

ABSTRACT

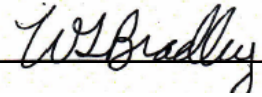
Thermal Degradation as a Function of Time and Temperature in a Coconut Shell Powder-Polypropylene Composite

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Due to increasing environmental awareness and the rapid depletion of nonrenewable resources, natural materials have become more common as fillers in polymeric composites. Coconut shell powder (CSP) as a functional filler in polypropylene has been shown to provide mechanical property enhancements. However, specific processing parameters for CSP-polypropylene composites have yet to be well defined. CSP will not be able to transition from a lab-scale natural filler to a full production, commercial natural filler, until the specific parameters for CSP-polypropylene processing are determined. Therefore, the focus of this research is to determine the effects of processing time and processing temperature on CSP-polypropylene composites. The two opposing phenomena in processing CSP-polypropylene composites are thermal degradation of the CSP and encapsulation of the CSP by the polypropylene matrix. The encapsulation of CSP in a polypropylene matrix effectively shifts the onset of CSP degradation to higher temperatures. Additionally the effect of small amounts of thermal degradation to the encapsulated CSP may enhance processing instead of inhibiting processing, as intuitively assumed.

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THERMAL DEGRADATION AS A FUNCTION OF TIME AND TEMPERATURE IN
A COCONUT SHELL POWDER-POLYPROPYLENE COMPOSITE

A Thesis Submitted to the Faculty of
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In Partial Fulfillment of the Requirements for the
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TABLE OF CONTENTS

DEDICATION	iv
CHAPTER ONE	1
Introduction.....	1
Purpose.....	1
Coconut Farming	1
High Value Application of Coconut Shell.....	5
CHAPTER TWO	8
Literature Review.....	8
Overview of Thermal Degradation	8
The Variable of Moisture.....	10
Degradation of Ligno-Cellulosic Natural Fillers	12
Recent Work on the Degradation of CSP-Polypropylene Composites.....	14
CHAPTER THREE	17
Experimental Plan and Procedures	17
Overview.....	17
Thermal Degradation Characteristics of CSP and Polypropylene	18
Thermal Degradation Characteristics of CSP-Polypropylene Composite	19
Correlation of Thermal Degradation to Loss of Mechanical Properties...	20
Maximum Allowable Processing Time for Different Temperatures	21
Extra Considerations	22
CHAPTER FOUR.....	23
Experimental Results	23
Thermal Degradation Characteristics of CSP and Polypropylene	23

Thermal Degradation Characteristics of CSP-Polypropylene Composite	33
APPENDIX.....	49
THE EFFECT OF MOISTURE ON CSP-POLYPROPYLENE COMPOSITES	50

DEDICATION

To my loving family, my supportive friends, my Thesis Director Dr. Bradley, and Jesus Christ who has marked my life and continues to bring light into dark places.

CHAPTER ONE

Introduction

Purpose

The objective of this research is to determine commercial processing parameters for coconut shell powder (CSP)-polypropylene composites. Thermal degradation of CSP-polypropylene composites occurs at high temperatures and negatively impacts the mechanical properties and the aesthetic qualities of the material. By studying the rate of thermal degradation as a function of time and temperature, the specific processing parameters associated with the upper bound of the CSP-polypropylene composite processing window were determined. Ultimately, these processing parameters will aid in the commercialization and mass production of CSP-polypropylene composites, which utilize discarded coconut shells purchased from poor coconut farmers.

Coconut Farming

In an attempt to both help poor coconut farmers and utilize the abundance of coconut shell waste, Baylor University researchers began researching high-value applications for coconut shell. One of the initial goals of the research initiative was to create an application that would at least triple the average annual income of coconut farmers around the world [1]. It is estimated that 11 million families around the world rely on coconut farming as their main source of income, which, on average, yields US\$500 a year [2]. This equates to less than US\$2 a day and is defined as absolute poverty or an “inability to maintain predictable access to the minimal amounts of food,

water, shelter, medicine and clothing necessary for survival” [3]. Coconut farmers make their living off of the coconut palm, which is tropical/subtropical vegetation that is found in high volumes along coastal regions near the equator. Coconut palms bear fruit year round and coconut fruit consists of three main parts: the husk, the shell and the white coconut meat called copra. The outside layer of the husk is a thin hard shell, but the inside layer of the husk is composed of soft fibers. Within the husk is the shell, which is “four times as hard as the hardest maple wood and ten times as hard as pine wood,” and within the shell is the copra [2]. Different parts of the coconut are shown in Figure 1, below.



Figure 1: Different Parts of the Coconut

Countries in South and Southeast Asia account for the majority of coconut growth around the world. The three biggest coconut growing nations in the world are Indonesia, India and the Philippines, and it is estimated that in these three countries 76 percent of the world’s coconuts are grown [4]. A high percentage of the population in these three countries lives in absolute poverty, and, as a matter of fact, coconuts are grown in many countries with high absolute poverty rates. This correlation between coconut growth and absolute poverty can be seen by comparing Figure 2, which shows the boundary lines of

coconut growth around the world and Figure 3, which shows the percentage of a country's population living below the absolute poverty line of US\$2 a day.



Figure 2: Coconut Growth Boundary [5]

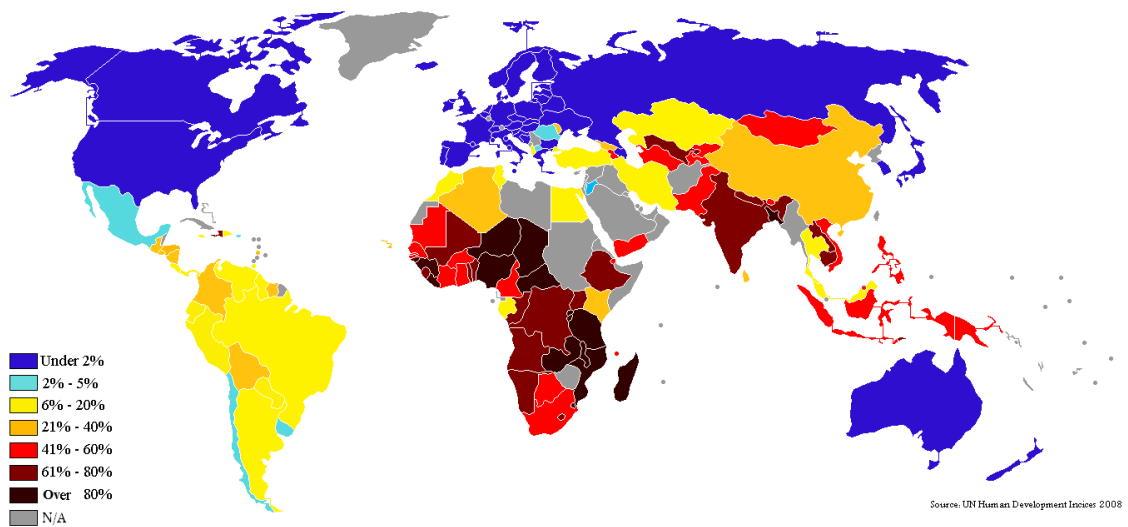


Figure 3: Percent of Population Living on Less Than US\$2 a Day [6]

When coconuts are harvested, the copra is extracted to sell, but the husk and the shell are discarded or used in low value applications that do not provide coconut farmers with much extra income. In many cases, coconut farmers must pay for the shells and husks to be picked up and taken to a landfill. Therefore, a high-value application of the husk and/or shell could greatly increase the annual income of millions of coconut farmer around the world. The extent of this research is concerned with high-value applications for coconut shell. According to the Food and Agriculture Organization of the United Nations, 5.5 billion coconuts grow every year, which amounts to 61 million tons of coconut. Unfortunately, 7.65 million tons of the 61 million tons of coconut grown every year is coconut shell waste [7]. According to Conroy, 85 percent of the world supply of coconut shells is used as cheap biomass fuel or trashed. The other 15 percent represents coconut shell activated carbons and coconut shell charcoal [2]. When studying the problem of coconut shell waste in Kenya in 1998, Indeglia calculated that coconut shell waste by volume would surpass all other biodegradable waste and equal 2.5 times the amount of all other biodegradable waste in Kenyan landfills by the year 2048 [8]. This problem is not isolated to Kenya. Coconut shell waste is a problem for most coconut growing countries around the world, and when landfill space fills up, many shells get dumped into the ocean. Figure 4 shows a city landfill in Mumbai, India, and the abundance of coconut shell is very apparent.



Figure 4: Municipal Dump in Mumbai, India [9]

High Value Application of Coconut Shell

One application of coconut shell that Baylor researchers discovered to be very promising was in using milled coconut shell as a natural filler in polymer composites. By processing the coconut shell in a hammer mill or centrifugal mill large coconut shell pieces could be made into fine coconut shell powder (CSP). Figure 5, below, displays different stages in processing and milling CSP.



Figure 5: Coconut Shell Processing: Stages of Milling

Hard CSP particles in a polymer matrix have an effect very similar to that of hard second phase particle strengthening in metals. Filling polypropylene with CSP at different weight percents, reinforces the polypropylene matrix and results in an increase in the tensile and flexural modulus of the composite over the unfilled polypropylene [2]. Figure 8 shows the result of using CSP as filler in polypropylene and the effect of weight percent loading on the tensile and flexural modulus.

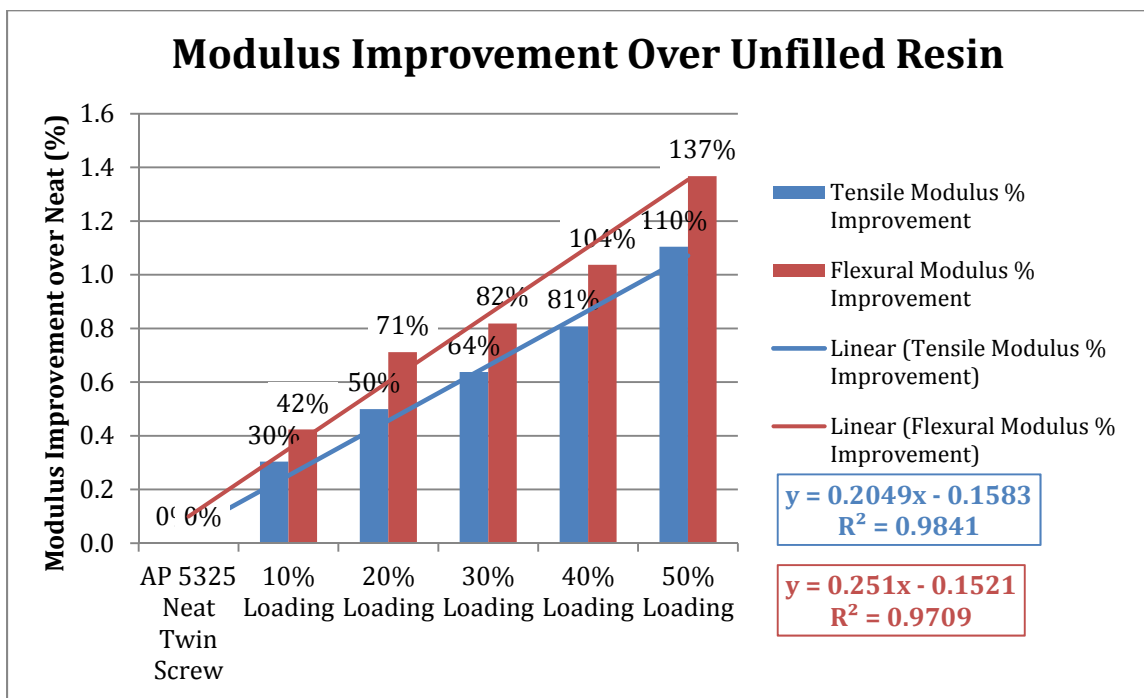


Figure 7: Modulus Improvement Over Unfilled Resin [2]

Not only does CSP prove to enhance the mechanical properties of polypropylene, but CSP as a natural filler in polypropylene also makes a great business case. Due to the volatility of crude oil, the price of polyolefins is not very stable and trends indicate that the price of polyolefins will continue to rise over the next couple of years. Thus, there are overall cost savings when using a natural filler like CSP, and displacing polypropylene for CSP is essentially trading a nonrenewable resource for a renewable resource that

reinforces the polymer matrix and improves the tensile modulus and the flexural modulus. Also, CSP as a functional filler in polypropylene has been show to increase tensile strength with good retention of impact strength.

The transition of a natural filler from lab-scale experimentation to commercial production is a combination of proven mechanical properties and an in-depth understanding of the processing parameter associated with the composite. In many cases in the polymer industry, the processability of a composite will supersede the mechanical property data, as long as the mechanical properties are not decreasing drastically. The mechanical properties of CSP-polypropylene composites have been proven, but not enough is known about the specific processing parameters for CSP-polypropylene composites to be able to give guidance to commercial compounders and injection molders on how to process the material. In order to facilitate a high-value application for coconut shell and produce a large enough demand for coconut shell to change the lives of poor coconut farmers around the world, the specific processing parameters are needed. Therefore, this research is focused on defining specific processing parameter for the upper bound of the processing window to aid CSP in moving from the lab to the market.

CHAPTER TWO

Literature Review

Overview of Thermal Degradation

The upper bound of the processing window is determined by the critical limit of thermal degradation of CSP-polypropylene composites. Thermal degradation of CSP-polypropylene composites occurs when the thermal energy being introduced to the composite is great enough to actually break the covalent bonds that are holding the polymer together and/or the covalent bonds that are holding the CSP together. The product of thermal degradation is, “fragmentation, production of a range of reactive free radicals, and more stable smaller molecules” [10]. Some of the free radicals produced from the thermal degradation will have a sufficiently low molecular weight and will be released as a vapor. The gaseous free radicals that are released due to the thermal degradation of polymers and other organic compounds are called volatile organic compounds (VOCs). VOCs can be carcinogenic and are considered health hazards.

Natural fillers are composed of different amounts of hydrogen, oxygen, and carbon. These atoms are bonded together in different ways to form a variety of complex microstructures. The strongest covalent bond in a synthetic polymer and natural polymer is a carbon-carbon bond. Hydrogen and oxygen bonds have lower thermal activation energies than carbon-carbon bonds. Thus hydrogen and oxygen bonds will break when exposed to substantial amounts of thermal energy. When the hydrogen and oxygen bonds in an organic material begin to break due to thermal degradation, a phenomenon known as charring begins to take place. Charring is a progressive process, in which the material

being thermally degraded loses its color and gets darker, until it turns black when all of the hydrogen and oxygen bonds are broken. Another problem with thermal degradation is chain scission, which is a specific type of bond breaking. Carbon-carbon bonds are considered the backbone of a polymer, and at higher temperatures, the carbon-carbon bonds begin to break, which gives a reduction in molecular weight and polymer strength [11]. This breaking of the carbon-carbon bonds that make up the backbone of the polymer is chain scission.

Weight loss due to volatiles is a simple way to monitor thermal degradation even though it does not directly capture all forms of degradation due to thermal energy. The degradation measured by weight loss can then be correlated with the consequential loss of mechanical properties. Changing surface appearance and odor can also be correlated with weight loss.

Polypropylene and other commodity plastics (e.g. PE and PVC) are processed around $210\text{ }^{\circ}\text{C} \pm 20\text{ }^{\circ}\text{C}$. Thermal degradation of the polymer is not an issue around these processing temperatures, and minimal chain scission takes place during polymer processing. However, most ligno-cellulosic biomasses (biomasses containing lignin, cellulose and hemicelluloses), which represent the majority of natural fillers, begin thermal degrading around $200\text{ }^{\circ}\text{C}$ [12]. Therefore, it is necessary to understand the thermal degradation of the natural filler as it relates to the specific processing temperature range of the chosen polymer. According to Rowell et al., when disregarding the onset of thermal degradation in natural fillers and processing at higher temperatures there is the, “possibility of ligno-cellulosic degradation and/or the possibility of volatile emissions that could effect composite properties.” Initial thermal degradation testing should be done

on a natural filler before composite processing by heating the filler to different temperatures in the polymer's specific processing temperature range and observing the weight loss due to thermal degradation (this testing should be done using specifically designed thermal degradation instrumentation).

The Variable of Moisture

When testing for weight loss due to thermal degradation in ligno-cellulosic fillers it becomes apparent that thermal degradation is not the only effect that contributes to a material's weight loss during heating. Commodity plastics are generally hydrophobic, and thus, absorb very little moisture. However, ligno-cellulosic natural fillers are hydrophilic, and therefore, have comparatively high moisture contents [13]. Heating a ligno-cellulosic filler will remove this moisture by diffusion and surface evaporation. When testing for thermal degradation at elevated temperatures, it is easy to differentiate between weight loss due to moisture desorption and weight loss due to thermal degradation because moisture desorption occurs primarily at lower temperatures than thermal degradation.

Moisture in a ligno-cellulosic polymer composite can effect both the processability of the composite, and the mechanical properties/aesthetic qualities of the composite. First, in polymer processing, water molecules act as plasticizers due to the low molecular weight of the water molecules compared to the polymer molecules. Figure 8 shows that an increase in the moisture content of a CSP-polypropylene composite can

cause a slight decrease in the apparent viscosity of the composite, which is a characteristic of plasticizers.

However, the effect of moisture on the apparent viscosity is minimal.

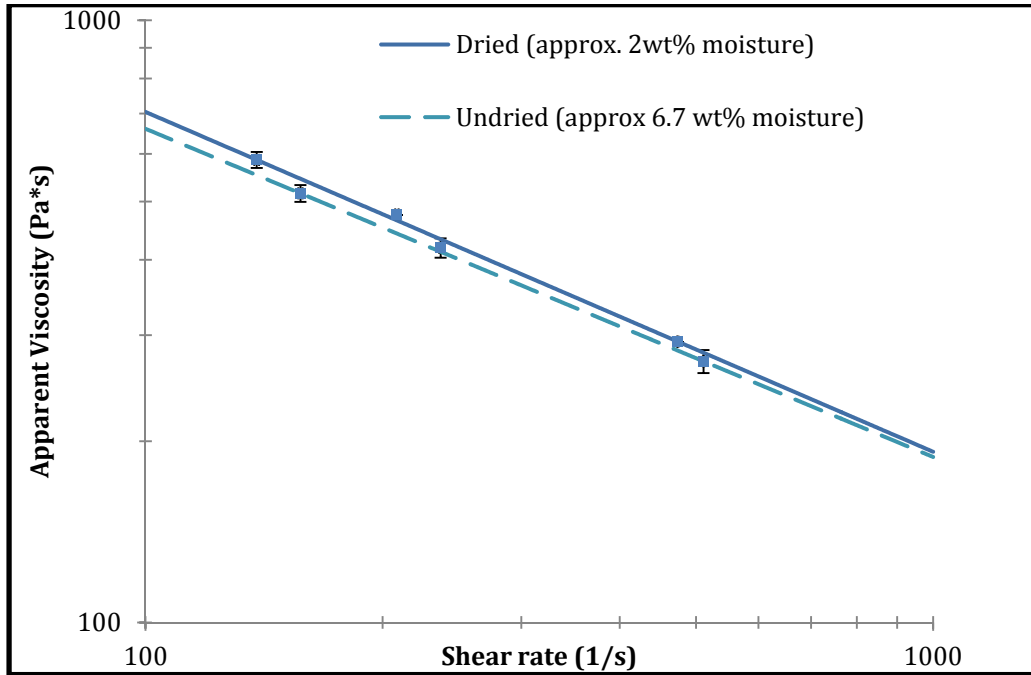


Figure 8: Effect of Moisture on Rheology with 20% CSP Loading at 180 deg C [14]

Second, moisture can adversely effect the mechanical properties and appearance of a composite [13, 15]. The negative effect of moisture on a composite's mechanical properties and appearance is very similar to the negative effect of thermal degradation on a composite's mechanical properties and appearance. The wood plastics industry has conducted extensive research into the effects of moisture absorption and the prevention of moisture absorption in wood plastic composites [16]. To give an idea of the variability of moisture content in ligno-cellulosic natural fillers, according to Klyosov, after 24 hours of water immersion, pressure treated lumber can absorb as much as 24 wt% water. Compare this value to the average moisture content in an ambient environment for

pressure treated lumber of around 6 to 8 wt%. In his thesis “The Efficacy of Using Coconut Shell Powder as a Filler / Reinforcement in Thermoplastic Composites”, Conroy shows that the average moisture content of coconut shell is around 5 to 9 wt% [2].

In this research, it is very important that the effects of thermal degradation are isolated from other variables such as moisture, so that the true effects of thermal degradation on a CSP-polypropylene composite can be studied. Therefore, a small portion of this research went into understanding the specific effects of moisture on CSP-polypropylene composites and trying to eliminate the effect of moisture on the final results. In order to remove moisture and kill microbials, it was recommended that CSP be dried at 160 °C for two hours [17]. These drying parameters were originally used in this research; however initial thermal degradation testing on dried and undried CSP compounded with polypropylene indicated that drying the CSP at 160 °C for two hours pre-degraded the powder before compounding. For this reason, multiple drying times and temperatures were experimented with, throughout the course of this research.

Degradation of Ligno-Cellulosic Natural Fillers

Ligno-cellulosic natural fillers are prone to thermal degradation around temperatures in the processing temperature range for polypropylene and other commodity plastics. For this reason, it is very important to understand what time-temperature combinations cause the natural filler to reach the critical limit of degradation. Understanding these time-temperature combinations provides the necessary insight to determine acceptable processing temperatures, within the processing temperature range for the chosen polymer. There is a variety of general research available regarding the thermal degradation of ligno-cellulosic natural fillers (i.e. wood [18], hemp [19]).

However, in order to determine a composite's upper processing bound and give guidance to commercial compounders and injection molders, a more focused approach to ligno-cellulosic degradation is necessary.

General research into the thermal degradation of coconut shell is also well documented. Macedo et al. gives a broad overview of the thermal degradation characteristics of coconut shell, and has the process of coconut shell heating broken down into five steps [20]. When heating a coconut shell across a range of temperatures, the first process to take place is moisture desorption. The moisture desorption step takes place between 25 and 150 °C and should not be damaging to the coconut shell because the onset of thermal degradation takes place after 150 °C, according to Macedo et al. The second step between 150 °C involves the elimination of remaining water molecules deep within the coconut shell, as well as the degradation of sclerenchyma cells, which are responsible for holding water in the shell. As the shell is heated up between 190 °C to 260 °C hemicellulose is degraded. The fourth step from 240 °C to 350 °C involves the degradation of cellulose, and then the final thermal degradation of the shell involves the breaking down of lignin between 280 °C and 500 °C. This multiphase degradation process speaks to the complex molecular bonding in lingo-cellulosic fillers. Conroy also gathered data on the thermal degradation of coconut shell. According to his findings, using a thermogravimetric analyzer (TGA), weight loss due to coconut shell degradation begins between 180 and 190 °C [2]. The discrepancy between the onset of degradation according to Macedo et al.'s research and Conroy's research reiterates that measuring thermal degradation as function of weight loss does not take into account all forms of degradation due to thermal energy. It is interesting to note that lignin is the most

thermally stable structural component because coconut shell is considered to be a lignin rich biomass, containing anywhere from 30 to 40 wt% lignin. How this high lignin effects the thermal degradation characteristics of coconut shell will be studied in the Experimental Results.

Recent Work on the Degradation of CSP-Polypropylene Composites

Recent research into the effects of thermal degradation of CSP-polypropylene composites on composite processing has yielded interesting results. Figure 9 and 10 reveal that thermal degradation lowers the apparent viscosity of CSP-polypropylene composites during processing. A 0.5 weight percent increase in the thermal degradation of the CSP-polypropylene composite amounts to a decrease in apparent viscosity from 500 Pa*s to 400 Pa*s. One reason for this drop in apparent viscosity is that the VOCs released during thermal degradation act as plasticizers, due to the low molecular weight of VOCs compared to the polypropylene molecules.

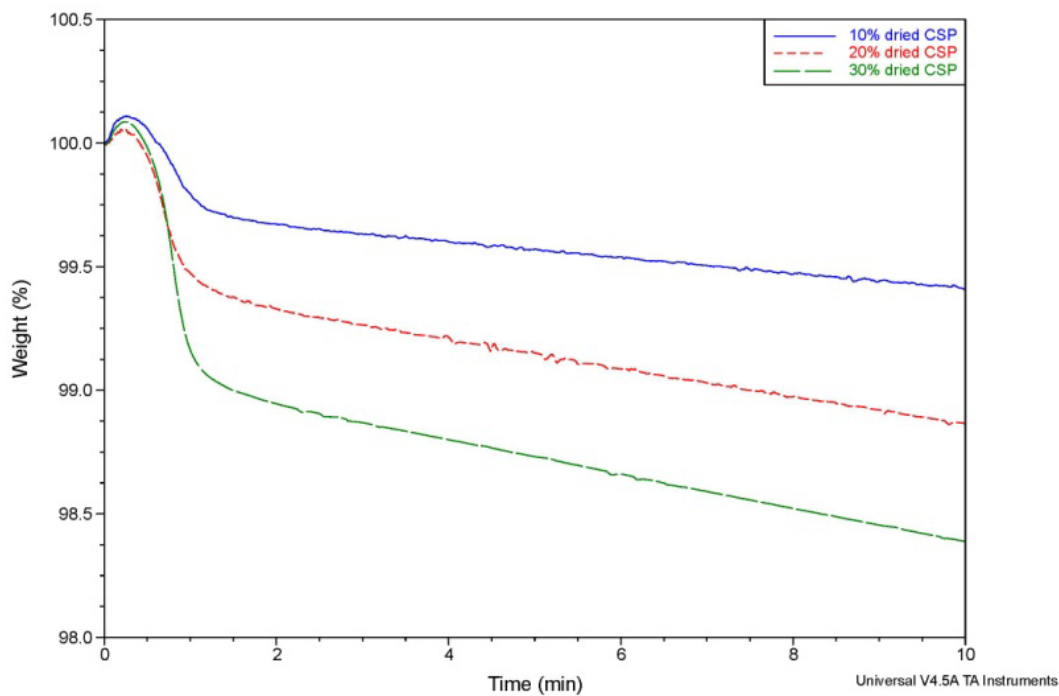


Figure 9: Thermal degradation of CSP filled PP at 210 °C [14]

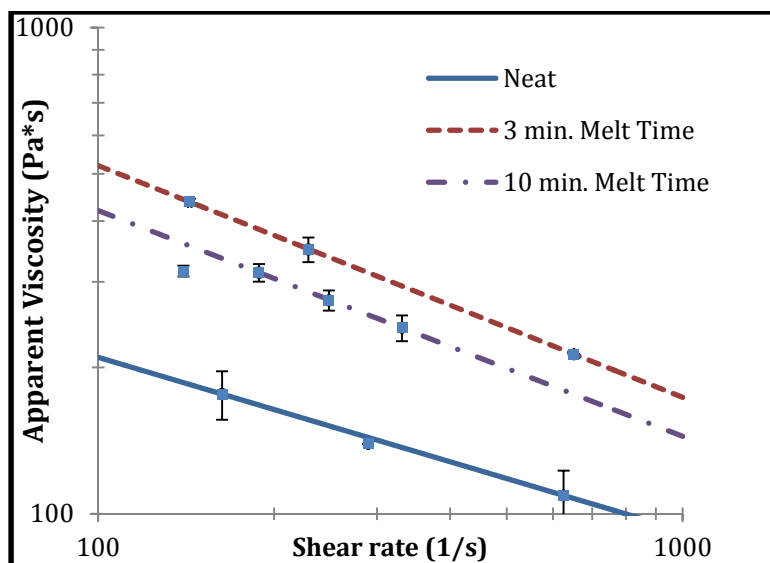


Figure 10. Effect on viscosity of thermal degradation of 30 wt% CSP filled PP copolymer at 210 °C [14]

These results showing that volatiles may act as plasticizers are similar to the results showing that water molecules may act as plasticizers; however it appears that a change of one weight percent of thermal degradation has a much bigger effect on the composite's

apparent viscosity than a change of one weight percent of moisture. Increasing amounts of thermal degradation has an overwhelmingly negative effect on natural composites, but its effects are not completely negative. It is apparent that processability is not a concern with increasing amounts of degradation.

CHAPTER THREE

Experimental Plan and Procedures

Overview

This research will address four questions associated with the thermal degradation of CSP-polypropylene composites as a function of time and temperature:

1. What are the thermal degradation characteristics of CSP and polypropylene individually?
2. What are the thermal degradation characteristics of CSP-polypropylene composites?
3. How do the mechanical properties of CSP-polypropylene composites change with degradation as measured by TGA?
4. Based on the critical limit of degradation, what is the maximum allowable processing temperature as a function of time for a CSP-polypropylene composite?

Materials:

- A wide spec. polypropylene (PP) copolymer with a melt temperature of 165 °C and an optimum processing range between 180 °C and 230 °C was used for the entirety of this research. The polypropylene was copolymerized with polyethylene, which both increases its resistance to oxidation and improves its impact strength at low temperatures. The findings made with this copolymer are generally applicable to other polypropylene homopolymers and copolymers.
- Coconut shell powder (CSP) with a particle size of less than 150 µm was used for the entirety of this research. The powder was made by milling an Indian species

of coconut shell with a centrifugal mill, and the median particle size is approximately 65 μm .

- The CSP-polypropylene composite used in this research was made by mixing, CSP, the polypropylene copolymer, and maleic anhydride polypropylene (MAPP) on weight percent basis. MAPP was loaded at 2 weight percent of the composite in every sample and the CSP was loaded at 20 weight percent of the composite, unless otherwise specified. A C.W. Brabender Single Screw Extruder was used to compound all composite mixtures. In order to minimize variability in compounding, temperature zones 1 (the hopper temperature zone), 2, 3, and 4 (the nozzle temperature zone) on the single screw extruder were set to 175, 185, 185, 210 $^{\circ}\text{C}$ respectively and the screw speed was set to 25 RPM.

Thermal Degradation Characteristics of CSP and Polypropylene

The thermal degradation characteristics of CSP and polypropylene are determined by the onset of degradation in the material and by the different thermally activated processes that are taking place at different temperatures. How these thermally activated processes influence the rate of degradation of CSP is also of importance. Studying the thermal degradation characteristics of CSP and polypropylene individually will provide insight into thermal degradation characteristics of the CSP-polypropylene composite. The thermal degradation characteristics of CSP and polypropylene were studied using a Thermal Analysis (TA) Q50 Thermogravimetric Analyzer (TGA). Thermogravimetric analyzers measure weight loss as it relates to thermal degradation. Not all of the thermal degradation that is taking place is recorded by a thermogravimetric analyzer, only thermal degradation that results in the release of volatiles. Two TGA testing methods

were used to capture the thermal degradation characteristics of CSP and polypropylene. The first testing method, referred to as ramp testing, involved heating a sample at a constant rate to a specified final temperature. Ramp tests display weight loss due to thermal degradation as a function of temperature. All ramp testing in this research utilized a ramp rate of 2 °C/min. A ramp rate of 2 °C/min allowed the sample to be heated relatively slowly, so that degradation at each temperature had more time to develop. A different ramp rate may yield slightly different results; however, the general thermal degradation characteristics will be the same. The second testing method, referred to as isothermal testing, involved heating a sample to a specified temperature as fast as possible and then holding the temperature constant for a specified time. Isothermal tests display weight loss due to degradation as a function of time at a specific temperature. Ramp testing is a good method for identifying the onset of thermal degradation and provides a broad view of a material's thermal degradation characteristics. Isothermal testing allows one to identify the thermal degradation characteristics of a material at a specific temperature and provides a more focused view of a material's thermal degradation characteristics. Isothermal testing is a good way to simulate a processing situation because polymer processing employs relatively isothermal conditions. All powder samples and all samples that were used in a comparison with powder samples had a mass of 13.5 ± 2 mg, to minimize variability due to significantly different temperature gradients within the samples.

Thermal Degradation Characteristics of CSP-Polypropylene Composite

Similar to the thermal degradation characteristics of CSP and polypropylene, the thermal degradation characteristics of CSP-polypropylene composites are determined by the onset

of degradation, the different thermally activated processes taking place at different temperatures, and the rate of thermal degradation. By studying the thermal degradation characteristics of CSP-polypropylene composites, it will be possible to predict the weight loss of the entire composite due to thermal degradation at different time-temperature combinations. The thermal degradation characteristics of CSP-polypropylene composites were studied in the same way that the thermal degradation characteristics of CSP and polypropylene were studied, by ramp and isothermal testing on the TGA. All pellet samples and all samples that were used in a comparison with pellet samples had a mass of 23.5 ± 2 mg, to minimize variability due to significantly different temperature gradients.

Correlation of Thermal Degradation to Loss of Mechanical Properties

The critical limit of thermal degradation is the amount of thermal degradation that corresponds to a noticeable decline in mechanical properties and aesthetic qualities. By understanding quantitatively the correlation between thermal degradation and mechanical properties, the critical limit of thermal degradation can be identified. This correlation takes into account the thermal degradation characteristics of CSP-polypropylene composites by providing the rate of degradation at the processing conditions. Then using these rates, one can relate the composite's thermal history in processing to amounts of thermal degradation. In this research, it is assumed that compounding with the single screw extruder, set to the previously specified parameters, results in a negligible amount of thermal degradation. Thus, in order to study the correlation between thermal degradation and mechanical properties, an Arburg Injection Molder was used to injection mold flexural and tensile testing bars at specific time-temperature combinations. The amount of thermal degradation at these specific time-temperature combinations was

extrapolated from the degradation characteristics of the composite, and the amount of thermal degradation of each flexural and tensile testing bar was related to its corresponding mechanical properties. Also, pictures of the flexural and tensile testing bars were taken using a Leica Binocular Microscope and the Baylor University Scanning Electron Microscope (SEM), in order to document the correlation between thermal degradation and appearance. Based on the thermal degradation-mechanical properties correlation and the qualitative correlation between appearance and thermal degradation, a critical limit of thermal degradation of CSP-polypropylene composites was determined. Procedural Note: When injection molding, all four temperature zones on the Arburg Injection Molder were set to the same temperature to get a more uniform heating of the molten plastic in the barrel. The temperatures indicated by the injection molder heater bands were as much as 5 °C lower than the actual temperature at the center of the strand. To simulate different processing times, molten plastic was held under heat in the barrel of the injection molder for a specified amount of time after the 1.5 minute dwell time before injection molding. Also, the injection molder screw was set to a speed 100 rpm for all samples. Flexural testing was done in accordance with ASTM D790-07 and tensile testing was done in accordance with ASTM D638-03. .

Maximum Allowable Processing Time for Different Temperatures

Due to the fact that thermal degradation is a function of time and temperature, there is not one maximum allowable processing time or one maximum allowable processing temperature. Instead for each temperature there is a maximum allowable time that the composite can be processed. The focus of this research is to give guidance to commercial compounders and injection molders on how to process CSP-polypropylene composites.

Therefore, the critical limit of degradation must be expressed in terms of processing parameters. Based on the determined critical limit of degradation and the rate of degradation at different temperatures in polypropylene's processing temperature range (180 to 230 °C), the maximum allowable time at each of these temperatures was calculated. Then nonlinear regression analysis was performed to find a function that best fit the data points and to characterize the maximum allowable processing time at any temperature in the processing range.

Extra Considerations

The effect of moisture on CSP was studied in-depth in this research and the effects are noted in the Appendix. The Appendix contains all information associated with the moisture content of a CSP-polypropylene composite. For measuring moisture, a Sartorius Moisture Meter was used and the temperature of drying was set to 120 °C, so as not to register any thermal degradation.

CHAPTER FOUR

Experimental Results

Thermal Degradation Characteristics of CSP and Polypropylene

This research is focused on giving guidance to commercial compounders and injection molders about the upper bound of the processing window for CSP-polypropylene composites. The upper bound will ultimately be depend on the critical limit of thermal degradation, but the thermal degradation characteristics of CSP and polypropylene individually are the building blocks, on which all of the subsequent research necessary to determine the critical limit of thermal degradation begins.

Determining the thermal degradation characteristics of CSP begins with ramp testing on the Thermogravimetric analyzer to obtain a global perspective of CSP degradation. Typical thermogravimetric analysis results are presented in Figure 13. A nitrogen environment is used to simulate thermal degradation taking place during polymer processing because molten plastic in an extruder or an injection mold is experiencing high heat in a poor oxygen environment. An air environment is used to simulate the oxidation of CSP in a furnace that allows for the circulation of air, which is the drying setup in this research.

The first thing to note when analyzing Figure 13 is the initial desorption of 5 wt% moisture. The moisture desorption process reaches its end when the weight loss derivative curve (dotted line) reaches zero. The weight loss derivative curve indicates the rate of weight loss at a given temperature, and it is helpful in identifying the onset of

thermal degradation. The onset of thermal degradation is determined by an increase in the weight loss derivative curve. Based on Figure 11, the onset of thermal degradation of CSP takes place between 170 and 180 °C. However, this degradation is very gradual, taking place at a rate of less than 0.1 wt%/°C until about 207 °C. Also, the nitrogen curve and the air curve begin to deviate from one another at approximately 193 °C, which indicates the onset of oxidation.

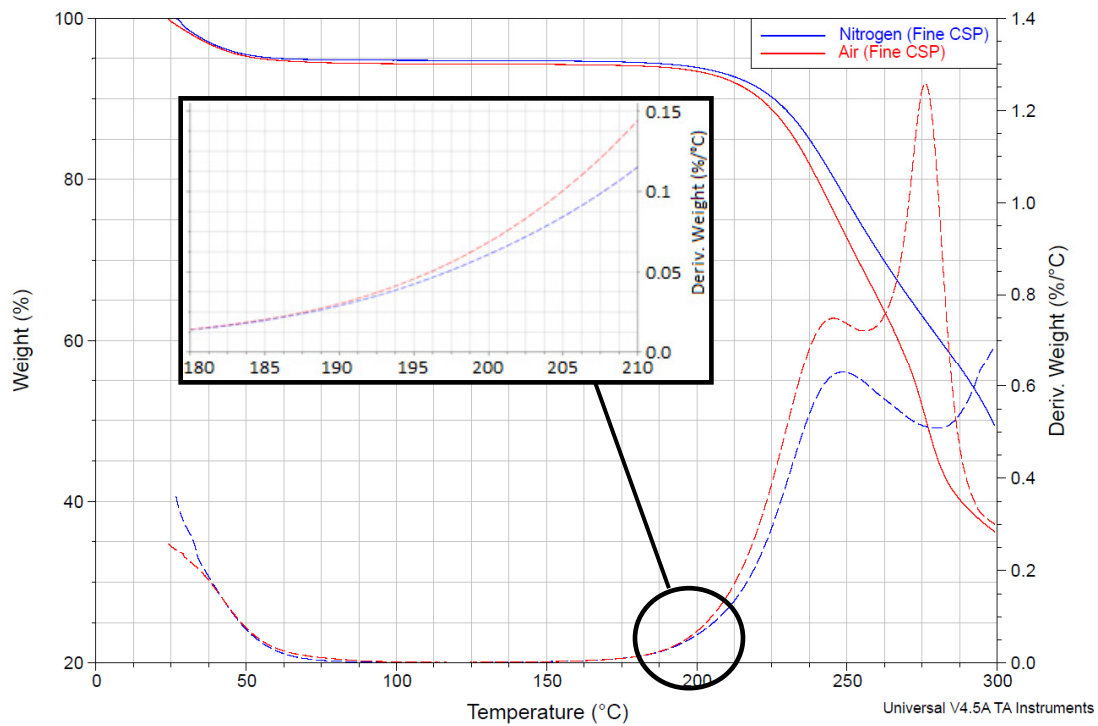


Figure 11: CSP Ramp Testing in nitrogen and air at 2 °C/min ramp rate

Compared to other lingo-cellulosic fillers, the onset of thermal degradation of CSP takes place at a relatively high temperature. A comparison between CSP and other commonly used natural fillers can be seen in Figure 12. The onset of degradation of CSP is between 170 and 180 °C. Comparatively, maple wood begins degrading as early as 130 °C, and pine wood, wheat straw, and walnut start to degrade around 160 °C. The onset of

thermal degradation of rice hulls at approximately 180 °C is the most comparable lingo-cellulosic filler to CSP out of all of the sampled fillers. The polypropylene used in this research has a melting temperature of 170 °C, which means that CSP encapsulation begins before any degradation to the CSP. Another important observation to make is that, compared to the other lingo-cellulosic fillers, the rate of thermal degradation of CSP between 180 and 210 °C is relatively slow. A relatively slow rate of thermal degradation means that CSP loses a relatively small amount of weight due to thermal degradation between 180 and 210 °C, which means that it should process well in the mid to low part of polypropylene's processing temperature range (180 to 230 °C). The advantage in thermal stability that CSP has over other commonly used lingo-cellulosic fillers could be attributed to the fact that CSP is relatively lignin rich, having a lignin content between 30 and 40 wt%.

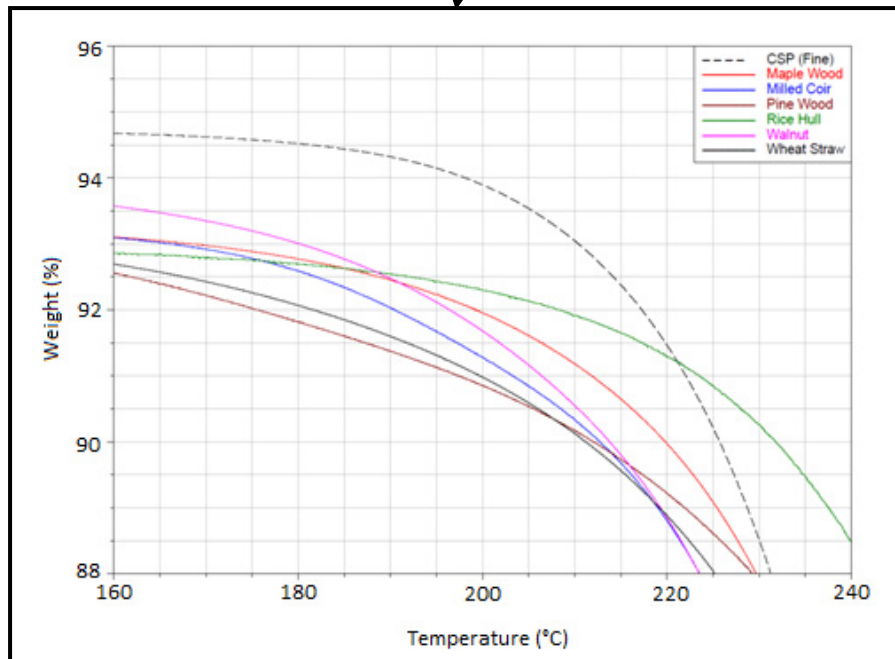
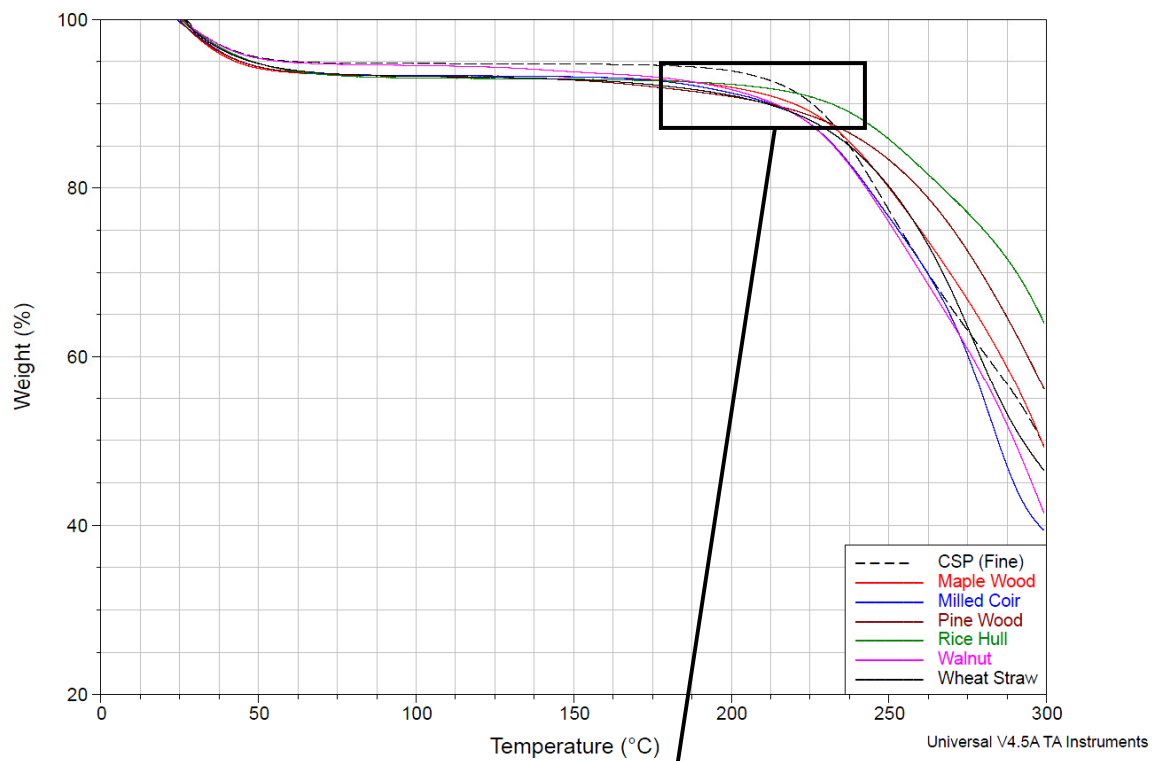


Figure 12: Comparison CSP and Commonly Used Natural Fillers with a 2°C/min ramp rate

Isothermal testing on a thermogravimetric analyzer was performed to gain a better understanding of the thermal degradation characteristics of CSP at eight different temperatures between 125 and 300 °C. The isothermal tests took place over a 500 minute time period, and the results are shown in Figure 13. Thermal degradation is a function of time and temperature, but it is more sensitive to changes in temperature. The thermal degradation of CSP follows a natural exhaustion process, $dW = (-R * W)dt$. Meaning that the change in weight of a CSP sample due to thermal degradation, dW , is equal to the rate of degradation, R , multiplied by the weight of the undegraded CSP, W . Thus the rate of degradation is a function of the amount of CSP that has not yet degraded, $\frac{dW}{W} = (-R)dt$. Solving this natural exhaustion process with the separation of variables method yields: $\ln(W) = -R * t$. Therefore, if weight loss due to thermal degradation is plotted on a logarithmic scale, weight percent over time should be linear with the rate as the slope.

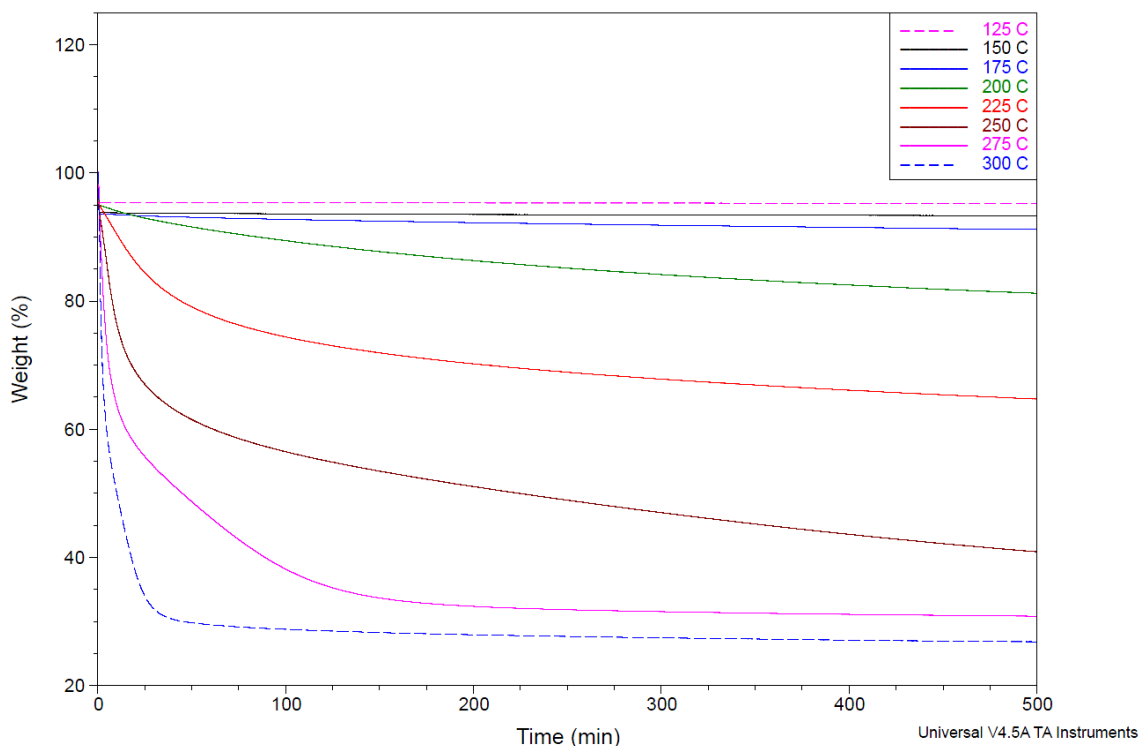


Figure 13: Isothermal Testing of CSP for 500 minutes

The data represented in Figure 13 can be seen with weight percent plotted on a log scale in Figure 14. When plotting weight percent on a log scale it becomes apparent that, at higher temperatures, the isothermal curve no longer behaves linearly. Instead at higher temperatures there is more than one linear region. The isothermal curves that correspond to temperatures between 125 and 200 °C appear linear on the log plot for the entirety of the 500 minute test, but the isothermal curves that correspond to temperatures between 225 and 300 °C appear to have multiple linear sections. It is assumed that different linear sections of the log plot correspond to the thermal degradation of a different structural element of CSP, and the nonlinear regions correspond to the depletion of a structural component and the transition into a different phase of degradation. Recall

from the literature review that the structural components of the coconut degrade at different temperatures:

Sclerenchyma Cell Degradation: 150 °C – 240 °C

Hemicellulose Degradation: 190 °C – 260 °C

Cellulose Degradation: 240 °C – 350 °C

Lignin Degradation: 280 °C – 500 °C

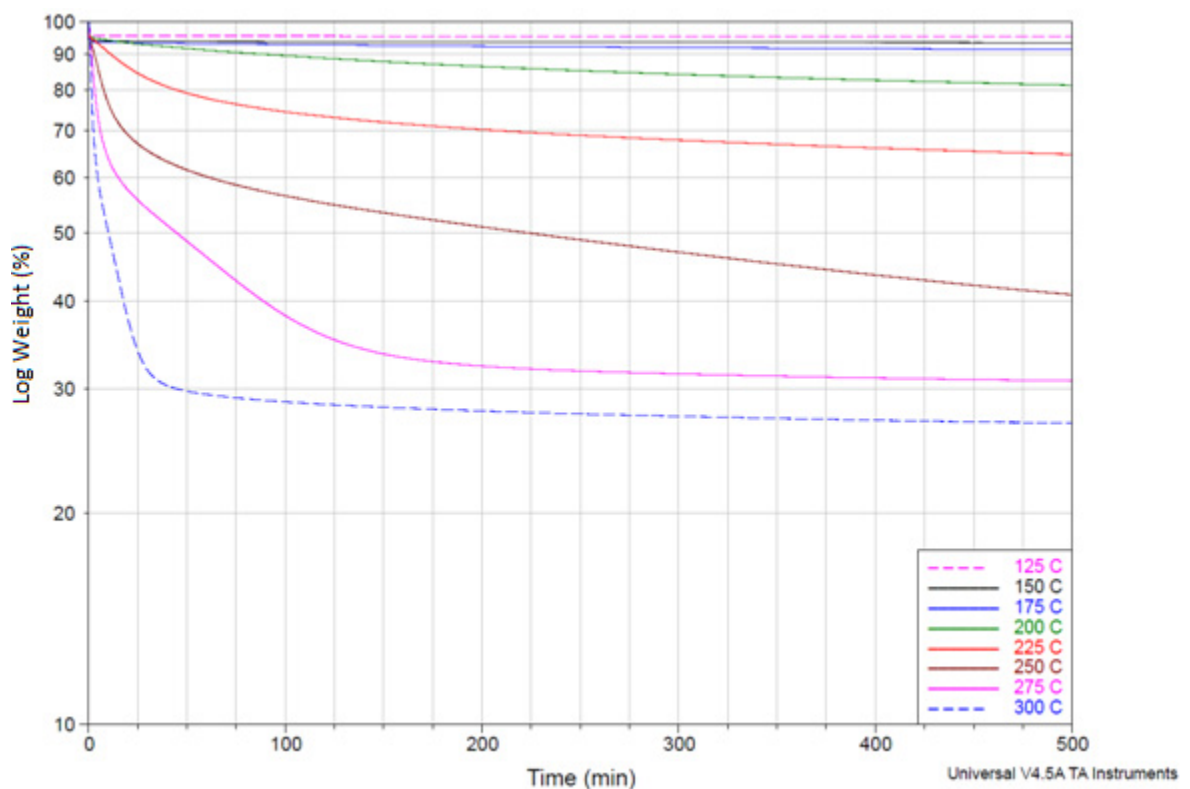


Figure 14: Isothermal Testing Graphed on a Log Scale

Thus, it would make sense that between 125 and 200 °C there is only one linear region on the log plot because sclerenchyma cells alone are being degraded. It appears that sclerenchyma cells and hemicellulose in the CSP are degrading between 225 and 250 °C, and the first linear section corresponds to the thermal degradation of both sclerenchyma cells and hemicellulose. Initially sclerenchyma cell degradation is the driving force for

the rate of degradation, but eventually the rate of sclerenchyma cell degradation slows down as the total elimination of sclerenchyma cells nears completion. Once the log plot becomes linear again, the sclerenchyma cells have been eliminated due to thermal degradation and hemicellulose is the only structural component degrading in the second linear region. Similarly, at temperatures between 275 and 300 °C, the initial degradation would be of sclerenchyma cells, hemicellulose, and cellulose, and once the sclerenchyma cells have been completely degraded, the hemicellulose and cellulose would degrade. Likewise, the complete degradation of hemicellulose would result in a linear region where only cellulose degradation is taking place. The degradation of these three structural components (sclerenchyma cells, hemicelluloses, and cellulose) at 275 °C for 500 minutes is shown in Figure 15.

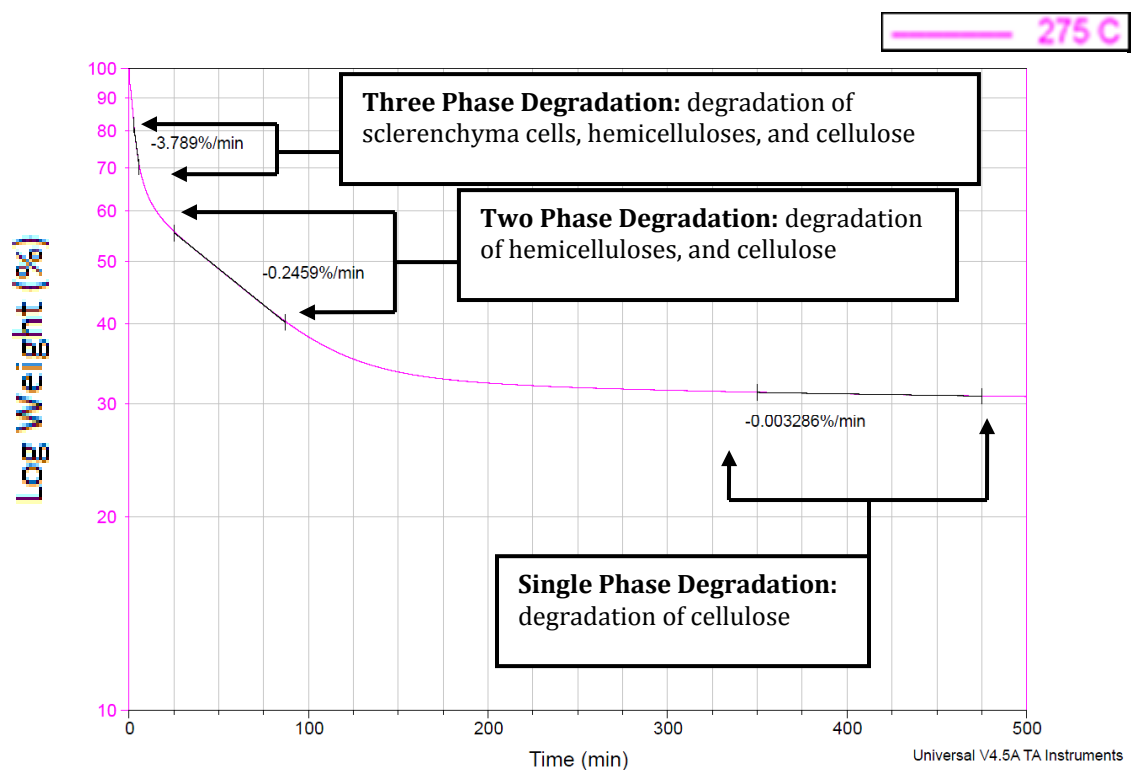


Figure 15: Multiphase Degradation of CSP at 275°C for 500 minutes

Each structural component that is being degraded has a different thermal activation energy, which is the reason why there are different phases of degradation. Each thermally activated process follows the Arrhenius equation, $R = Ae^{\frac{-\Delta H}{kT}}$, by which the rate of thermal degradation from the natural exhaustion process, R , corresponds to the frequency of attempt of the natural process, A , multiplied by the exponential of thermal activation energy for the process all over the bond energy, k , multiplied by the temperature, T . By taking the natural log of both sides, the Arrhenius equation becomes $\ln(R) = \ln(A) + \frac{-\Delta H}{kT}$. Based on this modified form of the Arrhenius equation, the natural log of the rate of single phase degradation is a linear function dependent on the inverse of temperature. Figure 16 shows the different phases of degradation. The single phase degradation processes fits a linear regression. The natural log of the rate of thermal degradation can be determined for any temperature along the regression. If CSP degradation is the main concern when processing CSP-polypropylene composites at a temperature of 200 °C or lower, then the maximum rate of degradation for CSP the specific processing temperature can be determined. Using this information the weight percent degradation over a specific processing time can be estimated. If the processing temperature is higher than 200 °C and less than or equal to 250 °C, the single phase degradation rate of the sclerenchyma and the single phase degradation rate of the hemicellulose can be calculated and the respective weight loss due to thermal degradation from each rate can be added together to get the total weight loss due to thermal degradation at that processing temperature. This assumes that the processing time is short enough that the two phase degradation (schlerenchyma and hemicellulose) is not in the

transition region. This amounts to a processing time, which, based on Figure 15, appears to be less than 10 or 12 minutes.

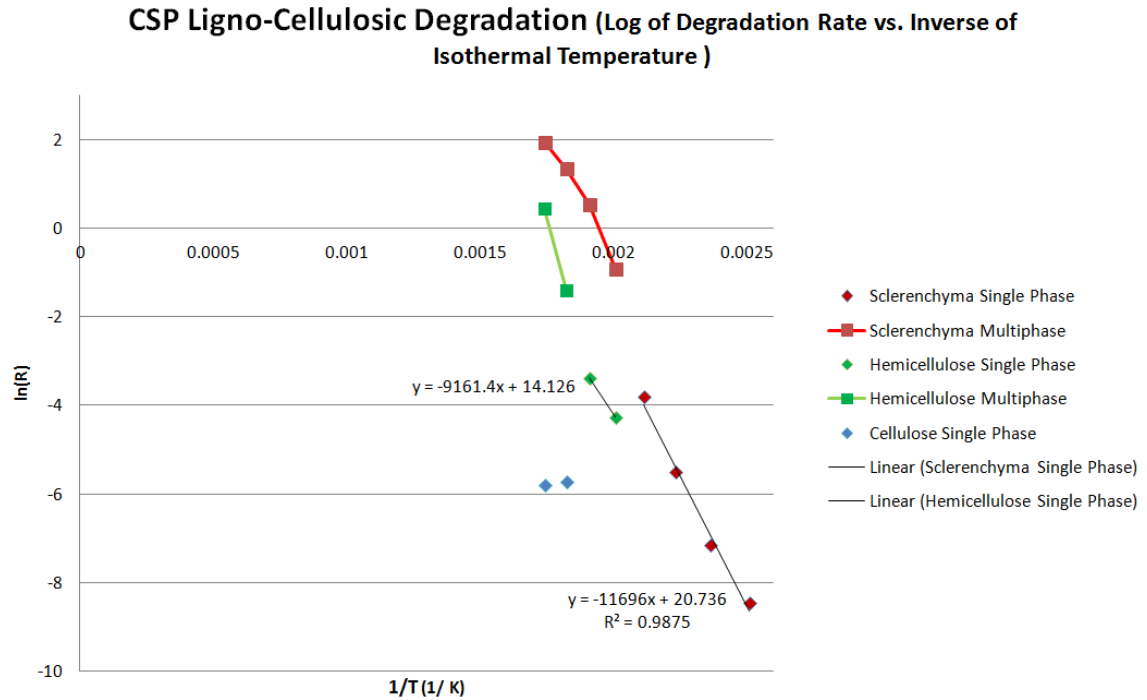


Figure 16: CSP Ligno-Cellulosic Degradation Phase Analysis

Understanding the thermal degradation characteristics of the CSP is very important because the thermal degradation characteristics of CSP- polypropylene composites largely depend on the thermal degradation characteristics of CSP. The thermal degradation characteristics of CSP-polypropylene composites also depends on the thermal degradation characteristics of the polypropylene copolymer. Ramp testing of the polypropylene copolymer used in this research is provided below in Figure 17. The processing temperature range for the polypropylene copolymer is between 180 °C to 230 °C, and thermal degradation of the polymer does not begin to take place until around 275 °C. Even after 275 °C, thermal degradation is very gradual (less than 0.1 wt%/°C of

degradation) until 350 °C. Therefore, the polypropylene copolymer should not thermally degrade at all during processing. However, polypropylene is very susceptible to oxidation and onset of oxidation takes place at 180 °C. The polyethylene that the polypropylene is copolymerized with provides some oxidative stability to the polypropylene copolymer, but even with the addition of polyethylene, the copolymer begins oxidizing around 180 °C.

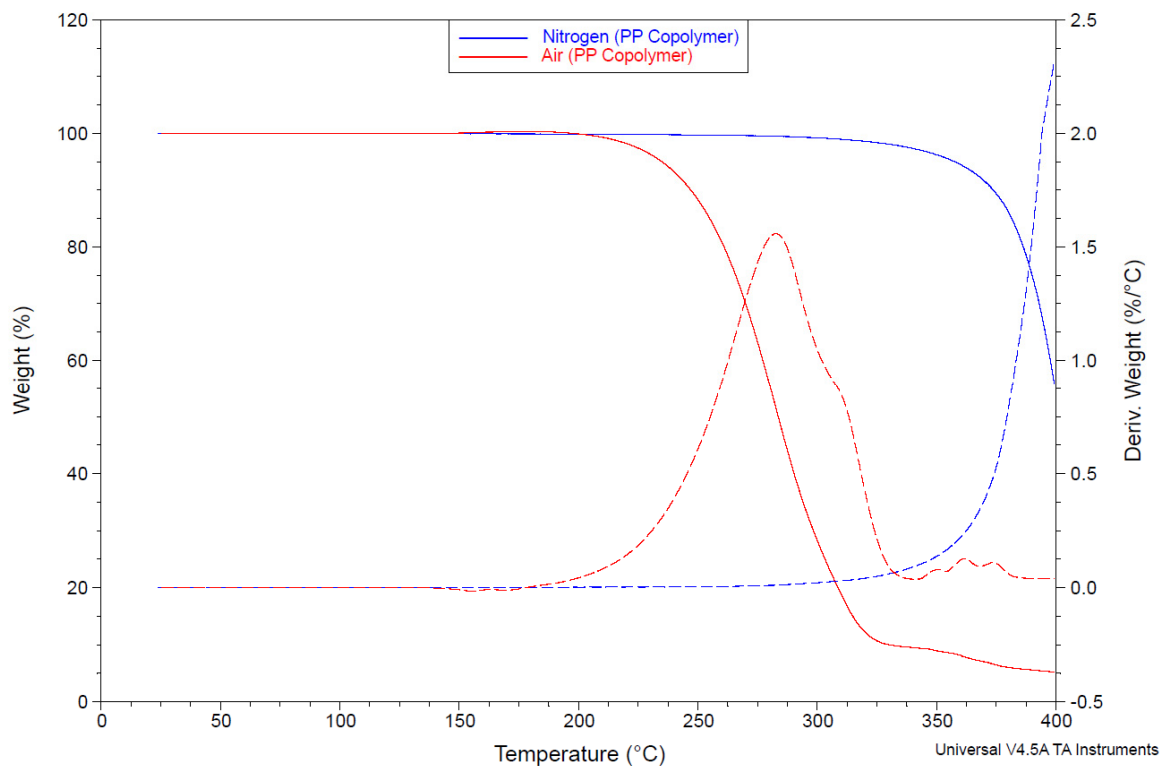


Figure 17: Ramp Testing of Polypropylene Copolymer with a ramp rate of 2 °C/min

Thermal Degradation Characteristics of CSP-Polypropylene Composite

If the ramp tests for CSP, polypropylene copolymer, and the CSP-polypropylene composite are plotted against each other, the correlation between CSP thermal degradation and the thermal degradation of the CSP-polypropylene composite should be

very obvious. Ramp tests of CSP, the polypropylene copolymer, and an undried 20 wt% CSP-polypropylene composite pellet, are shown in Figure 18. Referring to a CSP-polypropylene composite pellet as undried, means that the CSP was not dried before the composite was compounded, unless otherwise stated.

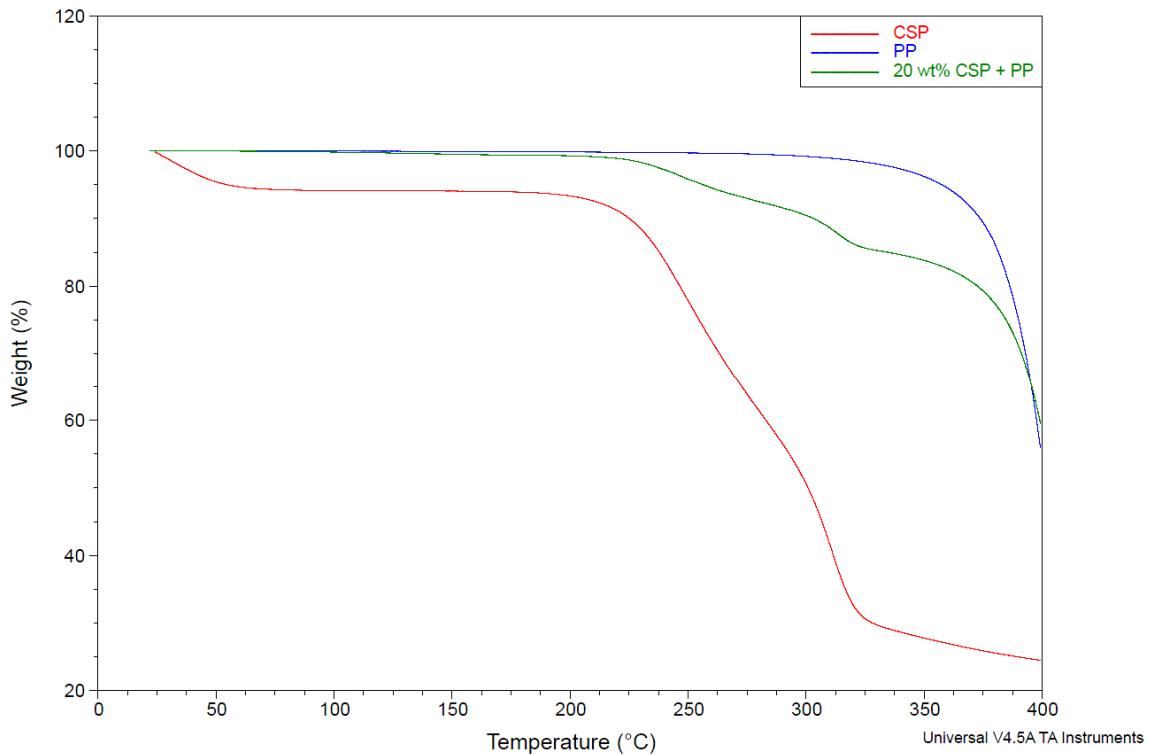


Figure 18: Ramp Testing: Constituents of Composite vs. Composite with ramp rate 2°C/min

As expected, the thermal degradation of the composite is dependent on the thermal degradation of CSP. The CSP loses less weight than the composite because CSP only represents 20 wt% of the composite. Notice that the shape of the degradation curve for CSP and the composite are the same before 350 °C, only the degradation slope of the composite is less steep. At 20 wt% CSP loading in the composite, 10 wt% thermal degradation to the CSP only means a 2 % weight loss from the overall sample. This also applies to the moisture content of a CSP-polypropylene composite because polypropylene

is hydrophobic. At 20 wt% CSP loading in the composite, 5 wt% moisture in the CSP only means 1 wt% moisture in the composite. For this reason, Figure 18 shows very little weight loss due to moisture desorption. The weight percent CSP in the composite is the limiting factor for both weight percent thermal degradation and weight percent moisture of the CSP-polypropylene composite.

A percent loading study was performed to study the degradation characteristics of CSP-polypropylene composites compounded with different weight percent amounts of CSP. As expected, by increasing the weight percent of CSP in the composite, the slope of the degradation curve became more negative and the composite lost more weight due to degradation at higher weight percent loadings of CSP. There were also some very interesting results pertaining to the onset of degradation for CSP when it is by itself and when it is encapsulated. Although the shape of the degradation curves of CSP and CSP filled composites appear to be identical, there is approximately a 20 °C difference between the onset of thermal degradation for the CSP and the CSP-polypropylene composite. This phenomenon can be seen in Figure 19.

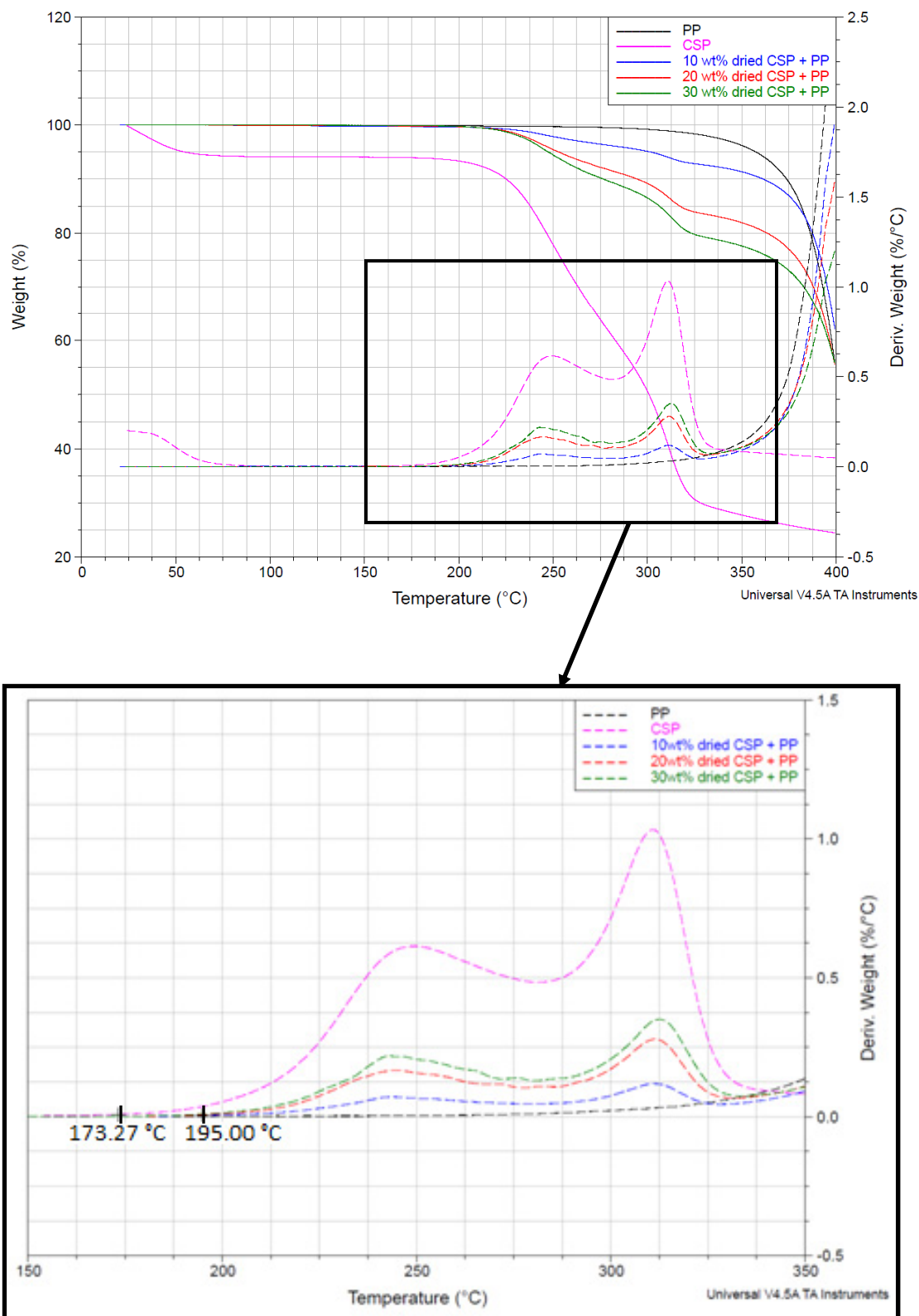


Figure 19: The Effect of Encapsulation and Loading Study with a ramp rate of 2°C/min

The onset of thermal degradation for CSP is approximately 173.27 °C, and the onset of thermal degradation for the encapsulated CSP is approximately 195 °C. There are a couple possible causes for this delay in the onset of degradation. First, it is possible that the temperature gradient through the CSP-polypropylene pellet is very big and the center of the pellet is not near as hot as the surface of the pellet, so CSP encapsulated in the pellet is actually 20 °C colder than the surface of the pellet. This would rather improbable, given the size of the pellet. There is 20 °C between the two degradation onsets and the ramp rate is 2 °C/min, meaning that the CSP-polypropylene pellet spends 10 minutes at a temperature above the melt temperature of the polypropylene copolymer (170 °C) and above its own thermal degradation temperature (between 170 °C and 180 °C) without any signs of weight loss due to thermal degradation. Another possibility is that the encapsulated CSP is thermal degrading and volatilizing at 173.27 °C, but the VOCs are trapped in the polypropylene matrix and cannot escape until the flow becomes less viscous at higher temperatures. However, this possibility requires more research to verify if that is, in fact, the case. For now it is important to note that the effects of encapsulation in delaying the onset of degradation and the fact that encapsulation can alter the rate of thermal degradation, make it very difficult to make a precise quantitative comparison between percent degradation of CSP and percent degradation of the CSP-polypropylene composite.

Thus in order to understand the different rates of degradation at different temperatures for the CSP-polypropylene composite, isothermal testing of composite pellets was necessary. The tests in Figure 20 are called isothermal simulations because the tests simulated an isothermal processing situation. All tests were performed over a ten minute time period, to get a good idea of the rate of degradation taking place.

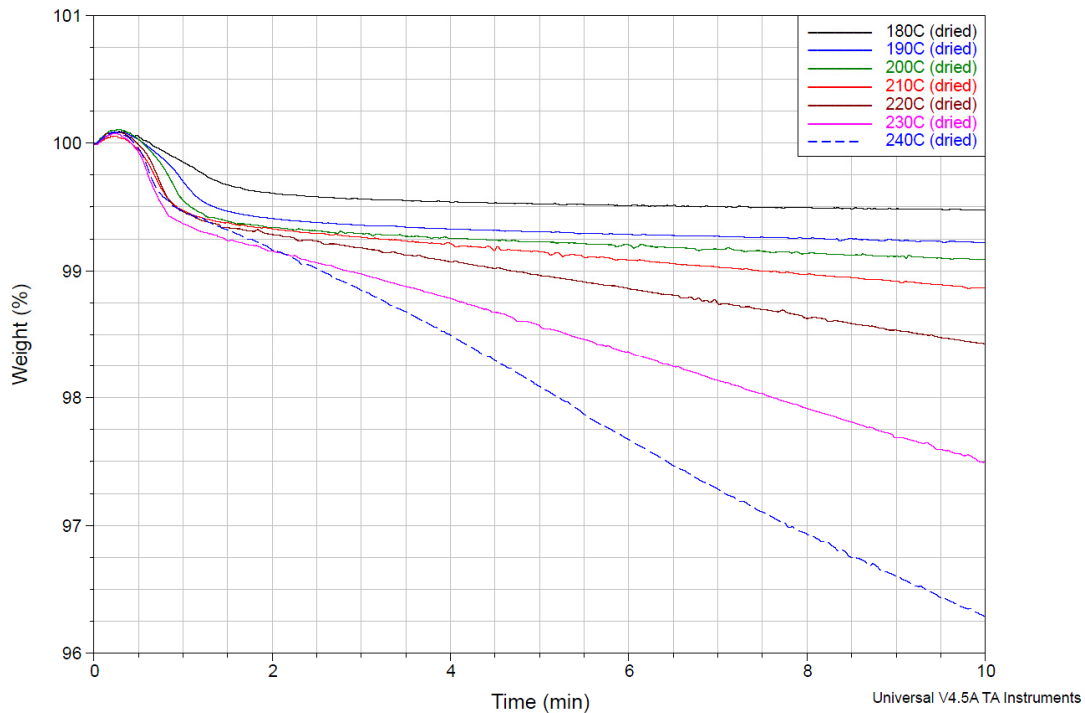


Figure 20: Isothermal Simulation of 20 wt% CSP Composite, all test were run for 10 minutes

The different temperatures tested in these 10 minute isothermal simulation tests, rang from 180 °C to 240 °C. From a molecular structure standpoint, this temperature range also corresponds to degradation of the schlerenchema cells and, at higher temperatures in the range, hemicellulose. Also, because the ten minute time test is complete before the isothermal test enters the transition region between different phases of degradation (the transition region is around 12 minutes at 250 °C), the isothermal plots can be graphed on

a log scale. This allows for a rate of degradation that takes into account both time and temperature, to be found, and this rate should be constant for each sample, until the phase transition region is reached. The tests run at 180 °C, 190 °C, and 200 °C should not have a transition region because the degradation at these temperatures is single phase and it is a function of schlerenchema cell degradation exclusively. Between 210 °C and 240 °C the thermal degradation taking place is two phase degradation (schlerenchem cells and hemicellulose). At these temperatures a transition region does exist; however, there is at least 12 minutes before that the thermal degradation enters that region and all.

Correlation of Thermal Degradation to Loss of Mechanical Properties

Using these isothermals to gather a rate of degradation for each temperature, the correlation between thermal degradation and mechanical properties was researched in hopes of determining the critical level of thermal degradation for a CSP-polypropylene composite. Thus testing was conducted in a way that utilized long processing times with an isothermal heating to degrade tensile bar and flexural bar specimens to levels of known degradation. First all the temperature zones on the Arburg injection molder were set to 200 °C. The dwell time for the injection molder is approximately 1.5 min. Three batches of tensile and flexural bars were made. The first batch had a standard dwell time, the second batch had a standard dwell time plus 5 minutes isothermal in the barrel of the injection molder. The last batch of tensile and flexural bars had a standard dwell time plus 10 minutes isothermal in the barrel of the injection molder. This same testing procedure was repeated for 220 °C heating zones. Table 1 shows the percent degradation of each of the injection molded bars based on processing time and processing temperature.

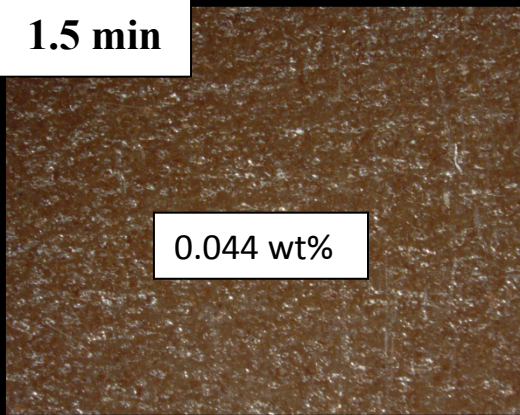
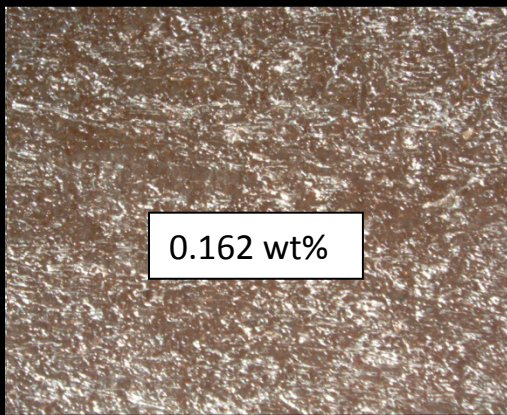
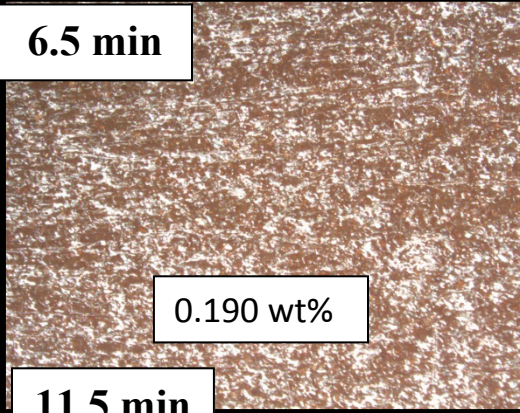
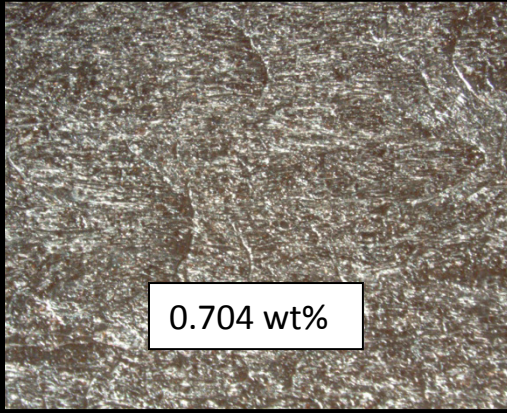
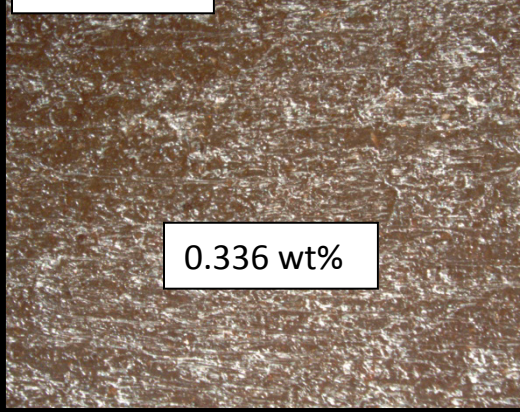
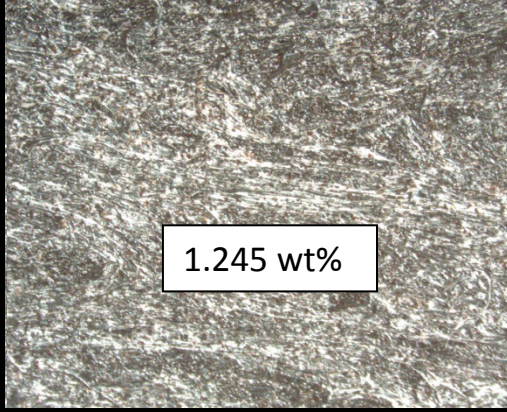
Table 1: Correlation between processing time and thermal degradation to composite and CSP

% Thermal Degradation of Composite				% Thermal Degradation of CSP		
Temperature	Time at Temperature			Time at Temperature		
	1.5 min	6.5 min	11.5 min	1.5 min	6.5 min	11.5 min
200 °C	0.044%	0.190%	0.336%	0.219%	0.950%	1.680%
220 °C	0.162%	0.704%	1.245%	0.812%	3.520%	6.227%

The percent degradation for this table was calculated using the linear rate of degradation for 200 °C and 220 °C from the log scale plot of isothermal simulations for CSP-polypropylene pellets. The rate of degradation in °C/min was multiplied by the time of the isothermal hold to get the percent degradation in the sample. It is important to note that the temperatures that the heating zones are set to correspond to the heater band temperatures on the surface of the molten plastic. A thermocouple was used to measure the actual temperature of the molten plastic as it flowed out of the injection mold. It was found that the actual temperature of the molten plastic ranged from 3 °C to 5 °C less than the temperature indicated on the heater band. However, when holding the molten plastic in the barrel of the injection mold for 5 or 10 minutes, the heater band temperature might have been more accurate than when the molten plastic was flowing through the injection mold. For this reason Table 1 represents the maximum possible degradation amounts for the specified time and temperature combination. The actual degradation could potentially be less than the specified amount, however, it can be assumed that the values in Table 1 are relatively close to the real values.

Table 2 displays this same information, but in a way that a 10X magnified picture of the surface of the tensile bar can be seen for each time and temperature combination.

Table 2: The appearance of thermal degradation corresponding to the processing situations

200 °C		220 °C	
1.5 min			
6.5 min			
11.5 min			

As the weight percent of degradation increases, the appearance of splay becomes more prominent. The images at 6.5 minutes and 11.5 minutes for the isothermal temperature of 220 °C have a dark tint because the degradation to the CSP in the composite has left the sample charred. The images with noticeable char would not be used from an aesthetics standpoint, and so on from the standpoint of appearances, 0.704 wt% degradation and up is definitely too degraded.

A further step in determining the critical degradation amount for CSP-polypropylene composites can be taken by comparing the mechanical properties of the CSP-polypropylene composite as a function of thermal degradation. Figures 21 and 22 show the flexural modulus and strain at break as they related to different levels of thermal degradation.

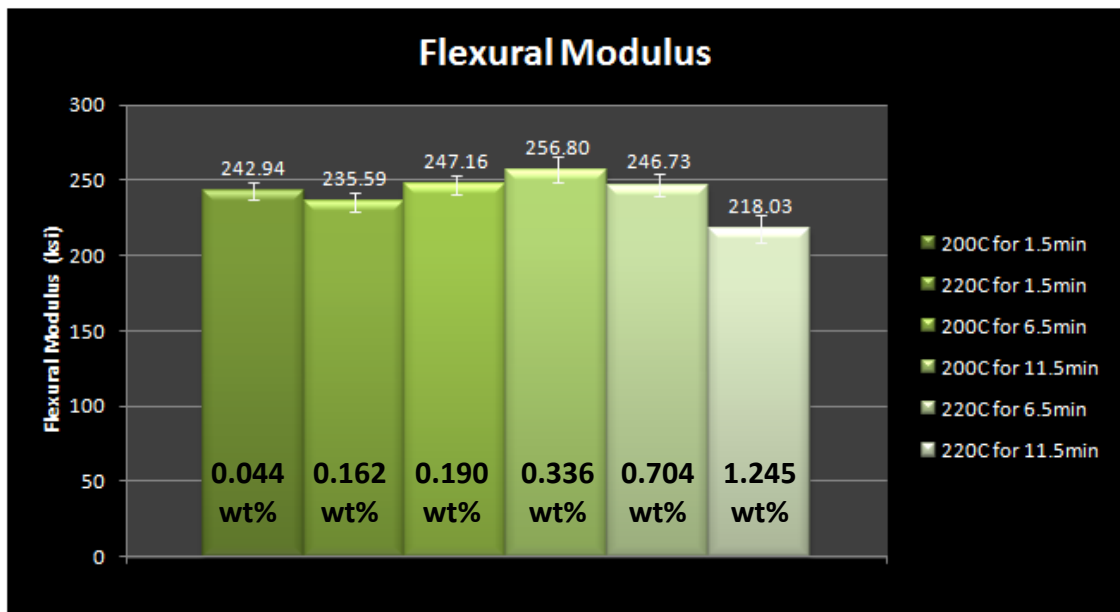


Figure 21: Flexural Modulus Compared to wt% Thermal Degradation

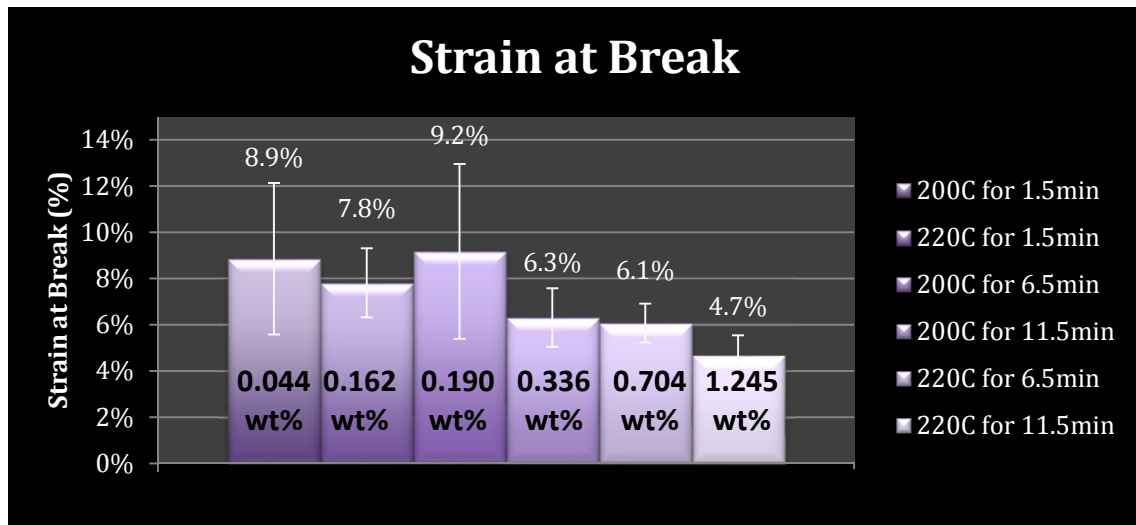


Figure 22: Strain at Break Compared to wt% Thermal Degradation

There is not a statistically significant change in the flexural modulus until the degradation gets close to 1.245 wt%. As the degradation increases, the strain at break decreases; however these results are also not statistically significant. More mechanical testing would have to be done to draw hard conclusion about the weight percent degradation and how it relates to the flexural modulus and the strain at break. In this research we decided to use the overall trend presented by the flexural modulus data and the strain at break data to draw certain conclusions. According to the overall trend of the data, it appears that thermal degradation has local effect on the mechanical properties of the composite. For this reason the global average mechanical properties such as the flexural modulus do not change very drastically in response to increases in thermal degradation. The only reason that the flexural modulus changes drastically between the 220 °C sample at 6.5 minutes and the 220 °C sample at 11.5 minutes is because at 1.245 wt% thermal degradation, there are enough local defects to cause a change in the global average. This is why strain at break is a more sensitive function to thermal degradation because strain at break is largely dependent on local defects. Strain at break, as well as tensile strength, and Izod

impact strength are sensitive to local defects and can be considered weakest link limiting properties. Izod impact strength was a mechanical property that was not tested in this research. CSP-polypropylene composites are known for having good retention of impact strength compared to other natural filler; however, it can be expected that Izod impact strength is an even more sensitive function of thermal degradation than strain at break. Therefore, impact strength will most likely fall drastically once the critical degradation limit is surpassed. Figure 23 reiterates that thermal degradation is responsible for local heterogeneities that cause drastic changes in strain at break properties and impact strength properties.

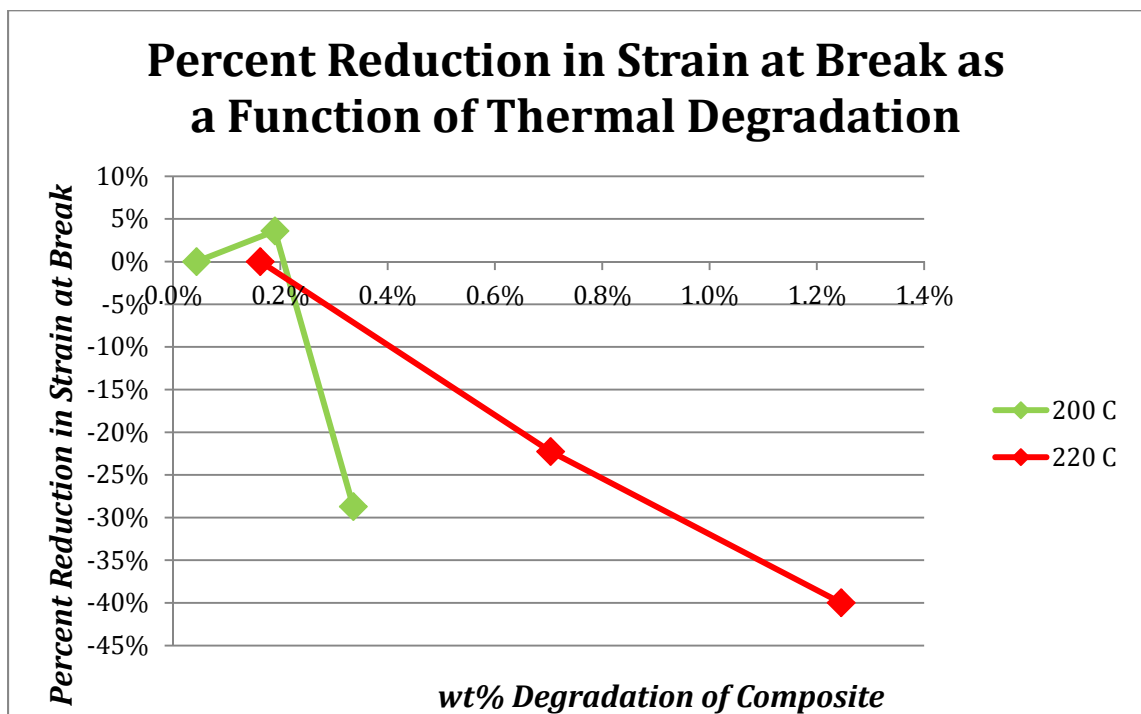


Figure 23: Percent Reduction in Strain at Break as a Function of Thermal Degradation

The reason that degradation causes local problems or defects rather than global defects is due to the fact that degradation is centered around CSP particles in the composite. When VOCs are released from the CSP during thermal degradation, they leave behind

microvoids, which makes it easier for cracks to form and propagate to the critical crack size in the material. The microvoids left behind by VOCs can be seen using a Scanning Electron Microscope (SEM). Figures 24 and 25 are 200X magnified fracture surfaces of tensile bars without degradation and with 1.245 wt% degradation respectively. The effects of escaping volatiles can be seen on the degradation picture.

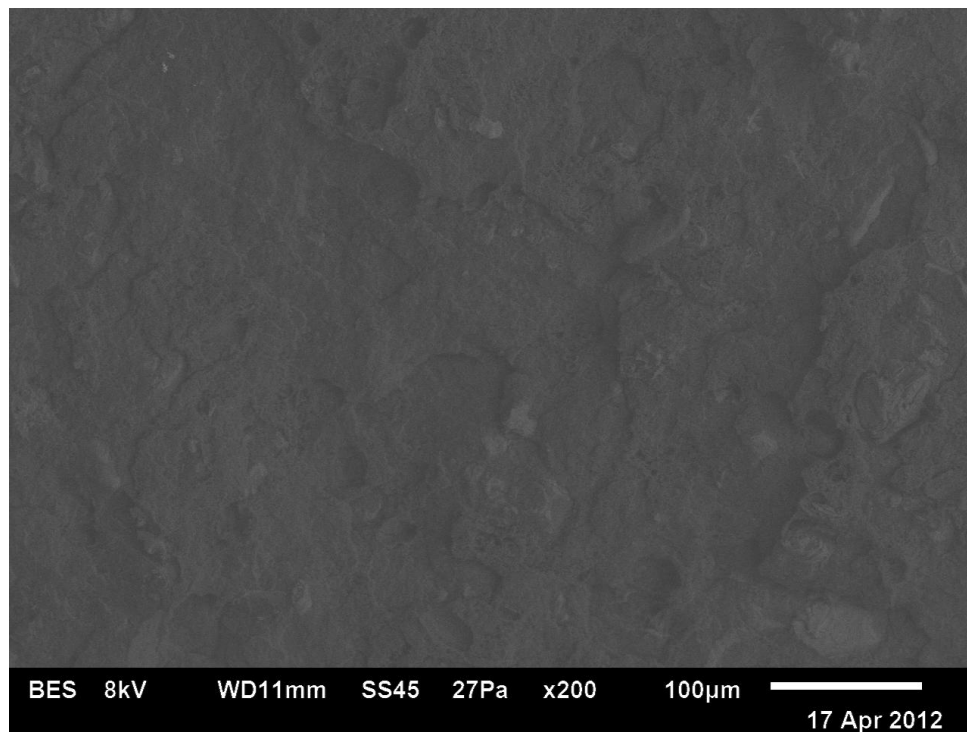


Figure 24: Minimal Thermal Degradation at 200x magnification with SEM backscatter

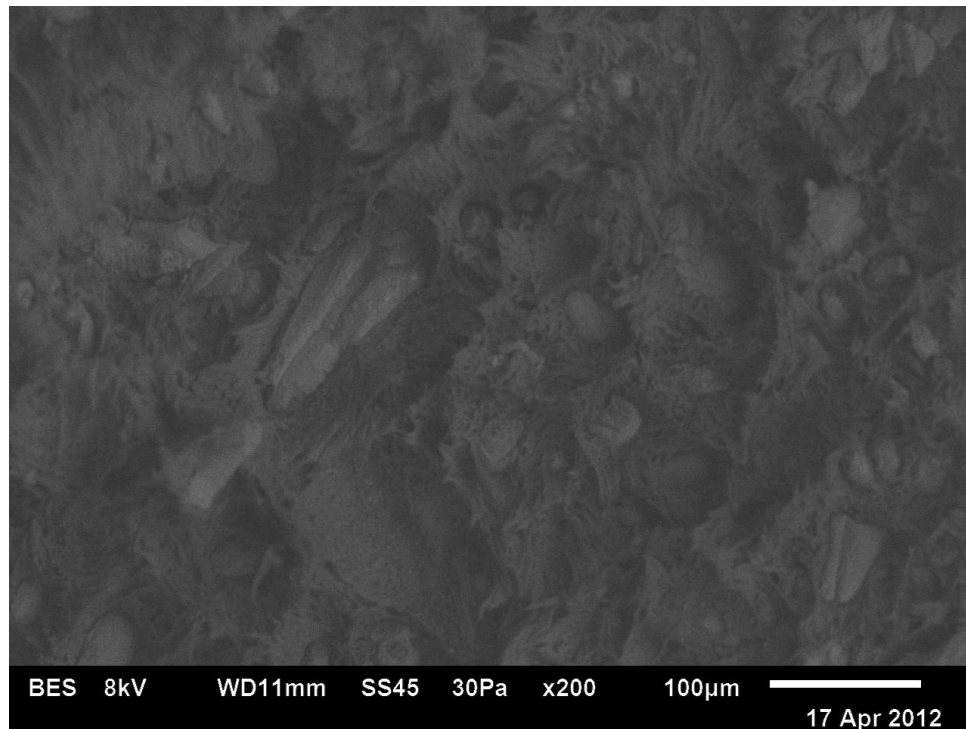


Figure 25: Maximum Thermal Degradation at 200X magnification with SEM backscatter

Figure 25 shows the fracture surface of a tensile bar that was injection molded at 220 °C after 1.5 minute dwell time and 10 minutes of sitting in the barrel of the injection molder at 220 °C. Comparing the surfaces of the thermal degraded tensile bar and the tensile bar with negligible thermal degradation, one notices a more texturized fracture surface for the tensile bar with thermal degradation. This is most likely caused by VOCs escaping from the CSP while the CSP is being degraded. The VOCs leave behind pockets or defects where crack propagation becomes easier and Figure 25 is the result.

Conclusion: Maximum Allowable Processing Time for Different Temperatures

Due to its lignin rich composition, coconut shell has good thermal stability compared to most other natural fillers. The polypropylene copolymer used in the CSP-polypropylene composite is processed between 180 °C and 230 °C and does not begin thermal degrading until 275 °C. CSP begins to degrade between 170 °C and 180 °C .

Therefore all of the thermal degradation of the CSP-polypropylene between 180 °C and 230°C, the copolymer's processing window, is due to thermal degradation of the CSP in the composite. However, CSP has a very gradual change in weight percent due to thermal degradation in the copolymer's processing temperatures (less than 0.1 wt%/ °C until around 225 °C). Thermal degradation of the composite is directly related to the wt% of CSP in the composite. Not all thermal degradation is necessarily bad, a very small amount of thermal degradation may, in fact, improve polymer processing. Yet too much thermal degradation is not only detrimental to the mechanical properties of the CSP-polypropylene composite but also the appearance of the CSP-polypropylene composite. Due to the variability of mechanical properties and due impart to small sample sizes for the tensile bars and flex bars that were tested. The mechanical properties do not provide much data that is statistically significant. Therefore, in order to have a stronger correlation between mechanical properties and thermal degradation, more mechanical testing needs to be done. Based on the data that is presented, it appears that thermal degradation causes localized defects due to VOC's escaping from the composite and leaving behind microvoid that make it easier for cracks to propagate through the material and reach a critical crack size. Thermal degradation does not have much of an impact on a global scale until the wt% degradation is a little over 1 wt%. After 1 wt% degradation, the local defects are so great that they begin to influence the global average in a noticeable way.

Based on the two main factors, appearance and somewhat correlated mechanical properties, the critical degradation level for CSP-polypropylene composites, as determined by this research is 0.366 wt% degradation of the CSP-polypropylene

composite, which is the same amount of degradation that took place after heating a CSP-polypropylene composite to 200 °C for 11.5 minutes. Based on this critical amount of degradation, the processing time for temperatures between 180 °C and 250 °C can be determined using the exponential function. Figure 26 shows the plot of time vs. temperature in CSP-polypropylene composite processing.

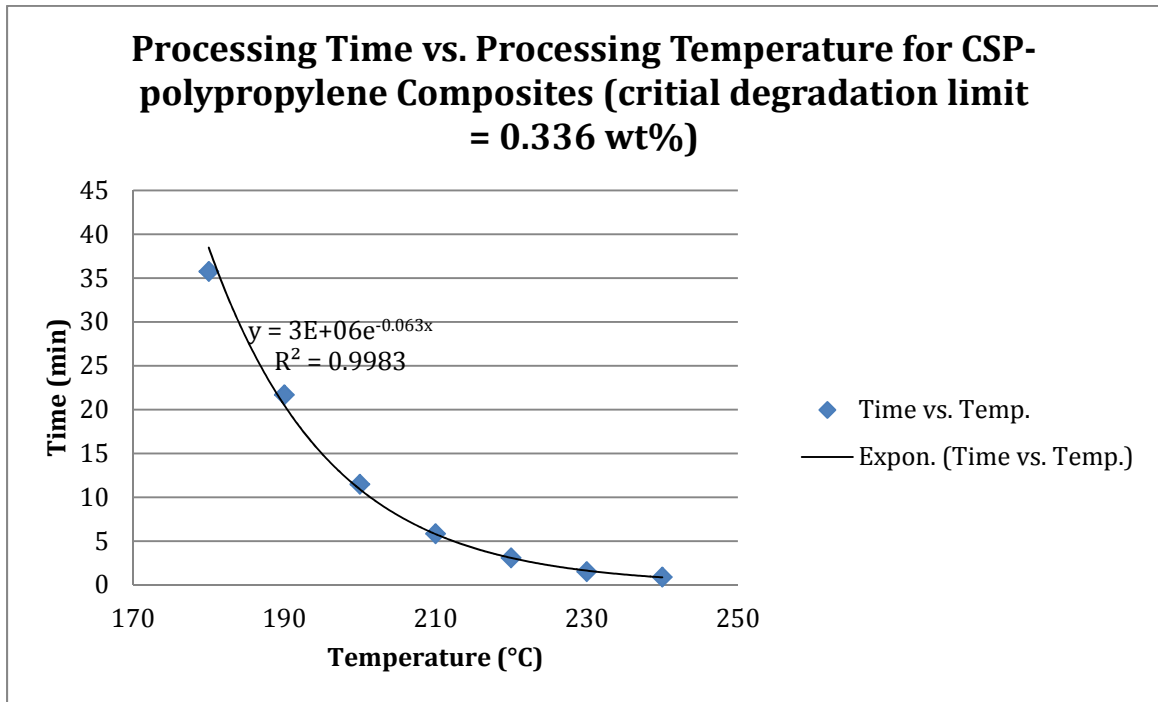


Figure 26: Processing Time vs. Processing Temperature For CSP-polypropylene composites

Table 3: Maximum Processing Time for Given Temperatures

Dried		
Temperature (°C)	Rate of Degradation (%/min)	Time (min)
180	0.009%	35.76
190	0.015%	21.69
200	0.029%	11.50
210	0.057%	5.86
220	0.108%	3.10
230	0.220%	1.53
240	0.370%	0.91

APPENDIX

THE EFFECT OF MOISTURE ON CSP-POLYPROPYLENE COMPOSITES

Now the question is in this section is: how can moisture be removed from the CSP, in order to isolate the thermal degradation of the composite? Moisture is an issue with all ligno-cellulosic fillers and adds variability to polymer processing. Moisture effects a polymer composite in a similar way to thermal degradation: decreased mechanical properties and increased surface defects. Figures A.1, A.2, and A.3 compare the effects of the presence of moisture and thermal degradation on the appearance of CSP-polypropylene composites, versus a CSP-polypropylene composite with negligible moisture and degradation levels. Lighting and magnification were kept the same when taking these images.



Figure A.1

Thermal Degradation

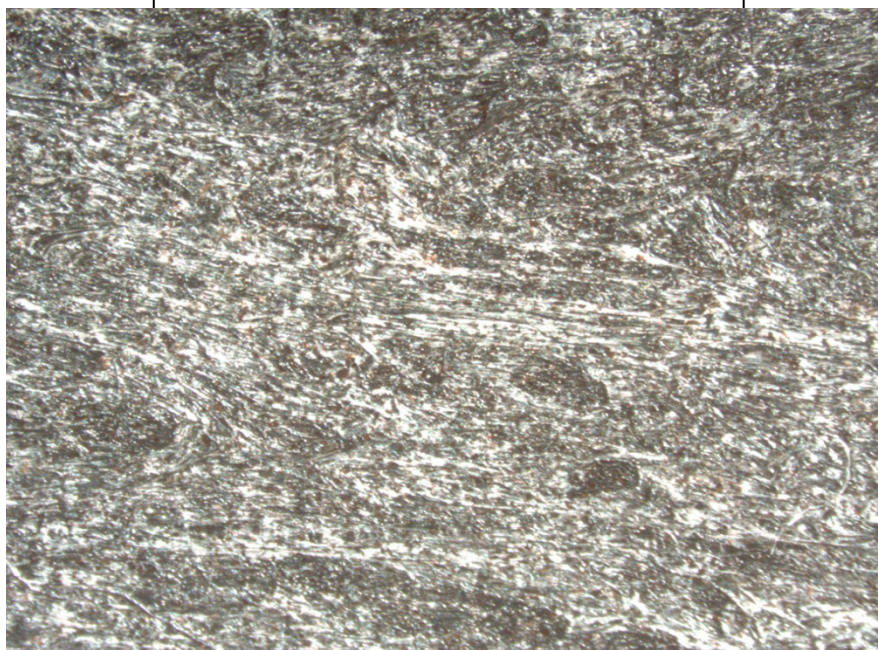


Figure A.2

Negligible Moisture and Thermal Degradation



Figure A.3

Figure A.1 displays the effects of moisture on the appearance of the CSP-polypropylene composite. The reason that the surface looks texturized is because during processing, the high temperatures turn the moisture to steam. Some of the steam makes its way to the surface, leaving behind pockets or microvoids in the space that the water once occupied and solidifies, causing the splay effect seen. The darkness of the image compared to the CSP-polypropylene composite with negligible amounts of moisture and thermal degradation is due to the light reflecting in different ways off of the splayed surface.

Figure A.2 displays the effects of thermal degradation on the appearance of the CSP-polypropylene composite. The picture was taken of a CSP-polypropylene tensile bar that was injection molded at 220 °C and left at that temperature in the barrel for 10 minutes after a 1.5 minute dwell time. The dark appearance is the effect of charring due to thermal degradation. There are also microvoids, created by escaping VOCs, but the splay effect is not quite as pronounced as it is in the moisture image. Figure A.3 displays a CSP-polypropylene composite with negligible amounts of moisture and thermal degradation. The reason this CSP-polypropylene composite appears lighter than the other two composites is because the surface is more homogenous and char free. Also, the absence of moisture means that there is no opportunity for steam to solidify at the surface.

Figures A.1 and A.2 have many similarities but at 10X magnification, the two images can be identified as being caused by moisture or thermal degradation. However, to the naked eye, it can be very difficult to differentiate between moisture and thermal degradation. For this reason, along with many others, it was imperative that the variable of moisture be eliminated. In order to be sure that test results were solely the effect of thermal degradation, moisture had to be removed. However, the real issue of removing

moisture is removing moisture in a timely manner without pre-degrading the CSP. For commercial applications, CSP drying must be done in a timely manner. Initially a drying of the CSP was done at 160 °C for two hours because this time and temperature also corresponded to the sterilization of microbials. Two hours is not too long and because CSP does not begin degrading until between 170 °C and 180 °C, it was assumed that no thermal degradation or oxidation would occur when drying at 160 °C. However, the Maxwell-Boltzmann distribution of kinetic energies says that oxidation and thermal degradation are possible at 160 °C. The subsequent isothermals in Figure A.4 show that both oxidation and thermal degradation of the CSP actually do take place over a two hour period.

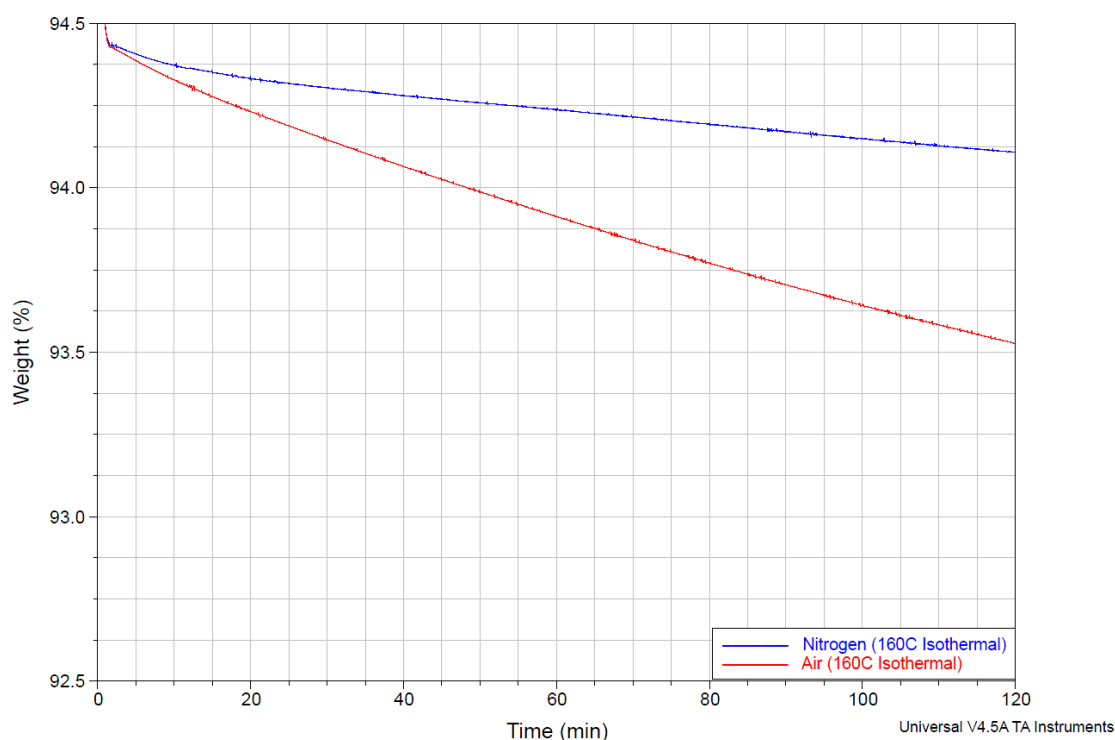


Figure A.4: Isothermal testing at 160 °C for 2 hours

Figure A.4 shows a two hour isothermal for CSP at 160 °C in both nitrogen (blue) and air (red). In this case, it is probably more appropriate to focus on the air isothermal because the furnace used to dry the CSP was not hooked up to a vacuum pump and air could circulate in the furnace. According to Figure A.4, after two hours, CSP loses a little less than 0.4 wt% due to thermal degradation and around 0.6 wt% due to oxidation. In total this amounts to only 1 % weight percent loss due to thermal degradation and oxidation. However, other drying temperatures were to make sure that no weight loss due to thermal degradation or oxidation occurred during drying. Figure A.5 shows the isothermal plots for other drying temperatures over a 500 minute period. Note that all of these isothermal results were run in an air environment, in order to simulate the conditions of drying the CSP in the furnace.

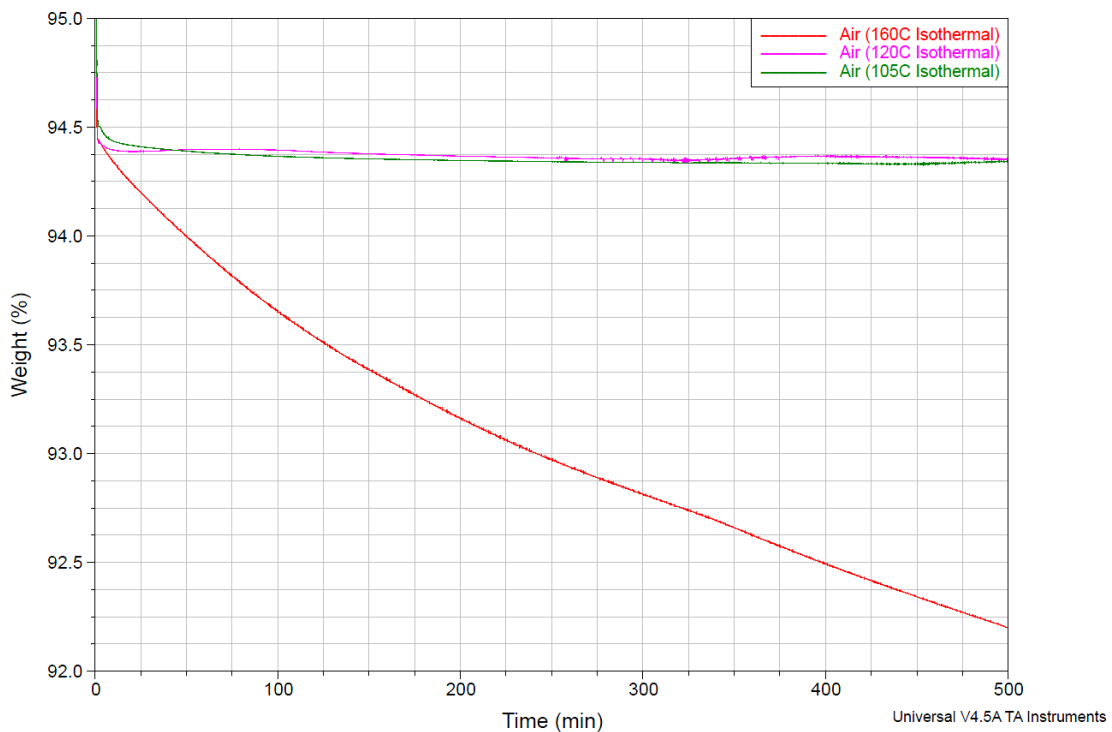


Figure A.5: Isothermal Testing for 500 minutes in Air at different drying temperatures

According to Figure A.5, after the initial moisture desorption, CSP at the temperatures of 105 °C and 120 °C is not being subjected to enough thermal energy for the activation energy barrier of any of the covalent bonds to be overcome.

After compounding CSP-polypropylene pellets with 10 wt%, 20 wt% and 30 wt% CSP that had been dried for different times and at temperatures, a ramp test was performed to compare the thermal degradation characteristics of dried CSP-polypropylene composites to undried CSP-polypropylene composites. The results for the 10 wt% CSP and 30 wt% CSP pellets are shown below in Figures A.6 and A.7.

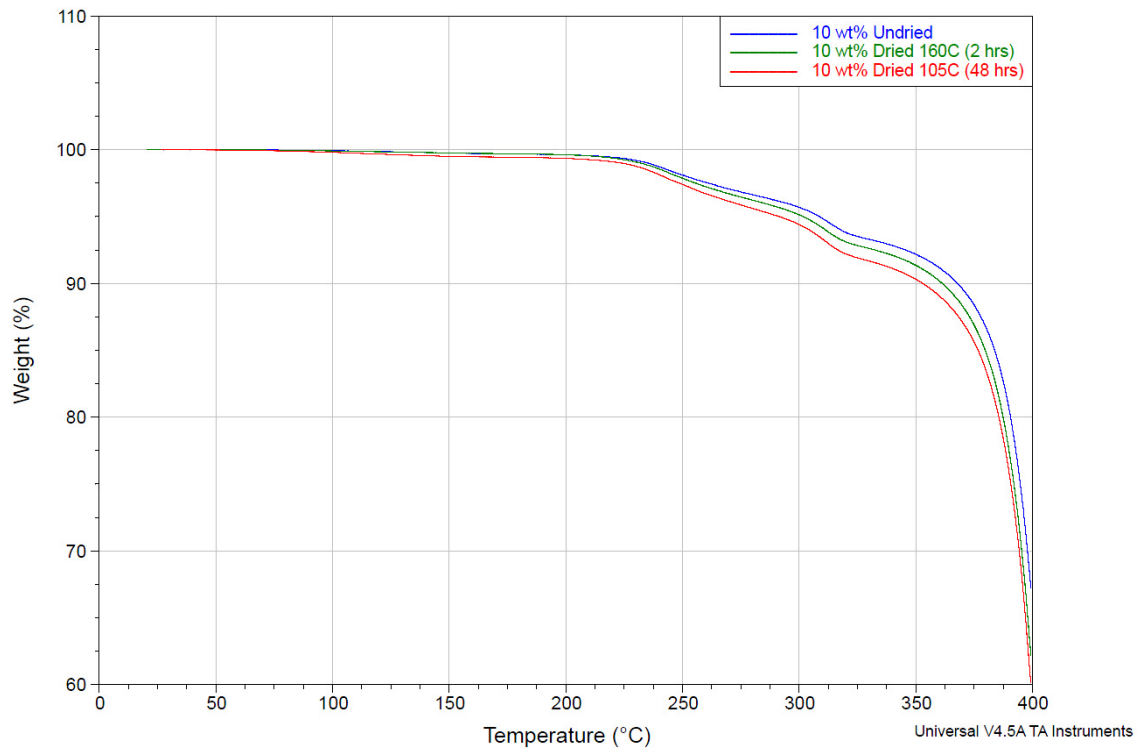


Figure A.6: Dried vs. Undried comparison of 10 wt% CSP composites

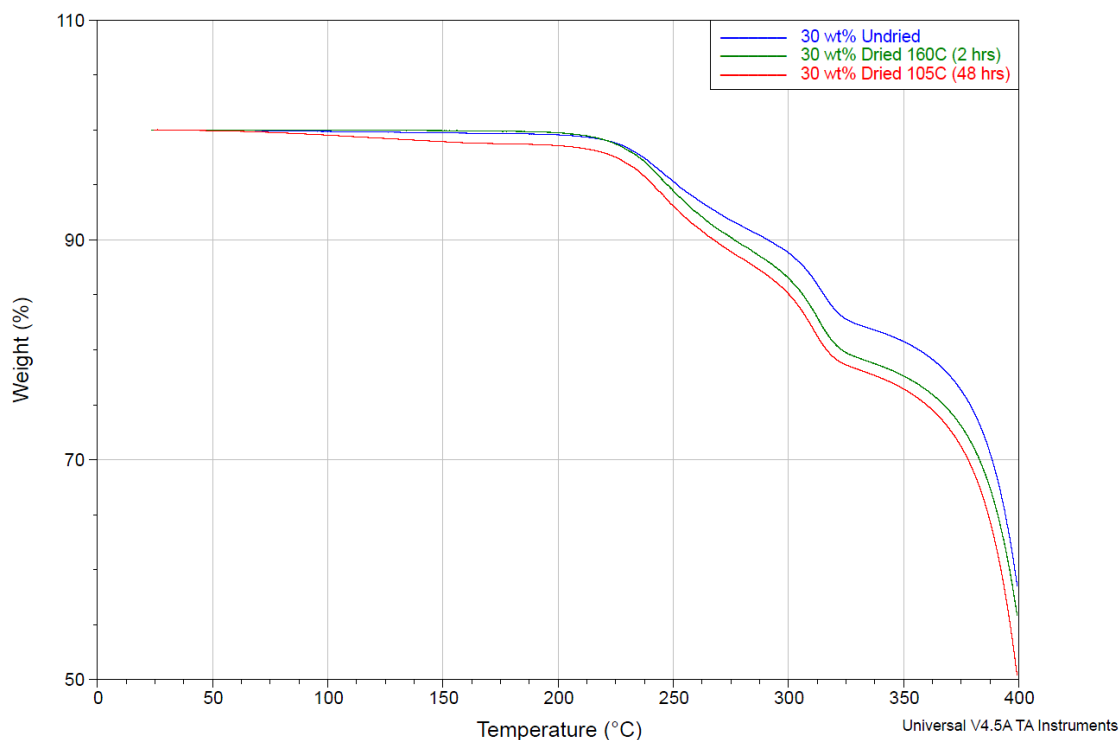


Figure A.7: Dried vs. Undried comparison of 20 wt% CSP composites

Figures A.6 and A.7 indicates that drying CSP before compounding causes the slope of the degradation curve to become steeper and potentially causes the onset of degradation to take place at a lower temperature. It would appear that the more moisture that is removed from the CSP, the steeper the slope of the degradation curve becomes. One hypothesis as to why the thermal degradation characteristics of the CSP change after a long exposure to high temperatures, is that long periods of time at high temperatures cause structural changes to the CSP. This would be analogous to baking something and not burning it. CSP should not degrade or oxidize at 105 °C, so the powder should not “burn”. Yet, being exposed to those kinds of thermal energies for a long time could change something in the molecular makeup of the CSP without the release of low molecular weight VOCs. One would need to take SEM pictures of the CSP to test this hypothesis. However, the change in the thermal degradation properties between the

undried CSP in the composite and the dried CSP in the composite is relatively insignificant, except for the 30 wt% CSP dried at 105 °C for 48 hours, but 48 hours is really an unrealistic drying time. This does beg the question, what does pre-degradation to the CSP look like on a thermal degradation ramp test. More testing is needed to get an idea for what the thermal characteristics of a pre-degraded CSP-polypropylene composite are. After encountering these problems with drying CSP, drying periods between 2 and 5 hours at 110 °C and 120 °C were used to remove moisture and reduce the variability that moisture causes.

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