performance Initiators. HB was also tested with Norox 925H as well as Norox HDP-75, both from Syrgis. HB and HA were tested with different initiators based on recommendations from the resin supplier. Each resin tested is listed below in Table 3, where GT125 is the parent laminate resin simulating a wind turbine blade, and GT80 is the current baseline repair resin.

Table 3: Resin Coding for each supplier

Resin	Supplier	Description
GT125	Reichhold	Parent Adherend VARTM Resin
GT80	Reichhold	Unsaturated Polyester (Current System)
RH	Reichhold	High Styrene Vinyl Ester
RL	Reichhold	Low Styrene Vinyl Ester
IP	Interplastic	Standard Vinyl Ester
AD	Ashland Performance Materials	Toughened Vinyl Ester
HA	Hexion	Toughened Vinyl Ester
HB	Hexion	Toughened Vinyl Ester

Resins RH and RL from Reichhold are both 100% vinyl ester resins. According to the supplier both these resins are pre-promoted thixotropic resins. It is especially important to use thixotropic resins for field repairs. Thixotropic means that the resin will not flow easily unless shear force is applied over time such as mixing. This allows for vertical repairs to be made without the repair laminate slipping off the main laminate due to gravity. These resins are manufactured to have high strength and toughness. Generally RH and RL are similar types of resins, except RH is a high styrene resin (about 42%) whereas RL is a low styrene resin (about 35%) [15,16]. Similar to RH and RL, IP is a 100% vinyl ester resin from Interplastic Corporation. This resin would fall into the low styrene category because, like RL, it has a maximum of 35% styrene. Again, it was formulated for hand layup and spray up applications typically geared towards the marine

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industry [17]. All three of these resins were tested by UND to confirm or deny the first hypothesis that high styrene vinyl ester resins would improve bond strength.

The next three resins (AD, HA, and HB) are all toughened vinyl esters. AD is a resin from Ashland Performance Materials. This is a new experimental vinyl ester resin that is toughened with polybutadiene copolymer [18]. While maintaining the superior properties of vinyl esters over unsaturated polyesters, toughened resins include elastomeric copolymer for increase fracture toughness. HA and HB are both toughened resins from Momentive Performance Materials, formerly Hexion Specialty Chemicals [19,20]. Both these resins are toughened using core shell rubber technology, the difference between the two being that HA and HB use 100 nm core shell particles and 200 nm core shell particles, respectively, as toughening agents.

Chemical Methods

The chemical portion test methods included differential scanning calorimetry and dynamic rheological testing. Together these methods were utilized to screen viable repair resin candidates. Each repair resin candidate was analyzed using DSC and rheology. For both baseline testing and new resins, isothermal DSC scans were run followed by a dynamic heat ramping DSC scan. Likewise, each resin, including the baseline, was tested using rheology.

DSC Measurements

A Perkin Elmer Jade DSC was used to perform the thermal analysis of the resins. Each sample was tested using hermetically sealed aluminum sample pans. Sample sizes for the DSC ranged from 12 to 20 mg. Each run consisted of an isothermal step holding at 25 ^{o}C for 300 minutes followed by a dynamic heat ramp from 25 to 250 ^{o}C at 10°C/min

[21]. The isothermal step measures the amount of energy given off during the exothermic reaction during the cure cycle. The dynamic heat ramp allows for calculation of any residual heat from any unreacted carbon-carbon double bonds. The residual heat is indicated by any heat flow present during the dynamic temperature scan. The heat generated during the isothermal scan (ΔH_{iso}) and the dynamic scan (ΔH_{res}) sum to the total amount of heat generated from curing. Using this data, the degree of cure can be calculated at any specified time using the following equation:

$$X = \frac{\Delta H_t}{\Delta H_{iso} + \Delta H_{res}}$$
Eq 1

where ΔH_t is the heat generated in time t, ΔH_{iso} is the heat generated during isothermal scanning, and ΔH_{res} is the residual heat from unreacted C=C. Each heat of reaction is obtained by taking the integral of the heat flow over time. We can then calculate the degree of cure for each resin at a given time [22].

Rheology

All rheological measurements were taken using an AR2000 controlled stress rheometer, manufactured by TA Instruments. Dynamic time sweep tests were performed at ambient conditions using 40 mm parallel plate geometry, an oscillating stress of 1.000 Pa, and a frequency of 1.000Hz. These conditions were chosen from running a preliminary experiment to establish that at this stress and frequency, the polymer remained in the linear regime. Oscillating frequency was chosen to prevent the polymer chains from aligning during the cure. This method better fits real production conditions used by LM. Each resin experienced the oscillatory shear stress until the storage modulus and elastic modulus crossed, indicating the approximate gel point of the resin.

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The resulting data were then used to determine the approximate gel time, indicated by a large and rapid increase in the complex viscosity:

$$\eta^* = \frac{\sqrt{G'^2 + G''^2}}{\omega}$$
Eq. 2

where

η^* = Complex Viscosity (Pa s)

G' = Storage Modulus (Pa)

G'' = Loss Modulus (Pa)

ω = Angular frequency (rad/s)

Mechanical Methods

Mechanical test methods included Mode I fracture toughness using double cantilever beam (DCB) testing and tensile fatigue. DCB mechanical testing was performed following ASTM Standard D 5528. This tests Mode I interlaminar fracture toughness of unidirectional fiber reinforced polymer matrix composites. Testing was done on a Shimadzu AG-IS Universal Testing Machine under displacement control at a crosshead rate of 0.1mm/min. Using a Retiga 1300 camera, crack propagation was monitored and recorded. Loads were applied stepwise for every 15mm of crack growth. This was done to prevent false loads to be recorded as the crack propagated. With the help of the Mechanical Engineering Department, the data was analyzed to obtain G_{Ic}, the mode I interlaminar fracture toughness. Figure 13 and Table 4, below, show the specimen and layup used for DCB testing.

30
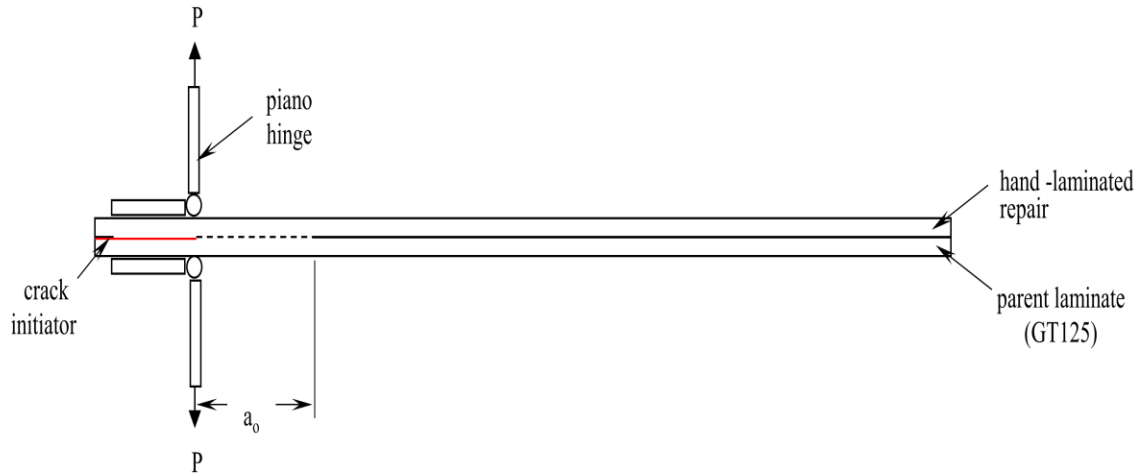
Figure 13: DCB Specimen for mechanical testing

Table 4: Fiber Stack layup used for mechanical DCB specimens

2x Biaxial	Repaired Laminate: Hand Lay-up (Upper adherend)
8x Combi	
CSM 300	
Crack Initiator	Tape
8x Combi	Parent Laminate: GT125 VARTM (Lower adherend)
2x Biaxial	

Following the static DCB testing, tensile fatigue testing was performed according to a LM Wind Power proprietary control instruction. This testing was done by LM Wind Power to measure the fatigue resistance of the baseline resin and the top three new repair resin candidates. Figure 14 and Table 5, below, show the specimen and layup used during the LM fatigue testing.

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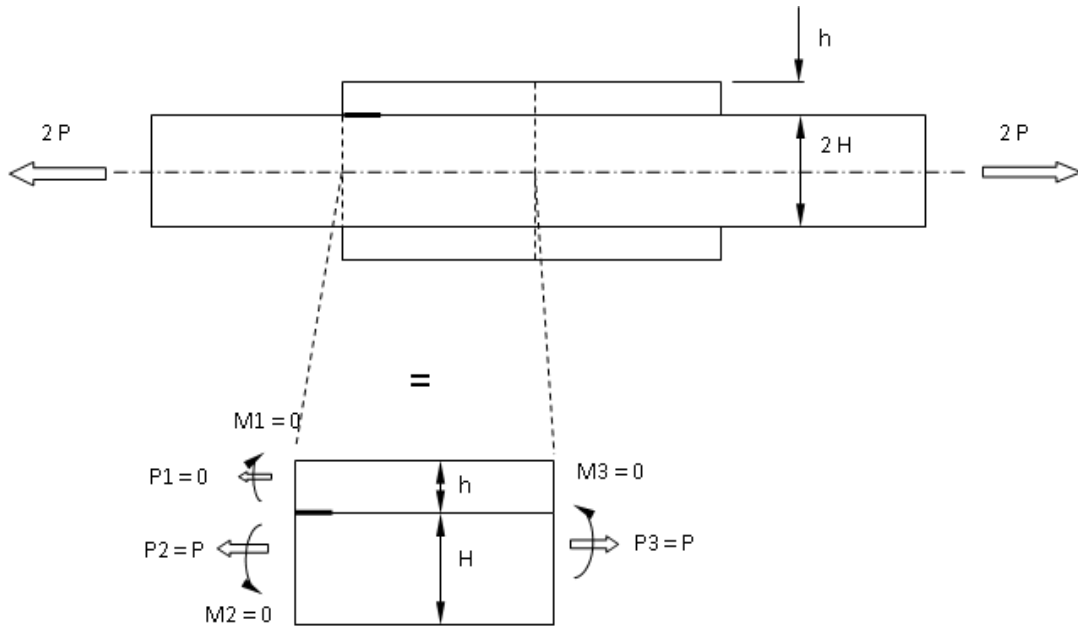
Figure 14: Tension fatigue testing specimen

Table 5: Fiber Stack layup for tension fatigue testing

1X Combi	Repair Laminate: Hand Layup
1X CSM	
4X Combi	Parent Laminate: VARTM GT125
4X Combi	
1X CSM	Repair Laminate: Hand Layup
1X Combi	

Sample Preparation

For the chemical testing, samples of neat resin were prepared in small glass vials. A known amount of resin was added to each vial and then the relative amount of initiator was added based on weight percent. The weight percent and type of initiator added for each resin tested is shown below in Table 6.

Table 6: Resin and Initiator combinations and levels tested

Resin	Initiator Type	% Initiator
GT80	Cadox M-50A	1.2
RH	Cadox M-50A	1.5
RL	Cadox M-50A	1.5
IP	Cadox M-50A	1.5
AD	Cadox M-50A	1.5
HA	Cadox M-50A	1.5
HB	Norox 925H	1.2
HB	Norox 925H	1.5
HB	Norox 925H	1.7
HB	Norox 925H	2.0
HB	Norox HDP-75	1.5
HB	Norox HDP-75	1.7
HB	Norox HDP-75	2.0

After initiation, the resin was mixed for at least one minute using a Maxi Mix II vortex mixer. Samples were then taken from the glass vial for DSC and rheology testing. DSC samples were crimped in hermetically sealed sample pans with weights ranging

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from about 10 to 20 mg. Rheology samples were placed between the 40mm parallel plate geometry with a gap of about 2500 microns.

Mechanical test specimens were prepared jointly with LM Wind Power engineers and the UND Mechanical Engineering Department. The DCB specimens were composed of a parent laminate and a repair laminate. The parent laminate used GT125 unsaturated polyester resin in a vacuum assisted resin transfer molding process (VARTM). To avoid any unaccounted factors, each parent laminate underwent a post curing cycle at elevated temperatures of 60 ^{o}C for 24 hours followed by 3 hours at 95 ^{o}C. Once the parent laminate was post-cured, it was ground and prepped for the application of the repair laminate. One complete ply of the parent laminate was ground off in preparation for the application of the repair laminate. Repair laminates of the baseline resin and new resin candidates were applied using the hand layup method. To maintain a high degree of cure for the repair laminates, the final composite was again post-cured at 40 ^{o}C for 16 hours prior to testing. Specimens measuring 35 cm long and 3 cm wide were cut from the prepared composite with a diamond band saw for DCB testing. Piano hinges were adhered to the composite using Araldite 2021 MMA adhesive.

Fatigue test specimens were prepared similar to the DCB specimens. The parent plate was prepared using the same method as the DCB samples; however the repair laminate was applied slightly different. Rather than apply repair laminate to only one side of the parent laminate, the repair laminate was applied to both sides of the parent plate.

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RESULTS AND DISCUSSION

Both the chemical data and mechanical data describe how each resin candidate behaves. The chemical data indicates how off the shelf resins behaved during the cure cycle. Each test resulted in the degree of cure and gel point for each resin. Both these parameters are important for a few reasons. It is desirable to reach a high degree of cure quickly for efficient output of completed parts. The gel point is even more important because it lets you know how much working time is available for the hand layup of a repair laminate. By utilizing the information from the data, a more desirable resin can be chosen to better meet the needs for repair laminates.

Coupling the chemical data with the mechanical data gives an overall picture of how a repair laminate will behave. Ultimately, the mechanical properties are the most important characteristics of the resin candidates. If a chosen resin candidate does not meet the mechanical requirements, it will automatically be excluded from possible solutions. Mechanical characteristics in both static and fatigue modes are essential to choosing a new viable repair resin.
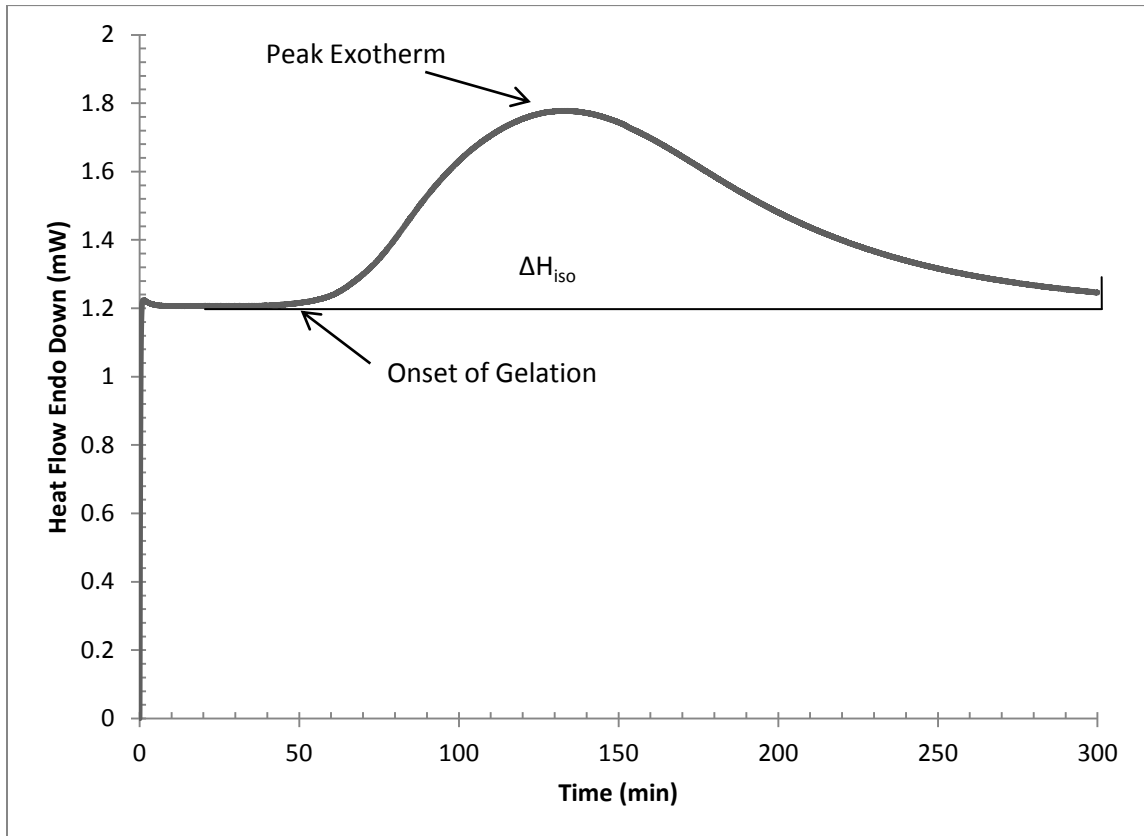
Chemical Results

The DSC data shows that each resin candidate tested reached a degree of cure in ranging from about 45% to 70%. Since the current repair resin GT80 had a degree of

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cure of 70.8% after five hours, it was desirable to have the new resin candidate reach near 70% or higher degree of cure after five hours. Table 7 below shows the degree of cure for each resin candidate. This was calculated using Eq. 1. As mentioned in Chapter 3, the area under the curve for the heat flow during isothermal DSC scans results in ΔH_{iso}. Likewise, ΔH_{res} is the area under the curve for the heat flow during the post isothermal dynamic DSC scans. Figures 15 and 16 show representative heat flow curves for the isothermal and dynamic DSC scans respectively. The resins that were chosen for this study were off the shelf from each resin supplier. Variance from resin to resin is likely due to the fact that Cadox M-50A is an initiator that was developed primarily for unsaturated polyester resins. Other than GT80, all the resins tested were vinyl ester resins. Although this information was known, to remove variables, Cadox M-50A was used to maintain consistency during testing. Because the testing done was preliminary and a screening design, the resins tested were not formulated by each supplier to meet our exact needs. The "off the shelf" resins were tested to make sure the research was on the right path towards choosing a new resin. Thus, each resin was tested and compared to GT80 with the intention of tweaking the resin formulation to better meet curing needs after selection. It should also be noted that HB, a toughened resin used Norox 925H as an initiator based on information from the resin supplier.

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Table 7: DSC Data for the baseline resin and each resin candidate

Resin	Initiator Type	% Initiator	ΔH_{iso} (J/g)	ΔH_{res} (J/g)	Degree of Cure (%)
GT80	Cadox M-50A	1.2	270.4	111.5	70.8
RH	Cadox M-50A	1.5	155.4	130.2	54.4
RL	Cadox M-50A	1.5	237.2	126.5	65.2
IP	Cadox M-50A	1.5	305.4	128.3	70.4
AD	Cadox M-50A	1.5	200.8	93.7	68.2
HA	Cadox M-50A	1.5	171.7	136.3	55.7
HB	Norox 925H	1.5	120.4	142.9	45.7

Figure 15: Representative Isothermal DSC Scan

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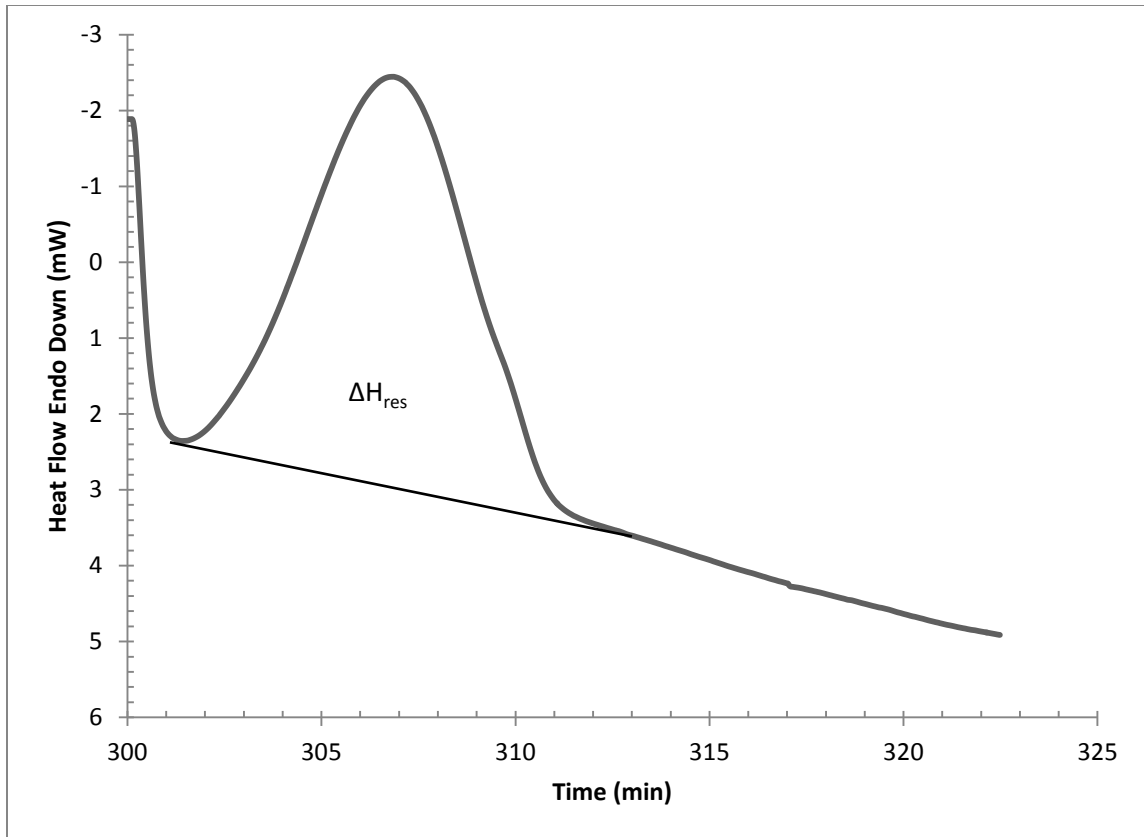
Figure 16: Representative Post Isothermal Dynamic DSC Scan

Coupling the DSC data with rheology data helps to give a clearer picture of the curing kinetics of each resin. Since the gel point of each resin is important for the working time needed to make repairs, it is imperative that this information be known. Table 8 shows the gel time data for the baseline resin and the new repair resin candidates. Figure 17 shows the resulting storage and loss modulus, G' and G", along with the complex viscosity calculated from Eq. 2 for a representative repair resin sample.

The rheology data shows that all resins tested except AD, had gel times similar to GT80. This is good as it allows enough time for the proper layup of hand laminate repairs. AD was sent as an unpromoted resin. Promoting the resin based on supplier gel

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time data, 0.2 phr of a 6% cobalt napthenate solution was used to promote the resin. Clearly, this gave a gel time of about 18 minutes. This quick of a gel time would be unacceptable for repair methods. To account for this, various promoter packages can be tested to allow adequate working time for repairs. In general, this applies to all resin candidates. However, the other candidates were pre-promoted per LM Wind Power's request.

Table 8: Gel Time Data for baseline and new repair resin candidates

GT80	Cadox M-50A	1.2	68
RH	Cadox M-50A	1.5	60
RL	Cadox M-50A	1.5	65
IP	Cadox M-50A	1.5	80
AD	Cadox M-50A	1.5	18
HA	Cadox M-50A	1.5	67
HB	Norox 925H	1.5	87
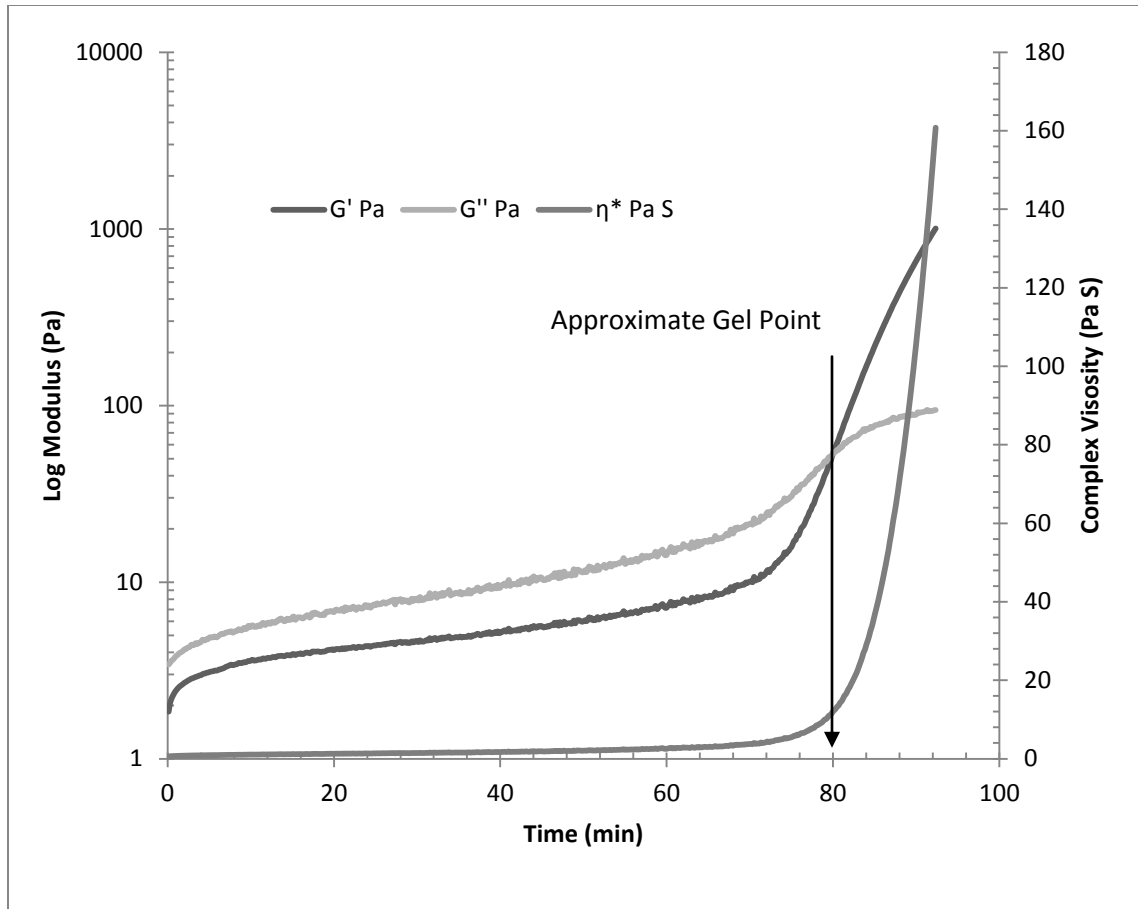
Figure 17: Representative Rheology Data for repair resin

The chemical data resulted in generally expected information. Using a five hour isothermal DSC scan, the achievement of about 60% degree of cure makes sense based on data from the baseline testing of the current repair resin that is well known by LM. As the polymerization progresses, it becomes more difficult for individual polymer chains to diffuse through the bulk, resulting in higher degree of cure. Although with thermoset resins the polymerization never ceases, the majority of the reaction occurs within a short period of time. Since LM lets repairs sit for at least 24 hours prior to shipment, achieving the degree of cure observed indicates that each resin candidate will cure in an acceptable timeframe suitable to LM Wind Power. This was proven after LM selected the resin they

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desired. Residual enthalpies showed that for thin and thick laminates using the new repair resin achieved 98% and 92% degrees of cure, respectively.

Since the resins tested were requested to come from the supplier as a pre-promoted resin with a gel time around 40 minutes the rheology data initially is puzzling. During the rheology testing small masses were used. It is widely accepted that large mass laminates experience higher peak exotherm temperatures and generate more heat than thin laminates. Since the rheology testing essentially simulated a thin laminate, the heat generated was easily dissipated to the surroundings. Because of the heat dissipation, the reaction progresses at a slower rate compared to a thick laminate which means that slower gel times will be observed. However, compared to the baseline resin, the gel times still met acceptable ranges required for the application of a hand laminated repair as required by LM Wind Power.

<div align="center">

Mechanical Results

</div>

Following ASTM D 5528, static DCB testing resulted in average interlaminar fracture toughness for each resin as shown in Table 9. It is shown that all resin candidates tested performed better than GT80 in the static tests. However, DCB testing was designed to screen the top three resin choices. RH was the best performing resin at just over twice as tough as GT80. Following RH, were HB and AD at about 1.5 times tougher than GT80.

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Table 9: Interlaminar Fracture Toughness, G_{Ic}, for each resin tested

Resin	Averaged G_{Ic}' at $a_o \sim 100$ mm
GT80	165 J/m^2
IP	225 J/m^2
AD	250 J/m^2
RL	230 J/m^2
RH	340 J/m^2
HA	175 J/m^2
HB	260 J/m^2

Using the top three new repair resin candidates, RH, HB, and AD, fatigue testing was performed by LM Wind Power. Figure 18 shows that RH, HB, and AD all are much better than GT80 in fatigue strength. The data shows larger strain for the resin candidates which means that they can support higher fatigue loads. This is based off of Equation 3 where:

$$\begin{bmatrix} \varepsilon_x \\ \varepsilon_y \\ \gamma_s \end{bmatrix} = \begin{bmatrix} a_{xx} & a_{xy} & a_{xs} \\ a_{yx} & a_{yy} & a_{ys} \\ a_{sx} & a_{sy} & a_{ss} \end{bmatrix} * \begin{bmatrix} N_x \\ N_y \\ N_s \end{bmatrix} \qquad \text{Eq. 3}$$

With uniform stiffness, a, higher strain, ε, means larger loads, N [4].

42
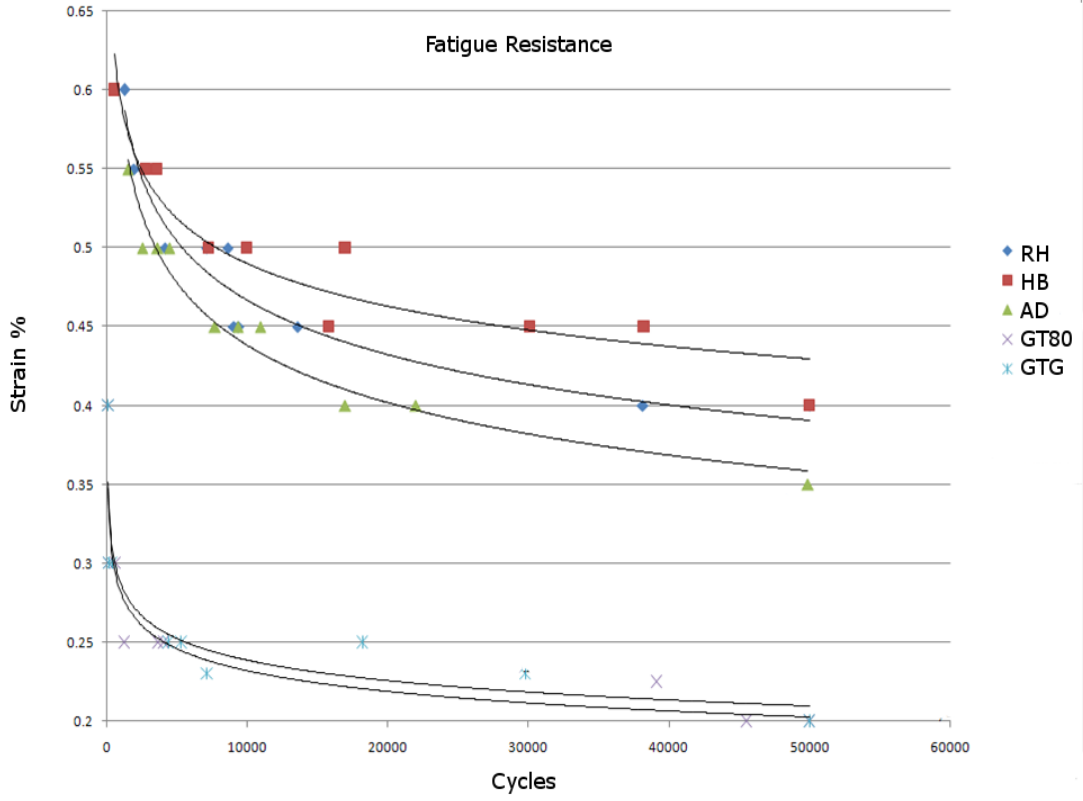
Figure 18: Fatigue Results for Top 3 Repair Resin Candidates

CHAPTER V

INITIATOR STUDY

Along with the repair resin testing, an initiator study was performed. It was hypothesized that without making changes to the resin formulation, choosing the optimal initiator type could improve the curing properties. Thermoset resins require the addition of free radical initiators in order to polymerize into a three dimensional crosslinked polymer network. When using unsaturated polyester and vinyl ester resins as a matrix, initiator types are almost always organic peroxides. Studies done by Norac Inc. have been done showing that variations in initiator do indeed affect the cure cycle of resins. Ingredients of initiators that may affect resin cure include the active oxygen content, which is related to the amount of hydrogen peroxide present, the initiator type, including methyl ethyl ketone peroxide (MEKP), cumyl hydroperoxide (CHP), acetyl acetone peroxide (AAP), and various blends of these initiators. It is important to know that hydrogen peroxide alone will kick off the curing reaction but it will not progress beyond the gel point. Because of this it is imperative that the main organic peroxide is present, either as a monomer, dimer, or trimer. Studies done at Norac Inc. have also shown that the amount of monomer, dimer, and trimer of the peroxide also can affect the cure. Norac Inc. has shown that with high dimer initiators, the gel time lengthens compared to the monomeric initiator.

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During the development of the new repair resin system, three organic peroxides

were studied. There were two MEKP initiators and one MEKP-CHP blended initiator.

Figures 19 and 20 show generic structures of MEKP and CHP initiators. Figure 19

shows the monomer and dimer forms of MEKP.
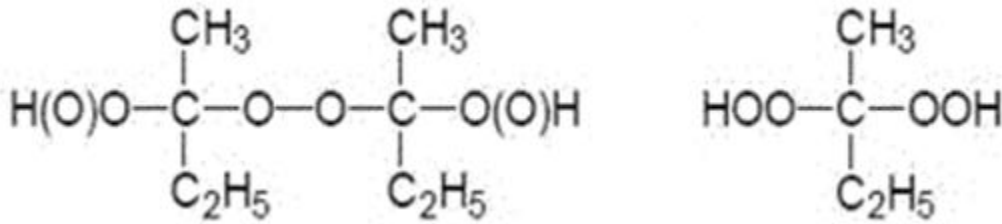
Figure 19: Dimer and Monomer forms of Methyl Ethyl Ketone Peroxide (MEKP) initiator
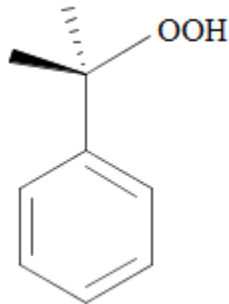
Figure 20: Cumyl Hydroperoxide Initiator.

Various initiators were tested with the new repair resin candidates including

Cadox M-50A, Norox 925H, and Norox HDP-75. Both Cadox M-50A and Norox 925H

are methyl ethyl ketone peroxide (MEKP). Cadox M-50A is a multipurpose MEKP

initiator from AkzoNobel that has been used for room temperature curing of unsaturated

polyesters. Cadox M-50A is considered a high hydrogen peroxide, high monomer

initiator. Similarly, Norox 925H is an MEKP initiator used for the room temperature

cure of unsaturated polyester and vinyl ester reins. Unlike Cadox M-50A, 925H is

considered a low hydrogen peroxide, medium monomer MEKP initiator. It has been specifically formulated by Syrgis Performance Initiators to reduce gas generation in applications using vinyl ester resins [23].

Unlike Cadox M-50A and Norox 925H, Norox HDP-75 is a blended initiator. HDP-75 is a three to one blend of MEKP and CHP, or cumyl hydroperoxide. It has been formulated by Syrgis Performance Initiators as a high dimer, low hydrogen peroxide initiator for use in room temperature cures of unsaturated polyester and vinyl ester resins. HDP-75 is designed mainly for vacuum infusion of resin, but because it is a MEKP-CHP blend, it was thought to provide a quality cure that could be used with the hand laminate repair system [24,25].

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Repair Initiator Study

An initiator study was performed on the top resin choices to help find an optimal

initiator package for improvements on the curing kinetics of the resin candidate chosen,

shown in Table 10.

Table 10: Initiators used for resin testing

Initiator	Supplier	Description
Cadox M-50A	AkzoNobel	MEKP
Norox 925H	Syrgis Performance Initiators	MEKP
Norox HDP-75	Syrgis Performance Initiators	High Dimer MEKP-CHP Blend
Norox MCP75	Syrgis Performance Initiators	Parent Adherend Initiator

Following the same procedures as the DSC and rheology testing, two initiators were

tested with the HB toughened vinyl ester resin. Syrgis Performance Initiators supplied

Norox 925H and Norox HDP-75 as initiators to test with the new repair resin. These

initiators were chosen for testing based on discussions between UND, LM Wind Power,

and Syrgis Performance Initiators. As discussed earlier, the rationale for using 925H was

that it is has a lower concentration of hydrogen peroxide and would result in reduced gas

formation during the cure. Likewise, HDP-75 was studied to determine if the MEKP-

CHP blend would ultimately achieve a more desirable cure.

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Each initiator was tested at various weight percent in both DSC and Rheology. Typically, resin suppliers have completed quality assurance testing before they ship resins to a customer and have determined a range of acceptable initiator concentrations to use during the curing process. Generally resin suppliers recommend using between 1.0% and 2.5% initiator for the curing of their resin. Based on these recommendations, Norox 925H was tested at 1.2, 1.5, 1.7, and 2.0%, while HDP-75 was tested at 1.2, 1.5, and 2.0%. With both initiators at each of the levels listed, HB toughened vinyl ester resin underwent isothermal DSC scans at 25 ^{o}C for five hours followed by a dynamic heat ramp from 25 to 250 ^{o}C. Similarly, HB underwent rheological testing at each level with both 925H and HDP-75 initiators at ambient conditions. Both initiators were tested at these levels to determine the optimum concentration that would give the best cure, appropriate gel time, and low peak exotherm required by LM Wind Power. The analysis of the resulting data was then done following the same methods described previously in the DSC Measurements and Rheology sections discussed in Chapter III.

Working with the supplier, HB was formulated with a promoter package to work well with Norox 925H at 1.5% w/w. Both 925H and HDP-75 showed good degree of cure with HB at the 1.5% w/w. Norox 925H, however, was closer to the desired gel point at 1.5% w/w. This is most likely due to the efforts the supplier put forth to provide a resin meeting the requirements of the new repair resin. At higher initiator concentrations, both 925H and HDP-75 showed low degree of cure and longer gel points. This is most likely due to radical terminations. Radical terminations occur when free radicals collide with other free radicals that cause the two radicals to kill each other off, leaving behind nonreactive polymer chains. This generally occurs between growing polymer chains. This sometimes occurs when too much initiator is added. Tables 11 and 12 show the results of DSC and Rheology testing using the two initiators. It is clear from the DSC data that at higher levels of initiator HB did not cure well with Norox 925H. Similarly, with HDP-75 as the initiator, as concentration was increased the degree of cure went down. This could be from radical terminations. However, the drastic differences between 1.7%, 2.0% 925H doesn't make sense compared to all the other levels tested with both 925H and HDP-75. Perhaps the resin is reacting differently with these concentrations of initiators because of the presence of the CSR particles.

The rheology data shows that the gel point for each initiator was rather long except for 1.5% 925H. Like earlier stated, this could be from low mass simulating thin laminates. However, the data continues to indicate that the use of 1.5% 925H initiator is the best level and type of initiator to use with HB. Again this is because Hexion worked hard in the formulation of their resin to meet the needs of LM Wind Power.

Table 11: Initiator study DSC results with HB

Resin	Initiator Type	% Initiator	ΔH_{iso} (J/g)	ΔH_{res} (J/g)	Degree of Cure (%)
HB	Norox 925H	1.2	92.6	102.9	47.3
HB	Norox 925H	1.5	120.4	142.9	45.7
HB	Norox 925H	1.7	5.51	257.9	2.1
HB	Norox 925H	2.0	18.4	244.9	7.0
HB	Norox HDP-75	1.5	158.1	170.2	48.2
HB	Norox HDP-75	1.7	103.7	224.5	31.6
HB	Norox HDP-75	2.0	71.3	256.9	21.7

Table 12: Initiator study Rheology results with HB

Resin	Initiator Type	% Initiator	Gel Time (min)
HB	Norox 925H	1.2	150
HB	Norox 925H	1.5	87
HB	Norox 925H	1.7	173
HB	Norox 925H	2.0	140
HB	Norox HDP-75	1.5	116
HB	Norox HDP-75	1.7	108
HB	Norox HDP-75	2.0	103

Blade Initiator Study

Like the repair resin initiator study, an initiator study was performed on the blade resin. This study was a spin-off of the repair resin project. Like the repair resin initiator study, it was hypothesized that choosing the right initiator would improve blade infusion and cure cycle resulting in a more uniform cure during blade production, thus reducing the number of repairs need during manufacturing.

Similar to the repair resin project, the blade initiator study used DSC and Rheology to collect data for the analysis of each initiator. LM Wind Power's blade resin, an orthophthalic unsaturated polyester was used for this study and five initiators were tested from Syrgis Performance Initiators including HDP-75, MCP-21, MCP-75, Norox 757, and Pulcat. MCP-75 is the current blade initiator and is a monomeric MEKP. HDP-75 was chosen because it is a high dimer MEKP initiator. Again, Norac Inc. has shown that high dimer initiators help to drive the reaction. MCP-21 is similar to MCP-75 where as both are MEKP-CHP blends, but MCP-21 is a two-to-one ratio of MEKP to CHP and MCP-75 is a three-to-one ratio of MEKP to CHP. Norox 757 and Pulcat were chosen to incorporate other initiators other than MEKP and CHP. Norox 757 is an acetyl acetone peroxide with a high active oxygen content used for room temperature curing during resin transfer molding of unsaturated polyester resins. Pulcat is a proprietary initiator from Syrgis Performance Initiators typically used in pultrusion. It was chosen purely from an academic approach to see what happens when used with unsaturated polyester resins. Using the same procedures from the repair resin study, the following data was collected using the five initiators with the blade resin.

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Table 13: Blade Initiator Data

Initiator Type	Wt. Percent	ΔH (J/g) ISO	ΔH (J/g) DYNAMIC	Degree of Cure (%)	Gel Time	Peak Exotherm Temp (°C)
HDP-75	1.2%	60.48	232.14	20.7	262.02	196.8
HDP-75	1.5%	233.77	206.74	53.1	218.18	101.1
HDP-75	1.7%	309.74	174.81	63.9	140.35	98.2
HDP-75	2.0%	259.91	156.11	62.5	135.69	96.3
MCP-21	1.2%	207.61	232.62	47.2	193.02	117.5
MCP-21	1.5%	338.61	153.32	68.8	144.19	116.2
MCP-21	1.7%	389.91	106.20	78.6	141.18	116.3
MCP-21	2.0%	407.44	165.14	71.2	99.69	114.6
MCP-75	1.2%	133.46	252.62	34.6	191.85	115.2
MCP-75	1.5%	294.87	183.91	61.6	163.65	116.3
MCP-75	1.7%	319.13	139.03	69.7	116.02	116.6
MCP-75	2.0%	351.16	113.06	75.6	95.02	115.9
Norox 757	1.2%	381.40	59.38	86.5	66.20	115.9
Norox 757	1.5%	422.10	71.94	85.4	41.90	113.3
Norox 757	1.7%	303.51	82.87	78.6	36.40	111.4
Norox 757	2.0%	363.68	55.54	86.8	41.52	62.0
Pulcat	1.2%	390.68	141.26	73.4	163.70	93.8
Pulcat	1.5%	292.10	105.44	73.5	148.20	89.2
Pulcat	1.7%	277.40	102.97	72.9	132.90	86.3
Pulcat	2.0%	301.34	100.61	75.0	100.70	85.2

(MCP-75 rows marked as BASELINE)

Blade Initiator Study Results

One of the main goals for this project was to decrease the overall cure time while increasing the working time. The initiators with the greatest degree of cure were PULCAT and Norox 757. By comparing the degree of cure of PULCAT with that of MCP-75, PULCAT displays approximately a 12% increase in the degree of cure over that of MCP-75 at 1.5% weight percent. This should effectively reduce the overall cure time for a blade. How much this will lower the overall cure time is yet to be determined and more research would be needed to quantify this time savings.

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Another observation noted about the degree of cure is the sensitivity to mass concentration that some initiators display. From Table 13 it is seen that MCP-75 is very sensitive to the weight percent of initiator in relation to the degree of cure. The degree of cure for MCP-75 varies from 35% cure at the 1.2% initiator concentration to 76% cure at 2.0%. PULCAT and Norox 757 display relatively small fluctuations in degree of cure with varying weight percent. PULCAT ranges from 73% to 75% cure throughout the 1.2% through 2.0% concentration and Norox 757 displays a range 79% to 87% over the same concentrations. Note that HDP-75 and MCP-21 display similar sensitivities to initiator concentrations as MCP-75.

Peak exotherm temperatures can also be determined from DSC analysis. It is well known that the peak exotherm temperatures given by DSC analysis are subjective to many factors. These factors include composite thickness, mass of the curing resin, and mold geometry. However, we are using the same size pans (i.e. mold) for DSC and the resin's weight is taken into account since heat flow is on a per gram basis. This allows us to make comparisons of peak exotherm temperatures given by different initiators, realizing that temperature is subjective to what is actually observed during blade production. Table 13 displays peak exotherm temperatures from each of the various initiators studied. From this we can see that Norox 757, and PULCAT have lower peak exotherm temperatures. Contrary to what is initially observed from this data, low peak exotherm temperatures from dynamic DSC runs means that the peak exotherm temperature is actually higher. This is because the heat flow peaks at a lower temperature meaning that more heat is given off from the curing reaction of the resin. Therefore PULCAT and Norox 757 experience the highest peak exotherm temperatures.

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The Rheology data is a necessary tool to completely study the performance of an initiator and the characteristics of the curing reaction. The most important characteristic gained from rheological data is the viscosity profile throughout cure. However, no apparent trends have been proven based on the viscosity profiles generated for each initiator at different concentrations.

Rheological data also allows us to estimate gel times for each initiator concentration. As shown in Table 13 and Figures 20 through 24, the gel time of each resin typically is reduced with increased weight percent initiator. All the initiators tested showed gel times similar to that of the baseline MCP-75 except Norox 757. Norox 757 gelled and cured much quicker than any of the other initiators tested.
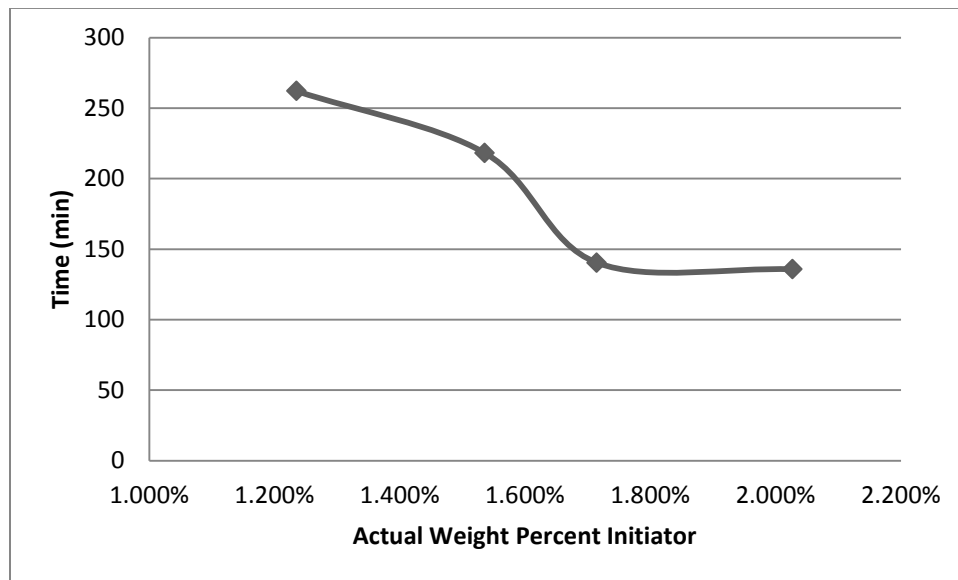
Figure 21: HDP-75 gel time vs. w/w% initiator

54
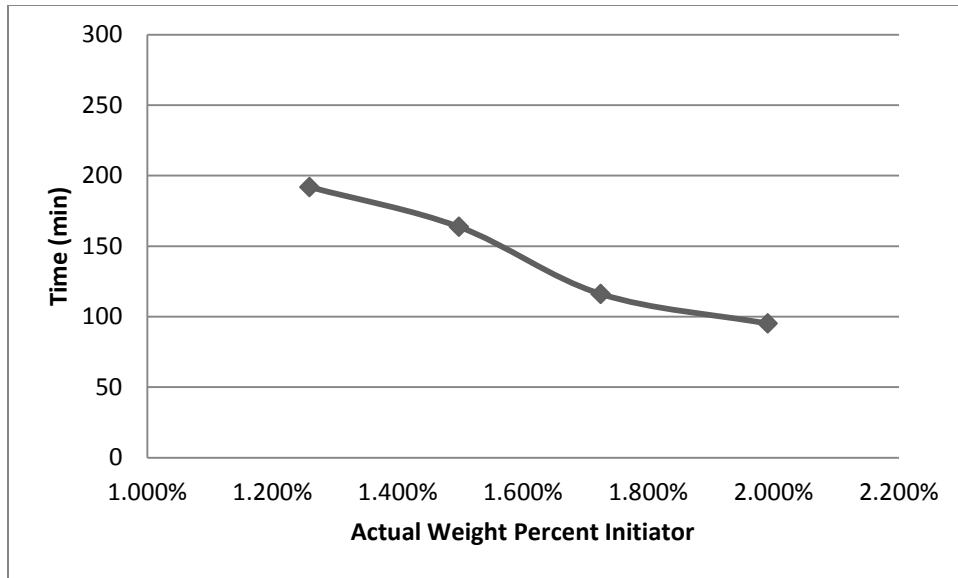
Figure 22: MCP-75 gel time vs. w/w% initiator
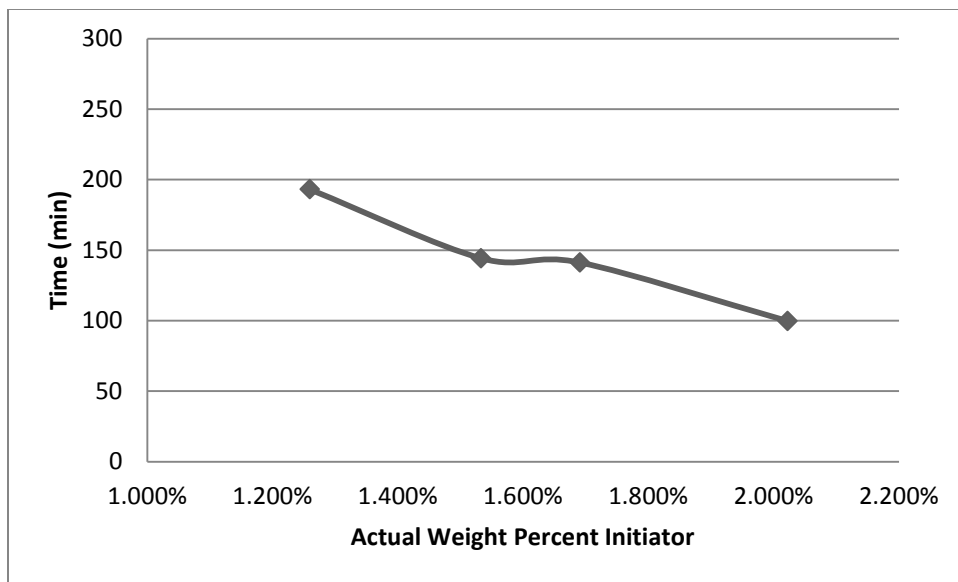
Figure 23: MCP-21 gel time vs. w/w% initiator

55
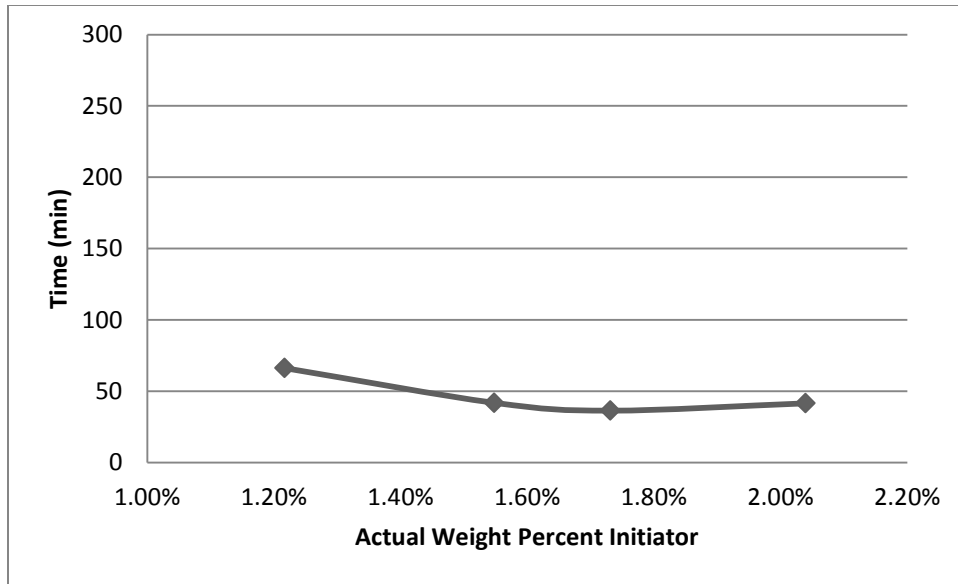
Figure 24: Norox 757 gel time vs. w/w% initiator
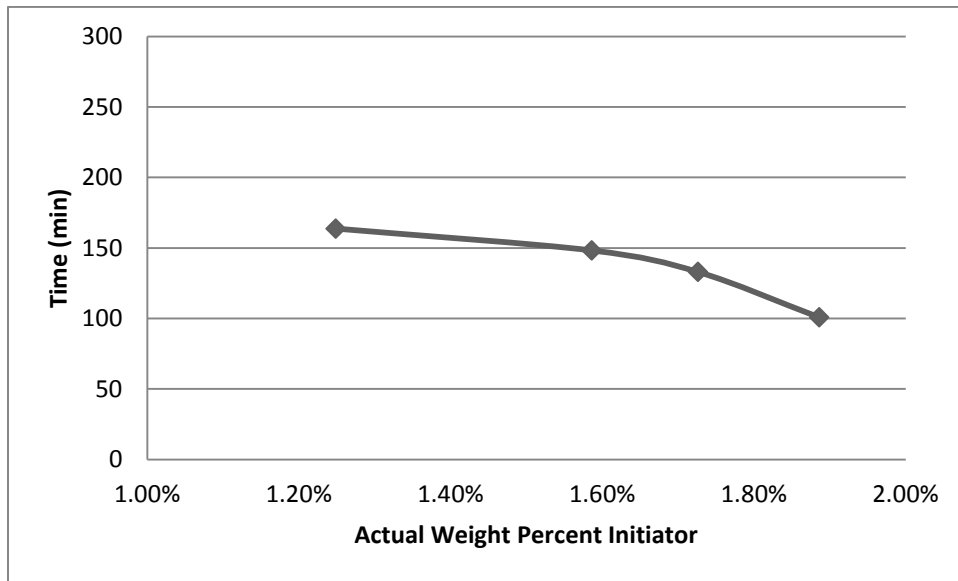
Figure 25: Pulcat gel time vs. w/w% initiator

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Blade Initiator Study Conclusions

Based on the data acquired, there is not an initiator that necessarily stands out as performing better than MCP-75. It is still unclear as to what viscosity is acceptable for good wetting during infusion and should be determined in the future. Compared to MCP-75 all the initiators tested fell within a similar range of viscosities, but no viscosity profile trends were able to be observed.

Coupling the DSC data and the Rheology data, PULCAT did indicate improvements. It has been shown that the gel times using PULCAT are similar to the current initiator system, but the degree of cure is higher. This leads to the belief that blades can be wetted out with the longer gel times, yet overall cure time is reduced. An ideal initiator would allow the blade to be fully wetted in say 45 minutes, gel in 60 minutes, and be 95% cured within a few hours. By using PULCAT as an initiator we may be able to reduce the overall cure time but it is far from an ideal case.

The data collected thus far does not allow for recommendations at this point on using an "improved" initiator versus the current MCP-75 package. More research needs to be conducted to define viscosities that are acceptable for good fiber wetting, as well as the minimum required working time. Both these factors are related to each other. For example, if a lower viscosity resin is available and can maintain said low viscosity after initiation, the wetting time can be reduced. Studies analyzing the flow of resin and wetting properties need to be performed to help determine this information.

CHAPTER VI

CONCLUSIONS AND RECOMENDATIONS

Coupling the chemical testing with the mechanical testing, all resins candidates performed better than GT80. The top three candidates, RH, HB, and AD underwent fatigue testing to determine which resin was superior. Although all three of the top resins performed well in fatigue, HB was superior.

Since HB performed the best, an initiator study was done to determine which initiator and what weight percent works best for the requirements of LM Wind Power. Testing was initially done using the current initiator Cadox M-50A. Visual results using this initiator showed a high level of porosity in the composite laminate. Discussions between LM Wind Power, UND, and Syrgis led to the choice of testing both Norox 925H and Norox HDP-75 as initiators with HB. Both of these initiators have relatively low concentrations of hydrogen peroxide compared to standard MEKPs. Studies done by Syrgis have shown that high hydrogen peroxide concentrations in initiators result in excess gas generation and porosity during curing. The supplier also worked to formulate the promoter package of HB to work well with Norox 925H. Due to these discussions, both initiators were tested, and it can be concluded that using 1.5% w/w 925H initiator works best with HB. This was confirmed when laminates were prepared and visually inspected showing a lower amount of porosity compared to Cadox M-50A.

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Based on the superior performance mechanically of HB, it has been recommended to replace the current repair resin with HB. The chemical testing also confirms that HB is within the curing requirements, and allows enough working time for efficient throughput. Although HB was the top choice, it was decided to ultimately go with RH. This resin was chosen over HB because unlike HB, RH is not a new experimental resin that is just coming into the market. RH is readily available globally and fits the needs of LM Wind Power. By switching to this resin choice, LM Wind Power should be able to reduce the scarf ratio of repairs and increase the integrity of their blades.

An initiator study was also performed as a spin off project of the repair resin project. The initiator study tested LM Wind Power's blade resin with four different initiators from Syrgis Performance Initiators. Each initiator type was chosen just to see what would happen with the blade resin. Using DSC and rheology, the four initiators were compared to the current initiator MCP-75. The data suggested that with each initiator tested, an initial spike in viscosity will occur. This is an undesirable trait because higher viscosity of the resin package results in a longer to for wet-out of the part. However, unlike MCP-75, HDP-75, and MCP-21, Pulcat did not show a gradual increase throughout the curing cycle at low weight percent initiator (1.2%). It did, however, gel in about half the time expected from the resin formulation. This leads us to believe that if Pulcat was used over MCP-75, that good wet-out may be achieved even with a shorter gel time. To prove that this is true, Pulcat would need to be tested in a VARTM system on top of the DSC and rheology testing and then compared to MCP-75. Due to financial and time constraints these tests were not performed. It is recommended that if LM Wind Power choses to further pursue this hypothesis, that infusion testing be performed with

Pulcat. However, at this time, there is no recommendation to change the initiator type based on the DSC and rheology data.

APPENDIX A: DSC DATA

Table A.1: Degree of cure for each resin and initiator tested from DSC

Resin	Initiator Type	% Initiator	ΔH_{iso} (J/g)	ΔH_{res} (J/g)	Degree of Cure (%)
GT80	Cadox M-50A	1.2	270.4	111.5	70.8
RH	Cadox M-50A	1.5	155.4	130.2	54.4
RL	Cadox M-50A	1.5	237.2	126.5	65.2
IP	Cadox M-50A	1.5	305.4	128.3	70.4
AD	Cadox M-50A	1.5	200.8	93.7	68.2
HA	Cadox M-50A	1.5	171.7	136.3	55.7
HB	Norox 925H	1.2	92.6	102.9	47.3
HB	Norox 925H	1.5	120.4	142.9	45.7
HB	Norox 925H	1.7	5.51	257.9	2.1
HB	Norox 925H	2.0	18.4	244.9	7.0
HB	Norox HDP-75	1.5	158.1	170.2	48.2
HB	Norox HDP-75	1.7	103.7	224.5	31.6
HB	Norox HDP-75	2.0	71.3	256.9	21.7

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Figure A. 1: GT80 25 °C isothermal DSC scan
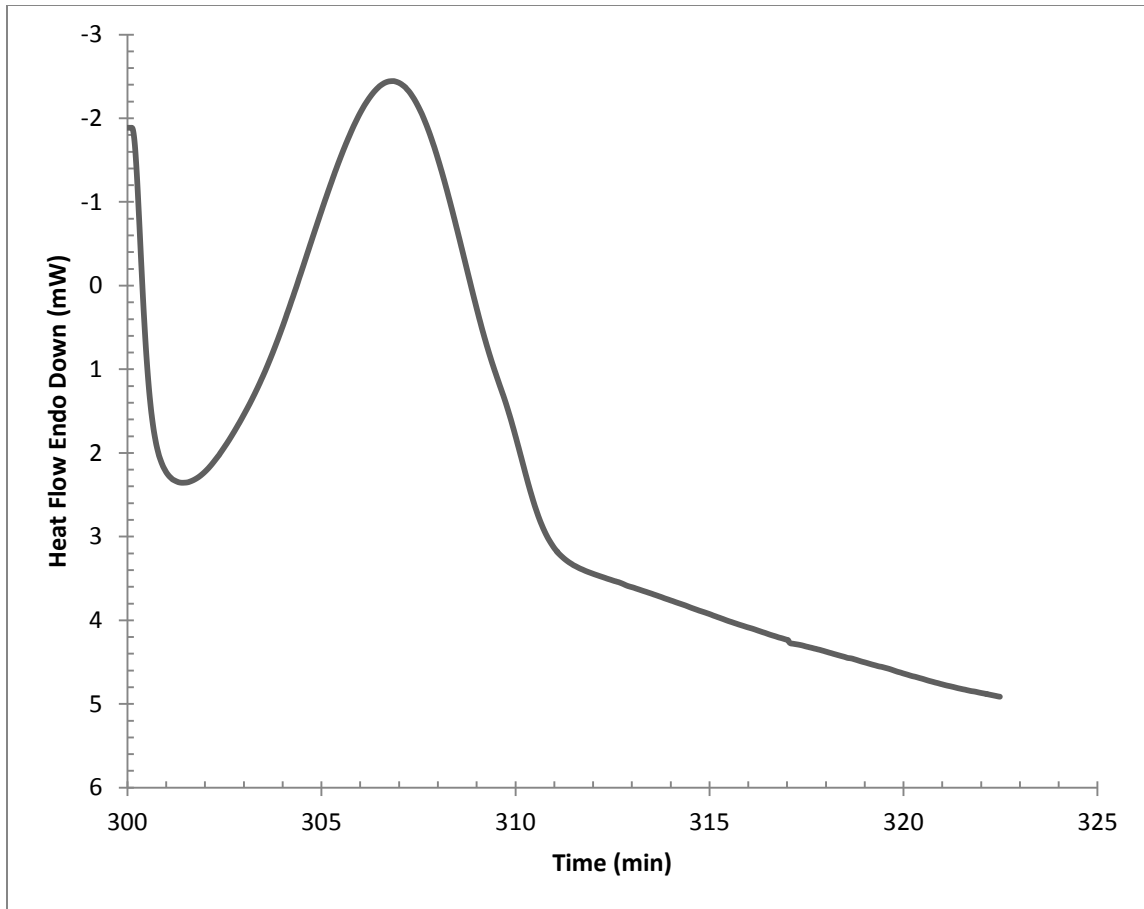
Figure A. 2: GT80 post isothermal dynamic DSC scan

Figure A. 3: AD 25 ^{o}C isothermal DSC scan

65
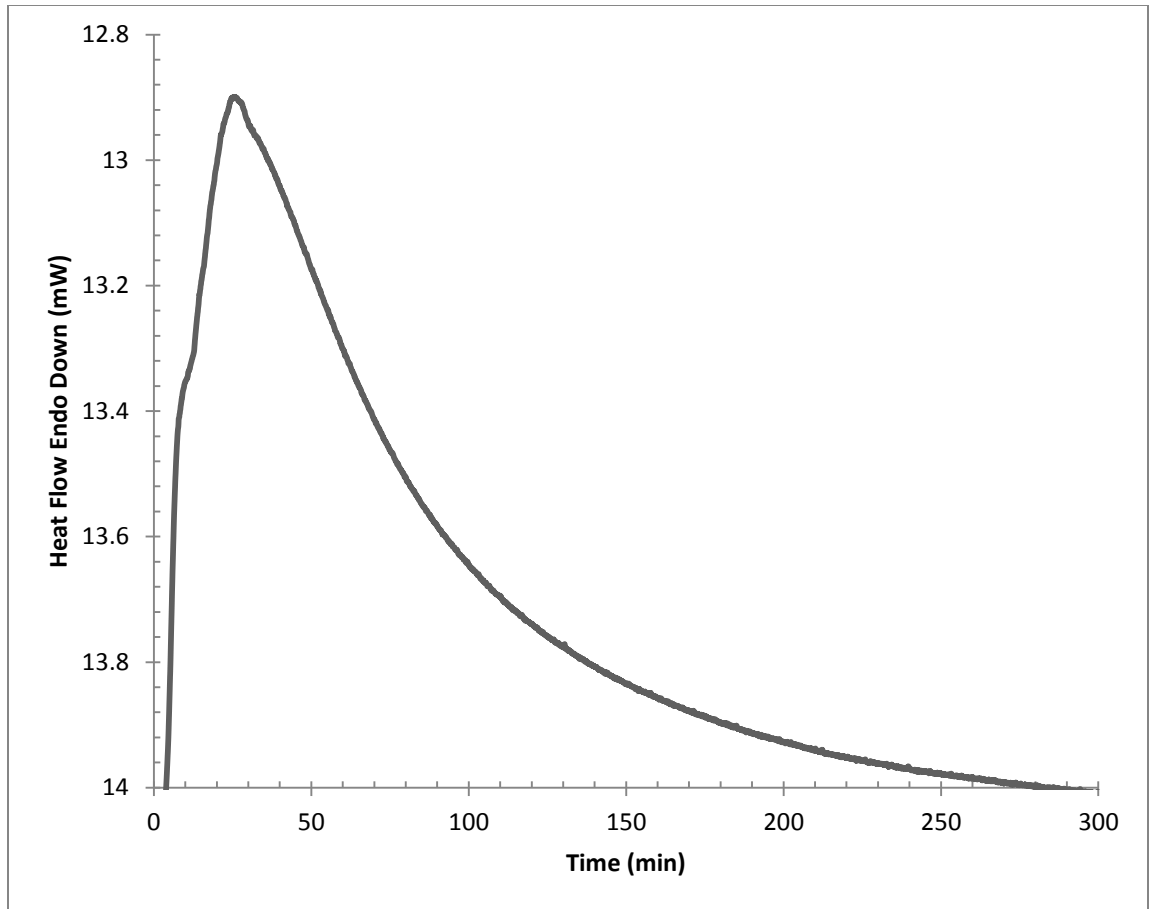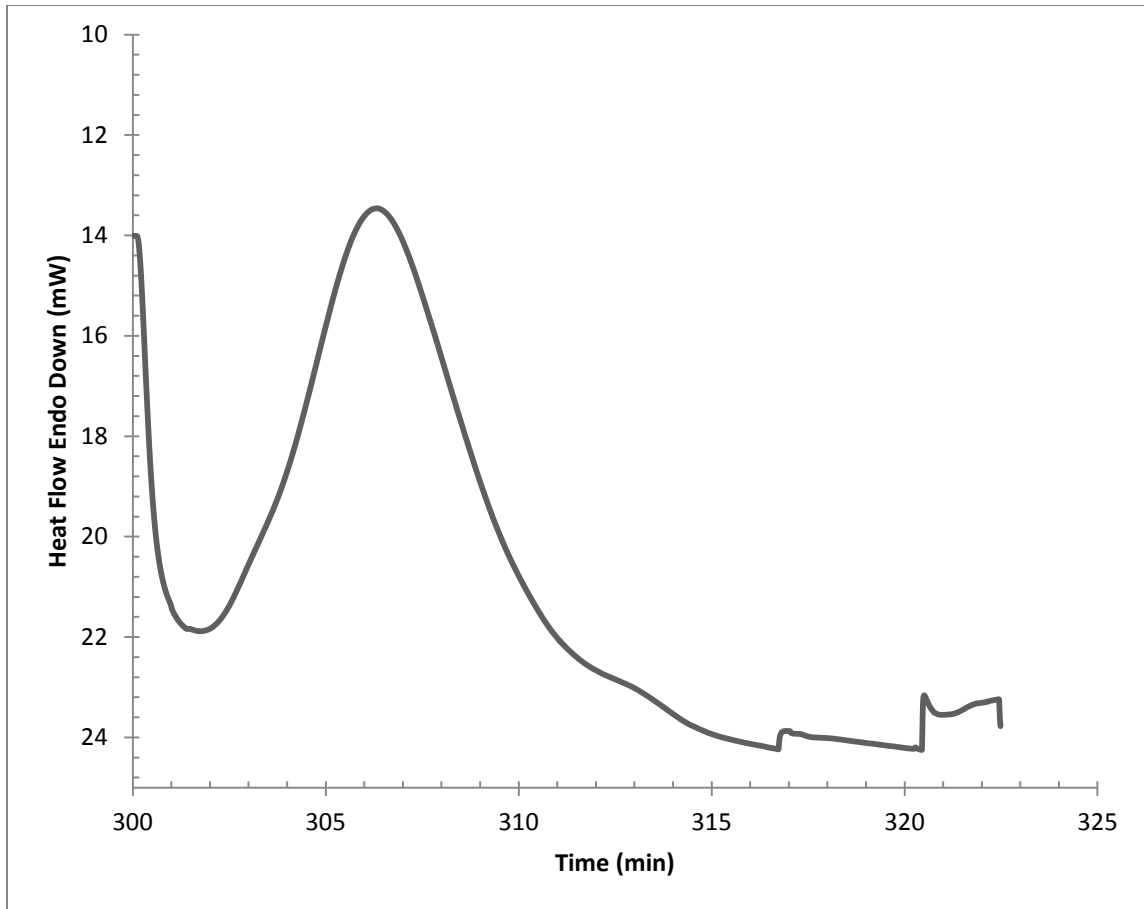
Figure A. 4: AD post isothermal dynamic DSC scan

66
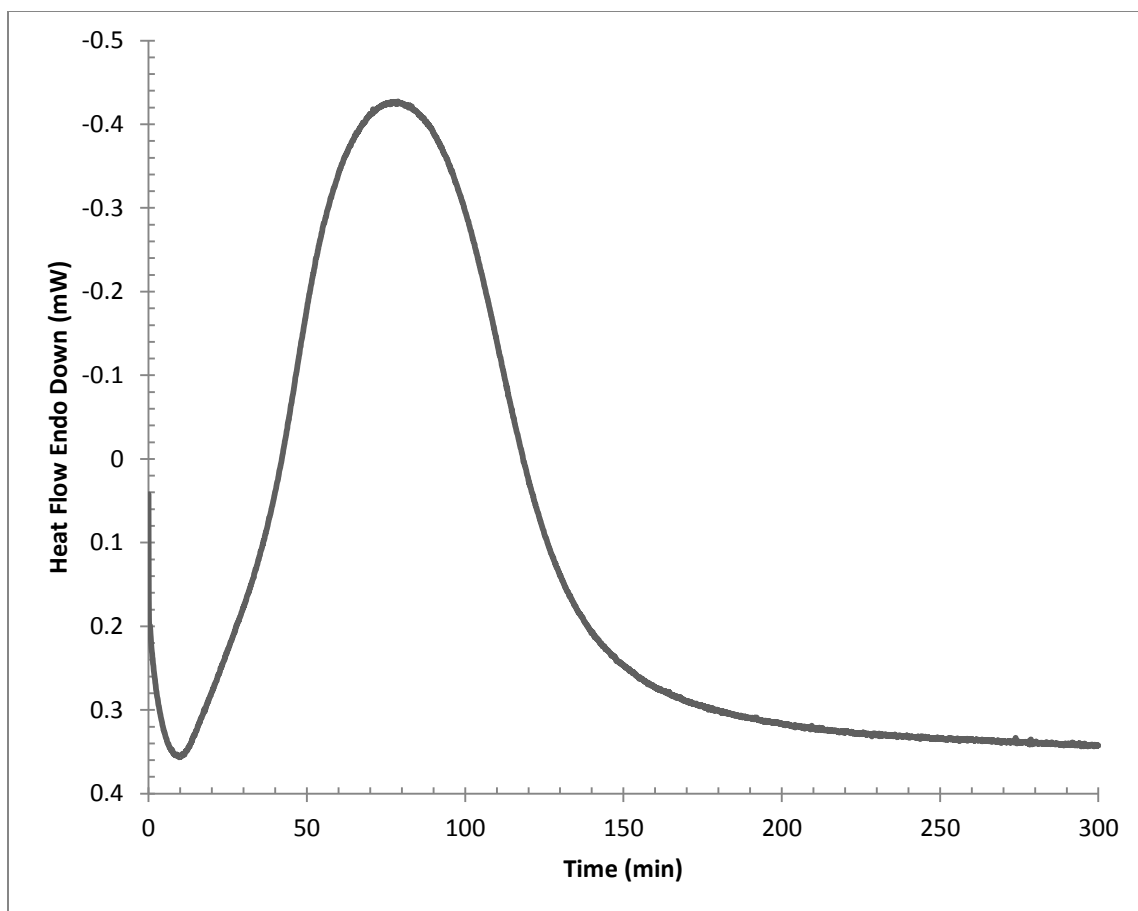
Figure A. 5: IP 25 °C isothermal DSC scan
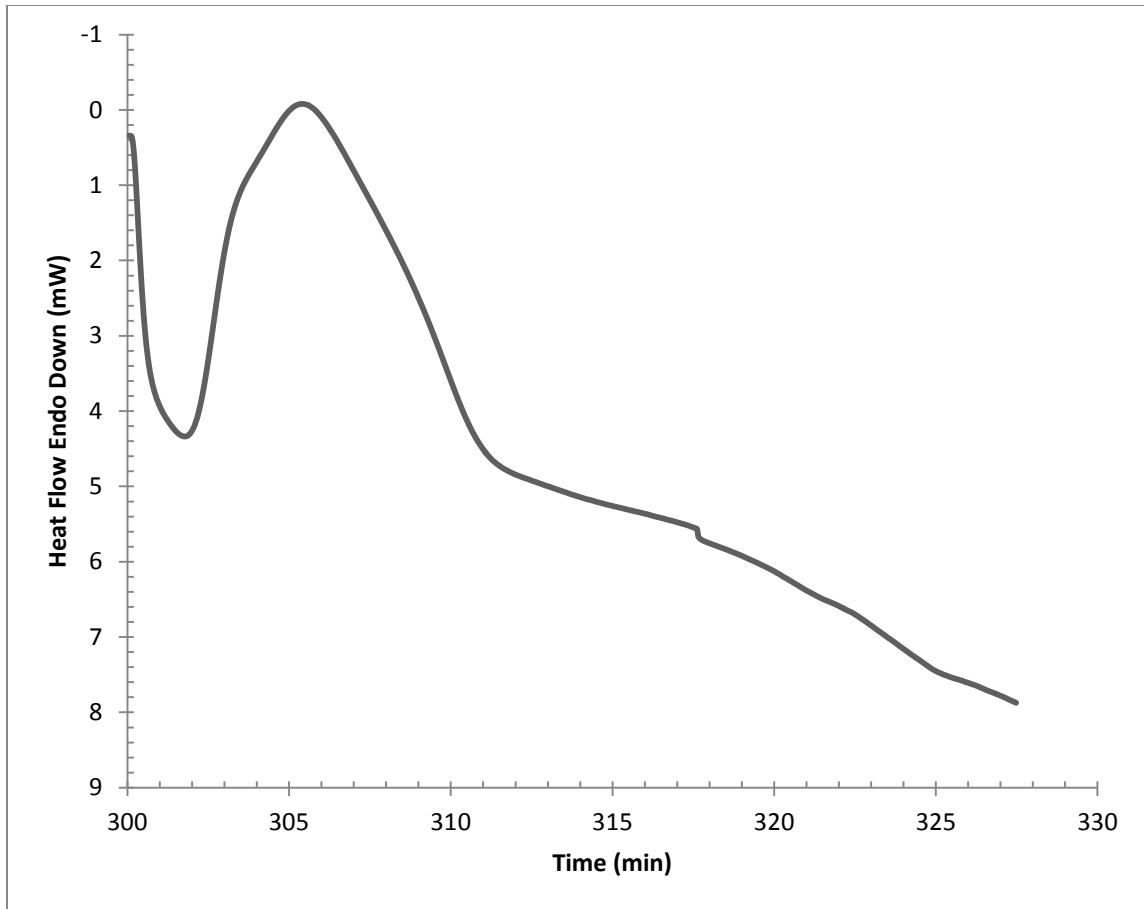
Figure A. 6: IP post isothermal dynamic DSC scan

68
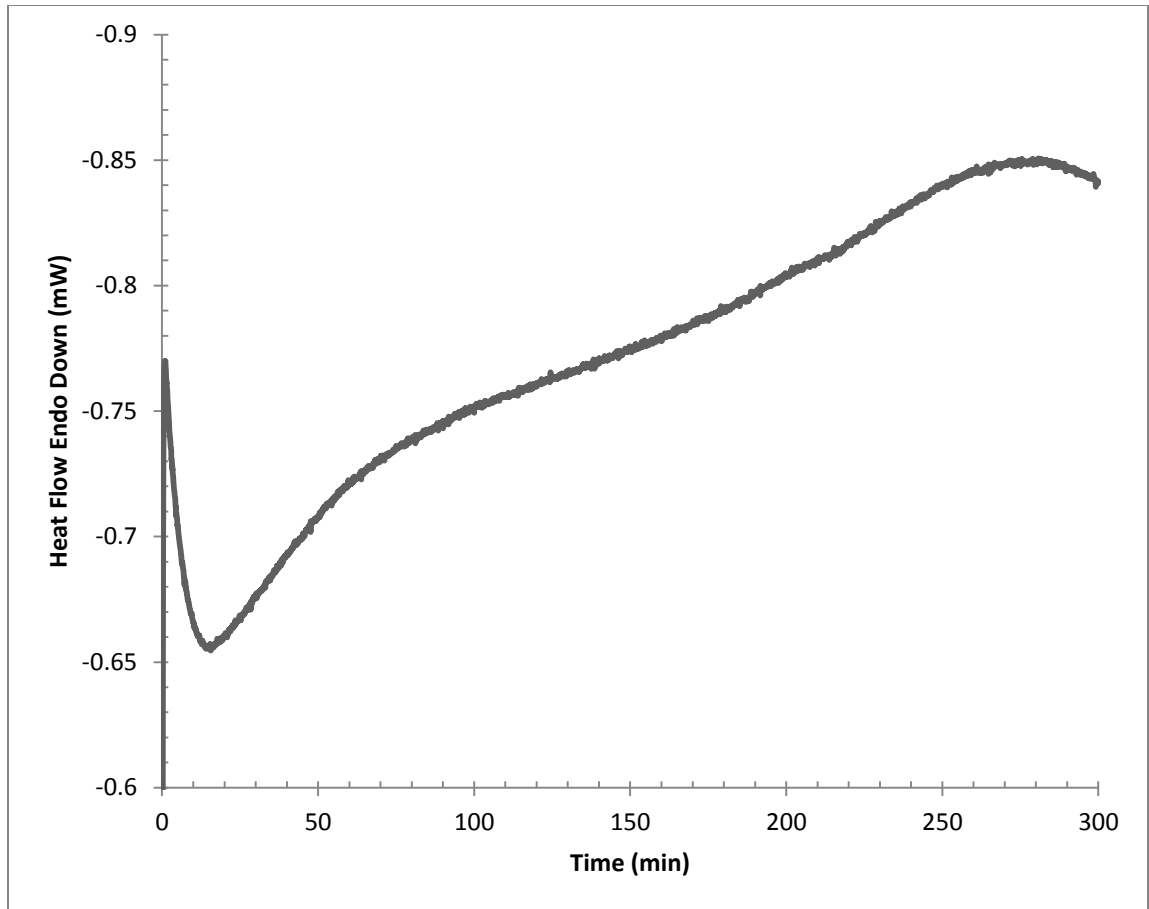
Figure A. 7: RH 25 °C isothermal DSC scan
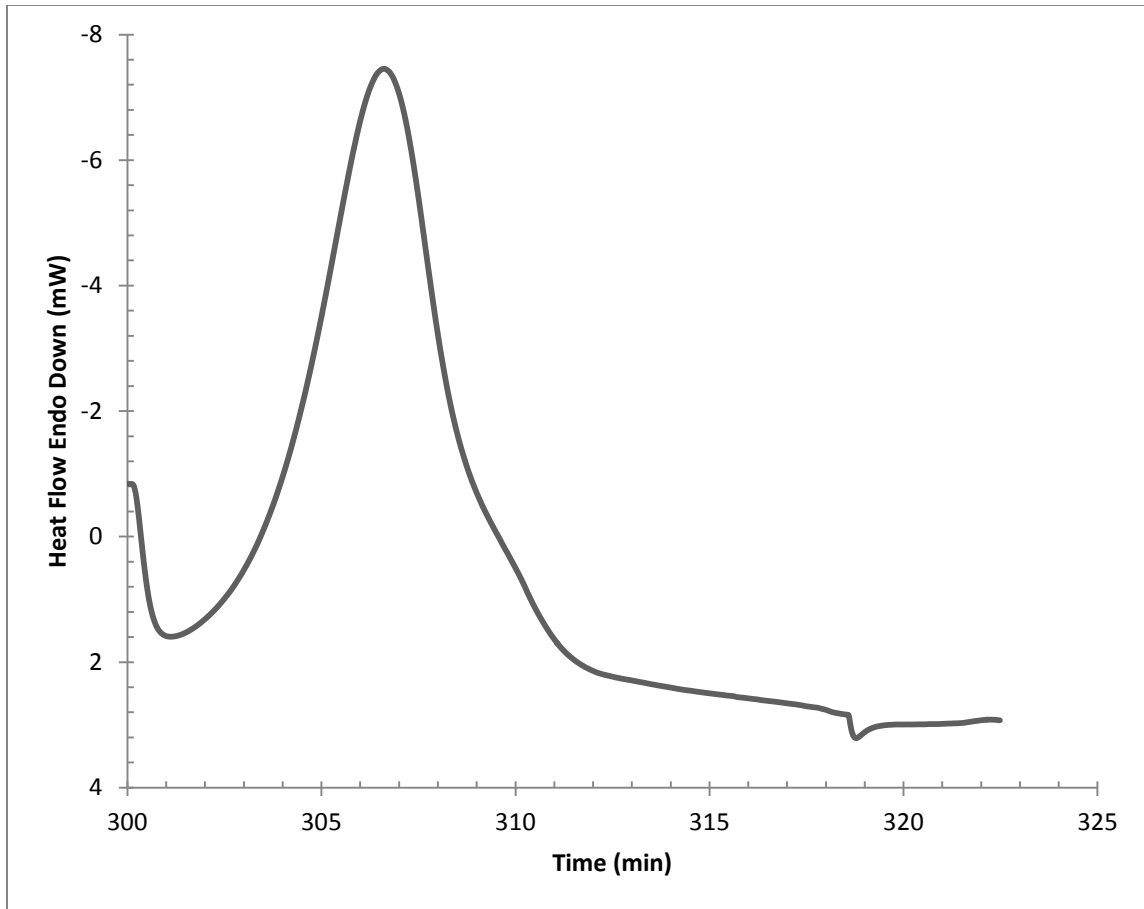
Figure A. 8: RH post isothermal dynamic DSC scan

70
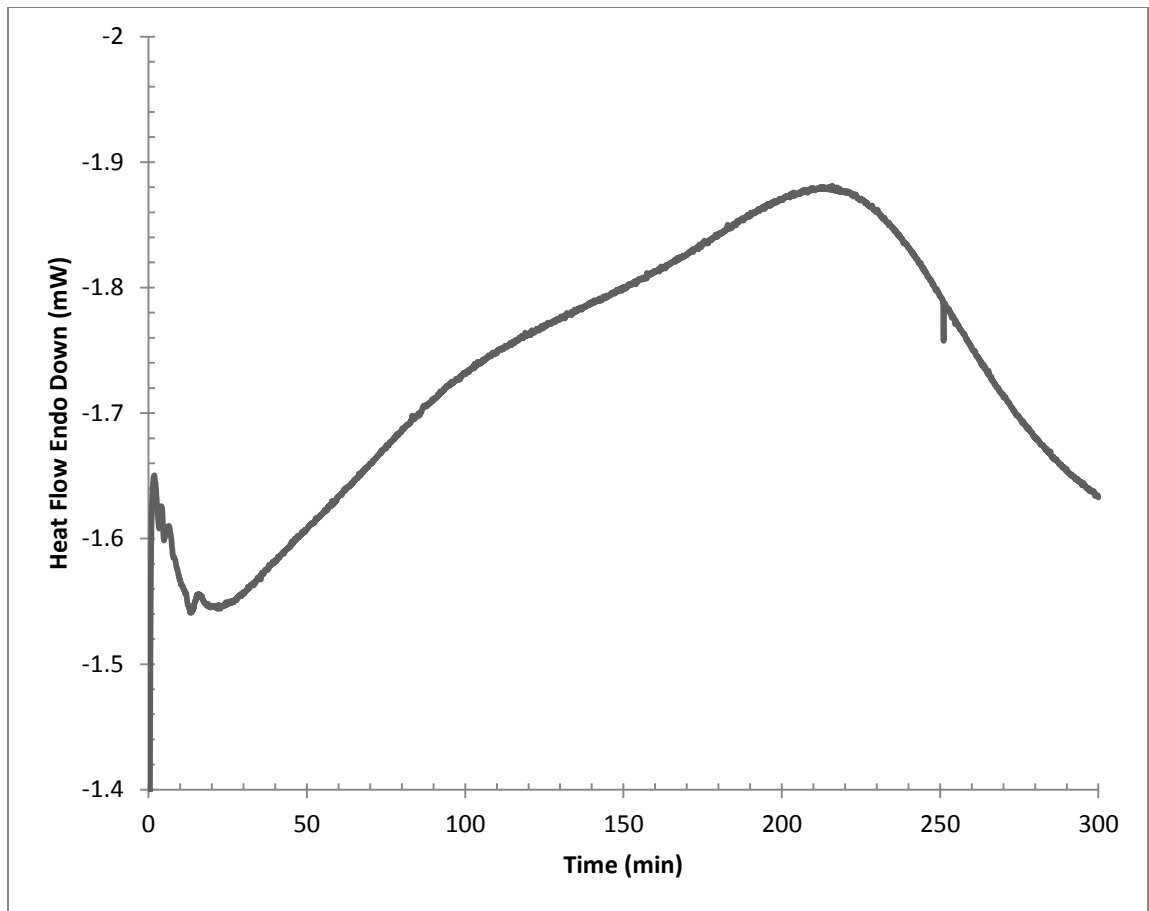
Figure A. 9: RL 25 °C isothermal DSC scan
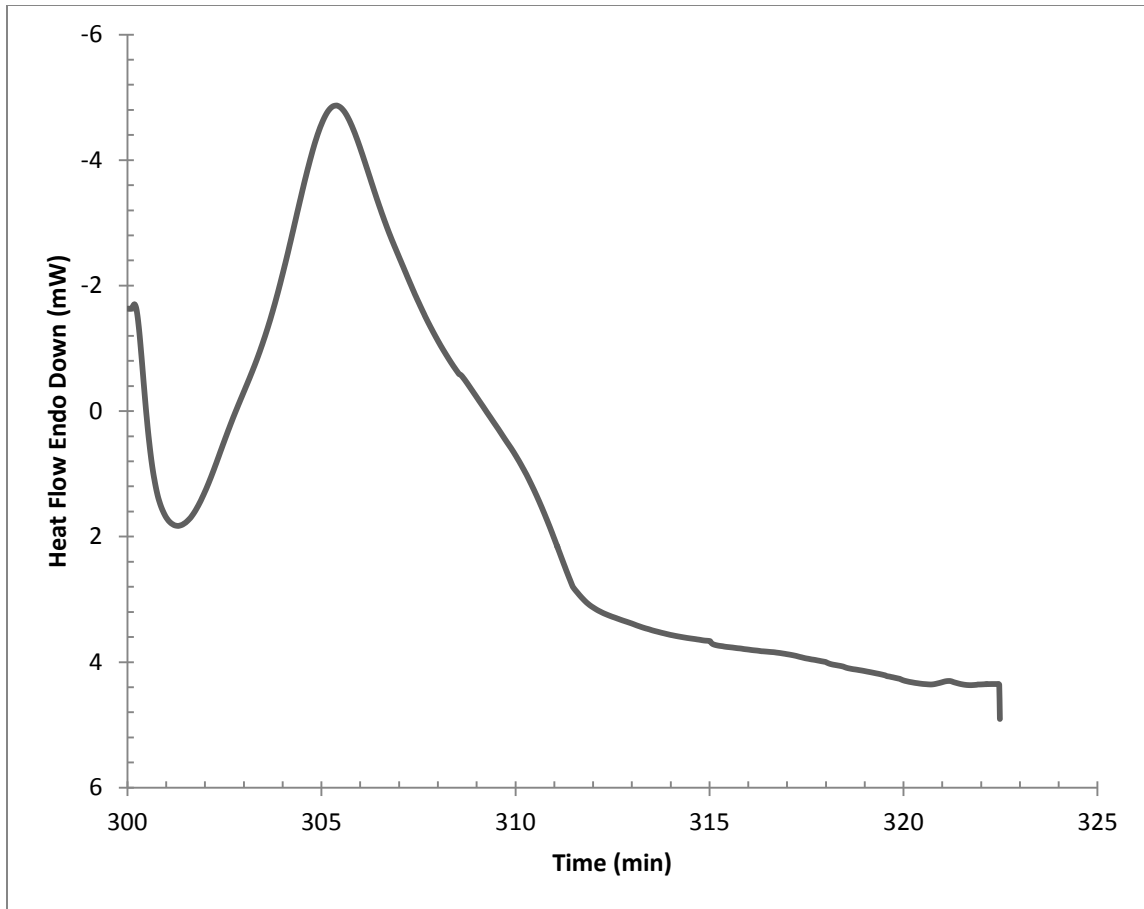
Figure A. 10: RL post isothermal dynamic DSC scan

72
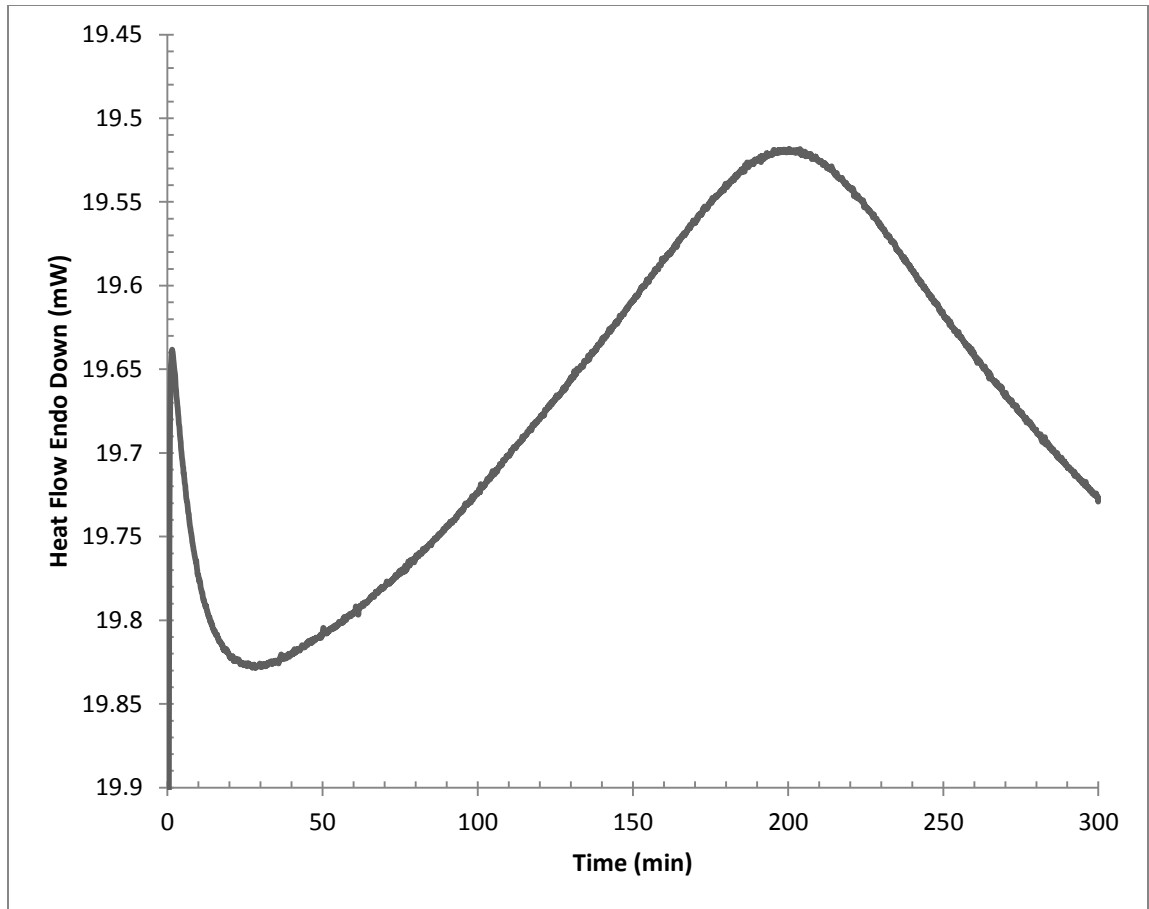
Figure A. 11: HA 25 °C isothermal DSC scan
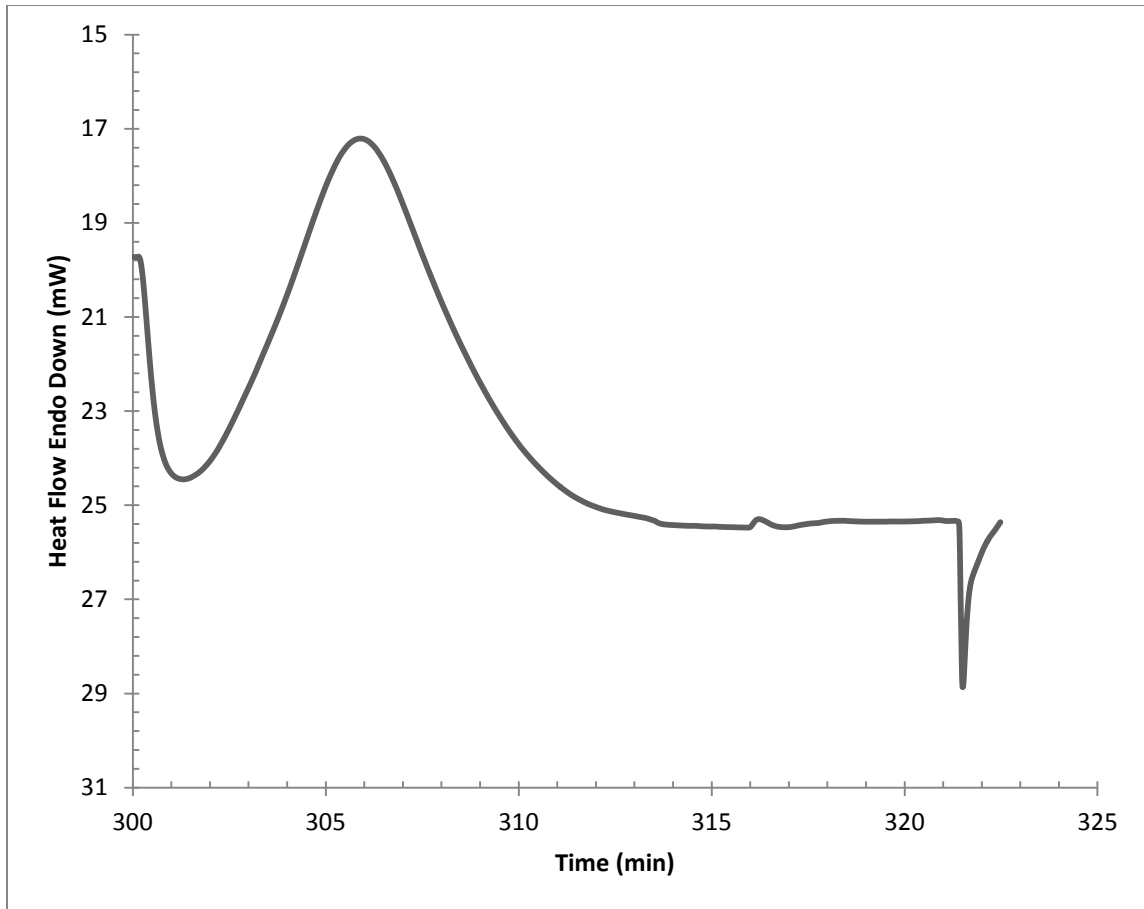
Figure A. 12: HA post isothermal dynamic DSC scan

74

Figure A. 13: HB 25 ^{o}C isothermal DSC scan with varying MEKP-925H initiator

75
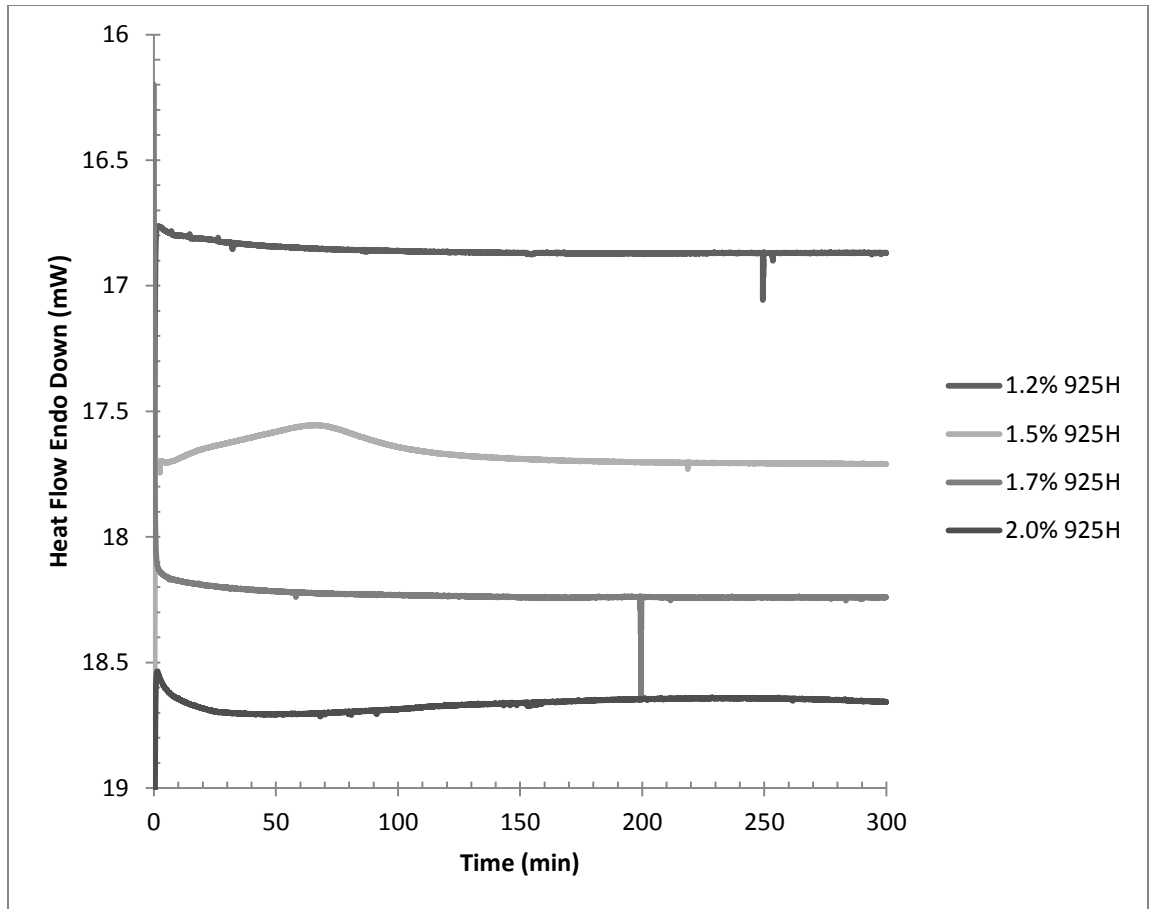
Figure A. 14: HB post isothermal dynamic DSC scan with varying MEKP-925H
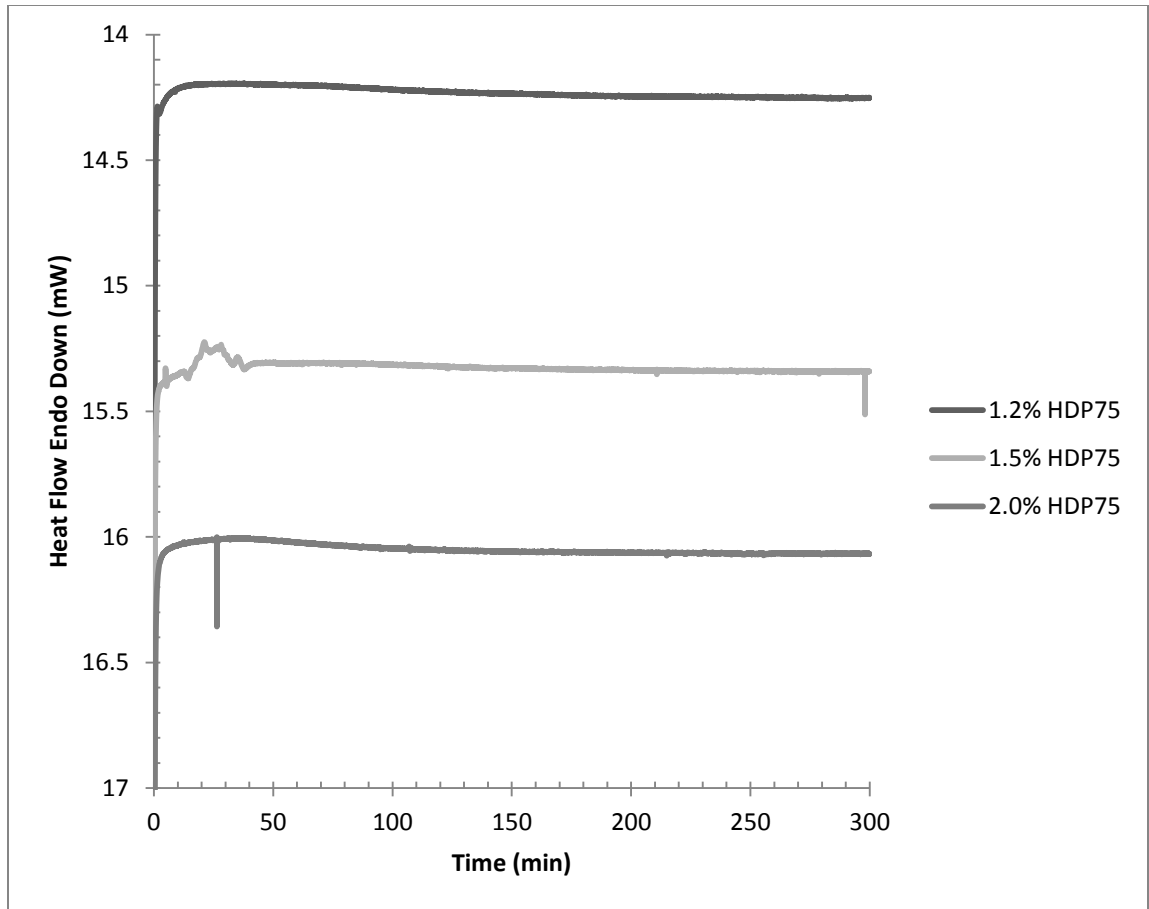
initiator

Figure A. 15: HB 25 °C isothermal DSC scan with varying HDP-75 initiator
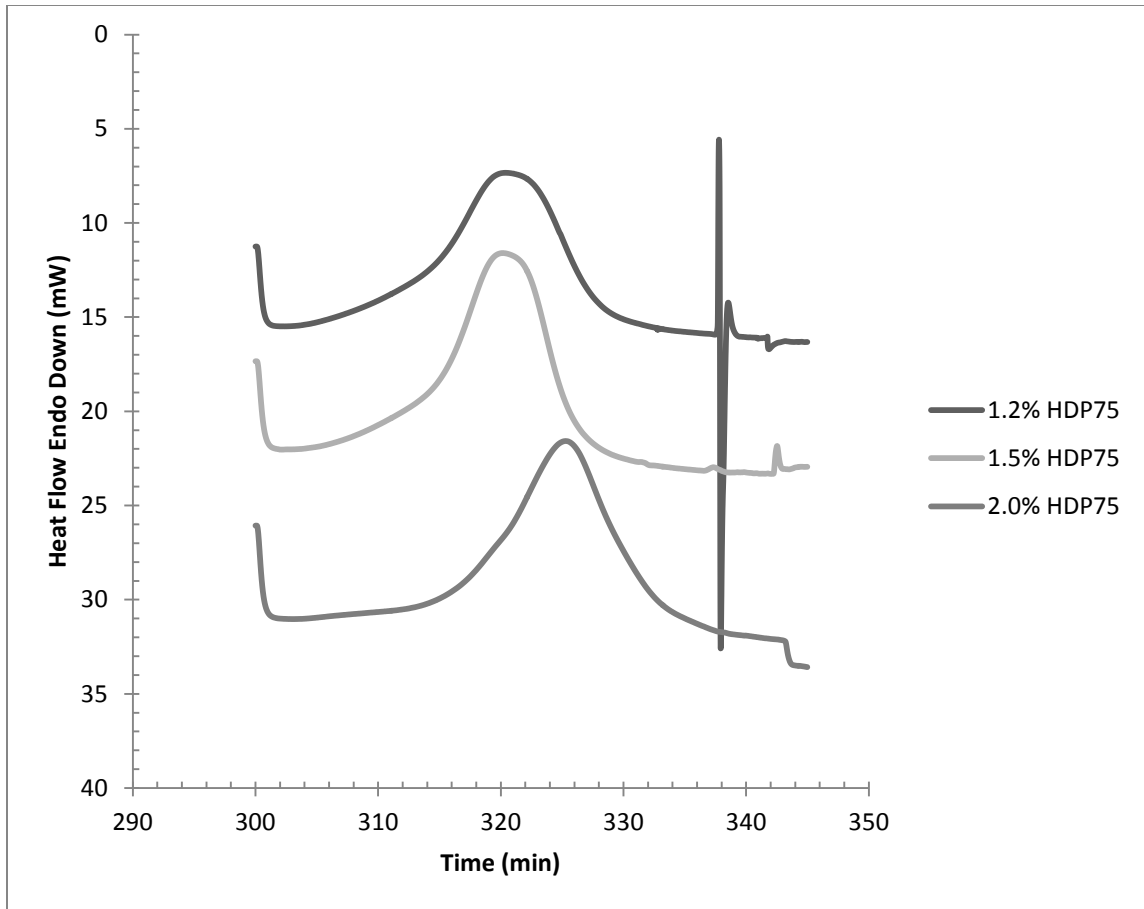
Figure A. 16: HB post isothermal dynamic DSC scan with varying HDP-75 initiator

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APPENDIX B: RHEOLOGY DATA
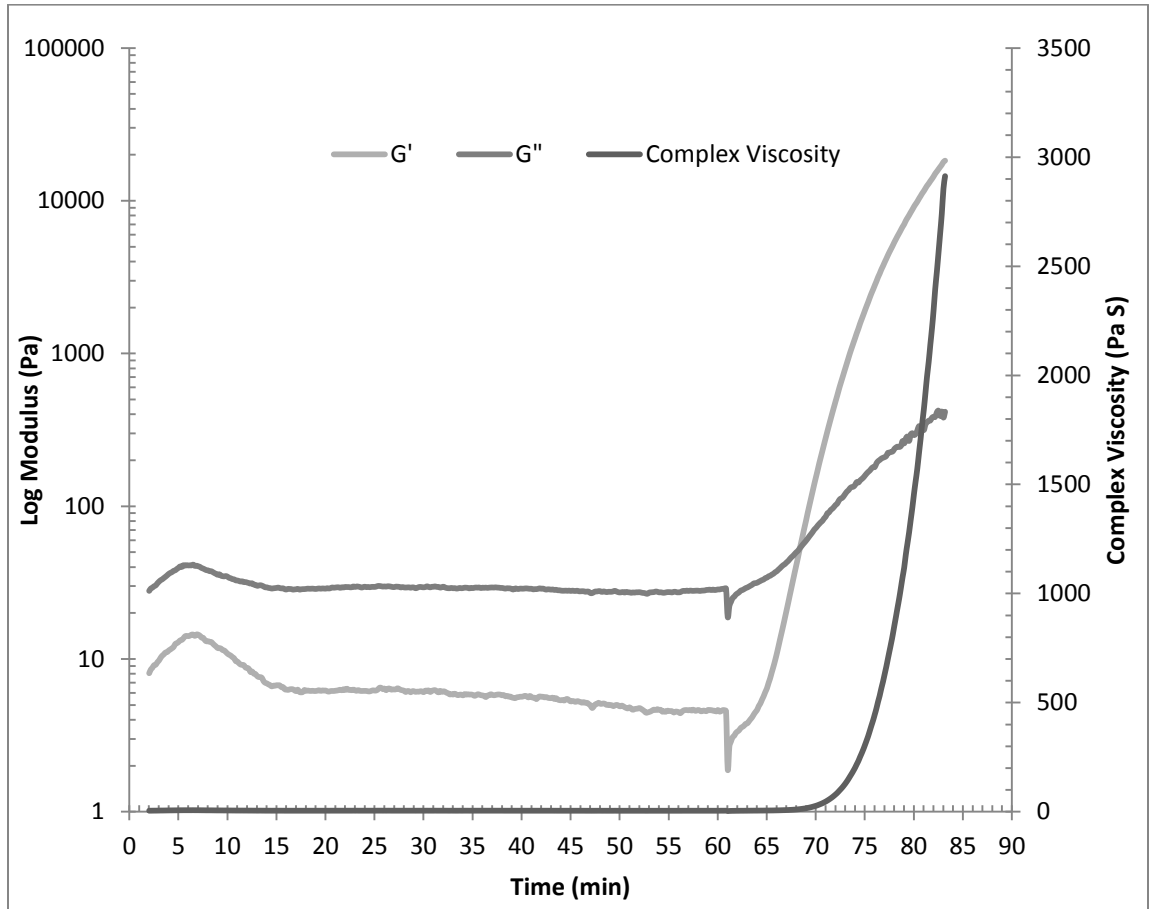
Figure B. 1: Rheological Testing of GT80 at Ambient Conditions
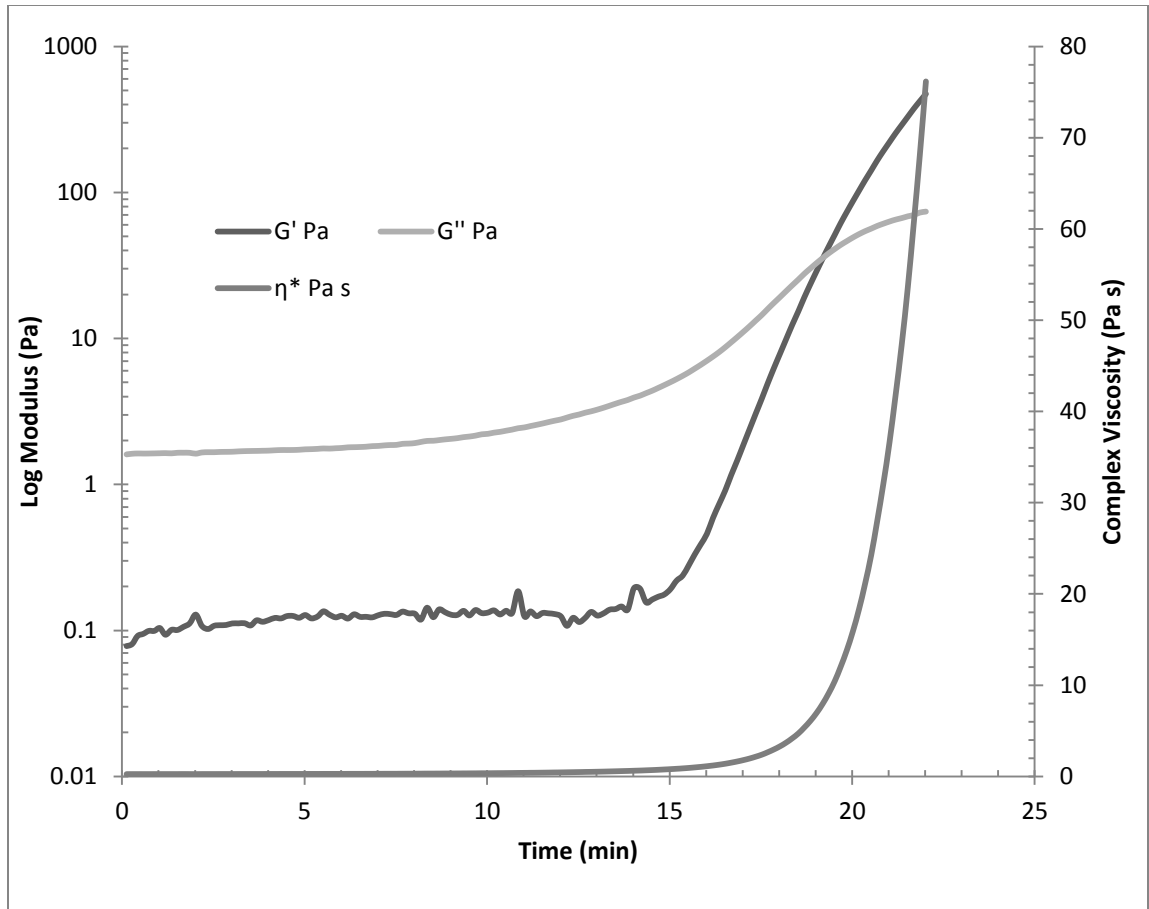
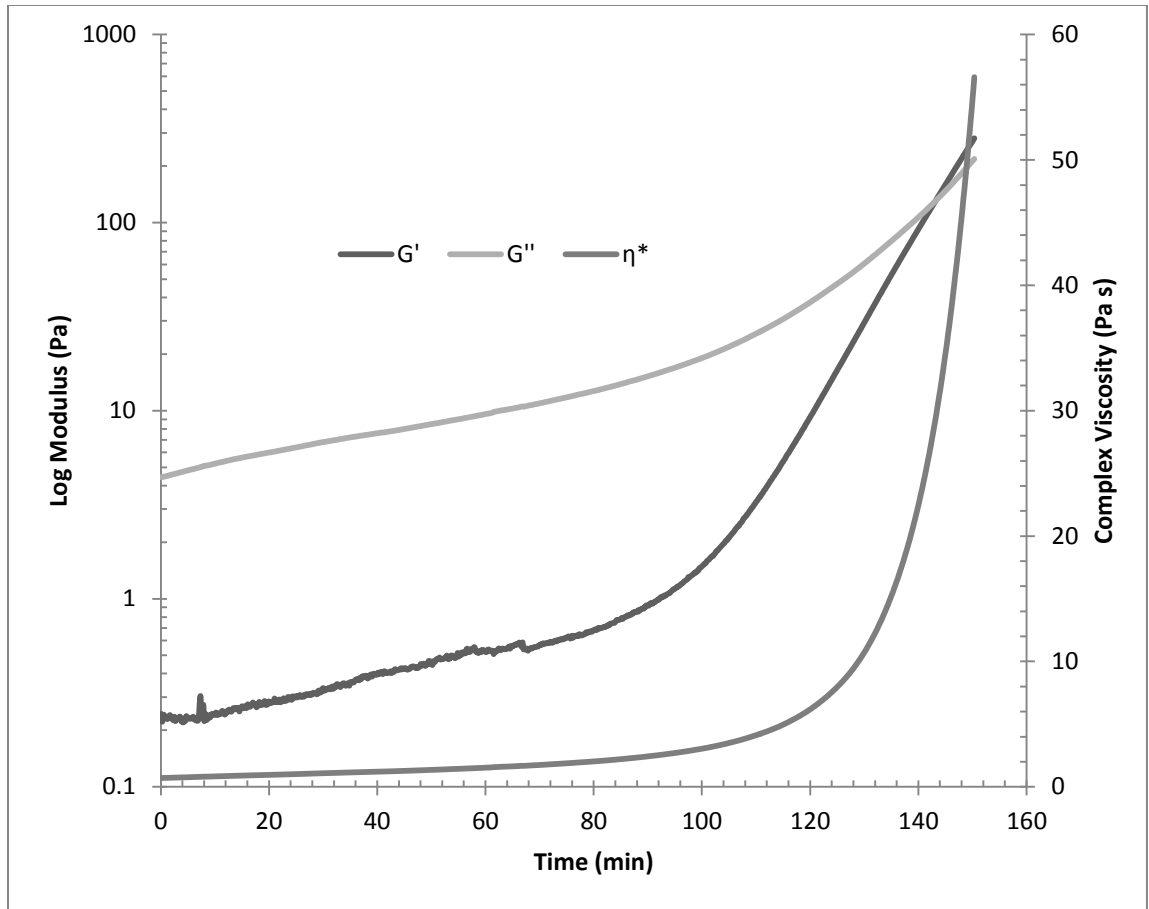**Figure B. 2: Rheological Testing of AD at Ambient Conditions**

80
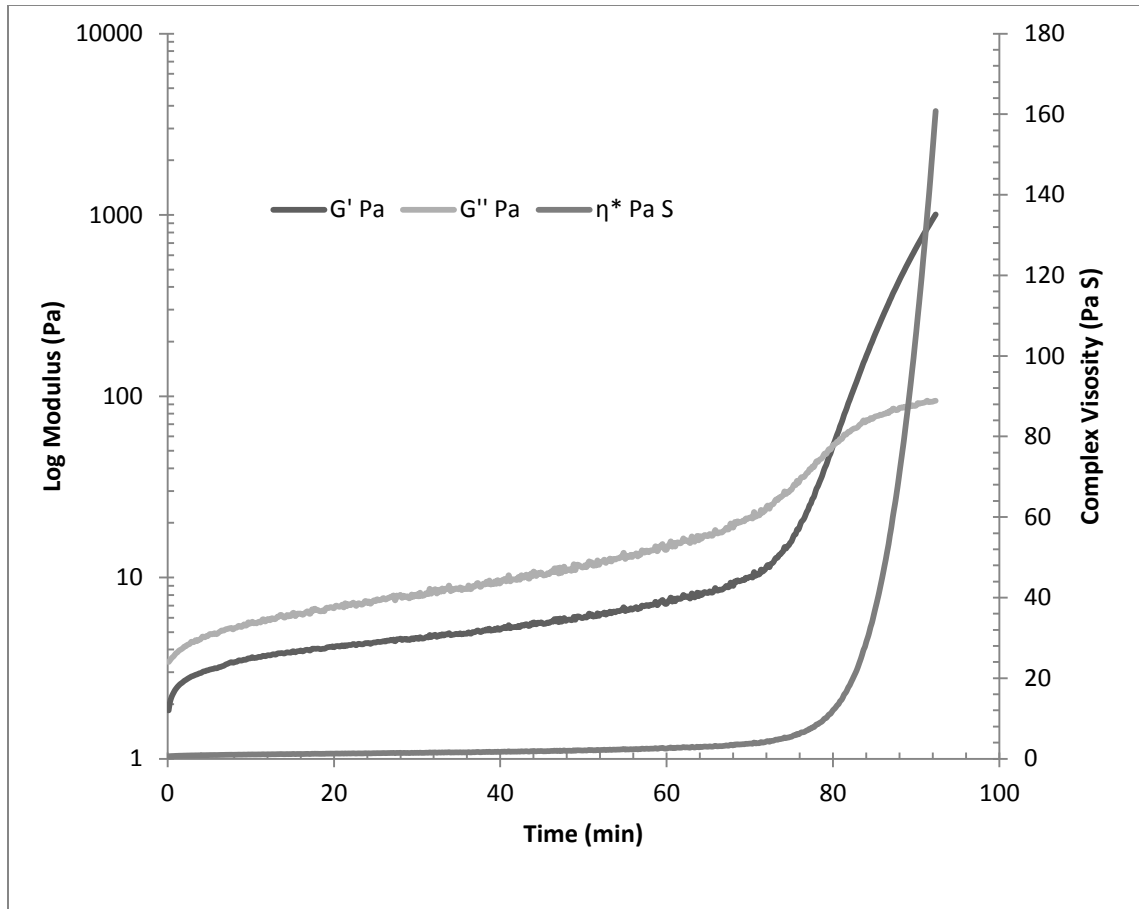
Figure B. 3: Rheological Testing of IP at Ambient Conditions

81
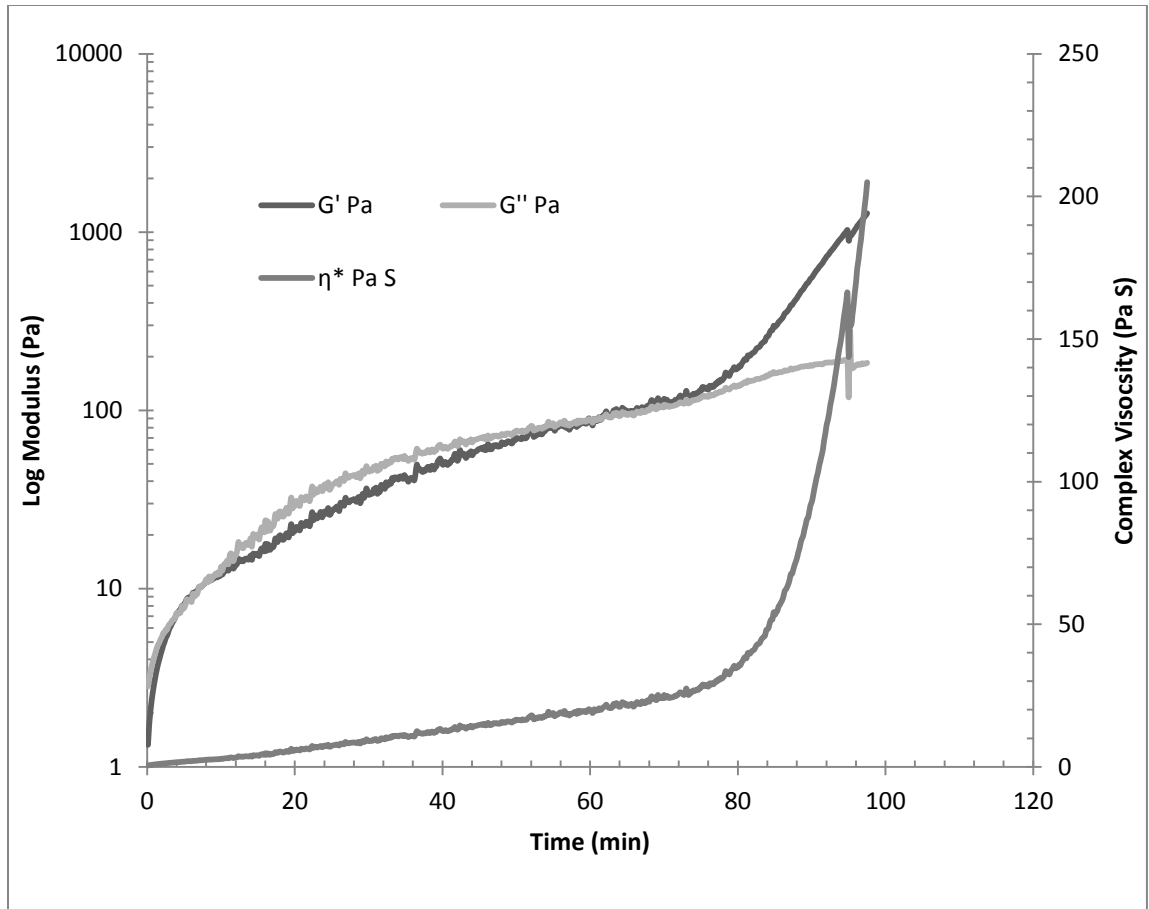
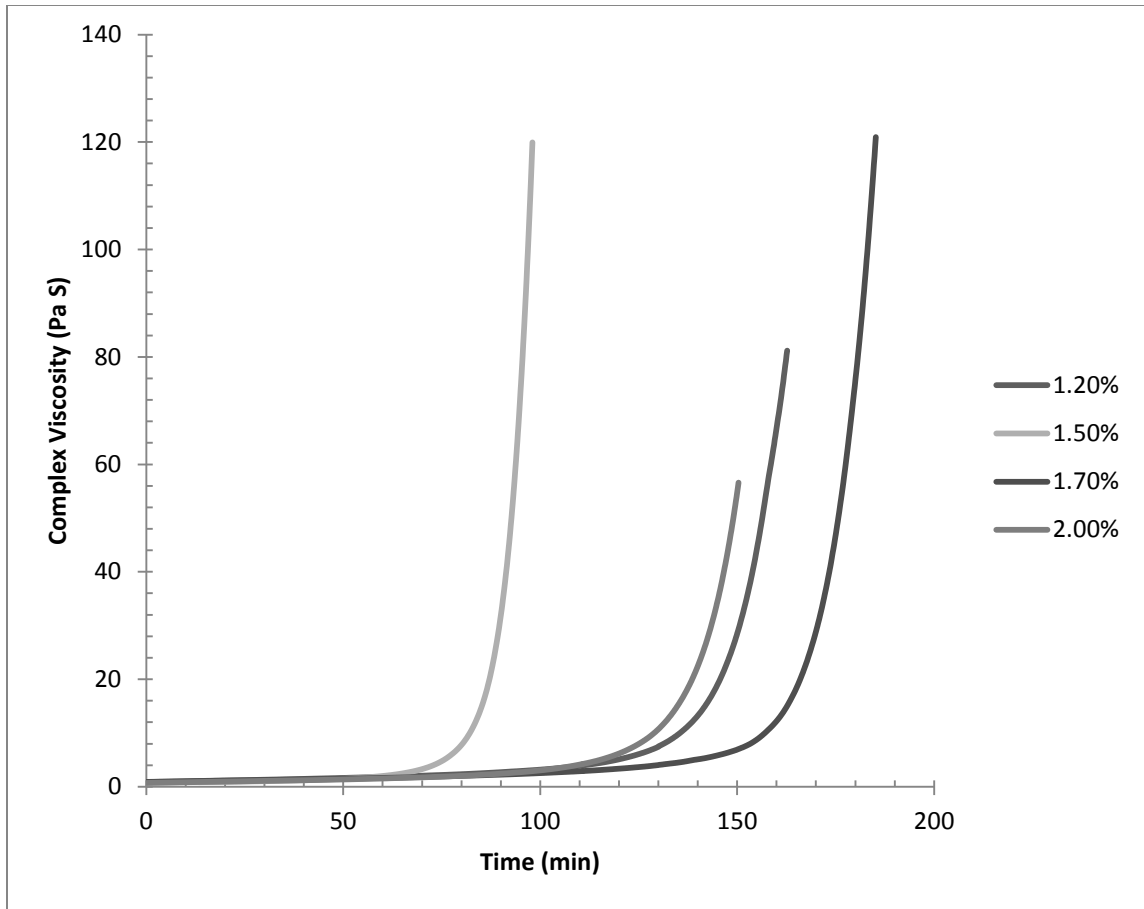**Figure B. 4: Rheological Testing of RH at Ambient Conditions**
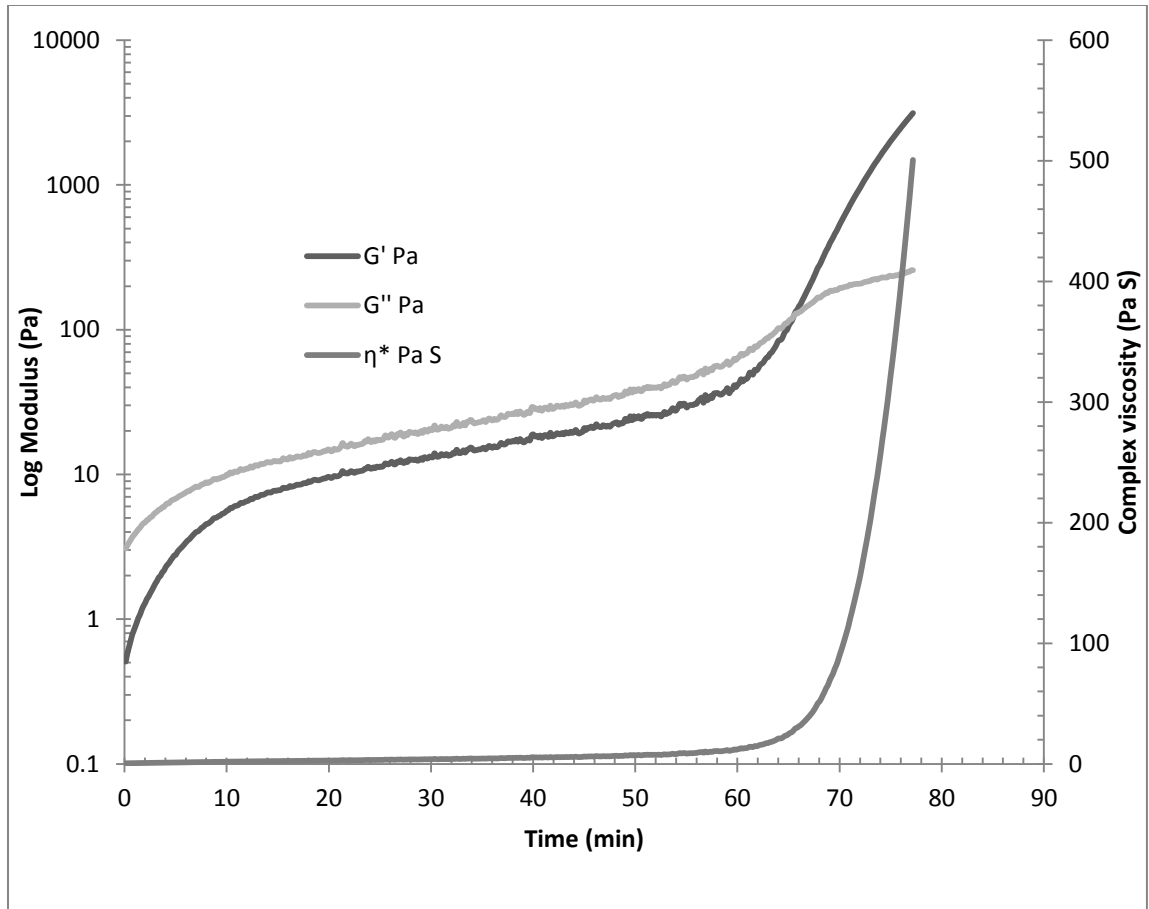
Figure B. 5: Rheological Testing of RL at Ambient Conditions
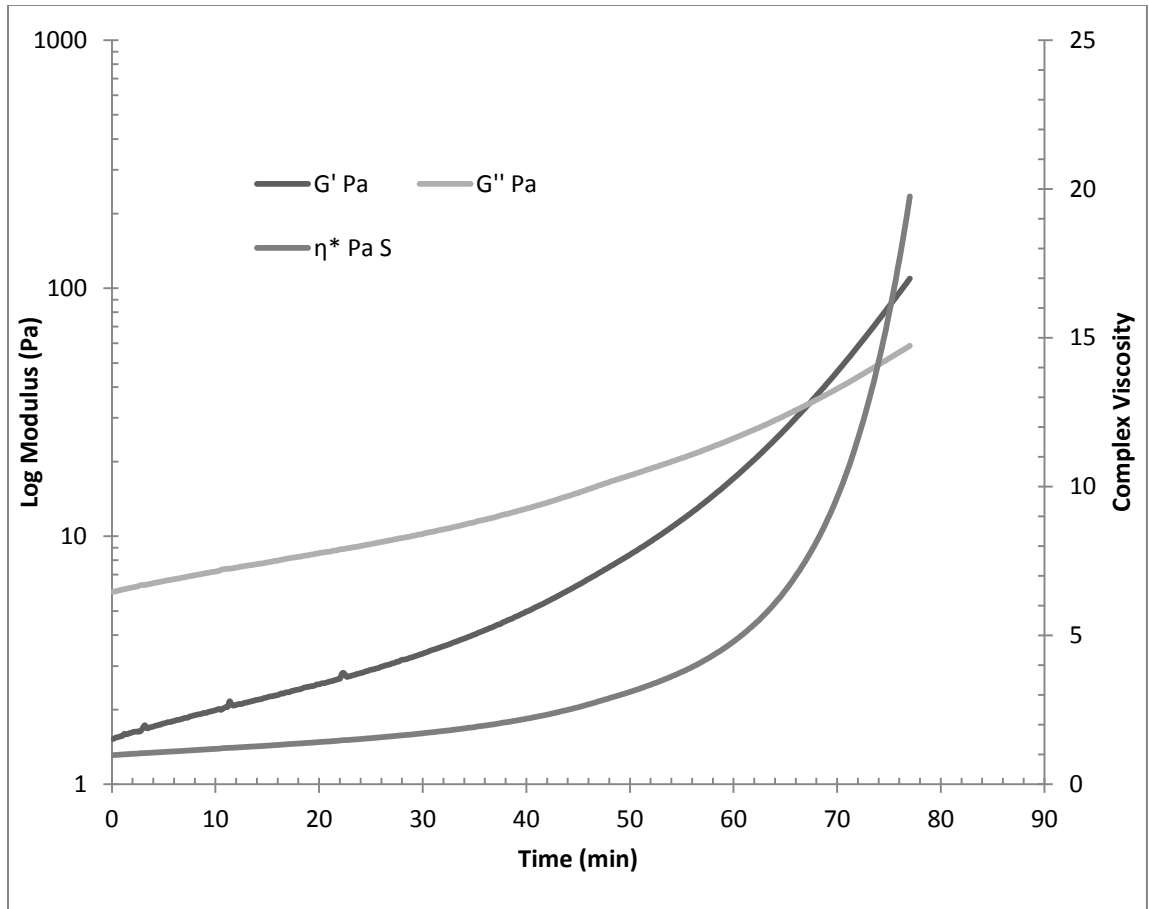
Figure B. 6: Rheological Testing of HA at Ambient Conditions

84
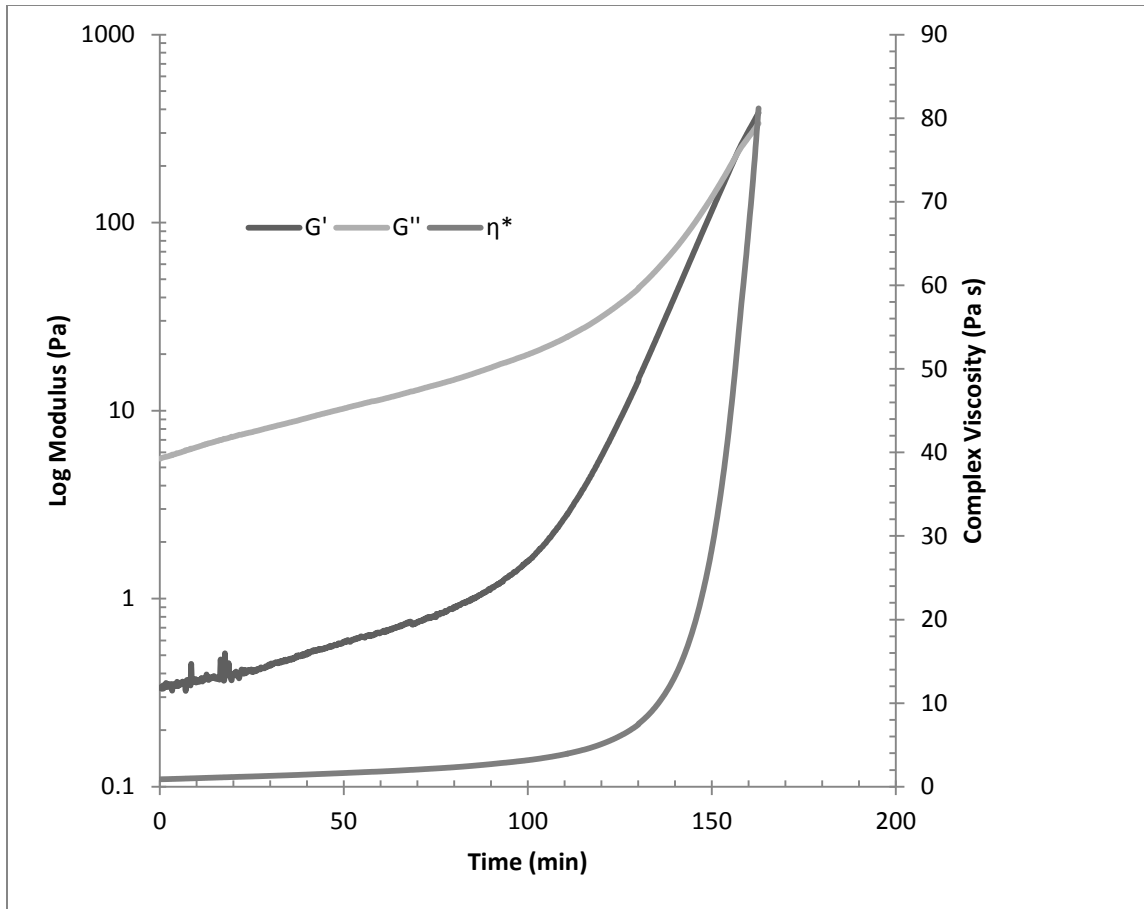
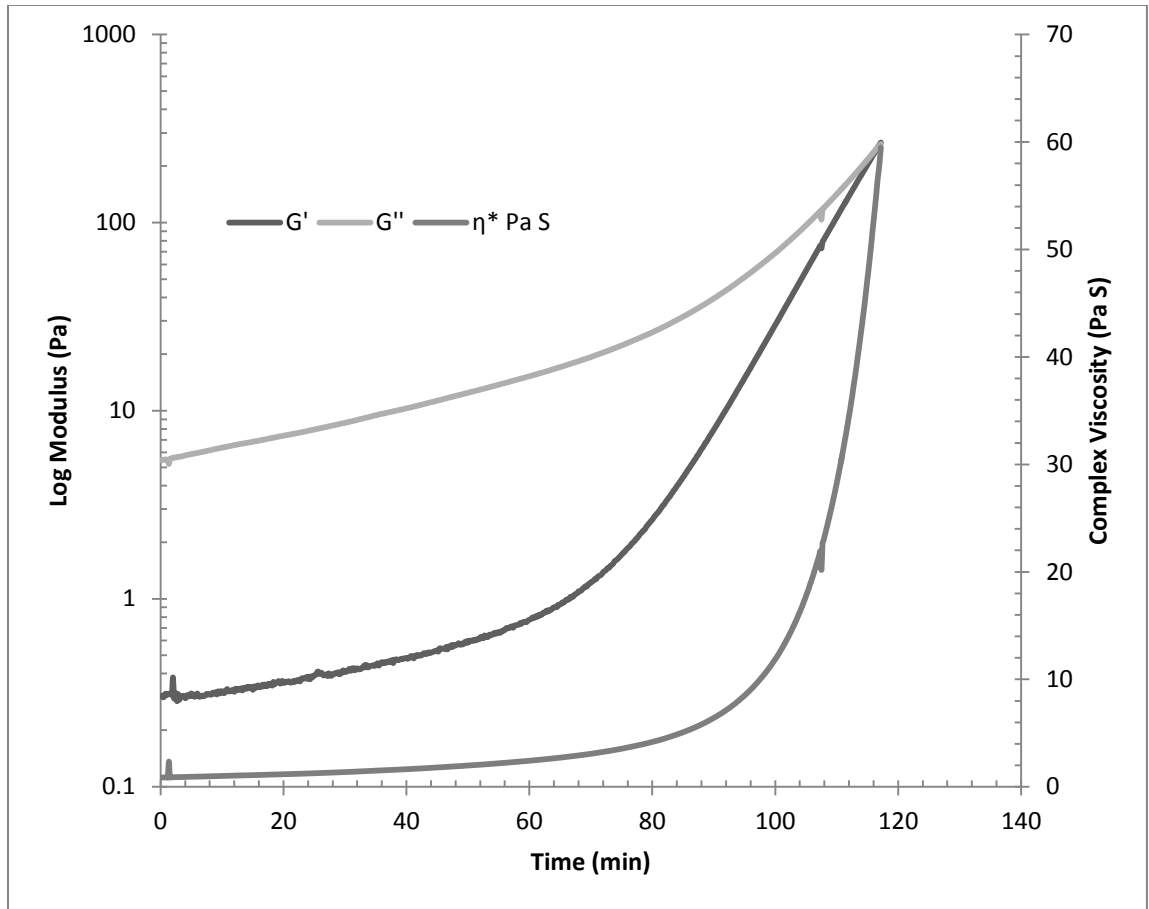**Figure B. 7: Rheological Testing of HB with 1.2% 925H at Ambient Conditions**

85
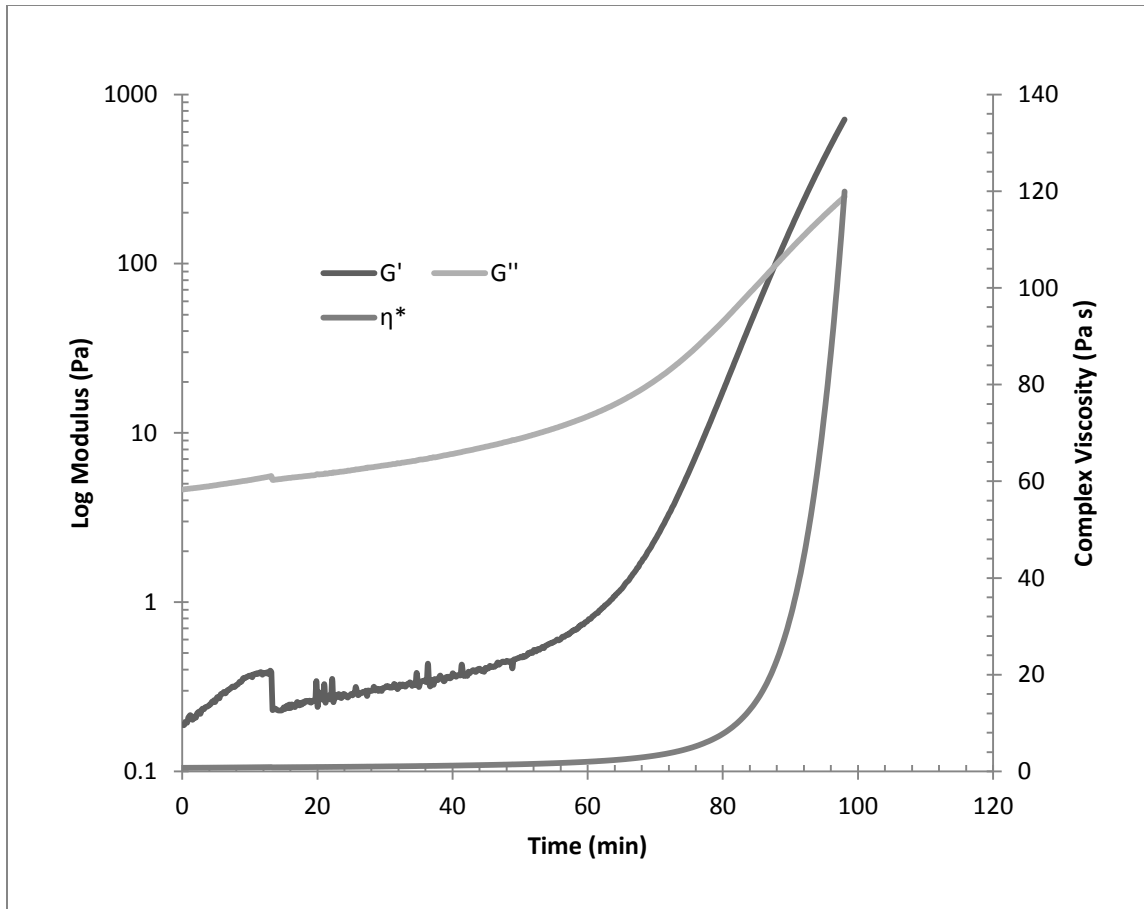
Figure B. 8: Rheological Testing of HB with 1.5% 925H at Ambient Conditions
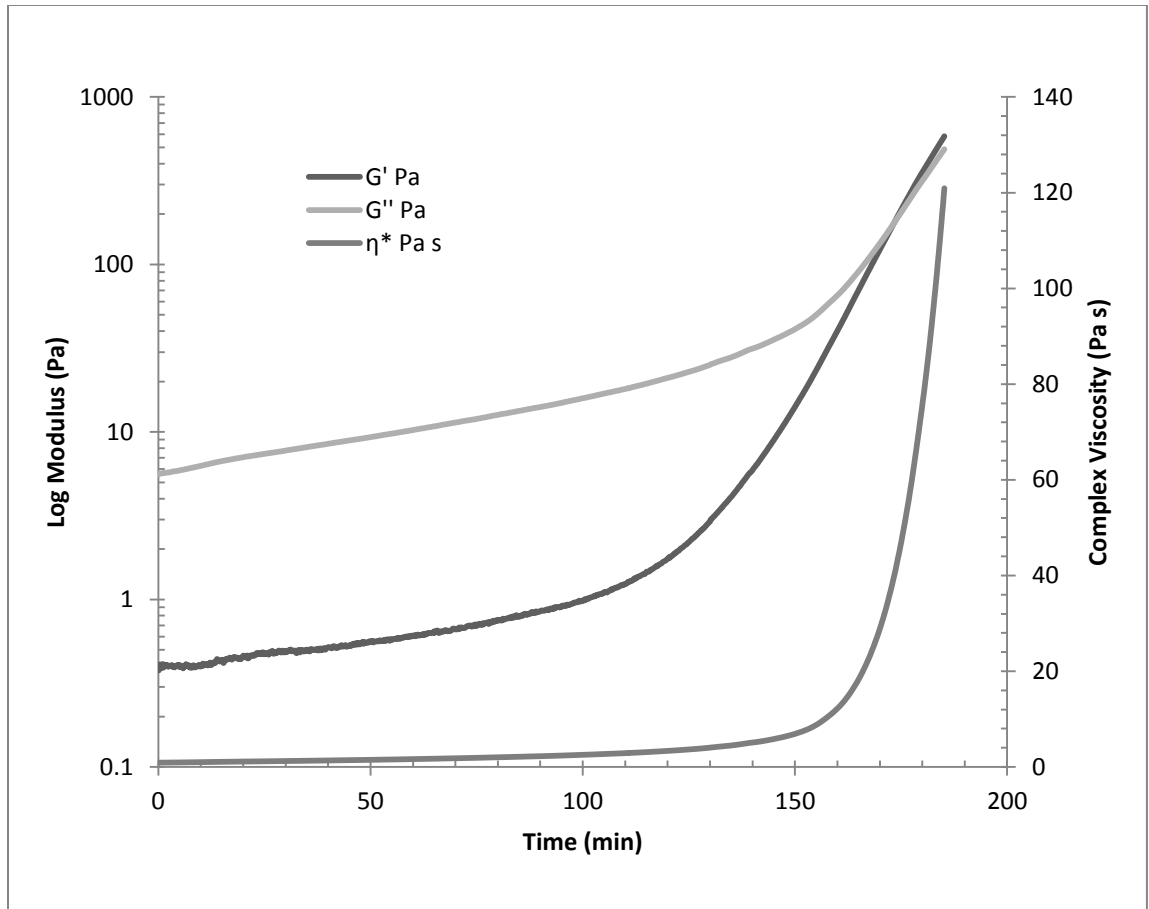
Figure B. 9: Rheological Testing of HB with 1.7% 925H at Ambient Conditions
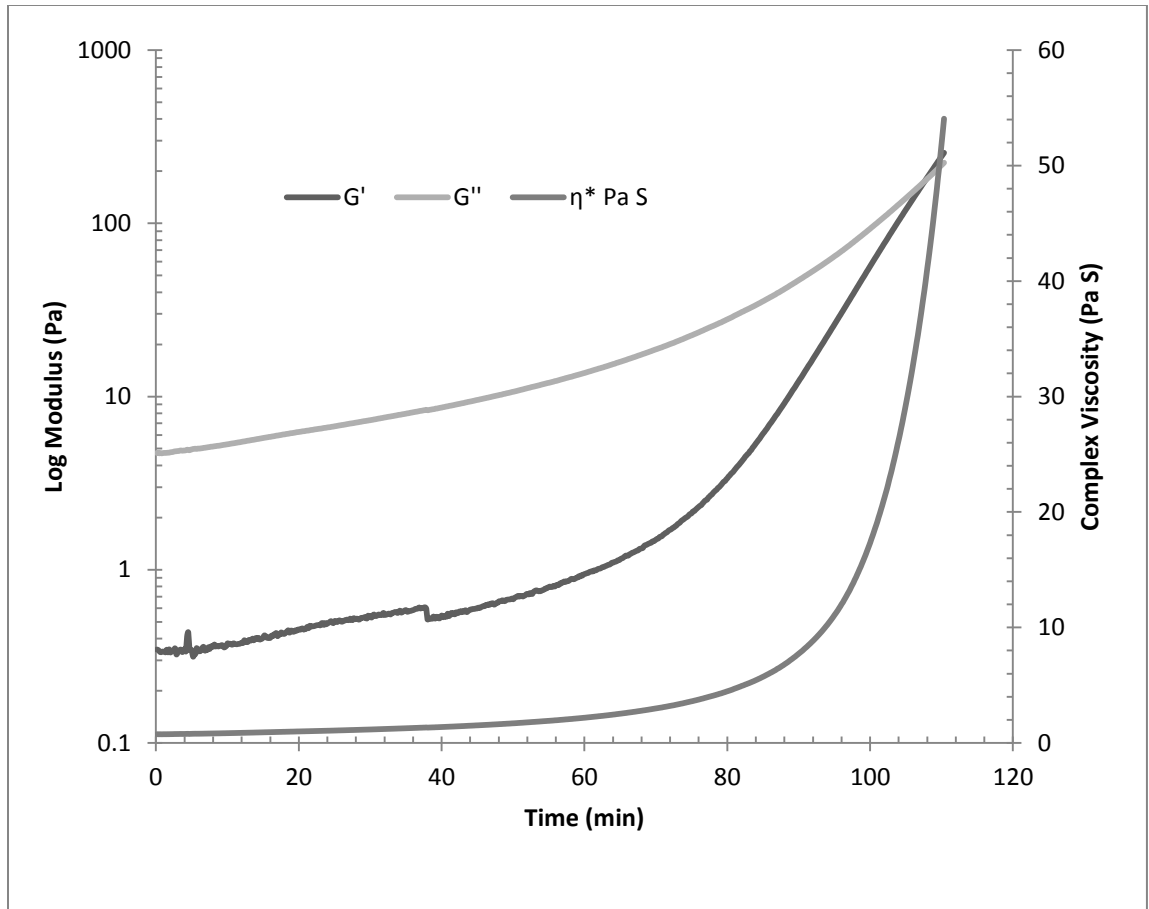
87

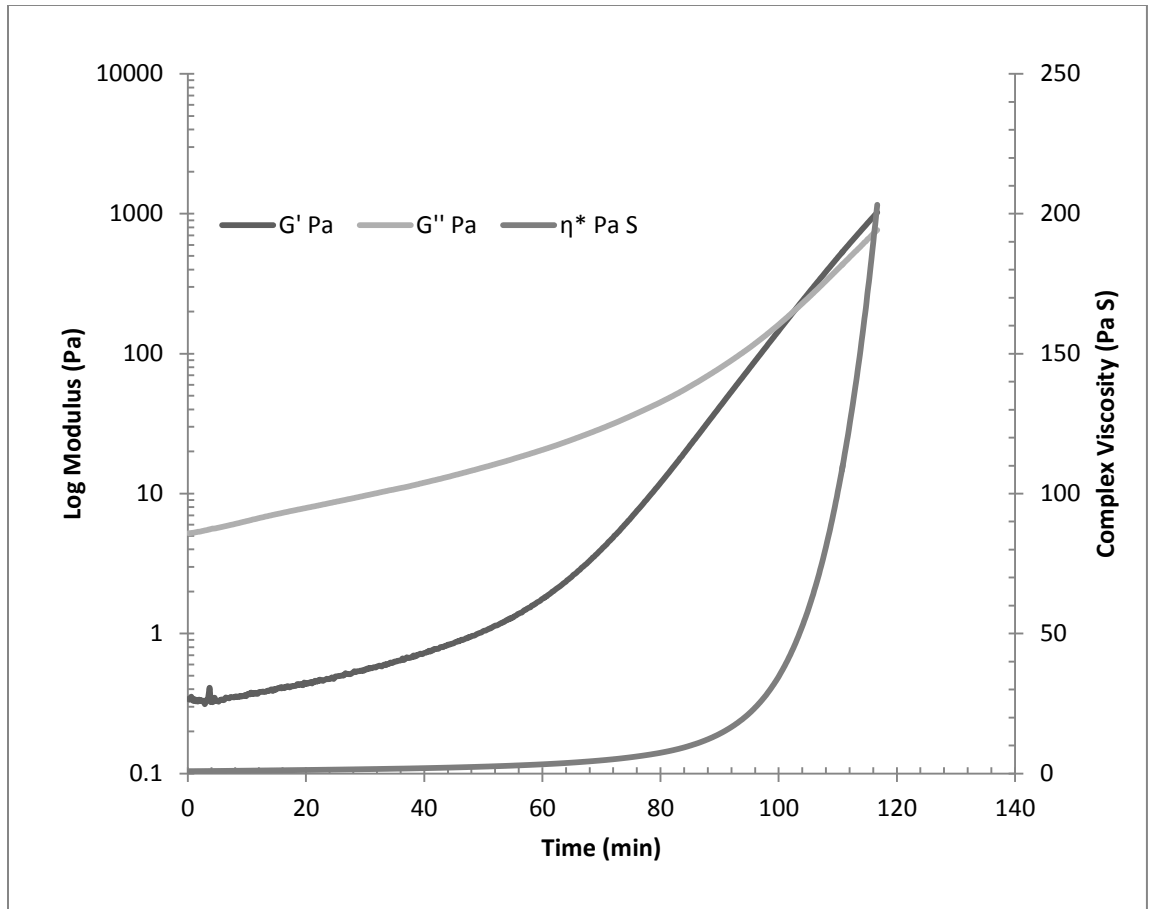**Figure B. 10: Rheological Testing of HB with 2.0% 925H at Ambient Conditions**

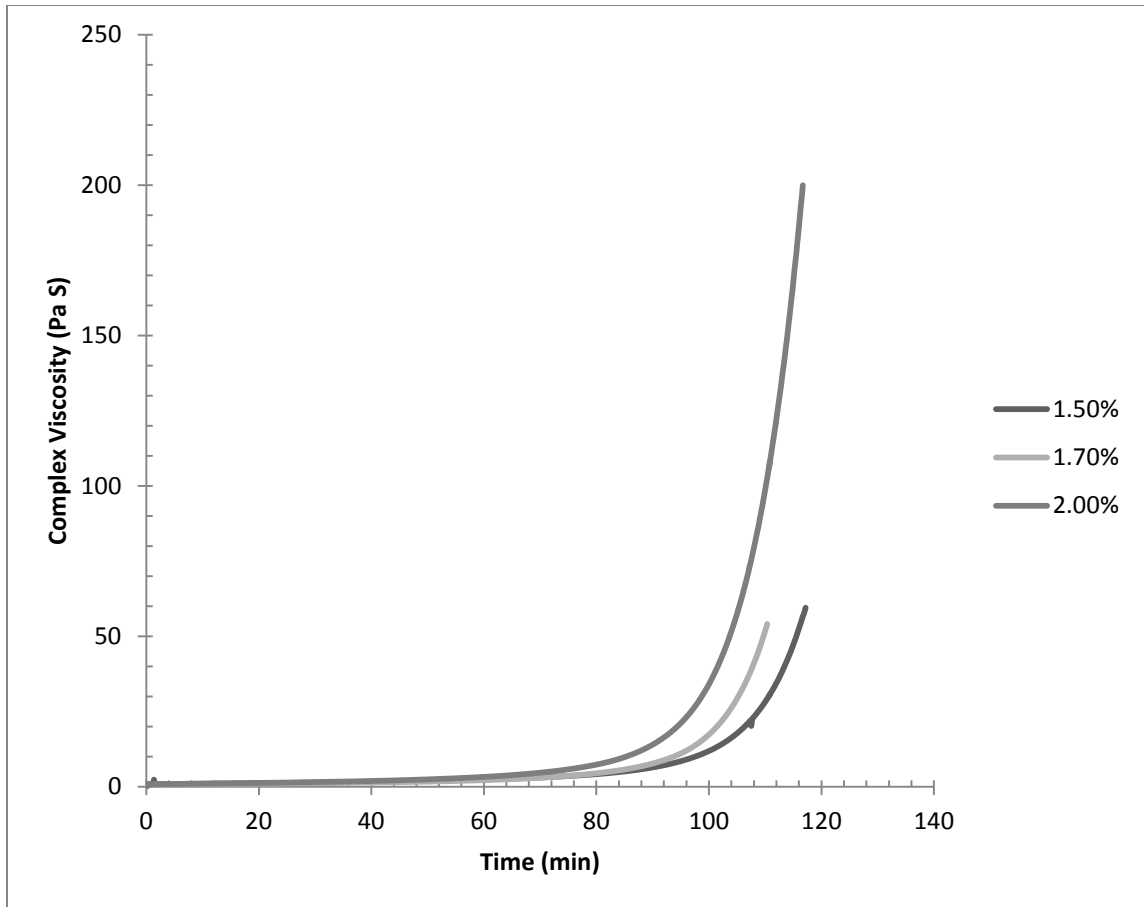**Figure B. 11: Complex Viscosity of HA with Varying 925H Concentration**

89

Figure B. 12: Rheological Testing of HB with 1.5% HDP-75 at Ambient Conditions

90

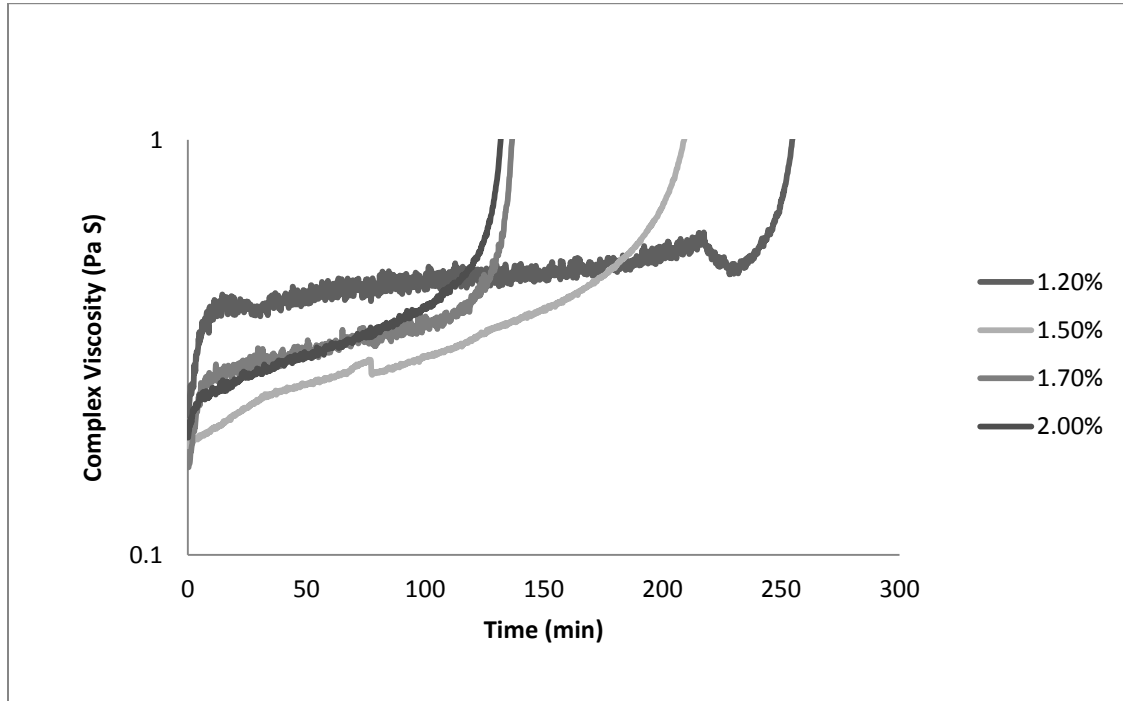**Figure B. 13: Rheological Testing of HB with 1.7% HDP-75 at Ambient Conditions**

91

Figure B. 14: Rheological Testing of HB with 2.0 % HDP-75 at Ambient Conditions
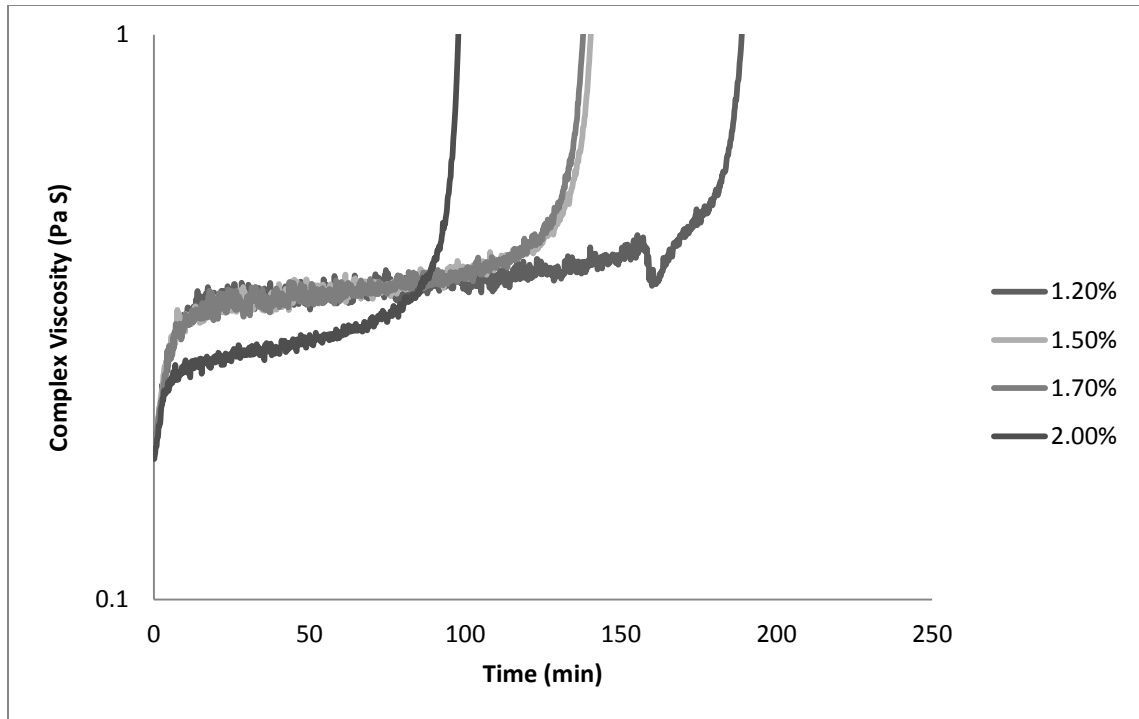
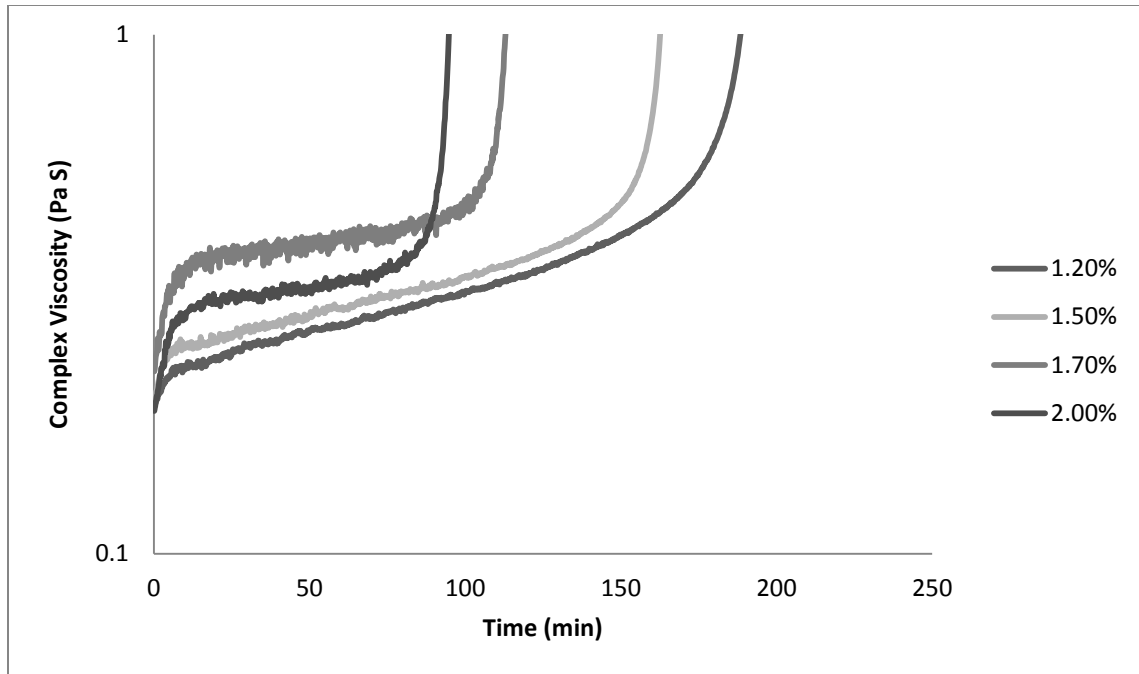**Figure B. 15: Complex Viscosity of HB with Varying HDP-75**

93

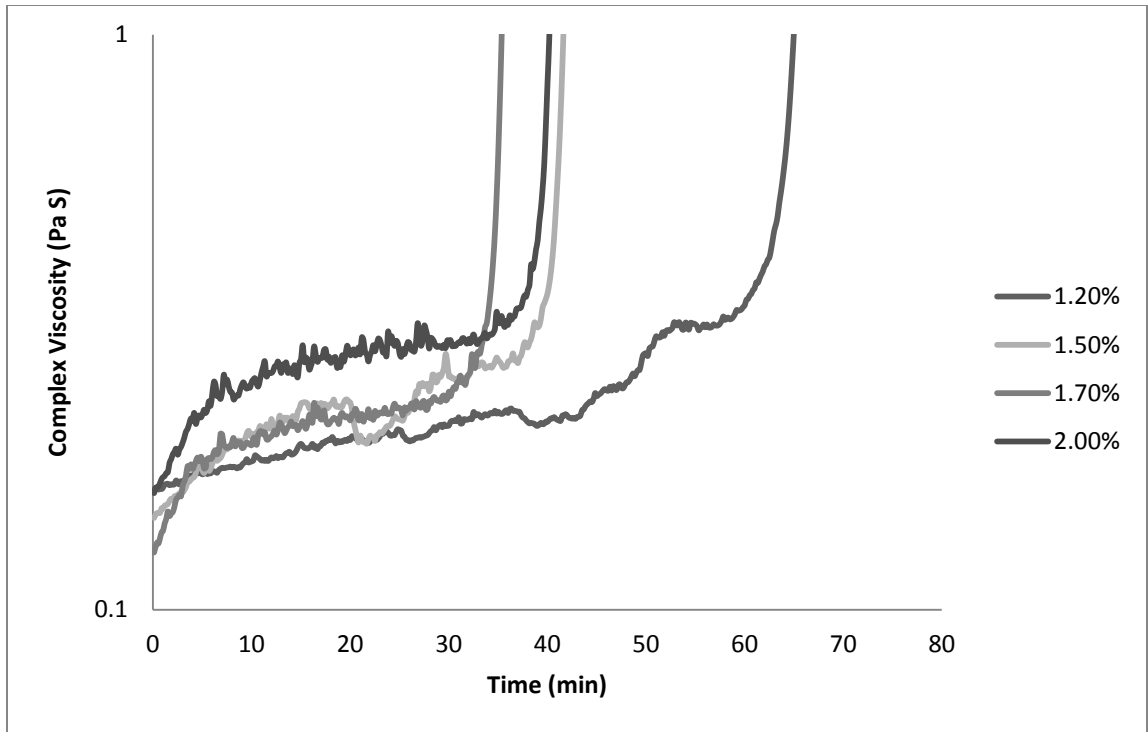# APPENDIX C: BLADE INITIATOR VISCOSITY PROFILES

Figure C.1: This figure displays the complex viscosity profile of HDP-75 at various mass concentrations

Figure C.2: This figure displays the complex viscosity profile of MCP-21 at various mass concentrations
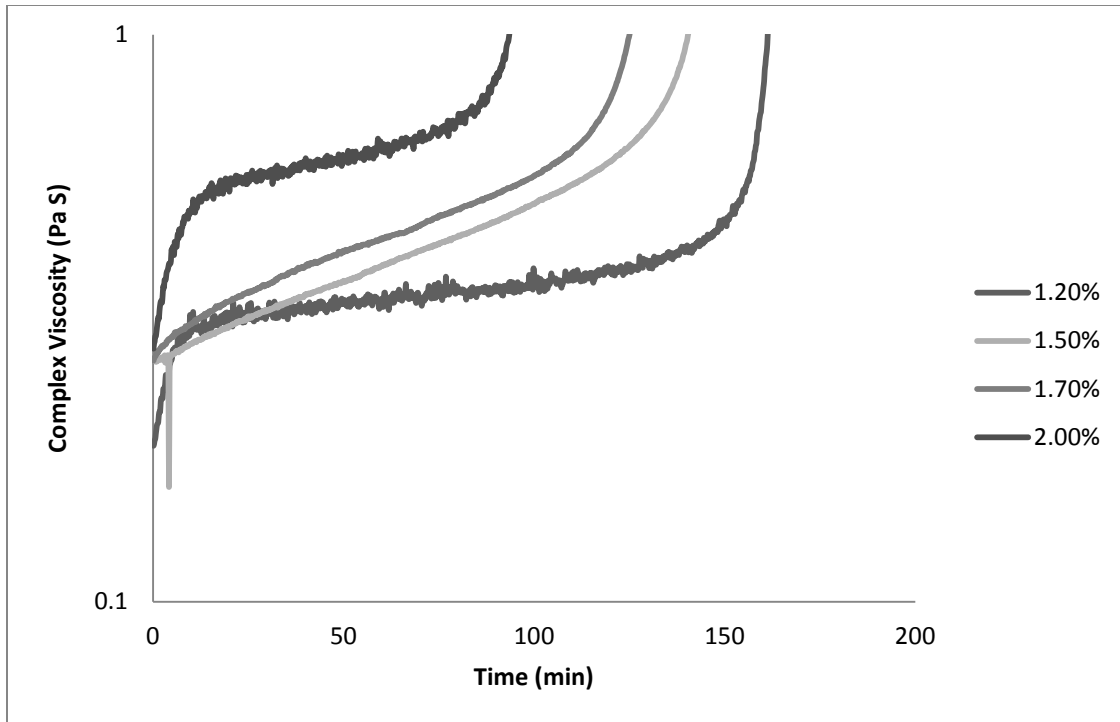
Figure C.3: This figure displays the complex viscosity profile of MCP-75 at various

mass concentrations

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Figure C.4: This figure displays the complex viscosity profile of Norox 757 at various mass concentrations

Figure C.5: This figure displays the complex viscosity profile of PULCAT at various mass concentrations

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