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Study of mechanical and thermal properties of soy flour elastomers

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Study of mechanical and thermal properties of soy flour elastomers

by

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DEDICATION

This thesis is dedicated to my family, friends, neighbors, classmates, and kids like myself that didn't or couldn't have the same opportunities that I have obtained.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS

ASTM	American Society for Testing and Materials
CB	Carbon Black
DMF	Dimethylformamide
DSC	Differential Scanning Calorimetry
DSF	Defatted Soy Flour
GCMS	Gas Chromatography/Mass Spectroscopy
NMR	Nuclear Magnetic Resonance
NR	Natural Rubber
PBAT	Poly(butylene adipate-co-terephalate)
SBR	Styrene Butadiene Rubber
SEM	Scanning Electron Microscope
SF	Soy Flour
SPC	Soy Protein Concentrate
SPI	Soy Protein Isolate
SS-NMR	Solid State Nuclear Magnetic Resonance
TGA	Thermogravimetric Analysis
TPE	Thermoplastic Elastomer
UV	Ultraviolet

ACKNOWLEDGEMENTS

ABSTRACT

Bio-based plastics are becoming viable alternatives to petroleum-based plastics because they decrease dependence on petroleum derivatives and are more environmentally friendly. Raw materials such as soy flour are widely available, low cost, lightweight, stiffness and have high strength characteristics, but weak interfacial adhesion between the soy flour and the polymer poses a challenge. In this study, soy flour was utilized as a filler in thermoplastic elastomer composites. A surface modification called acetylation was investigated at soy flour concentrations of 10 wt%, 15 wt% and 20 wt%. The mechanical properties of the composites were then compared to that of elastomers without a filler. Chemical characterization of the acetylated soy flour was attempted in order to understand what occurs during the reaction and after completion.

In the range of tests, soy flour loadings were observed to be inversely proportional to tensile strength for both the untreated and treated soy flour. However, the acetylated soy flour at 10 wt% concentration performed comparable to that of the neat rubber and resulted in an increase in tensile strength. Unexpectedly, the acetylation reaction increased elongation, which reduced stress within the composite and is believed to increase the adhesion of the soy flour to that of the elastomer.

In the nuclear magnetic resonance (SS-NMR), the intensity for the treated soy flour was larger than that of the untreated soy flour for the acetyl groups that were attached to the soy flour, particularly, the carbonyl function group next to the deprotonated oxygen and the methyl group next to the carbonyl. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) indicated that the acetylated soy flour is slightly more

thermally stable than the untreated soy flour. The treated soy flour also increased the

decomposition temperature of the composite.

CHAPTER I

INTRODUCTION

Approximately ten billion kilograms of synthetic rubber are produced annually with a vast majority of these petroleum-based materials being placed in landfills once they exceeded their useful life (Threadingham, 2011). Because of the growing concerns regarding depleting petroleum reserves and the environmental effects of petroleum-derived polymers, bio-based polymer alternatives are becoming increasingly popular. The easy availability and biodegradability of renewable raw materials, such as protein and starch, have led to a growing number of polymer applications. Soy products in particular show significant potential to be used in the synthetic polymer industry according to the 2011 Omni Tech report "Rubber Compounds: A Market Opportunity Study" (Brentin, 2011).

1.1   Background

1.1.1   Styrene Butadiene Co-polymer Rubbers

Styrene butadiene co-polymer rubber (SBR) is a synthetic rubber that has been utilized as an alternative to natural rubber. The synthetic rubber market is dominated by SBRs, which account for 50% of the tire industry (Dick, 2009). The chemical structure of SBR is shown in Figure 1.

Styrene butadiene rubbers are elastic polymers that are derived by the polymerization of petroleum by-products. Styrene butadiene rubber can be produced using either an emulsion process or a solution process, depending on the desired mechanical properties. In the emulsion process, styrene and butadiene monomers are emulsified with soap as the emulsifying agent.

The solution-processing route for SBR provides products with higher purity because of the lack of soap residues (Dick, 2009).
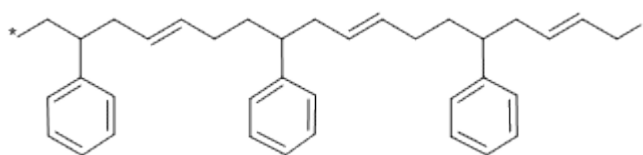
Figure 1: Chemical structure of styrene butadiene rubber (SBR) (Chemical Book, 2010)

Styrene butadiene co-polymers are thermoplastic elastomers (TPE) that are typically used to replace natural rubber. They are referred to as thermoplastic rubbers and are usually a mix of a plastic and a rubber. Thermoplastic elastomers are easy to process, have lower cost of processing, and can be recycled, making them more "green" compared to thermosets (McKeen, 2010).

Carbon black is the most common filler used in SBRs and can be utilized as a reinforcing additive. Its particle size, shape, and surface chemistry play an important role in its reinforcing capabilities, and its ability to adsorb to hydrocarbon elastomers makes it the filler of choice. Carbon's black hydrophobic surface chemistry allows for better adhesion and dispersion in polymer matrices to create a composite but it produced from petroleum. Soy protein can be utilized as an alternative filler to carbon black. It is cheaper and more environmentally friendly, but its hydrophilic surface is one drawback in why it is not incorporated within polymer composites. (Keller, 2012).

1.1.2   Soy Protein

Soy protein is widely available, abundant in nature, and has a molecular mass ranging from 8 to 600 kDa. Proteins are heteropolymers that can contain up to 20 different polymerized amino acids. Amino acids are organic compounds that are composed of amine ($-NH_2$),

carboxylic acid (-COOH), and a specific side chain that is specific to each particular amino acid. Each individual amino acid is connected to another through a peptide bond containing a carbon unit, from one amino acid, double bonded to a nitrogen, from another amino acid). According to Reddy *et al.*, proteins tend to be folded into secondary, tertiary, and quaternary structures and are stabilized through hydrophobic interactions, hydrogen bonding, and electrostatic interactions among the amino acids. Other stabilization methods include strong covalent crosslinks and disulfide bonds. In order to utilize soy proteins in material applications, an unfolding and realignment of the proteins must be accomplished before a new, three-dimensional network can be formed and stabilized (Reddy, Mohanty, & Misra, 2010).

According to Weber, the two most prevalent soy protein fractions are referred to as 7S, which represents 35%, and 11S, representing 52% of the protein. Conglycinin is the main constituent of the 7S fraction, representing more than 50% of the fraction, while glycinin represents the principal components of 11S (Lagarón, 2011). Minor fractions include 2S (8%) and 15S (5%) (Weber, 2010).

Soy protein is typically available in the form of soy concentrate, soy isolate, soy meal, or soy flour with varying protein content in each form. Soy isolate contains 90%, soy concentrate 65%, soy flour approx. 56%, and soy meal 40% protein. During the design and engineering of many plastic and material applications, soy isolate is the most commonly used because of its –NH$_2$, -OH, and –SH side groups that are easy to modify. However, soy isolate is more costly than the other forms of soy protein.

The most common amino acids present in soy protein are aspartic acid and glutamic acid. Both have hydroxyl side groups resulting in them being hydrophilic. It is assumed that higher percentages of protein content (i.e. soy isolate has ~90% protein) within the soy by-product can

contribute to the hydrophilic nature because of the higher distribution of hydroxyl groups (–OH) on the surface of soy protein. An example of this is given in Table 1 where it details the typical compositions of soy flour, concentrate, and isolate (Reddy, Mohanty, & Misra, 2010). Soy flour offers the advantage of high strength and lower cost compared to soy isolate but the hydrophilic nature is still an issue.

Table 1: Standard composition of soy flour, concentrate, and isolate

Component	Flour	Concentrate	Isolate
Protein	56	72	90
Carbohydrates	33.5	17.5	0.3
Fat	1.0	1.0	0.1
Fiber	3.5	4.5	0.1
Ash	6.0	5.0	3.5

1.1.3   Rule of Mixtures

When creating composites, one of the key concepts in modeling the mechanical and thermal behavior is homogenization of the filler and the polymer, because the phases differ in modulus. However, various properties can be predicted based on a composite's constituent materials. In particular, the rule of mixtures is utilized to predict various composite properties under the following assumptions:

- The fibers (particles) are uniform, parallel, and continuous.

- There is perfect bonding between the fiber and the matrix.

- Longitudinal load produces equal strain in both the fiber and the matrix.

However, in this study the model that closely resembled the composites created followed the inverse rule of mixtures because the composite is loaded in the transverse direction of the fiber. Here, the assumption was that the stress will be the same in each component and that the Poisson contraction effects will be ignored. The fact that the soy flour particles are dispersed in

the matrix of the polymer led us to use the Takayanagi model. The Takayanagi model for predicting the Young's modulus for the composite investigated in this study is shown in Eq. 1.

$$E = \left[\frac{\emptyset}{\lambda E_R + (1-\lambda)E_p} + \frac{1-\emptyset}{E_p} \right]^{-1} \qquad (1)$$

Where: $\emptyset$: volume fraction of fiber E_R: Modulus of Fiber
                λ: volume fraction of polymer E_p: Modulus of Polymer
Equation 1: Equation for the Takayanagi Model of the Inverse Rule of Mixtures

1.2   Research Objectives and Approach

Soy flour can be utilized as a filler in thermoplastic elastomer or TPE composites and as a low costs alternative to soy protein isolate; however, lack of interfacial adhesion can reduce the final composite's mechanical properties. The goal of this research was to investigate the mechanical properties of elastomer composites with soy flour as a filler and compare these properties to those of the neat elastomer. Mixing hydrophilic soy flour with hydrophobic TPE was a concern because the soy flour and elastomer components are incompatible and it was theorized this fact could result in composites with limited mechanical properties. To overcome this obstacle, a surface modification was proposed to reduce the hydrophilic nature of the soy flour. In particular, the hydroxyl groups (-OH) on the protein as well as the carbohydrates in the soy flour were replaced with more hydrophobic functional groups.). Because of the success seen in the Kumar study, we proposed look at similar pretreatment of soy flour as a composite filler for rubbers, and in particular thermoplastic elastomers. In addition it is important to note that this work focusses on soy flour, which is high in soy protein in order to assure that final composition could be cost effective (Kumar, 1994).

This surface modification was accomplished by an acetylation reaction, which is an esterification reaction that replaced the hydroxyl groups (-OH) on the surface of the soy with

more hydrophobic acetyl (-COCH$_3$) groups. After the acetylation reaction, composites were fabricated containing treated and untreated flour as well as a control group without soy flour. The mechanical properties were examined through tensile testing, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Chemical characterization of the treated soy flour was also performed by carbon solid-state nuclear magnetic resonance (SS-NMR), proton NMR, and gas chromatography mass spectroscopy (GCMS). Dispersion of the soy particles was characterized using scanning electron microscopy (SEM).

CHAPTER II

LITERATURE REVIEW

In recent years, renewable fillers have been investigated as a substitution for synthetic fillers such as glass fibers and in the case of rubber, carbon black. Renewable filler have the potential of being are abundant, widely available, and more cost effective compared to their petroleum counterparts. Renewable materials, such as soy protein and other soy products, have been explored as key components in plastics and adhesive applications because of their relatively low environmental impact and strength characteristics (Reddy, Mohanty, & Misra, 2012) (Zhang & Chen, 2010).

Soy proteins can demonstrate good adhesion if hydrolyzed and even function as plastics but exhibits poor water resistance unless they are chemically modified such as cross-linking. In most studies, water stability was enhanced by the substitution of polar functional groups with less polar functional groups provides the material with better water resistance properties (Xu *et al.*, 2012). For example, successful chemical modification has been seen in wood flour and plastic composites (Kumar 1994).

In 1994, Kumar investigated a variety of methods to chemically modify wood and found that acetylation had the greatest potential because it improved dimensional stability and resistance to biological degradation (Kumar, 1994). Increased mechanical properties and thermal stability was seen after acetylation of wood flour prior for the fabrication of plastic wood flour composites (Çetin, 2011). Because of the success seen in the Kumar study, we proposed to look at similar pretreatment of soy flour as a composite filler for rubbers, and in particular thermoplastic elastomers. In addition it is important to note that this work focusses on soy flour,

which is high in soy protein in order to assure that final composition could be cost effective. In

addition, esterification has proven to increase adhesiveness and water resistance of soy protein

adhesives by replacing the hydroxyl groups with more hydrophobic ester groups (Wang, Sun, &

Wand, 2006). The chemical reaction with acetic anhydride converted amine and hydroxyl

groups to amides and esters when used in the application of wood flour (Xu *et al*., 2012). This

process and prcedure of acetlyating wood flour was adapted to be used in the fabrication of soy

flour elastomer composites.

As mentioned in the previous chapter, SBR incorporates carbon black as a filler in rubber

composites (Kutz, 2011). Typically, carbon black and silica are the two main fillers used in

rubber, with carbon black dominating 90% of the filler market in the rubber industry. Carbon

black is produced from petroleum resources or natural gas and generates carbon dioxide as a by-

product (Jong, 2013). The surface chemistry and ultraviolet (UV) absorption of carbon black

play key roles in it selection as a filler in rubbers. With the same logic, soy protein can be

integrated into elastomer composites by changing the functionality of the soy protein. While the

soy protein may not be as effective in UV stabilization, it may serve as a low cost filler.

The functionality of soy protein/ soy flour are affected by changes in composition,

hydrolysis, and conformation. These properties are influenced by the heating treatment applied to

the protein to promote denaturing (Radha & Prakash, 2009) (Reddy, Mohanty, & Misra, 2012).

According to Zhang, currently soy protein in bioplastics research is classified into two

types: "as a thermoplastic material for neat soy protein plastics or as a matrix polymer, and as

filler for thermoplastics or thermosetting resins." Chemical modification has also been

investigated and proven to improve the physical and mechanical properties soy protein plastics

(Zhang & Chen, 2010) (Grewell, Carolan, & Srinivasan, 2013).

Soy protein is sensitive temperature and pH and will unfold/melt under both elevated temperatures and pressures, a process known as denaturing. The majority of the functional groups on soy proteins are polar, while petrochemical plastics tend to be non-polar; therefore, the resulting interfacial adhesion between the two is poor. "Improving interfacial adhesion by adding an appropriate compatibilizer or coupling agent in the blends have proved to be an efficient means to obtain improved mechanical properties" (Zhang & Chen, 2010. Soy protein has been blended with non-degradable polymers such as poly(butylene adipate-co-terephthalate) (PBAT) (Chen & Zhang, 2009); polyurethane (Chen Y. Z., 2007), and styrene-butadiene latex

In 2004, Lei Jong compared defatted soy flour (DSF) and soy protein isolate (SPI) as fillers in elastomer composites, in particular in styrene-butadiene rubber with small amounts of carboxylic acid. Because soy protein contains a significant amount of carboxylic acid and substituted amine groups, Jong utilized a styrene butadiene rubber (SBR) latex with small amounts of carboxylic acid to increase interaction between the filler and the rubber. He found that both fillers increased tensile strength but reduced elongation. However, the DSF composites had higher moduli and, as the soy flour concentration increased, the tensile strength for DSF was slightly lower than that of the SPI, except for in the 30% composite. The soy flour (SF) exhibited slighty better tensile strength than SPI and could possibly be a better filler when testing with higher loading concentrations (Jong, 2005a) (Jong, 2005b) (Jong, 2005c).

 Later, Jong compared the previously collected data with those of soy protein concentrate (SPC) and SBR latex. He concluded that the addition of soy concentrate potentially increased the interaction between the filler and the rubber. He found that DSF fillers created a significant increase in shear elastic modulus (230-fold) at 30% compared to unfilled rubber and CB composites (Jong, 2008) .

Jong also compared the effects of DSF in SBR latex composites to those of carbon black, which is normally incorporated in rubber composites as a filler. In this study, he found that compared to carbon black the soy protein fillers showed better elastic modulus and yielded better recovery behavior. Later studies compared the dynamic and viscoelastic behavior of SBR latex and natural rubber (NR) composites with DSF and CB fillers, respectively (Jong, 2013).

Reddy *et al*. reported that dry processing of soy protein for plastics is easily adaptable to industrial-scale operations; however, its narrow processing window presents a disadvantage. One method to overcome this issue is the destructurization of the soy protein through either chemical additives or mechanical forces. To increase the reinforcement effects of the renewable filler, blending of the fiber with flexible polymers was proposed as a desirable approach (Reddy, Mohanty, & Misra, 2012).

Huang *et al*. investigated optimized processing conditions for creating soy protein/starch based plastics using a twin-screw extruder and an injection molding machine. They reported an optimal injection molding temperature at 130 ℃ with a moisture content of 10–14%. Also, water absorption was reduced by adjusting the pH of the protein/starch based plastic samples to that of the isoelectric point of the soy proteins (Huang, Chang, & Jane, 1999).

To improve the processibility of the soy protein as well as to overcome its hydrophilic nature, John and Bhattacharya attached anhydride groups to polyesters. This technique improved the compatibility between the soy protein (concentrate, flour, and isolate) and the polyester. Their data reported an improvement in the blend's mechanical properties. They also reported that the mechanical properties were dependent on the crystallinity, melt strength, and protein and polymer interaction within the blend (John & Bhattacharya, 1999)

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The objectives of this study was to utilize acetylation as a viable surface modification to change the hydrophillic nature of the soy flour to that similar to the hydrophobic nature of the TPE. A systemized method for processing the soy flour and TPE composites neeeded to be developed. Overall, it was hypothesized that the acetylation reaction would enhance the mechanical properties of the soy flour elastomers compared to the untreated soy flour elastomers but not to that of the neat elastomer with no soy flour

CHAPTER III

EXPERIMENTAL

3.1   Materials

Soy flour used in the experimental work was 7B grade and was purchased from Archer

Daniels Midland (Decatur, IL). According to the MSDS, the soy flour contained 53% protein,

9% fat, 32% carbohydrates, and 18% dietary fiber per 100g of material. The polymer used was a

thermoplastic elastomer (TPE) with a trade name of Dynaflex^{TM} and a product number of

G2755-1000-00. Dynaflex^{TM} was a styrene butadiene block co-polymer with a specific gravity of

0.878 g/cm^3 purchased from PolyOne (Avon Lake, Ohio).

3.2   Methodology

3.2.1   Acetylation of Soy Flour

3.2.1.1 Drying of Soy Flour

Moisture was eliminated by placing the soy flour (SF) in an oven at 100°C for 12 h.

Before acetylation, the soy flour was sieved with 1.18mm mesh in order to reduce the particle

size of the SF incorporated within the matrix of the polymer. Each soy flour concentration was

calculated based on percent weight of a 50g batch of TPE. Five grams, 7.5 grams, and 10 grams

of soy flour were measured for each 50g batch of TPE for the 10wt %, 15wt %, and 20wt %

formulation, respectively.

3.2.1.2 Chemical Modification: Acetylation

All chemicals used were purchased from commercial suppliers and used as received. All reactions were performed under a fume hood at ambient temperatures and pressure. As stated in the introduction, the goal of the acetylation was to replace hydroxyl groups (-OH) on the surface of the soy flour with acetyl groups (-OCOCH$_3$). This specific procedure was developed from previous publications creating wood flour composites (Özmen, 2013; Çetin, 2011;Jebrane, 2007; Hill & Jones, 1996).

In the initial acetylation processes, ten g of defatted soy flour was transferred into a 250 mL round bottom flask containing a solution of dimethylformamide (DMF) (10.23g, 14mmol/g SF) and acetic anhydride (57.17g, 56mmol/g SF) in the presence of potassium carbonate (K$_2$CO$_3$) (1.5g, 1.1mmol/g SF) (Fang, 2012). The reaction in Figure 3 reacted at 100°C for 3 hours. Once the reaction completed and cooled to room temperature, the mixture was poured in a flat bottom flask. The mixture was then allowed to precipitate by sitting undisturbed in a fume hood for 3 days. After the flour precipitated, washing is needed to remove unreacted substances and by products. The mixture was then washed 3 times with deionized water and then 3 times using a büchner funnel with a 4/1/1 mixture of toluene, acetone, and ethanol. The liquid was evaporated using a rotary evaporator. The flour was washed from the flask using acetone and poured into a 9x6x1 in. metal pan. Deionized water was mixed with the treated flour in the metal pan and then placed in a freezer at -20^{0}C. The treated flour was freeze dried at -42^{0}C for 72 hours and then pressed into a powder using a mortar.

The acetylation procedure was later refined after the precipitation stage because the fabricated samples had a strong odor of vinegar from the acetic anhydride suggesting the chemical reaction had not been completed. In more detail, after the soy flour precipitated in the flat bottom flask, a 200mL soxhlet extractor (I.D. 50mm) was utilized to wash the solution with deionized water for 24 h. Next the mixture was washed with a soxhlet with a 4/1/1 mixture of toluene, ethanol, and acetone for 24 h.

After washing, the treated soy flour was placed in an oven at 100°C for 24 h. The treated soy flour was then transferred to a 20mL vial until used in the extrusion process. To confirm the proposed chemical pathways, chemical characterization of the treated soy flour was also performed by carbon SS-NMR, proton NMR, and GCMS. Where applicable these resulted were compared to untreated soy flour. These techniques are detailed in the following sections.
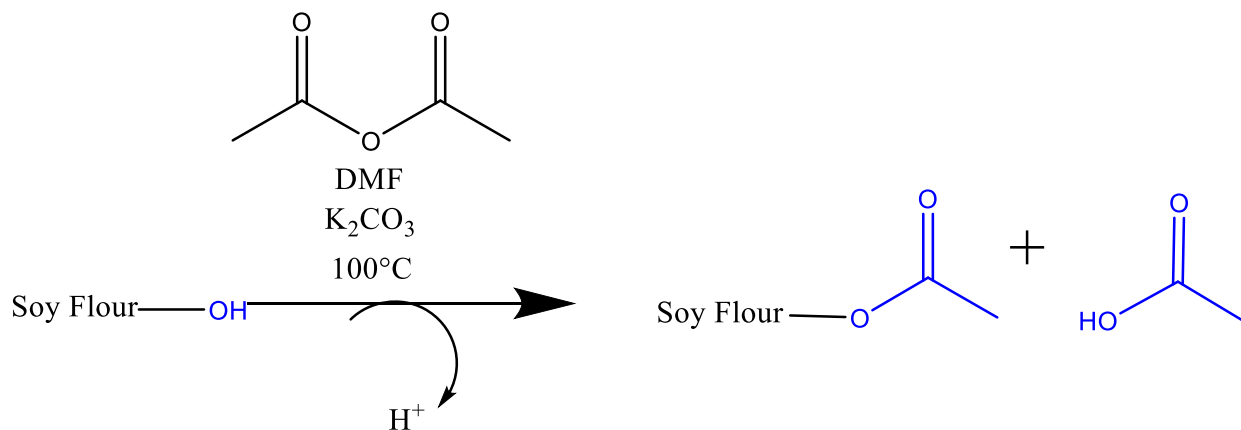

Figure 2: Acetylation reaction of soy flour

3.3   Chemical Characterization of Soy Flour

3.3.1 ^{13}C SS-NMR

In order to narrow the interactions among the functional groups that were modified, particular the carbonyl and the methyl from the acetyl group, a carbon (^{13}C) solid state NMR was

used to analyze the previous connections on the soy flour molecule. A method commonly known as gated decoupling was applied to suppress the representation of $-CH_2$ and $-CH$ groups on the molecule to make a direct comparison of what acetyl groups attached to the soy flour. A ^{13}C solid state NMR was collected using a AVIII-600 NMR spectrometer with a bore 14.1 tesla superconducting magnet from Bruker Corporation (Billerica, MA and Karlsruhe, Germany).

3.3.2 ^1H NMR

A ^1H NMR was collected using a VXR400 NMR spectrometer that features a narrow bore 9.4 tesla superconducting magnet from Oxford Instruments (Abingdon, Oxfordshire, England), a $^2H/^1H/BB$ 5 mm liquids probe from Bruker Corporation (Billerica, MA and Karlsruhe, Germany), and an NMR spectrometer from Varian (Agilent), Inc. (Santa Clara, CA). The system is operated by VNMR running on a Sun UltraSPARC computer.

3.4   Compounding of Composites

Soy flour particles (untreated and treated) were filtered with a 1.18 mm sieve. Soy flour particles and elastomer pellets are mixed with a single-stage, single screw Brabender (19.05 mm, 30:1 (L/D)) with four temperature zones was purchased from C.W. Brabender Instruments in South Hackensack, NY. Samples were extruded at 165 °C and 60 rpm through a 3 mm circular die. Formulations were created by mixing 10 wt%, 15 wt%, and 20 wt% concentrations of treated and untreated soy flour with the TPE. The treated soy flour elastomer composites were mixed in the same fashion as the untreated soy flour. This procedure was developed through screening experiments of mixing the soy flour and the elastomer in the extruder. In more detail,

thermal degradation of the soy was minimized and was evident of discoloration and odor. In addition the manufacturer recommended processing conditions taken into consideration.

The pellets were compression molded into dogbone samples according to ASTM D638. Nine grams of pelletized elastomer and/or elastomer composites was added to a dogbone sample mold. For the soy flour composites, the mold was then heated for 8 minutes and then compressed at 176 °C for 5 minutes with 5 tons of force. Samples were allowed to condition for 2 d before beginning mechanical property testing in standard atmospheric conditions. For the acetylated soy flour composites are heated at 149°C for 8 minutes and then compressed for 5 minutes with 5 tons of force. The soy flour composites are compression molded at a different temperature because the soy flour degrades at a temperature higher than 149°C. Again, this process was developed through trial and error of my personal visual conformation of a proper cohesive sample. Samples were allowed to set for at least 72 h before they were tested. The mechanical properties were examined by tensile testing and thermal analysis was completed using TGA and DSC.

3.5   Tensile Testing

Dogbone samples were created according to ASTM D638. An Instron 5569 tensile testing machine (Norwood, MA) was used with non-contacting video extensometers. Sample dimensions were 115mm in length, 25mm in width, and a grip distance of 33mm. The crosshead speed was 300 mm/min. Averages of sample measurements were compared to each formulation and was deemed statistically significant if the average fell into the standard deviation of a particular formulation.

CHAPTER IV

RESULTS AND DISCUSSION

The goal of this research was to compare the mechanical characteristics of thermoplastic elastomers (TPEs) filled with various grades of soy flour. It was theorized that in order to enhance the mechanical properties of soy flour/TPE composites, the hydrophilic nature of the soy flour and the hydrophobic character of the TPE would limit mixing and mechanical properties. In order to minimize this issue, the soy flour was treated with an acetylation process .In more detail, the hydroxyl groups (-OH) on the surface of the soy flour were replaced with more hydrophobic acetyl groups ($-OCOCH_3$).

4.1   Tensile Testing

Five samples were compounded with the following general formulations:

- Control, net TPE

- Non-treated soy flour/TPE composites

- Treated soy flour/TPE composites

The level of soy flour concentrations ranged from 0 (control), to 10 wt%, 15 wt%, and 20 wt%. The mechanical properties that were examined were ultimate tensile strength, modulus, elongation, and axial strain. During extrusion, mixing became difficult for formulations higher than 20 wt% without the use of plasticizer or liquid that would increase the wettability of the flour and the TPE. Formulations are shown in table 2.

**Table 2: Composition of treated, untreated, and control soy flour elastomers**

Samples	Soy Concentration (wt. %)
Elastomer (TPE)	0
Acetylated Soy Flour (ASF)	10 15 20
Soy Flour (SF)	10 15 20

The average ultimate tensile strength, figure 3, of the control group (0 wt% soy flour) was 1.32±0.221 MPa. For the other samples, the strength was generally inversely proportional to the soy flour concentration. Untreated soy flour elastomer composites exhibited a strength of 0.882±0.294 MPa, 0.773±0.087 MPa, and 0.737±0.143 MPa for the formulations with 10 wt%, 15 wt%, and 20 wt%, respectively.

It was hypothesized that the acetylation reaction would improve the strength of the composites and this was proven to be true. However, it was not anticipated that a formulation would exhibit equivalent strength to that of the neat TPE. With increasing SF content, fracture cites were created within the polymer matrix, which lead to failure. The acetylated soy flour (ASF) appeared to have more uniform mixing and therefor has less stress concentration within the composite at lower SF loadings. However at higher levels, the ASF may have agglomerated resulting in stress concentration sites.

The 10 wt% ASF formulation displayed strength comparable to that of the control group (1.32±0.184 MPa); however, the 15 wt% and 20 wt% formulations displayed maximum tensile stress of only 1.07±0.144 MPa and 0.836±0.183 MPa, respectively. The acetylation of the SF increases the interfacial adhesion among the hydrophobic groups of the ASF and the TPE.
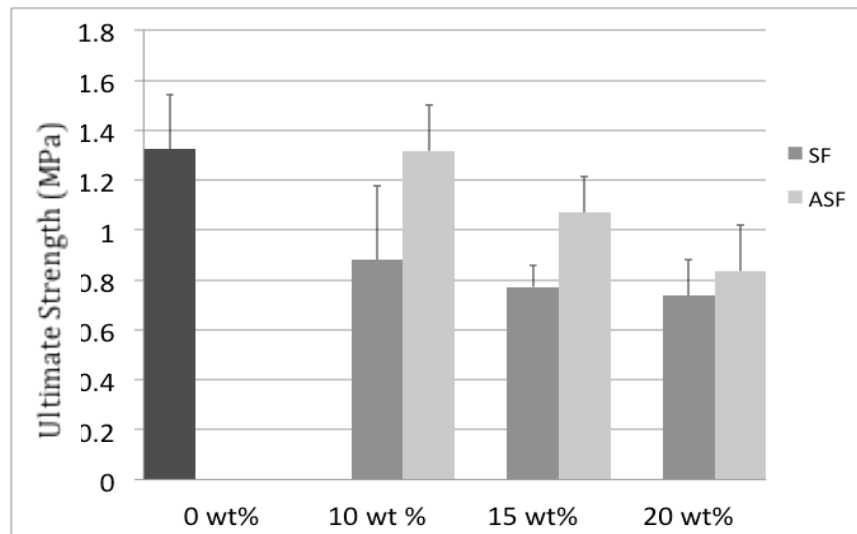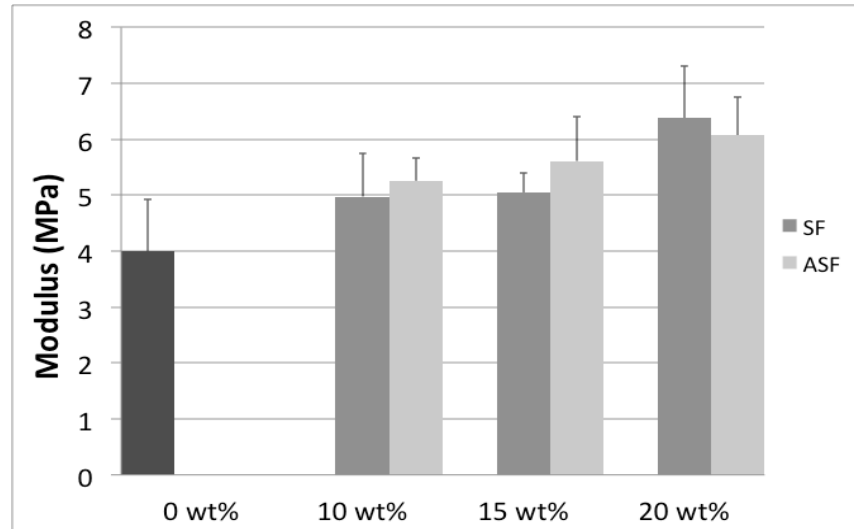

Figure 3: Tensile strength of the control elastomer, acetylated soy flour, and untreated soy flour

The modulus of the treated and untreated composites were proportional to the soy flour concentration, figure 4. The control group had a modulus of 4.00±0.918 MPa. The untreated groups' moduli were 4.97±0.775 MPa, 5.05±0.348 MPa, and 6.39±0.916 MPa for the range of formulations. Similar, the treated groups' moduli were 5.25±0.409 MPa, 5.61±0.795 MPa, and 6.07±0.676 MPa. The increase in SF loadings also increases the relative stiffness of the elastomer composite. With an increase in stiffness, flexibility is loss in the composite which if excessive can be an undesirable feature.

The data also shows that if the same weight percent of ASF or SF is added to the elastomer about the same amount of stiffness is present within the composite. In more detail, adding SF increases the modulus almost at the same rate for both the untreated and the treated

samples for the 10 wt%, 15 wt%, and 20 wt% samples. It is believed that the acetylation

promotes better ASF/TPE adhesion as well dispersion and evenly distributes the applied loads
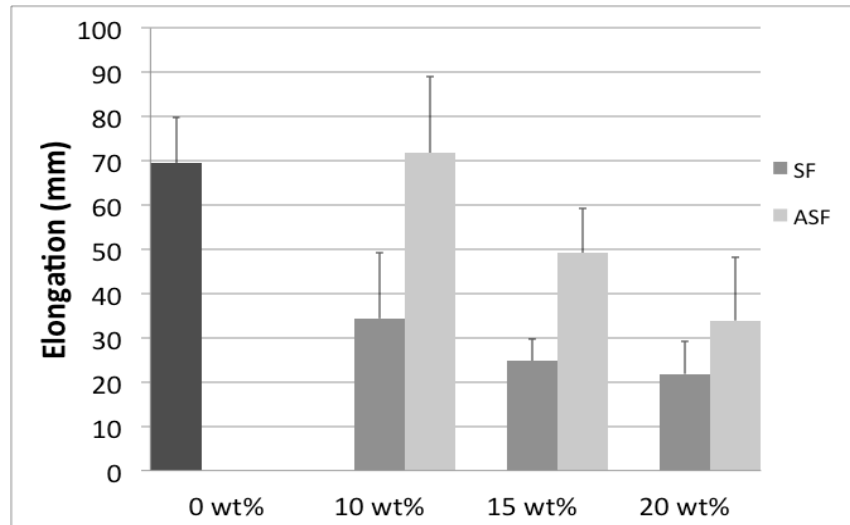

**Figure 4: Modulus of the control elastomer, acetylated soy flour, and
untreated soy flour composites**

during testing within the composite.

Elongation, figure 5, was generally inversely proportional to the soy flour concentration.

Maximum elongation for the control group was 69.5±10.2 mm. The untreated groups' elongation

was measured at 34.4±14.9 mm, 24.8±5.06 mm, and 21.8±7.30 mm for the varying formulations.

Reduced elongation as SF loadings increases corresponds with the findings of Jong in the

"*Characterization of Defatted Soy Flour and Elastomer Composites*". Here, Jong explains that a

lower elongation compensates for a higher tensile stress within the composite because it the filler

increases the immobility of the matrix. Unexpectedly, the addition of ASF loadings increases the

elongation at break. Particularly, the elongation for the 10 wt% acetylated soy flour elastomer

composite exhibited an elongation of 71.8±17.3 mm, which was slightly higher than that of the

control group. While statistically there is no difference, this did demonstrate that it is possible to

add 10 wt% SF without loss in mechanical properties of the TPE composite. For the 15 wt% and

the 20 wt% acetylated formulations, elongations of 49.2±9.93mm and 33.9±14.4mm,

respectively, were measured. The reduction of elongation in SF and TPE composites accounts


**Figure 5: Elongation of the control elastomer, acetylated soy flour, and
untreated soy flour composites**

for the increase in tensile stress at break which was confirmed in figure 4 and in figure 5.

4.2   SEM Images

Scanning electron microscopy (SEM) images were utilized to observe and understand the

morphology of the SF/TPE composites. Figure 6 (a) and (b) shows the mixing between the soy

flour and the elastomer polymer at 10 wt% at 50x magnification. At this magnification, it can be

seen that untreated soy flour aggregates, figure 6a, were larger than those of the acetylated soy

flour. Aggregates are still present in the ASF/TPE composites but are significantly smaller in

size compared to the SF/TPE composites. The surface area of the SF was increased by the

acetylation reaction resulting better dispersion and distribution of the ASF particles. This

phenomenon was shown more clearly in figure 7 (a) and (b) at 150× magnification.
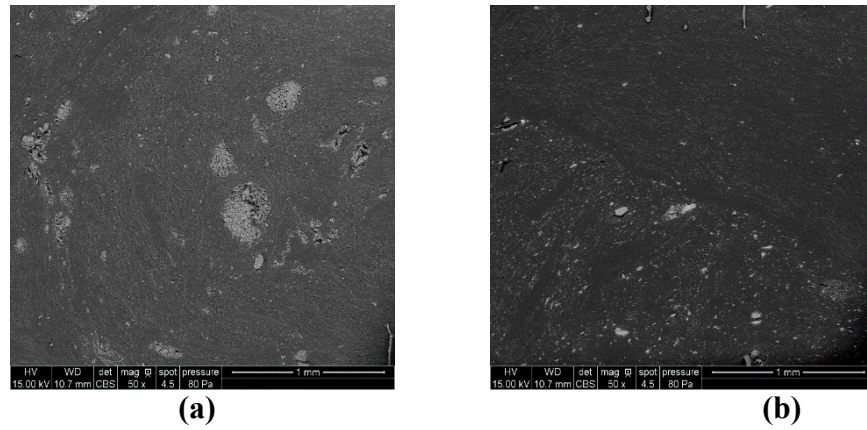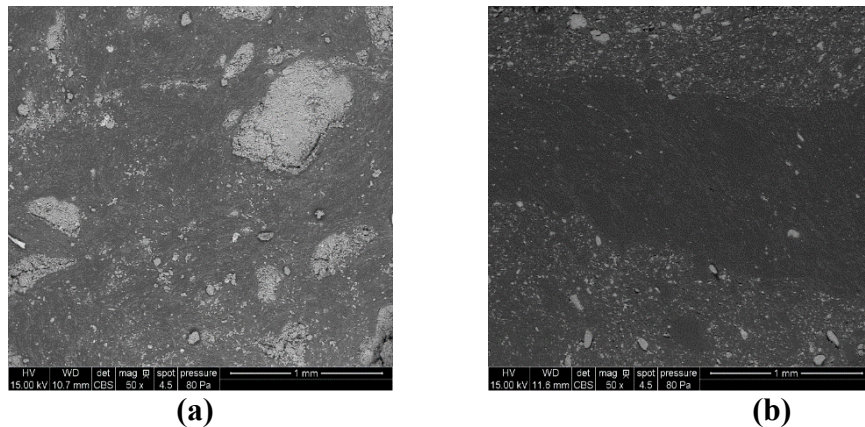
Figure 6: SEM Images of (a) SF and (b) ASF at 10 wt% and 50x magnification
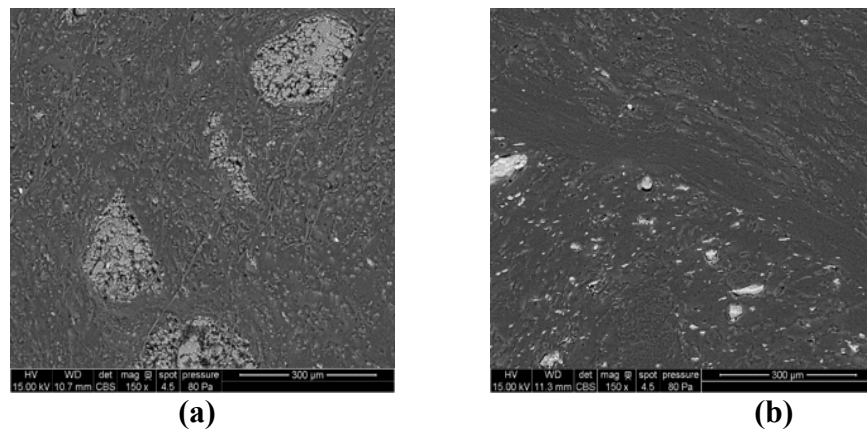
Figure 7: SEM Images of (a) SF and (b) ASF at 10 wt% and 150x magnification

Composites of SF and ASF at 20 wt% and 50x magnification are shown in figure 8 (a) and figure 8 (b). These SEM images compared to previous ones show that as SF and ASF loadings increase, the dispersion of the particles within the TPE matrix is more concentrated than at 10 wt%. In figure 8 (a), the varying particle sizes increases the amount of stress within the composite and reducing tensile strength by creating fracture cites within the matrix of the polymer. Figure 8 (b), appears to have better dispersion of the ASF particles because of the

increase adhesion of the ASF to the polymer. These results support the theories that the mechanical properties are enhanced as a result of better mixing.


(a)   **(b)**

Figure 8: SEM Images of (a) SF and (b) ASF at 20wt% and 50x magnification

4.3 Thermal Analysis

4.3.1 TGA

Figure 9, 10, and 11 displays the change in mass versus temperature for each of the elastomer composite formulations with 10 wt%, 15 wt%, and 20 wt% SF and ASF content. The decomposition temperature is usually inversely proportional to the addition of SF to the polymer. This is related to the low thermal stability of SF compared to TPE. Summaries of the decomposition temperatures are shown in Table 3, from TGA measurements.
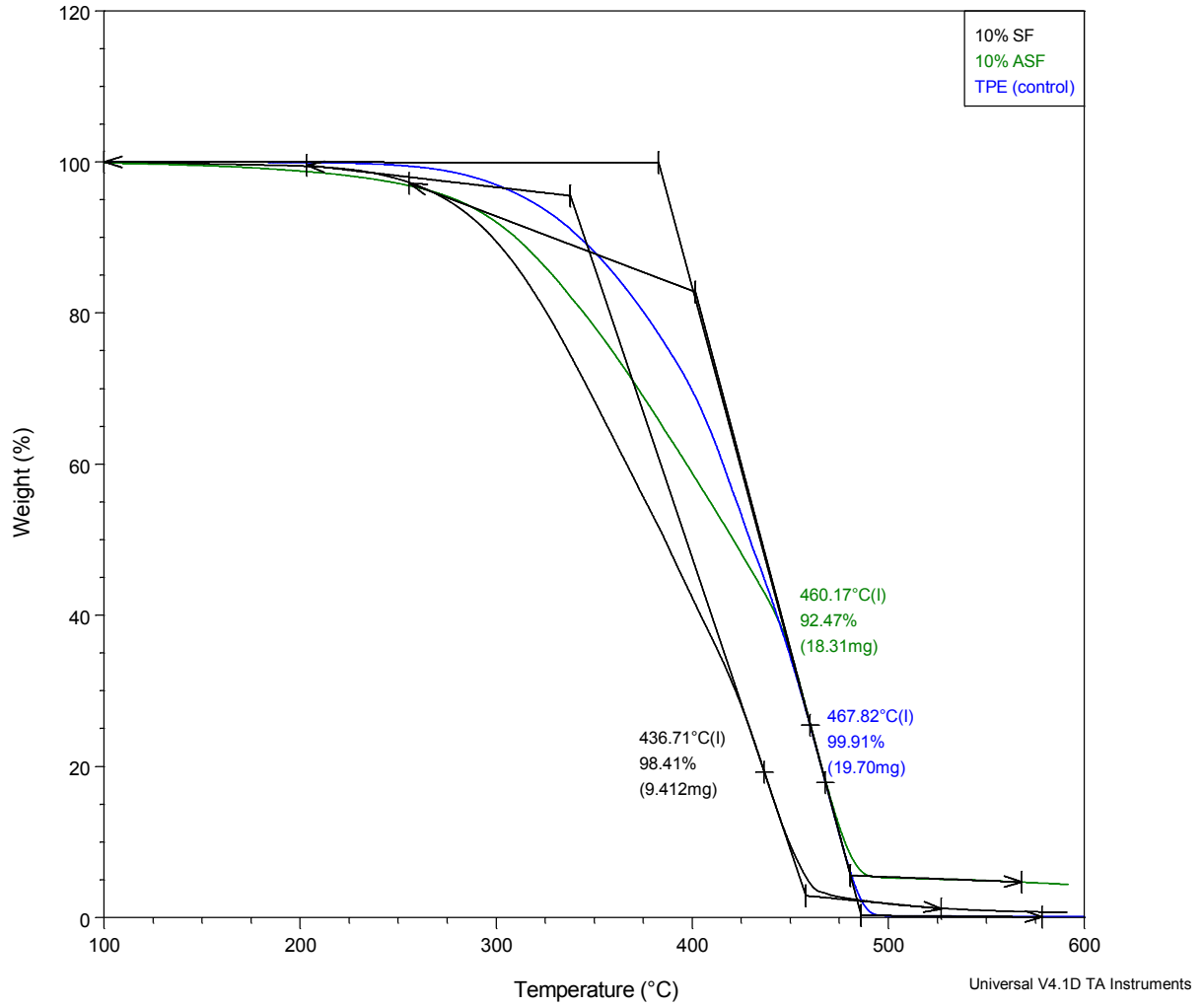
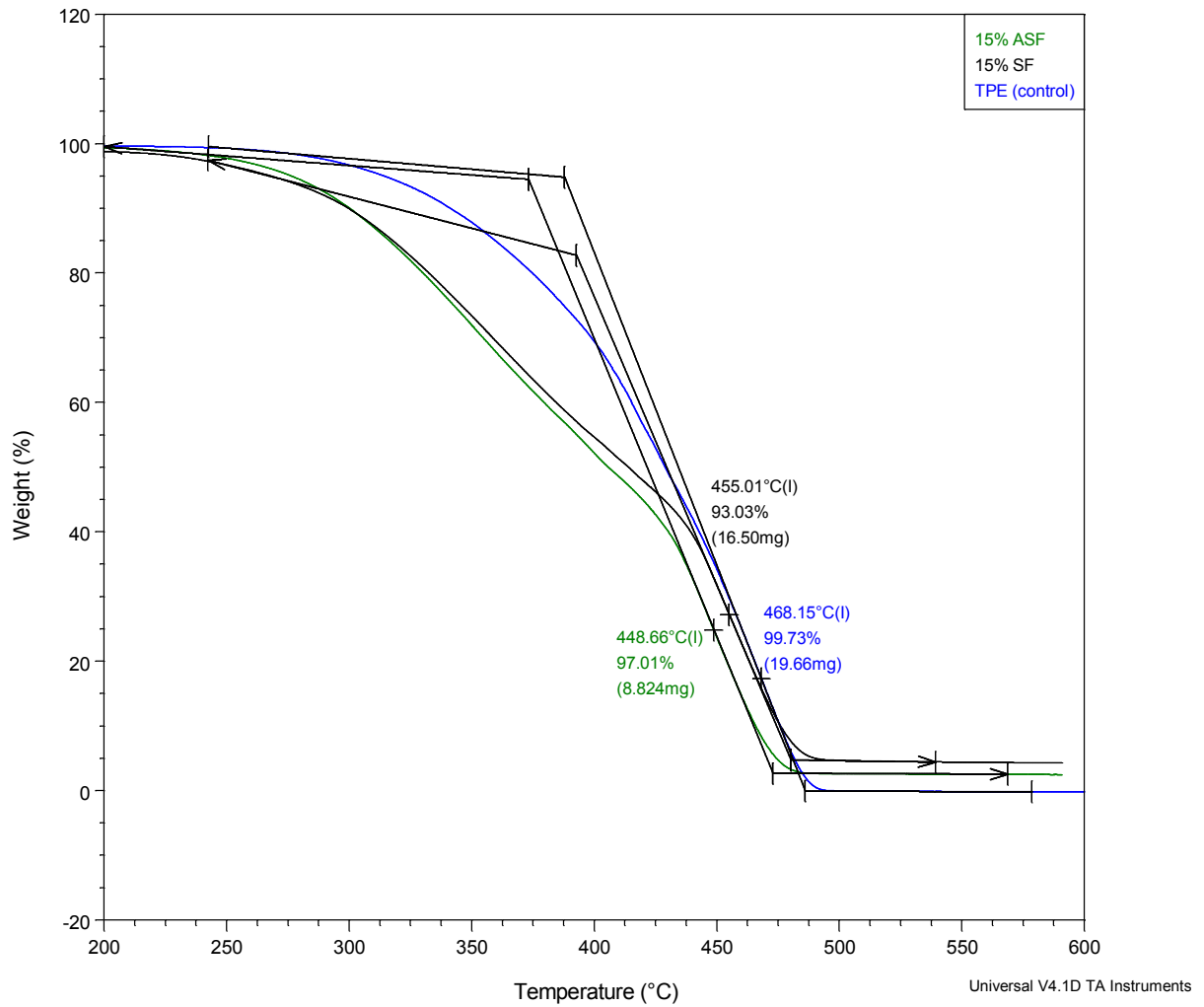**Figure 9: TGA of 10 wt% soy flour elastomer composites**

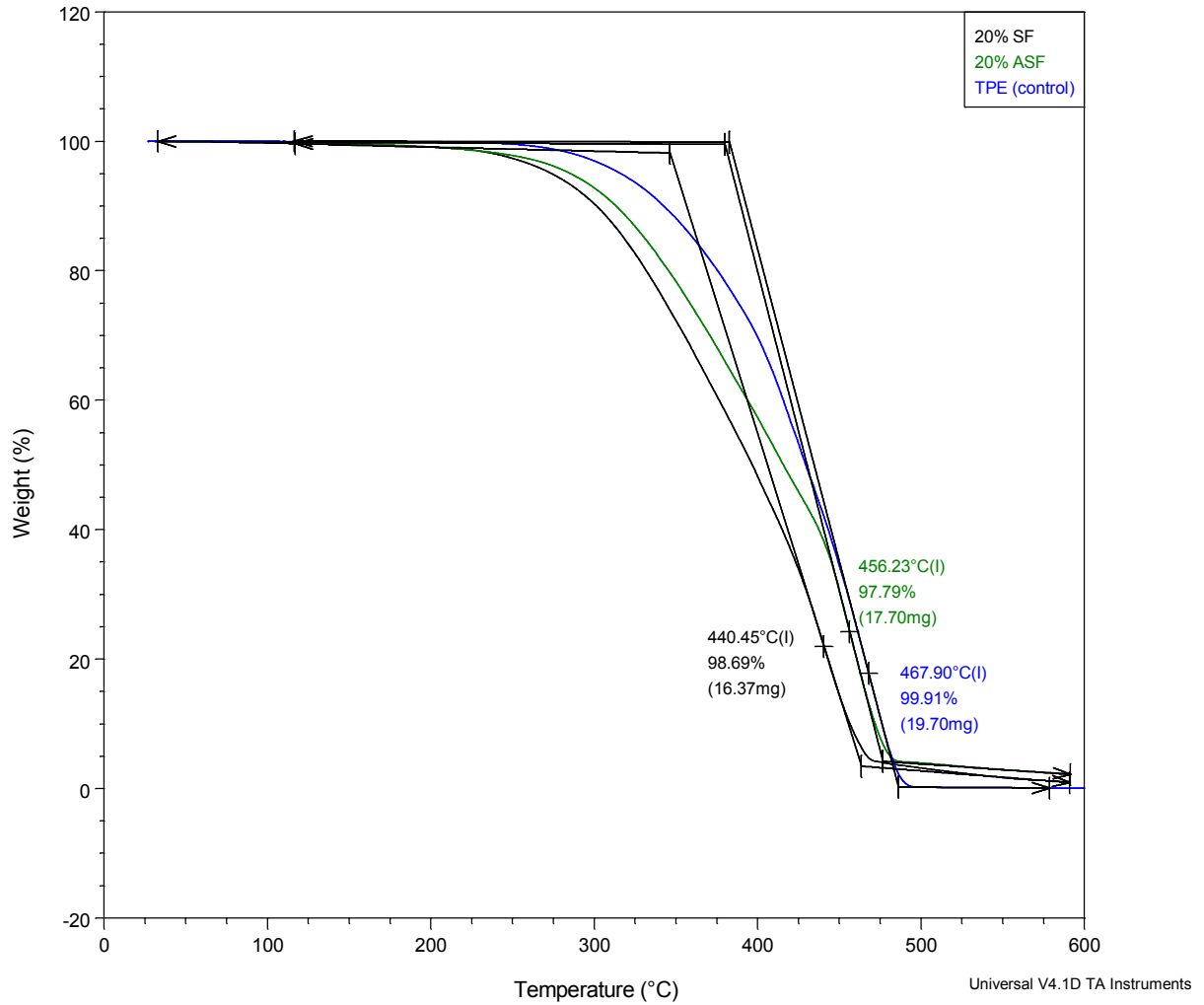**Figure 10: TGA of 15 wt% soy flour elastomer composites**

Figure 11: TGA of 20 wt% soy flour elastomer composites

Table 3: Decomposition temperatures of untreated and treated soy flour elastomer composites

| Sample %	Decomposition temperature (°C)
0 Soy (Control)	467.90
10 wt% SF	436.71
15 wt% SF	455.01
20 wt% SF	440.45
10 wt% ASF	460.17
15 wt% ASF	448.66
20 wt%ASF	456.23

Figure 11 shows the decomposition temperatures of pure soy flour (294.7 °C) and acetylated soy flour (321.7 °C). It is seen that the ASF is more thermally stable compared to the SF and could be the result of the increased adhesion to the TPE that increase the thermal stability of the TPE composites. The replaced hydroxyl groups had drawn water into the soy flour molecule, therefore, increasing the thermal stability of the protein. This leads the general increase in the thermal stability of the composite as well.
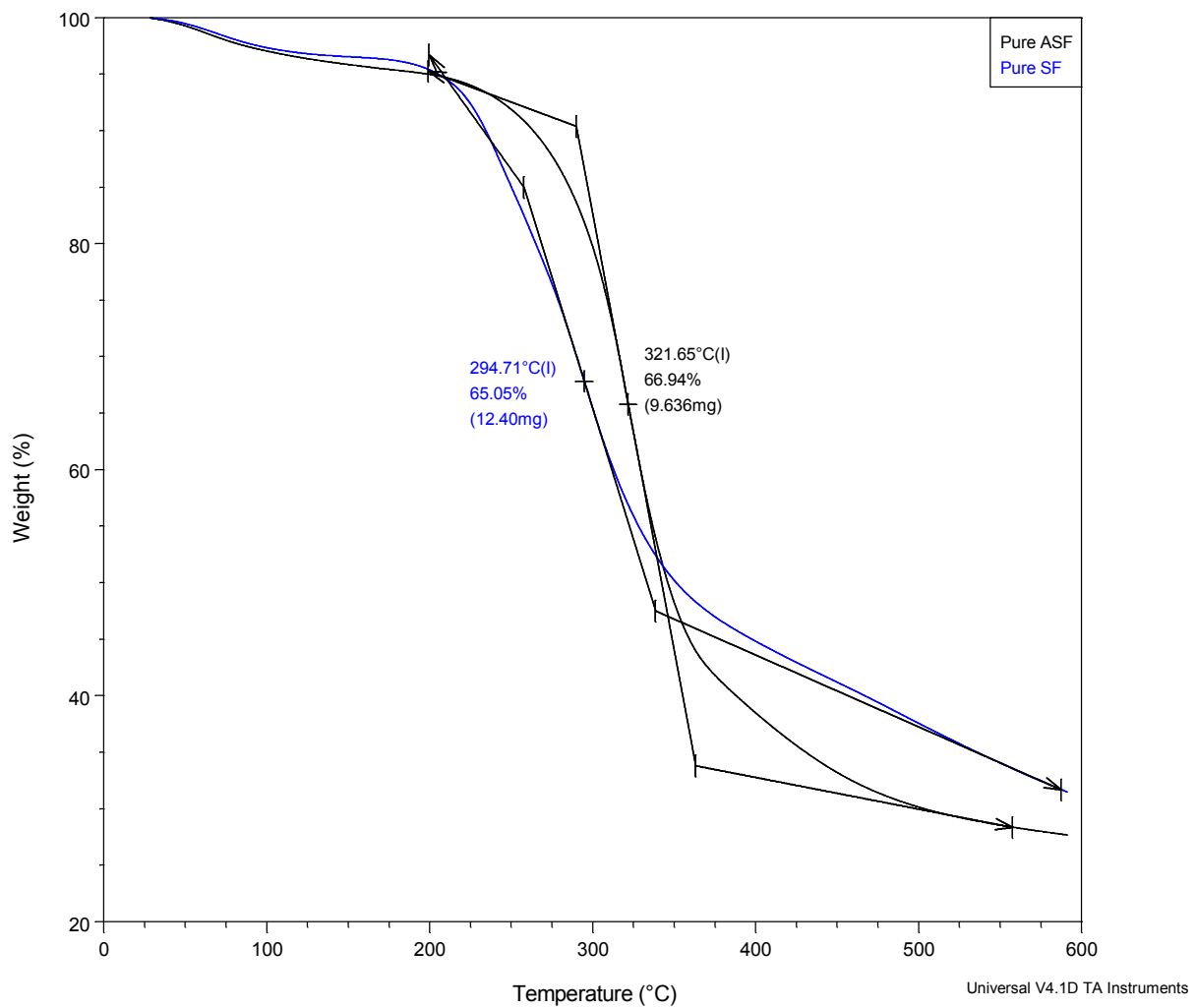

**Figure 7: TGA of pure ASF and pure SF**

4.3.2   DSC

Differential scanning calorimetry (DSC) measures thermal changes in a material that do not involve the change in a substance's mass. Two basic types of DSC were studied: heat flux and power compensated. Heat flux DSC was utilized in this research study. In figure 12, 13, and 14, the melting temperature, offset temperature, and the area underneath the curve are displayed on the DSC curves for the 10 wt%, 15 wt%, and 20 wt% formulations, respectively. The DSC results for each of the formulations were compared to those of the control group.
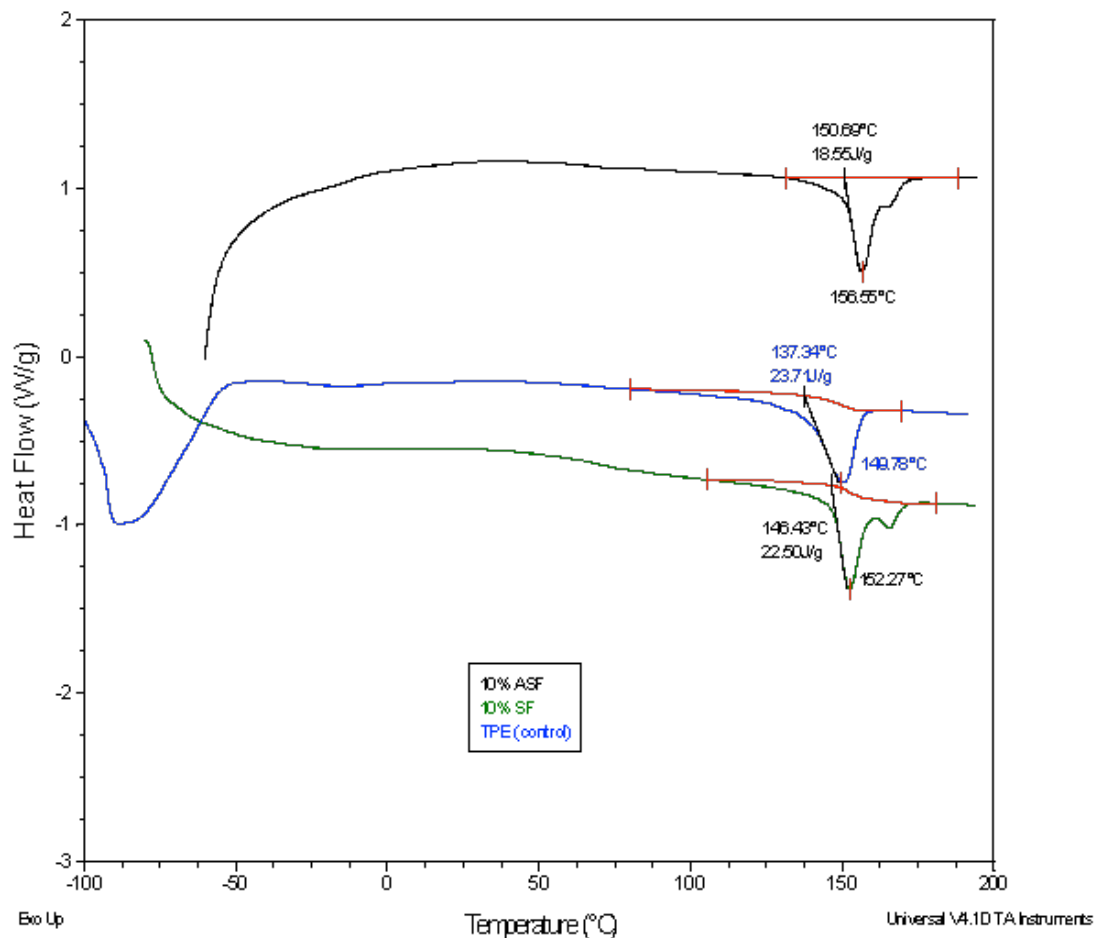
Figure 8: Heat flux DSC of 10 wt% soy flour elastomer composites
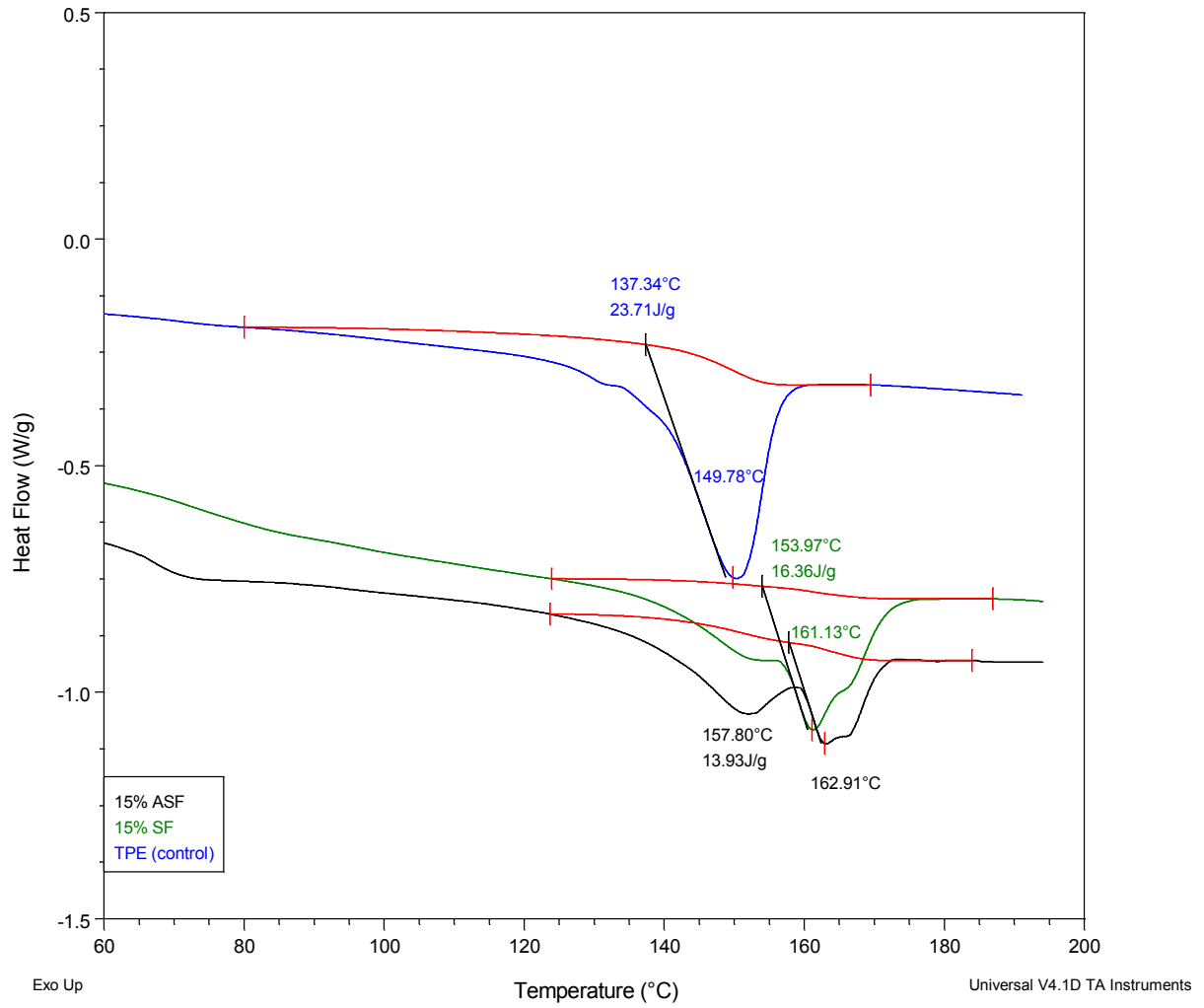
Figure 9: Heat flux DSC of 15 wt% soy flour elastomer composites
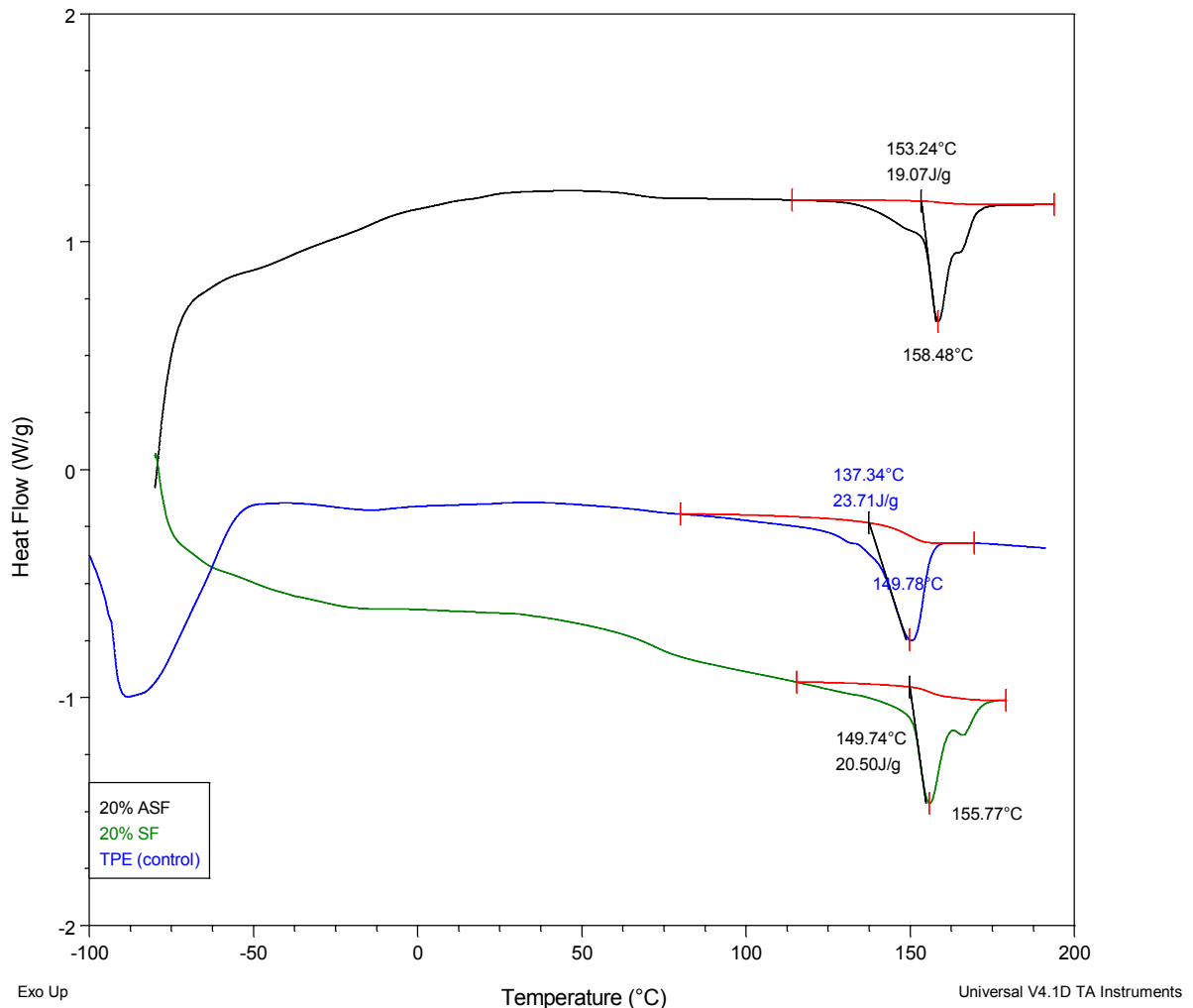
Figure 10: Heat flux DSC of 20 wt% soy flour elastomer composites

There are two meting temperatures for the control group of each of the DSCs indicating that the TPE is a two-phase system which is further supported by the SEM image in figure 7 (b). The thermal stability of the composites tends to increase as the soy flour concentration increases The melting temperature for the ASF/TPE composite at 10 wt%, 15 wt% and 20 wt% was higher (150.6°C, 157.8°C, 153.2°C) in contrast of the control group (137.3°) indicating that the acetylation reaction increases thermal stability by reducing the intake of water within the soy and

overall the polymer. The melt temperature for the untreated soy flour was 113.9°C and decreased

to 94.5°C for the treated soy flour. Even though the acetylation reaction reduces the thermal

stability of the soy flour, it increases the thermal stability of the composite because of the better

compatibility of the ASF with the TPE.

4.4   Chemical Characterization

4.4.1 ^{13}C SS-NMR

To confirm the chemical pathway of the proposed acetylation of soy flour, various

methods were used, including nuclear magnetic resonance (NMR) spectroscopy. Normally,

NMR is used in the application of detecting proton (^{1}H) connectivity on a molecular structure

and are measured in chemical shifts, or delta (δ), and has a unit value of part per million (ppm).

Chemical shift values are typical and indicate a reference point for connections of functional

group(s) connectivity. Since there is an abundance of proton connectivity on a typical protein

molecule and the soy flour was insoluble, carbon (^{13} C) solid state NMR was utilized. A method

called gated decoupling was used to narrow the range of detected signals. Gated decoupling

allows for tightly coupled groups (CH_2 and CH) not to be detected but allows for carbons

attached to oxygen as well as CH_3 groups to be detected. In the gated decoupling spectrum,

figure 15, there is significant difference in the area under the curve between the treated and

untreated soy flour occurred at δ 172.67 ppm and 19.88 ppm. The chemical shift at δ 172.67 ppm

references a carbonyl attached to an oxygen creating an ester functional group. The chemical

shift of a methyl group attached to a carbonyl is referenced at δ 19.88 ppm. The intensity level

for the treated soy flour is higher than that of the untreated soy flour indicating that there was a

higher percentage of acetyl and methyl groups on the surface of the soy flour supporting the

theory that chemical pretreatment resulted in a reduction of hydroxyl group
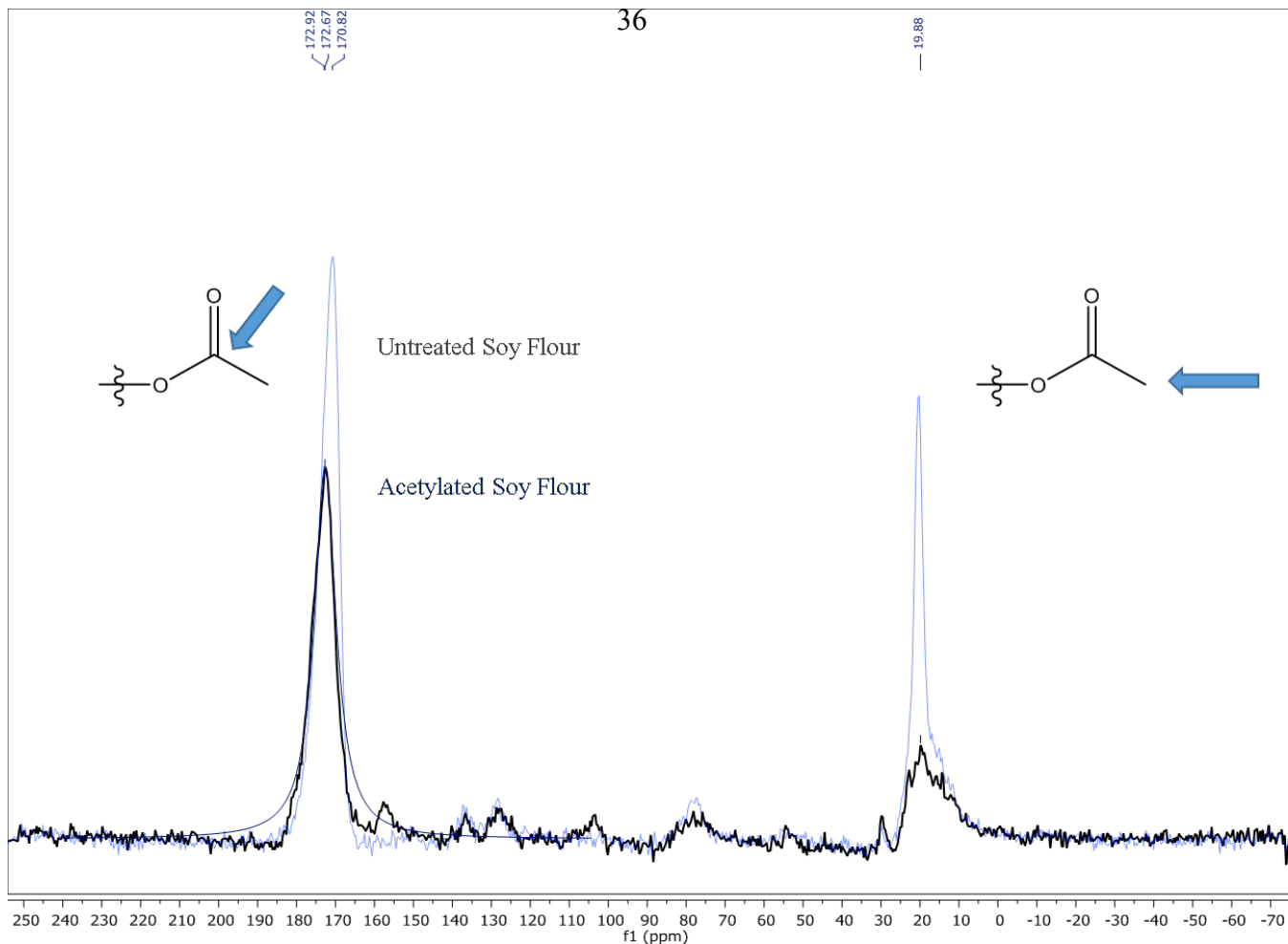
**Figure 15: ¹³C Solid State NMR spectrum of treated and untreated soy flour with gated decoupling**

4.4.2 GCMS

A GCMS was completed of the liquid run-off from the soxhlet extraction. This analysis technique was used to gain a better understanding of the reaction and if the desired product was attained. This test method was a restrictive of sampling a solid product thus the sample was a concentrated liquid dissolved in chloroform. When tested, a total of 3 mass specs were analyzed. One of the mass spectrums was the chloroform that the concentrated sample was dissolved in and was ignored. A similarity analysis of the other 2 spectrums compared the mass fragmentation to that of other molecules. The two molecules that the tested samples most resembled are that of $C_{18}H_{32}O_{16}$, figure 16, which is concentrated with hydroxyl groups, and

$C_{28}H_{32}O_{16}$, figure 17, which is concentrated with acetyl groups. These molecular structures are similar representations to ideal reaction products that are found in figure 2 in chapter 3. In general the acetylation of the water soluble carbohydrates replaces the OH side groups with $OCOCH_3$.
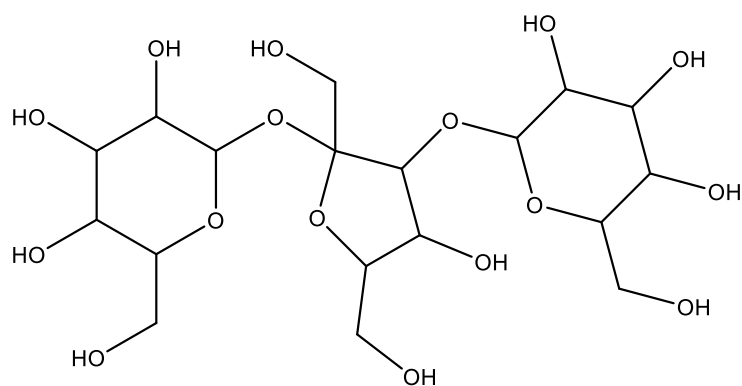
Figure 16: Chemical structure of $C_{18}H_{32}O_{16}$
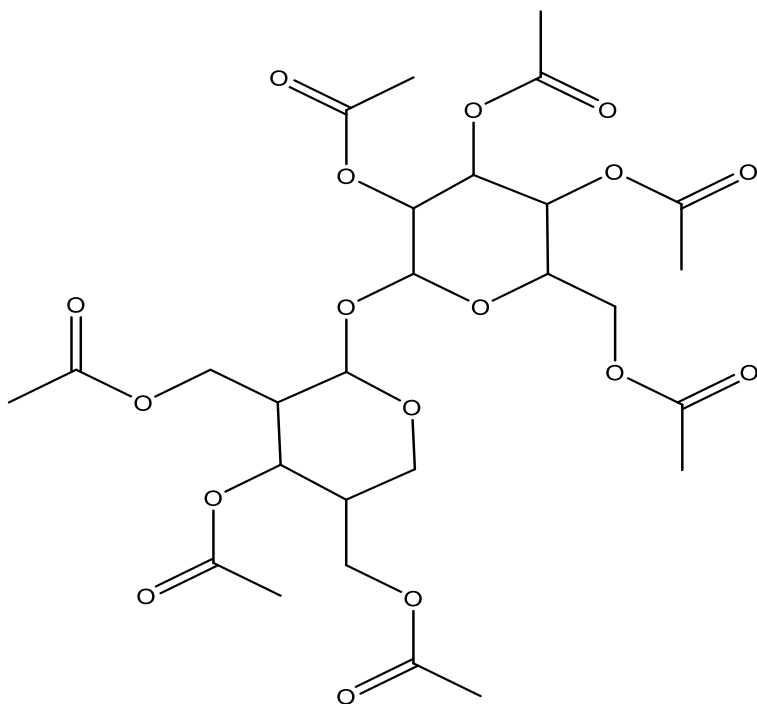
Figure 17: Chemical structure of $C_{28}H_{32}O_{16}$

CHAPTER V

CONCLUSIONS

The results of this study suggested that soy flour is a viable filler alternative in thermoplastic elastomer composites, although, a surface modification to the soy flour, acetylation, is needed. Tensile strength for all soy flour composites decreased as soy flour concentration increased. Specifically, the composite with 10 wt % acetylated soy flour exhibits equivalent tensile strength to that of the neat elastomer. Generally, as soy flour concentration increased so did modulus but unexpectedly, elongation increased as well at the 10 wt % formulation. This data indicated that there could be better adhesion of the soy flour to the elastomer mainly because of the increase in elongation at the 10 wt % concentration.

In both the SEM images of untreated and treated soy flour, aggregates are formed in the polymer matrix. The untreated soy flour formed larger aggregates in the elastomer matrix than that of the treated soy flour. The larger aggregates were possible fracture cites within the composite and was believed to cause failure. The smaller aggregates of the acetylated soy flour appeared to have better dispersion within the matrix creating a more cohesive composite.

In the SS-NMR, we can conclude that the reaction was completed as proposed. Using the method of gated decoupling to reduce the amount of signals present on the spectrum, the intensities of the acetyl groups on the treated soy flour were larger than that of untreated flour. DSC and TGA analysis indicated that the acetylated soy flour is slightly more stable than the untreated soy flour by increasing the decomposition temperature of the composite.

Future investigations should examine the exact role that protein has on the thermal stability and adhesion of the soy flour. Better chemical characterization techniques will be used

to understand the chemistry behind the acetylation reaction. Surface area will also be measured

to capitalize on better adhesion of the soy flour and the elastomer.

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