

IN-SITU POLYMERIZATION OF
POLYLACTIC ACID/MONTMORILLONITE NANOCOMPOSITES

THESIS

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Master of SCIENCE

by

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ABSTRACT

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SUPERVISING PROFESSOR: GARY BEALL

There is a great interest in finding a renewable plastic to reduce the need for petroleum-based plastics, such as polyethylene terephthalate (PET). The benefits in waste reduction and reducing dependence on oil would be ethically and economically beneficial. A leading contender to help replace these plastics is polylactic acid (PLA). It has similar properties to leading petroleum-based plastics, with the added benefit of being made from a renewable resource, although some properties could be improved, namely the heat distortion temperatures and water permeability. This research focuses on improving these properties by the addition of organoclay platelets. These nanoclays have

been shown to improve the mechanical, thermal, and permeation properties of various polymers. It is the scope of this research to define a method for improving PLA to the point that it can be used in food packaging films and apparel.

CHAPTER 1

INTRODUCTION

Petroleum-based plastics are not sufficient for the new ecological awareness taking place in the world markets, and are limited by the amount of oil left in the reserves that support the industry. The price of oil is high and supplies will eventually run out. The production of oil-based plastics is also quite energy intensive. One of the most immediate concerns with petroleum-based plastics is the amount of space they take up in landfills, up to 25% nationwide (1), and their low rate of biodegradability, thousands of years. All of these factors lead to a need for a less energy intensive and more biodegradable polymer.

In 1780 Scheele discovered lactic acid as a chemical component of sour milk. Then in 1881 Avery first produced it for commercial use (2). Lactic acid is very common biologically; it can be obtained industrially through a natural fermentation process from many different sources such as beets, corn, sugarcane, *etc.* The commercially available monomer is corn-based and available from Natureworks, L.L.C. based in Omaha, Nebraska. They are the world's largest provider of PLA plastics. The corn they ferment to obtain the monomer is made from low grade animal foodstuffs not intended for human consumption so that it doesn't directly take away from human food stores (1), (see Figure 1). There are also research efforts aimed at producing lactic acid from biowaste (18).

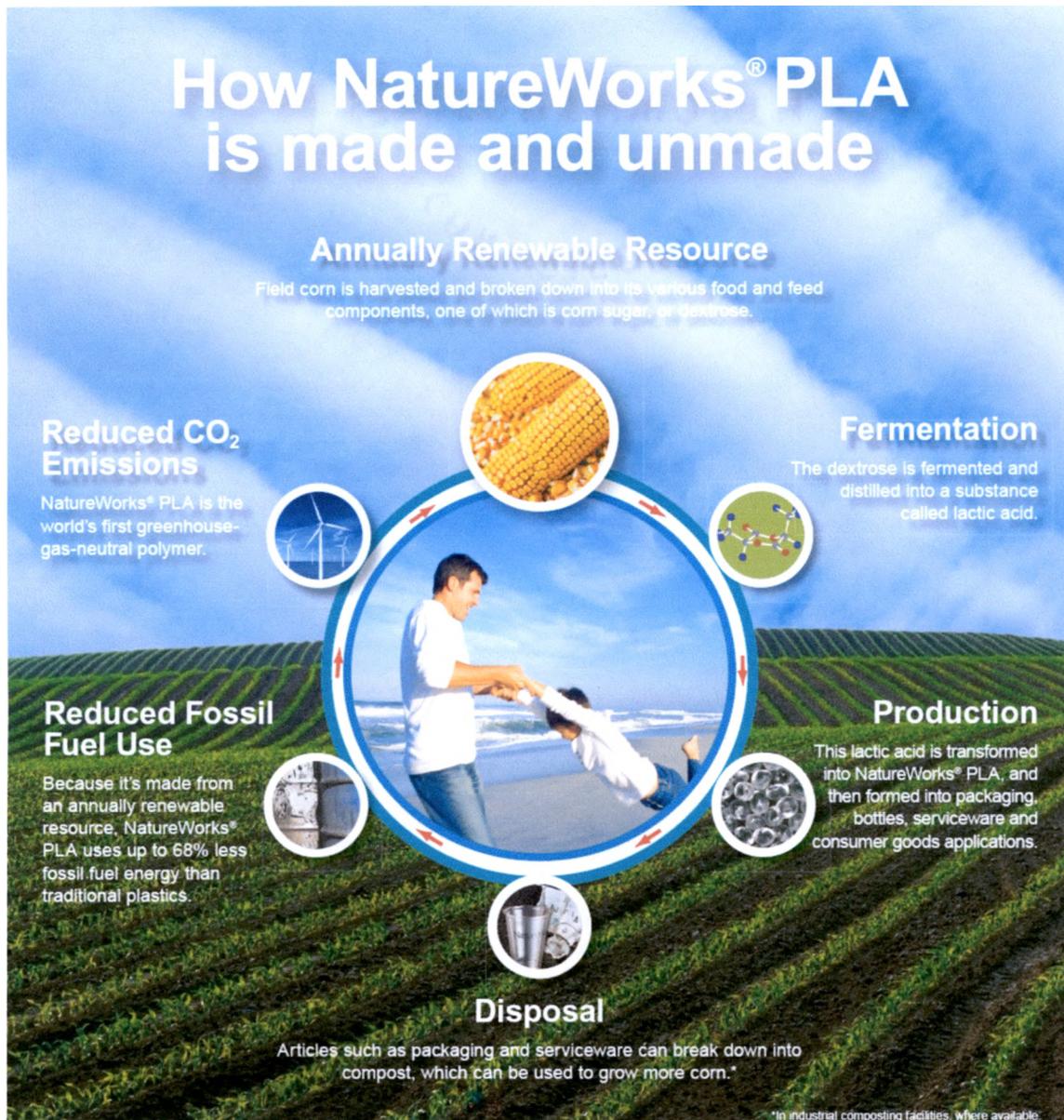


Figure 1. Flow chart of Natureworks PLA plastics (19)

Polylactic acid is a promising substitute for petroleum-based polymers, such as polyethylene terephthalate (PET). Polylactic acid is a plant-based plastic that is considered a renewable resource, and is biodegradable under composting conditions. In

addition, its cost has also become more comparable to petroleum-based plastics with the methods and production scale instituted by Natureworks.

Preliminary attempts at polymerization of lactic acid have shown that high molecular weights can be obtained ($>100,000$ g/mol) (3). After testing, it was observed that the mechanical, decomposition, and gas permeability properties were similar to petroleum-based polymers. These properties were similar, but less than ideal, to those needed for commercial use as a commodity polymer. In particular, the heat distortion temperature of PLA makes it of limited usefulness in food packaging, where sterilization is needed prior to filling containers, and in fabrics where higher heat settings on irons will scorch the fabric. Nevertheless, interest in improving these properties has increased with the global concern of petroleum products stress on the environment and economy, as previously discussed. The idea of an efficiently produced, biodegradable polymer derived from a replenishable resource is a great incentive for further consideration and research on the topic.

Lactic acid must be made into a cyclic dimer to eliminate the water produced by the condensation to form the ring. When regular lactic acid is polymerized, water is a by-product. This water by-product is the main factor in low molecular weight polymers because it hydrolyzes the chains as they are formed. Dehydration of lactic acid oligomers yields a cyclic dimer which is distilled to remove water (2).

High molecular weight polylactic acid is obtained from a ring opening reaction using a lactide and a stannous octoate catalyst/initiator system (4, 5), (see Figure 2).

PLA's UV stability, especially for clothing purposes. Outside the body, polylactic acid is biodegradable under high temperature and moisture conditions within 90 days (7,9). The price for producing a pound of polylactic acid is now under \$1. With respect to energy, PLA uses 65% less than petroleum plastics in production and produces 68% fewer greenhouse gases (1).

Current issues with PLA range from engineering, to ecological, to application. One of the main engineering and ecological dilemmas is that current production uses corn kernels. Ideally a method needs to be developed to extract the lactic acid from the husks and biowaste, so foodstuffs themselves are not used.

The application problem is the one that this research effort is focused upon. For untreated PLA the heat distortion temperature is 65 °C, which won't allow for steam sterilization in the food packaging process or ironing in apparel products (8). Also, the gas permeability is too high to keep food fresh for the lengths of time necessary to ship and be sold. In addition, the water permeability of PLA is 172 g/m²/day versus 1.1g/m²/day for PET (9,10).

The focus of this project will be to improve the heat distortion temperature and water permeation properties of polylactic acid for use as biodegradable food packaging films and clothing. This is a continuation of a previous project where various types of organoclays were added to the polymerization of PLA to improve the heat distortion temperature and lower the gas permeability compared to the pristine polymer (11). By introducing a clay component into a polymer system the thermal and permeation properties have been shown to improve substantially with additions as low as 1-5 weight percent (12).

Other plastics such as ϵ -caprolactone have shown increases in both thermal and mechanical properties from addition of organoclays at these low weight percentages (13,14). This is because the Cloisite clays are analogous to sheets of paper. They have a high planar aspect ratio and can act as reinforcement and barriers to gas permeation.

Between these sheets are exchangeable cations (see Figure 3). These cations are useful to aid in exfoliation of platelets and initiation of chains on the clay surface by exchanging these cations for quaternary ammonium compounds. These quaternary ammoniums serve two purposes: they open up the clay galleries and serve as hydroxide initiators for the polylactic acid chains.

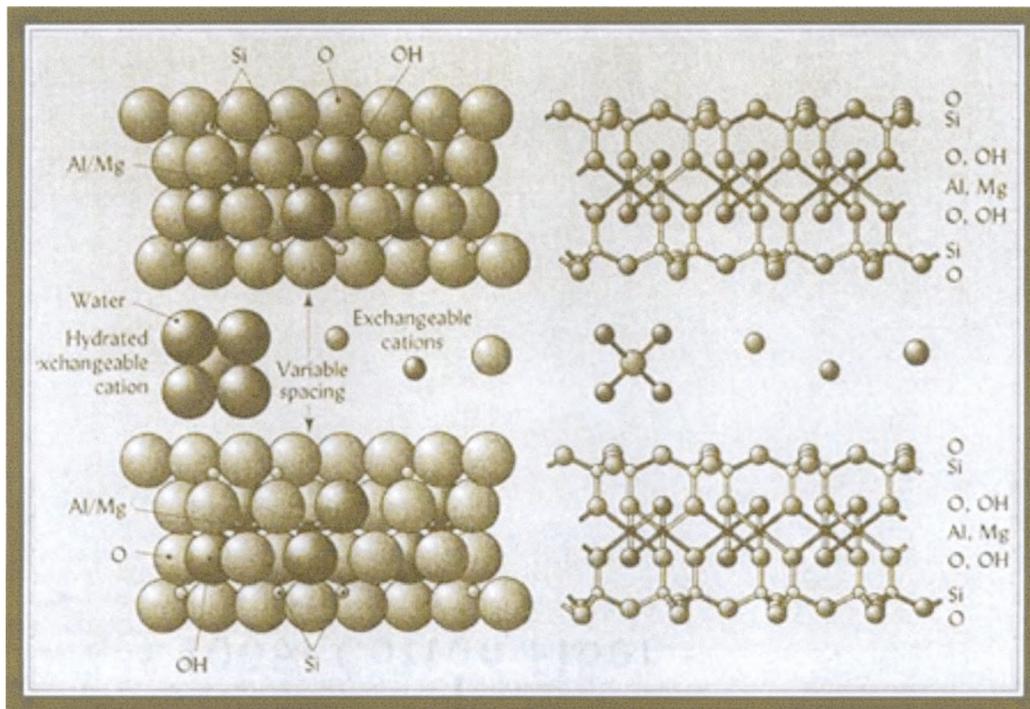


Figure 3. Generic Montmorillonite Clay Structure (21)

Structurally, adding thin layers of clay in between the polymer chains acts as a reinforcing agent that doubles as solid obstacles to deter gas molecules from penetrating the nanocomposite system, consequently elongating the useful storage time for food packaging (15,16). Previous research found that there is also a constrained polymer region around these clay platelets that causes crystalline-like behavior (22). This constrained polymer region also contributes to the improved thermal and permeability properties. With this one addition the mechanical strength and thermal behavior of the system is raised as the ability for gas permeability is lowered.

The challenge with these clays is getting the platelets to exfoliate instead of staying intercalated in the system. The property increases are maximized with exfoliated systems since the maximum surface interaction is produced. An exfoliated system has a homogenous composite of plastics and clay (see Figure 4). This uniformity decreases the gas permeability by giving the gas molecules a maze to traverse before passing through the polymer (15,16).

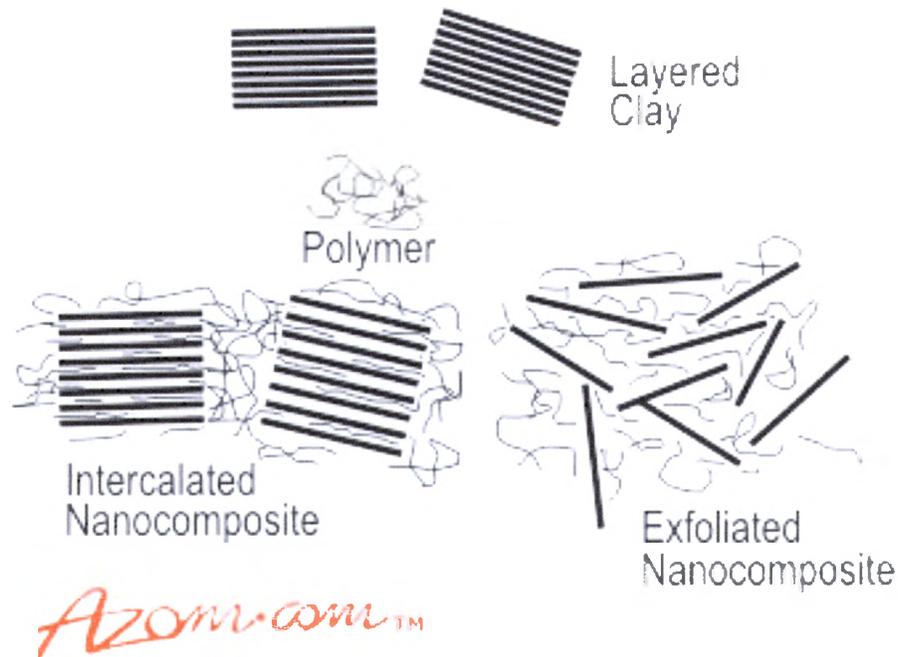


Figure 4. Differing levels of Platelet separation (23)

The research contained in this thesis is aimed at understanding and solving problems that occur upon introducing the clay into the system. Striking a balance between functional molecular weight and sufficient composition of clay to obtain the desired properties is the aim of this research.

Previous work done on this project has lead to several problems and possible solutions for obtaining the desired polymer matrix. After problems were encountered with lower than expected molecular weights, it was surmised that the initiators on the organoclay and necessary surfactants are hindering the molecular weight.

Previous research was successful in polymerizing pure PLA up to a molecular weight of 300,000 g/mol. Such high molecular weights show that the chosen

polymerization technique was able to form long chain polymers. But the nanoclay polymers that were made were all well below the target of 75,000 g/mol, which is the molecular weight that Natureworks, L.L.C. sells commercially. So several clay samples with different quaternary ammonium salts with differing amounts of initiator groups on the surface of the clay were prepared and used in polymerization. It was determined that a ratio of octadecyl ammonium (ODA) (no activation groups) with triester quaternary ammonium (TEQ) (one activation group) was best suited to control the number of chains initiated from the surface (3,11,12). These experiments still did not achieve the desired molecular weight. Additional experiments were conducted with silane coupling agents to passivate hydroxides on the clay edges since it was suspected that they might be acting as initiators.

In an attempt to disperse the clay during polymerization, the clay was sonicated for a period of time in dry toluene. It was hoped that sonication would open up the galleries in the clay enough to allow the dimer to infiltrate so the chains would polymerize from the clay surface and cause exfoliation through the chemical process.

CHAPTER 2

MATERIALS AND METHODS

2.1 Drying Toluene:

Unpurified toluene contains sulfur impurities. To purify the toluene before transferring into the still the following procedure was used (17):

1. Refrigerate H_2SO_4 to make sure the reaction stays below 30°C . This will keep the toluene from being sulfonated.
2. Shake twice with cold H_2SO_4 at a 100mL:1L sulfuric acid to toluene ratio in a separatory funnel.
3. Rinse once with distilled water.
4. Rinse once with 5% NaOH and again with distilled water.
5. Shake and store over CaCl_2 Add to still as needed.

2.2 Clay Preparation:

The necessary ratio of quaternary ammonium salts to clay to get the proper number of activation groups along the surface of the platelets was calculated and prepared according to the following procedure:

1. Add 20g of Na^+ Cloisite Clay to 400-500mL distilled water and stir *via* Dispermat at 2000-3000 rpm for 15-20 minutes.
2. Heat to 80°C while stirring with a stir bar.

3. When using silane edge treatment, 5.25g of aminopropyltrimethoxysilane purchased from UCT Specialties, L.L.C. was added to the heated slurry while Step 4 was performed.
4. Protonate ODA purchased from Sigma Aldrich with HCl by mixing 4.18g of 90% active ODA with 1.28 mL of concentrated HCl in 100mL of distilled water.
5. Add ODA chloride and 3.32g TEQ purchased from Akzo Nobel to clay slurry at 80°C and let heat for 2 hours.
6. Wash excessively with hot distilled water until AgNO₃ added to filtrate produces no precipitate.
7. Vacuum filter to remove water and dry clay in 70°C oven overnight.
8. Pulverize clay with a mortar and pestle. Then, brush through a 325 mesh US sieve and store in a 70°C vacuum oven.

2.3 Monomer Purification:

To purify the cyclic lactide dimer a recrystallization procedure was required. The method received from Natureworks, L.L.C. was used:

1. Place 100g of unpurified monomer from Natureworks, L.L.C. in a flask with a mixture of still-dried toluene and THF. Heat to 65°C until melted.
2. Transfer to an air-free filter flask and cool to room temperature (see Figure 5).
3. Filter toluene/THF mixture. Rinse twice with same mixture.
4. Dry under vacuum overnight.
5. Transfer to dry box. The purified dimer is not exposed to atmosphere after the final rinse.



Figure 5. Air-Free Filter Flask (left) and Toluene Still (right).

2.4 Initial Neat Polymerization:

The first polymerization performed in this research was a neat monomer polymerization to establish the polymerization method and conditions. This

polymerization was conducted with 5g of purified lactide dimer and tin(II)octoate catalyst left in the dry box over the course of many months from previous projects.

The vial was then capped and brought out of the dry box directly into 180°C oil bath. These values were previously shown to get a 40,000:1 monomer to catalyst ratio, calling for an 8 hour polymerization.

2.5 Polymerization:

The polymerization is carried out in 20mL glass vials with Teflon tape around the threads to maintain a moisture-free atmosphere for polymerization.

1. The vials are rinsed with distilled water and dried in an oven for 30 minutes at 120°C along with a spatula and a 50 μ L syringe and either aluminum or glass tray.
2. All items are immediately taken out of the oven and directly to the dry box where they are cycled into the argon atmosphere.
3. Dimer (5g) and 14 μ L of tin(II) 2-ethylhexanoate are both transferred to the vial, which is then sealed.
4. Take directly from dry box to 180°C oil bath for 2-4 hours (see Figure 6).

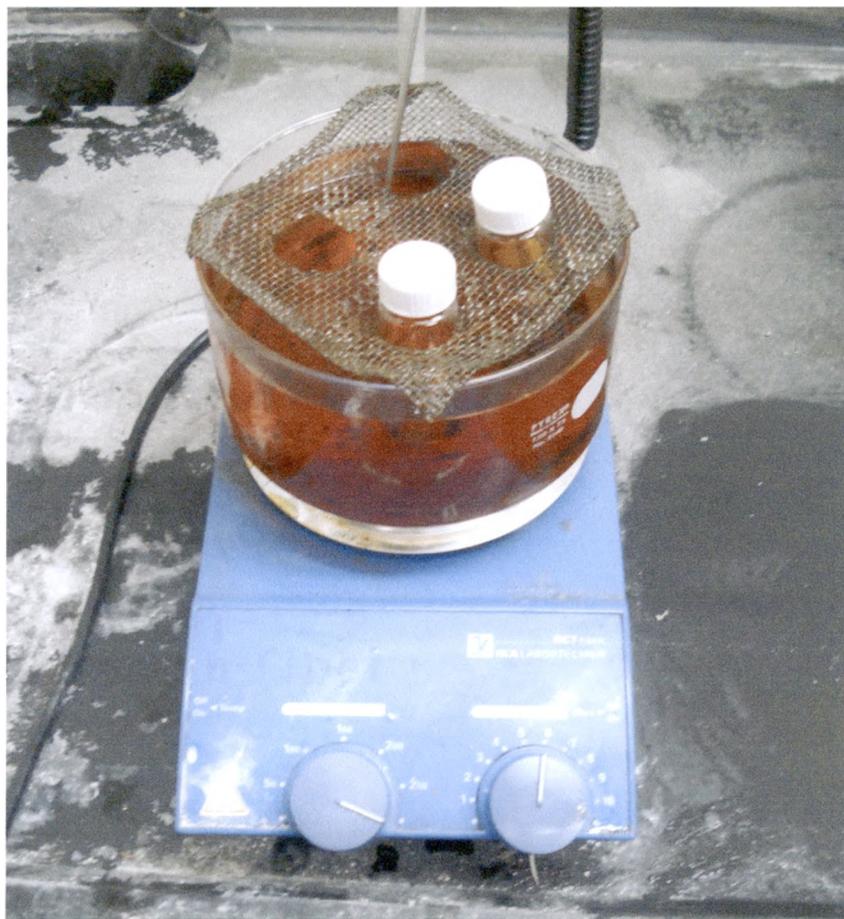


Figure 6. Polymerization Setup

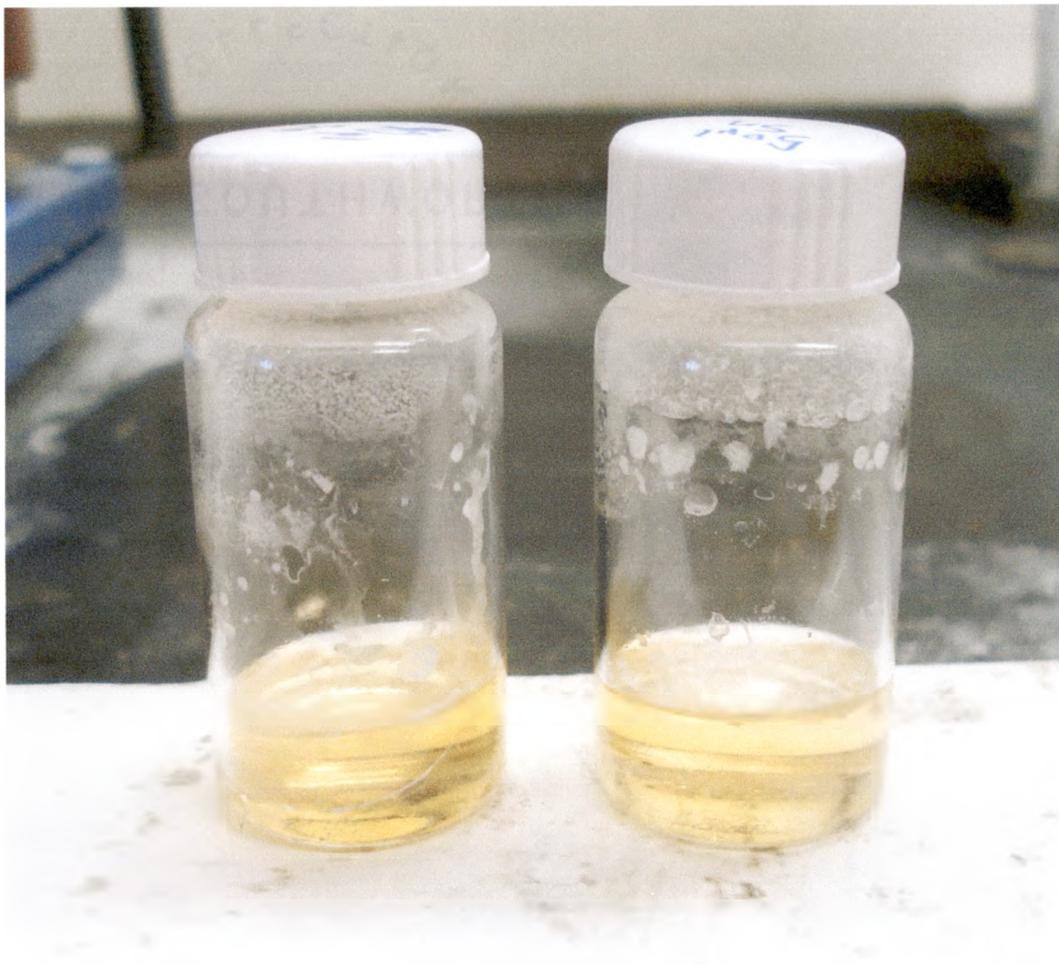


Figure 7. Neat Polymers

2.6 Nanoclay Polymerization:

The polymerization procedure for synthesizing a neat polymer was utilized. The beginning steps were the only difference.

1. The clay was taken from of the vacuum oven and immediately capped to limit the amount of moisture absorbed from the atmosphere.

2. The clay was transferred to a dried and tared vial on a scale and immediately capped.
3. Dried toluene was transferred into a vial with clay and immediately sonicated at 30 kHz and 100W for 10-15 minutes.
4. Slurry was taken out of the sonicator and capped, then transferred to dry box and continued with same polymerization procedure shown above.

All these steps were focused on limiting the amount of time that the clay is exposed to the atmosphere so that water is not present during polymerization.

2.7 Analysis:

Molecular weight was determined using a Waters HPLC setup. A Waters 600 controller and pump was connected to a series of three Waters columns, two HR 4 and a HR 4E. These fed into a Waters 2410 Refractive Index Detector and Waters 2487 Dual λ Absorbance Detector. The 254nm peak was used to determine the molecular weight based on a polystyrene calibration curve.

The samples (25mg) were dissolved in 5mL of HPLC-grade chloroform. Then they were filtered through a 0.45 μ m Teflon filter. A portion (50 μ L) of sample was then injected into the sample loop and run through the HPLC at 1mL/min for 45 min.

The thermal properties were tested as follows.

For thermal gravimetric analysis:

1. The sample (10-15 mg) was placed on the balance of the TGA Q50.
2. The sample was heated in an inert argon atmosphere.
3. The results were plotted on a weight vs. temperature plot.

For differential scanning calorimetry:

1. The sample (10-15 mg) was measured in a tared weighing pan and lid for the DSC Q200.
2. The pan and lid were pressed together using a Perkin-Elmer press.
3. The sample was weighed again to confirm the weight was maintained before placing it in the DSC Q200.
4. The results were plotted on a heat flow *vs.* temperature plot.

For dynamic mechanical analysis:

1. The sample was placed in a silicon mold and heated to 180°C to facilitate melting.
2. After the sample melted, a cleaned and dried stainless steel syringe was used to stir and puncture gas bubbles within the sample.
3. The sample was allowed to melt back to shape at heat and Step 2 was repeated as necessary.
4. The sample was then cooled to room temperature in a press to obtain a uniform sample.
5. Once cooled, the sample was sanded until all sides were parallel along both lengths and polished to remove any stress lines that would cause stress fractures during analysis.
6. The results were plotted on storage modulus and loss modulus *vs.* temperature plots.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Initial Neat Polymerizations

The first polymerization conducted was done using the parameters previously discussed (section 2.4). The monomer melted quickly in the oil bath and appeared transparent. Within forty-five minutes the sample was still viscous and slightly darker in color. From one-and-a-half to three-and-a-half hours the sample grew noticeably darker in color. After seven hours the run was stopped earlier than planned due to the dark brown color.

This was not an ideal sample and was used as a preliminary run to become familiar with the technique. It was determined that the toluene needed to be purified before being dried in the stillpot. The still used to dry and store toluene was killed and restarted at this time, and the old dimer was replaced by purified dimer. Even being stored in the dry box it was determined prudent to replace the existing dimer in case it had decomposed due to the many months of storage, or in the event that the laboratory atmosphere had contaminated the dry box during this time.

For the next set of polymerizations a volume of 2.499 μ L of 0.0347M catalyst for 5g of monomer was calculated to yield 75,000 g/mol. So the next polymerization set was two runs with excess catalyst, Vials #1 and #2, and two runs with the calculated volume of 2.5 μ L of 0.0347M, Vials #3 and #4.

Table 1. Neat Polymerization Reaction Vial Contents

Vial #1	5.0g lactide dimer	8.0 μ L of 0.0347M catalyst
Vial #2	5.0g lactide dimer	8.0 μ L of 0.0347M catalyst
Vial #3	5.0g lactide dimer	2.5 μ L of 0.0347M catalyst
Vial #4	5.0g lactide dimer	2.5 μ L of 0.0347M catalyst

Within an hour of being placed in the oil bath Vials #1 and #2 displayed a darkened color. Within three hours of the start of the polymerization Vials #3 and #4 started to show some darkening. After the full 8 hours passed the samples were removed from the oil bath. GPC analysis showed that Vial #4 had a molecular weight of 36,772.0 g/mol. The low molecular weight was most likely due to the thermal breakdown over time from excess catalyst or duration of the polymerization. If the catalyst had become concentrated over time the excess in the reaction would increase the rate of reaction causing thermal breakdown.

3.2 Polymerizations with Varying Catalyst Volumes

To determine whether the catalyst or atmospheric contamination was to blame a set of samples with varying catalyst volumes was run:

Table 2. Neat Polymer Volume Ladder Samples

Vial #5	5.0g of lactide dimer	15.00 μ L of 0.0347M catalyst
Vial #6	5.0g of lactide dimer	50.00 μ L of 0.0347M catalyst
Vial #7	5.0g of lactide dimer	115.0 μ L of 0.0347M catalyst

After an hour Vials #6 and #7 darkened. By five hours Vial #5 was darkening. The GPC results performed for Vials #5 and #7 showed molecular weights of 25,429 g/mol and 36,613 g/mol, respectively. This shows that the large difference in catalyst concentration did not show a difference in molecular weight, but the cause of the low molecular weights was inconclusive.

A following set of sample runs with a ladder of 0.0347M catalyst volumes of 0.00 μ L, 50.00 μ L, 100.0 μ L, 150.0 μ L. There was little difference in color among the final samples. GPC analysis was not performed on these samples, but the continuous trend of dark brittle polymers led to the conclusion that over the course of the polymerization the laboratory atmosphere was seeping into the vial caps. The vial with no catalyst did not polymerize; it recrystallized on cooling to room temperature.

3.3 Attempts to Eliminate Atmospheric Contamination

The following polymerizations were done with the intention of finding the best way to ensure the polymerizations occurred in an inert atmosphere. The first set of samples in this series was run with Teflon tape placed around the threads of the vials inside the dry box to give a tighter seal. The samples were prepared as before with a 0.0347M catalyst volume ladder of: 75.00 μ L, 100.0 μ L, 125.0 μ L, 150.0 μ L. Within four

hours all four of the samples were darkly colored. This indicated that the polymerization was not acceptable and the samples were taken out of the oil bath.

Next, an attempt to polymerize in a vial with argon flow was made. One 5.05g sample with 115.0 μ L of 0.0347M catalyst in a septum-capped vial with a syringe feeding argon into the vial and an evacuation syringe to facilitate flow was placed in the hot oil bath. After a full, eight-hour polymerization the sample was dark to the point of being black. On investigation it was found that the release syringe was not releasing pressure. Another reaction under the same conditions yielded similar results. From this it was determined that the relatively small gauge needles being used for purging were insufficient.

The next polymerization attempted was done with a slightly larger gauge needle and a bubbler to monitor gas flow. Within four hours there was no argon flow and the sample was black in color, similar to obsidian.

3.4 Neat, High-Molecular Weight Polymerizations

The next set of samples was done after diluting a new sample of catalyst. The molar ratio of the newly diluted catalyst was 10,000:1. The molar ratio was achieved with a 10% solution of Sn catalyst in dried toluene. Following this model a value of 14.0 μ L of 10% catalyst solution was calculated for a proposed MW of 200,000 g/mol.

Using the new catalyst concentration a series of samples containing 5.0g of purified dimer and 14.0 μ L of catalyst was run. Also, the polymerization time was lowered from eight hours to two hours because of the increased molar concentration. The variable was

the amount of argon purging each vial received. This was to determine the best method for achieving the high molecular weights needed and avoid coloration.

Table 3. Sample Set with Argon as a Variable

Vial #8	sealed in the dry box and not introduced to argon or laboratory atmosphere
Vial #9	purged with argon for 30 seconds
Vial #10	continuously purged with Ar until the flow was hindered as evidenced by lack of flow through the bubbler
Vial #11	same as Vial #10 with a stir bar added to see if mixing would promote further polymerization

At the end of the polymerization it was noted that the darkness of the polymers was in the following descending order: Vial #8>#9>#10>#11. Vial #8 was noticeably darker in reference to the other samples, but all four were not as dark as the previously run samples. Upon completion of the reaction the vials were opened and examined by GPC. The molecular weights were as follows:

Table 4. Molecular Weight of Argon Variable Samples

Vial #8	193,203 g/mol
Vial #9	122,487 g/mol
Vial #10	99,598.0 g/mol
Vial #11	185,536 g/mol

The high molecular weights showed that the catalyst was the limiting factor in previous polymerizations, more so than any atmospheric leaks. The lower molecular weights in Vials #9 and #10 showed that the Ar flow actually caused lower molecular weights. This was likely due to the fact that the argon tank used was not equipped with an oxygen scrubber to ensure an inert atmosphere, and any oxygen or water present in the atmosphere would cause a decreased molecular weight.

Vial #11 had the second highest molecular weight even though it was exposed to the untreated argon. This indicated that the presence of the stir bar aided in polymerization. This is surprising in that the magnetic stir bar was suspended over the surface of the plate. Because of this, the stir bar was active for only twenty minutes of the polymerization before the polymer was too viscous to allow further stirring.

3.5 Initial Nanoclay Polymerizations

For the first nanoclay polymerization the silane-treated TEQ/ODA clay was used. It was hypothesized that the edge treatment from the silane would limit the amount of initiators present in solution and allow for higher molecular weight. For the same reason the first reaction was with 1% by weight clay-to-dimer. The contents of the vials are shown in Table 5.

Table 5. Initial Nanoclay Reaction Vial Contents

Vial #12	2.0mL of dried toluene, 0.05g of silane-treated TEQ/ODA clay, 5.0g of dimer, 14.0 μ L of 10% catalyst solution
Vial #13	2.5mL of dried toluene, 0.05g of silane-treated TEQ/ODA clay, 5.0g of dimer, 14.0 μ L of 10% catalyst solution

The variable toluene volume was to determine which gave better exfoliation of the clay within the system. The final product had poor exfoliation as the clay was concentrated on the bottom and unreacted monomer on the top of the reacted product. This unreacted monomer indicated an incomplete polymerization and the lack of exfoliation showed that the procedure needed to be improved. Since both samples were incomplete it was determined that the variable solvent volume had no appreciable effect on exfoliation.

3.6 Attempts to Improve Exfoliation

The first attempt to improve the exfoliation was to add propylene carbonate, a known organoclay activator, to the toluene. The samples were prepared as follows:

Vial #14- 5.0g of lactide, 0.05g of silane-treated TEQ/ODA clay, 14.0 μ L of

Sn(II)octanoate, 4.0mL of dried toluene sonicated at 35 kHz and 100W with three drops of propylene carbonate for ten minutes. The clay was not exfoliated so one more drop of propylene carbonate was added and sonicated for an additional ten minutes. The clay still was not exfoliated so three more drops were added and sonicated for an additional twenty minutes.

Vial #15- 5.0g of lactide, 0.05g of silane-treated TEQ/ODA clay, 14.0 μ L of

Sn(II)octanoate, 4.0mL of dried toluene sonicated at 35 kHz and 100W with three drops of propylene carbonate for twenty minutes.

After the two hour polymerization Vial #14 was clear and looked complete while Vial #15 was unfinished. Neither of these samples were determined to have good exfoliation

from visual analysis. So, the next set of samples that was run was to test whether ether would be a more appropriate solvent.

Table 6. Variable Solvent Sample Contents

Vial #16	5.0g of lactide, 0.05g of clay, 14.0 μ L of Sn(II)octanoate, 4.0mL of dried toluene
Vial #17	5.0g of lactide, 0.05g of clay, 14.0 μ L of Sn(II)octanoate, 4.0mL of petroleum ether

The clay did not dispense well in Vial #17 and the petroleum ether completely evaporated during sonication. Vial #16 was not polymerizing after three hours. As it cooled it turned into a white crystalline solid, which indicated there was a large amount of unreacted monomer in solution.

3.7 TEQ/ODA Clay without Silane Treatment

After analysis of the previous results the clay used was switched from the silane-treated clay to the TEQ/ODA clay that was not silane edge treated. A variable amount of catalyst was also introduced in this set of samples to see if the excess catalyst would be needed due to the excess initiators present on the clay surface. The extra catalyst could also react with unwanted water present in solution that would hydrolyze the dimer and hinder polymerization. The contents of the samples are shown in Table 7.

Table 7. Nanoclay Without Silane Treatment Reaction Vial Contents

Vial #18	5.0g of lactide, 0.05g of TEQ/ODA clay, 2.5mL of toluene, 14.0 μ L of 10% catalyst solution
Vial #19	5.0g of lactide, 0.05g of TEQ/ODA clay, 2.5mL of toluene, 14.0 μ L of 10% catalyst solution
Vial #20	5.0g of lactide, 14.0 μ L of 10% catalyst solution

Both Vials #18 and #19 were sonicated at 20 kHz and 100W for ten minutes each. Vial #20 was a control to see that the new batch of purified monomer that was made immediately before this set was indeed pure.

After four hours Vial #20 was polymerized and golden in color, which indicates that the purified lactide was pure and polymerizable. Vial #18 was unpolymerized. It was more viscous than melted dimer, but still not solid, indicating a lack of polymerization. Vial #19 was polymerized, but had bubbles in the polymer. It is believed that these bubbles are from evaporated toluene being trapped as the polymer chains grew. This sample was analyzed with the GPC and showed a very unsatisfactory molecular weight of 10,147 g/mol.

The clay used up to this point had been dried in an oven overnight and then stored in a cabinet in a sealed vial. Because of the low molecular weight displayed in the previous run the clay was dried again in a 70°C oven overnight to drive off excess moisture. TGA analysis indicated that the dried clay still had 1.25% by weight water present (see Figure 8). The procedure for Vials #18 and #19 was duplicated naming each #21 and #22,

respectively. At the end of three hours both looked like they had undergone some amount of polymerization, but there was a noticeable amount of unreacted monomer on top of each. This was enough of an indication of an incomplete reaction that GPC analysis was not done (see Figure 9).

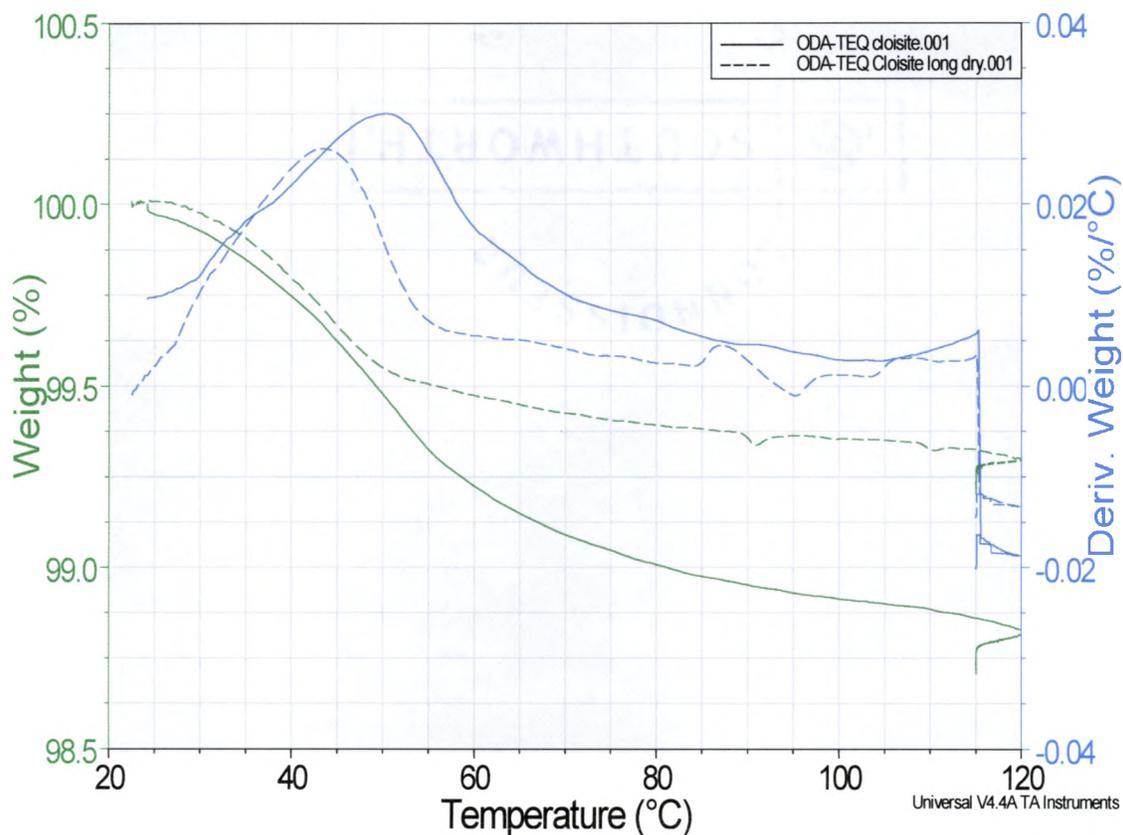


Figure 8. TGA Analysis of Dried and Vacuum-Dried TEQ/ODA Clay



Figure 9. Incomplete Nanoclay Polymerization. Notice the excess crystallized lactide with clay trapped inside along the walls of the vials.

It was also evident that proper exfoliation was not occurring due to the samples heterogeneous nature (see Figures 10 and 11).



Figure 10. Heterogeneous Clay-Polymer Mixture. Notice the darker clay regions.



Figure 11. Heterogeneous Clay-Polymer Mixture. Another angle.

3.8 Vacuum-Dried Clay Polymerization

The reason for the low molecular weights and unreacted monomer was still thought to be the presence of water in the clay structure. The clay was then placed in a 70°C vacuum oven at 30 in. Hg for five days. Further TGA analysis of this extensively dried clay indicated that it now had 1% by weight water present in the clay layers.

This next run was done with the excessively dried clay to see if the reduced H₂O content was enough to complete a polymerization without excess unreacted lactide present. The contents are shown in Table 8.

Table 8. High Molecular Weight Sample Vial Contents

Vial #23	5.0g of lactide, 0.05g of TEQ/ODA clay, 2.0mL of dried toluene, 28.0μL of 10% catalyst solution, sonicated at 20 kHz and 100W for ten minutes.
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After a three hour polymerization there was less unreacted lactide present in the reaction vial and it was a solid, indicating a level of polymerization. There are still bubbles present in the plastic from the evaporating toluene. It was observed that the clay migrated to the top of the polymer by the end of the run. This migration may possibly be from an association between the toluene bubbles and the clay as the bubbles move through the polymer.

GPC analysis showed that Vial #23 had a molecular weight of 84,661 g/mol. This peak was a much smaller peak than the oligomer and dimer peaks, but the large chains are present. This sample proved more flexible than previous PLA samples, and very

resistant to repeated blows with a mortar in an attempt to crack it open to obtain a GPC sample.

An X-ray diffraction analysis of the nanoclay sample showed that there was a level of intercalation, not necessarily exfoliation of the clay platelets (see Figure 12).

Nevertheless, further analysis was conducted to see how the properties were improved.

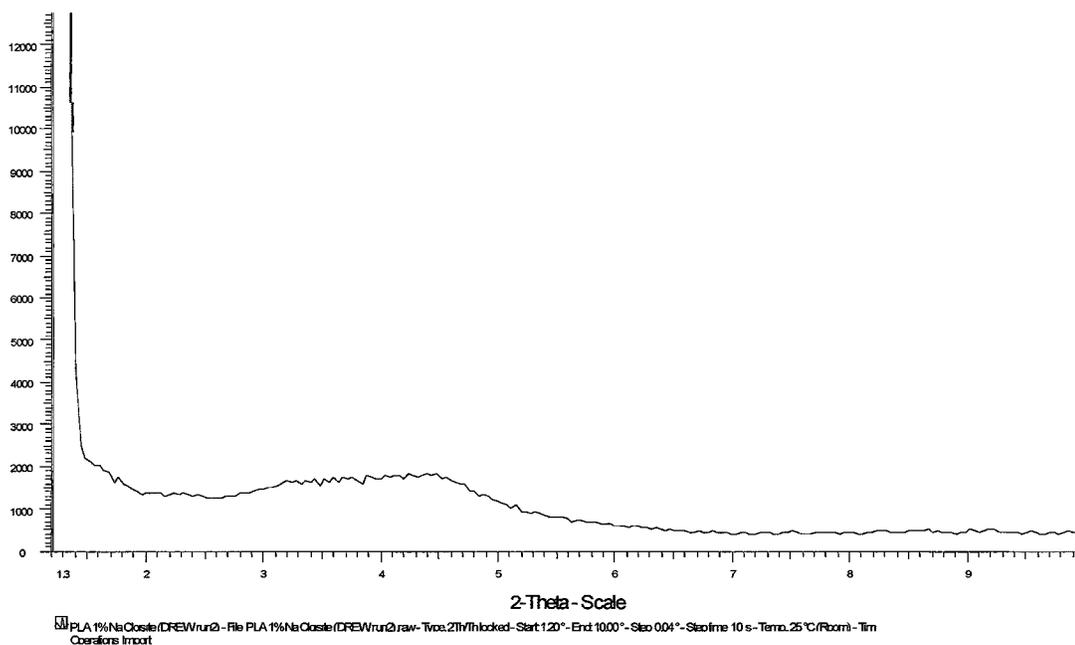


Figure 12. X-Ray Diffraction of Initial Successful Nanoclay.

The TGA analysis showed a difference in behavior of the nanoclay from the commercial PLA samples we have available (see Figure 13).

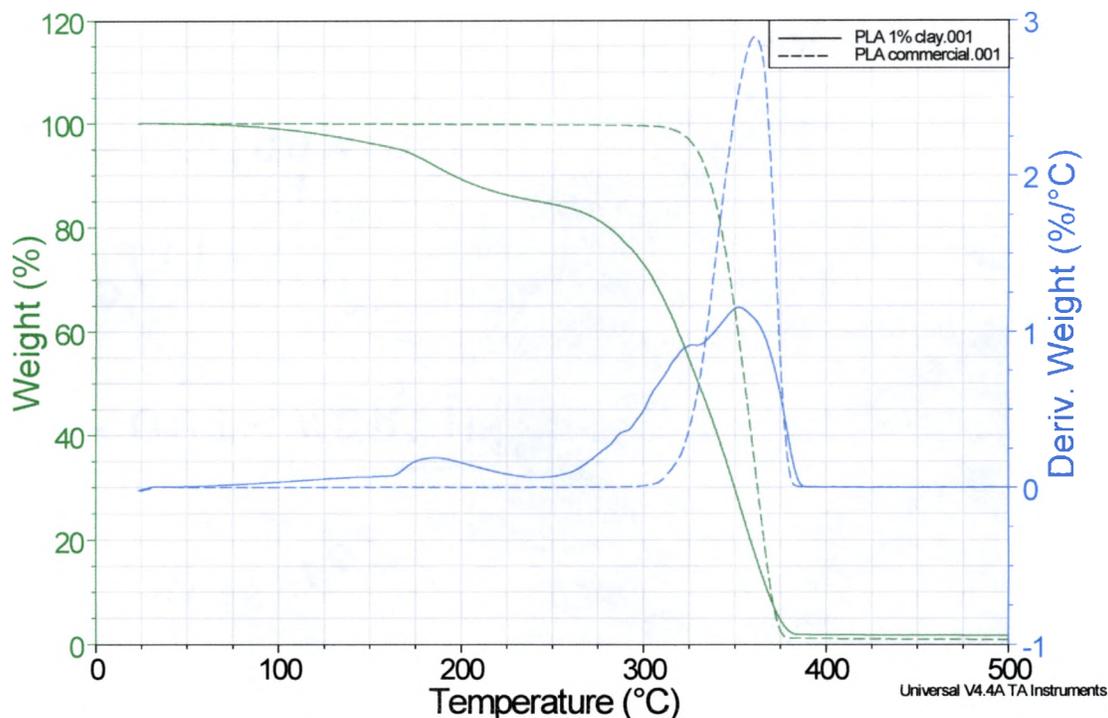


Figure 13. TGA Analysis of Nanoclay (solid) vs. Commercial PLA (dashed)

As can be seen, the 10% loss point was 140°C less in the nanoclay composite. The early decrease in weight can be attributed to toluene still present in the polymer matrix. The second decrease would be the decomposition of the surface treatment on the organoclay. After the Surface treatment of the organoclay breaks down the amine would form amides and break down the PLA.

The DSC comparison between the commercial and the nanoclay polymers showed a similar T_g for the nanoclay. But there is a definitive crystalline peak and consequent melting point in the nanoclay sample (see Figure 14).

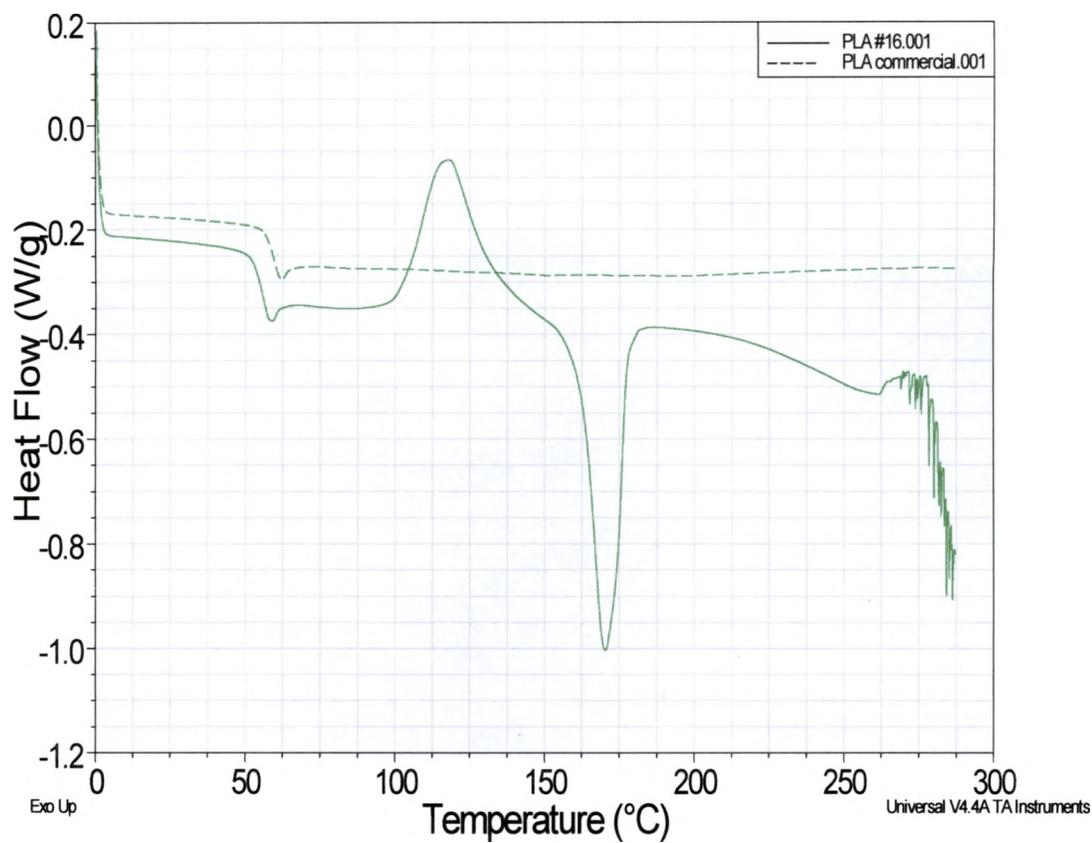


Figure 14. DSC of Nanoclay (solid) and Commercial PLA (dashed)

These findings made it very interesting to get the results from a DMA analysis of the nanoclay polymer. Dynamic mechanical analysis would be the conclusive test to determine whether the mechanical properties of the nanoclay are significantly improved over the commercial polymer (see Figure 15).

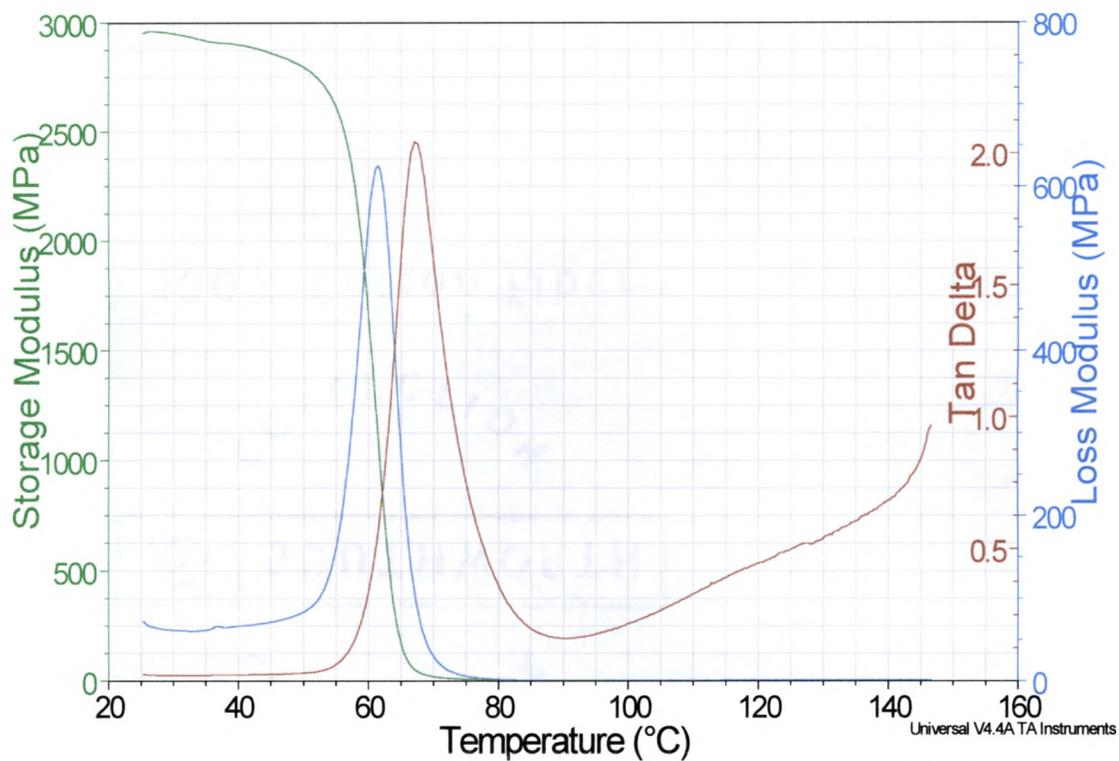


Figure 15. DMA Analysis of Commercial PLA

The X-Ray diffraction was promising as it showed much improved exfoliation over the previous nanoclay samples (see Figure 16).

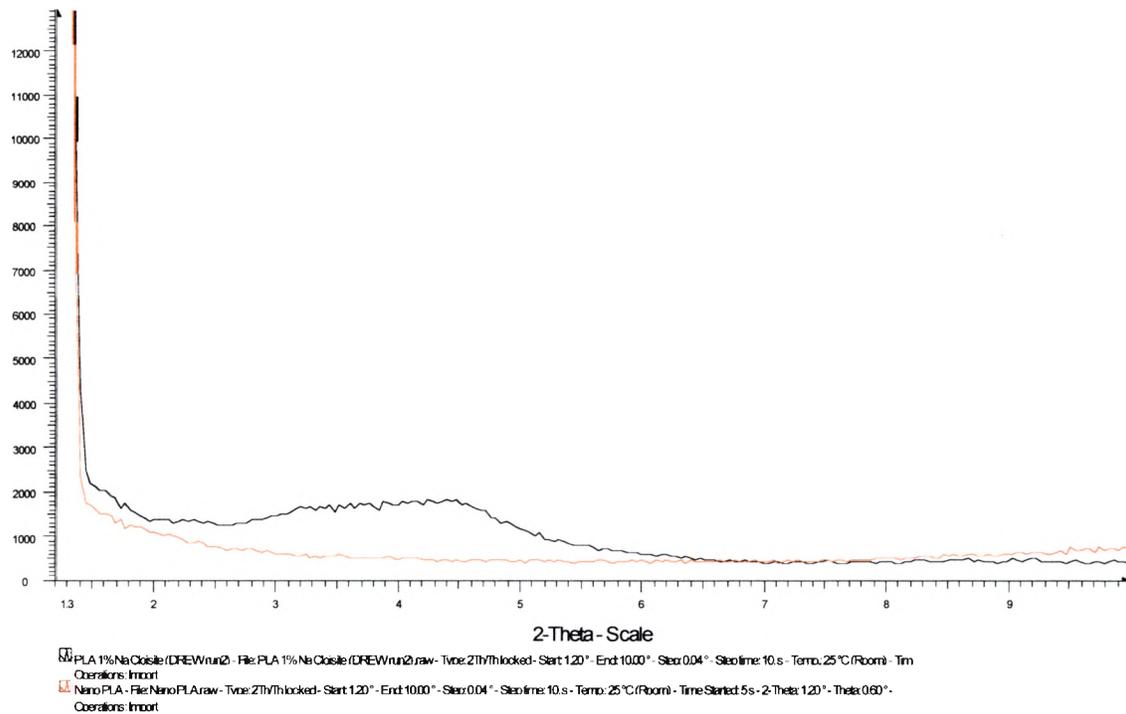


Figure 16. XRD Analysis of Initial High Molecular Weight Nanoclay (black) and the More Sonicated Sample (red)

While making the DMA bars for analysis it was difficult to clear the sample of bubbles. A DMA sample with bubbles would give inaccurate results because each gas pocket would be a point of failure as load was applied. The original sample became dark and brittle after heating too long in an oven to remove gas pockets and melt into a mold.

Because of the poor sample quality of the first attempt, another set of polymerizations was run using the same protocol as before. The only change was an increased amplitude of sonication in an attempt to improve exfoliation. Vials #24 and #25 were sonicated at 20 kHz and 100W for ten minutes. Vial #26 and #27 were sonicated at 30 kHz and 100W for ten minutes. The TGA and DSC analysis of these

samples showed that the vials with the increased amplitude of 30 kHz and 100W showed improved 10% loss and T_g values over the vials sonicated at 20 kHz and 100W (see Figures 17 and 18).

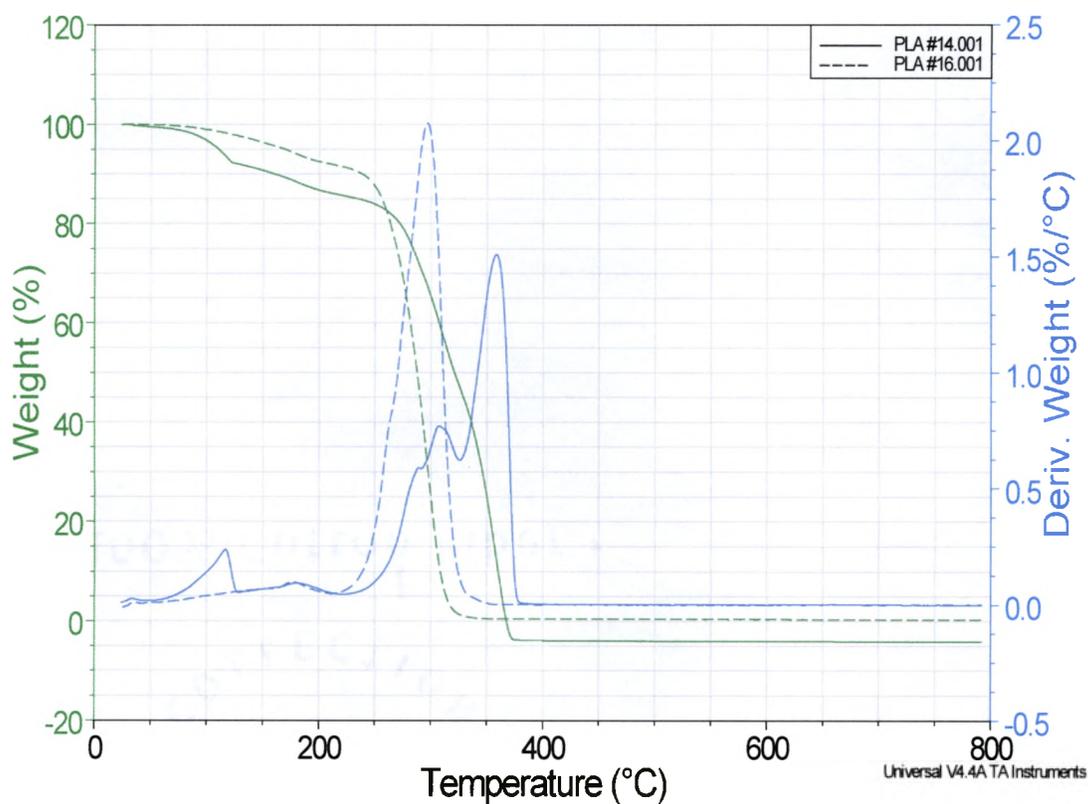


Figure 17. TGA Analysis of Samples #25 and #27.

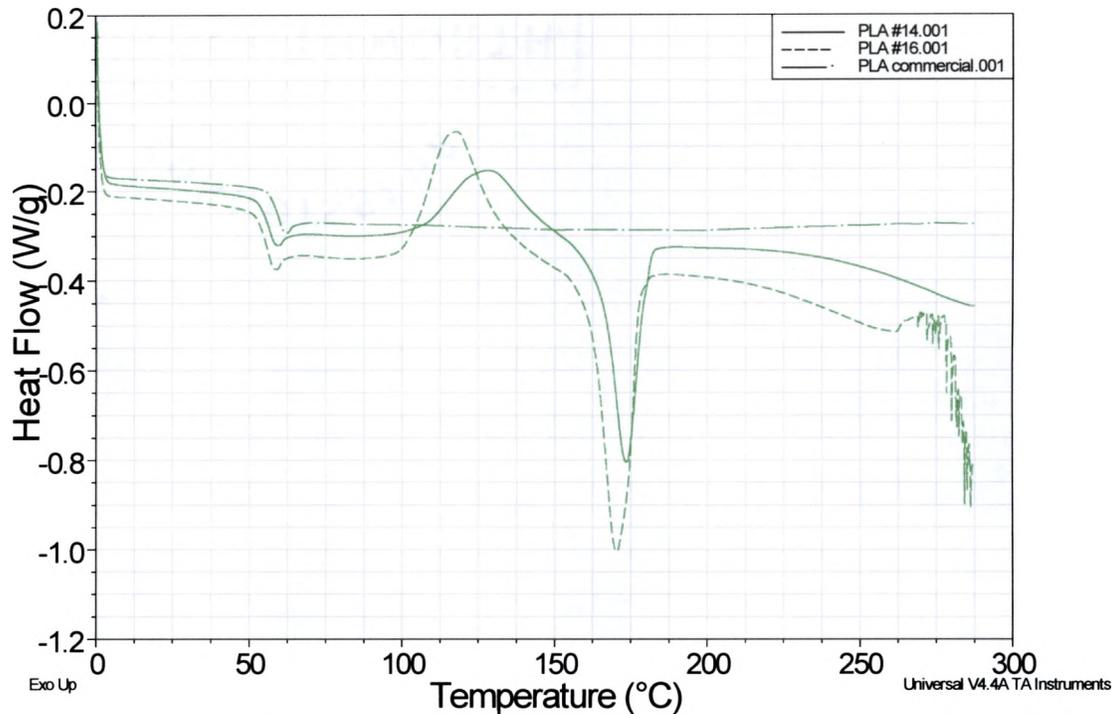


Figure 18. DSC Analysis of Commercial PLA and Vials #25 and #27. Notice the T_{gS} of all three samples are similar. The obvious difference is the presence of crystalline peaks in the nanoclays from the constrained polymer regions. Also note the earlier melting points of the nanoclay samples.

The DMA analysis shows an increase in storage modulus with a sharp decrease in loss modulus (see Figures 19 and 20). This shows an increase in stiffness for the nanoclay. This is further evidenced by the fact that the final sample of the commercial polymer was bowed and had lost its original dimensions. The nanoclay sample was run twice and maintained very close to its original dimensions. It was run twice due to the inability to retrieve the data from the first run. Being run twice may have added to the amount of crystallinity present in the polymer and affected the final analysis along with

the contaminants present from production of the sample. Though not ideal these results are promising for further research.

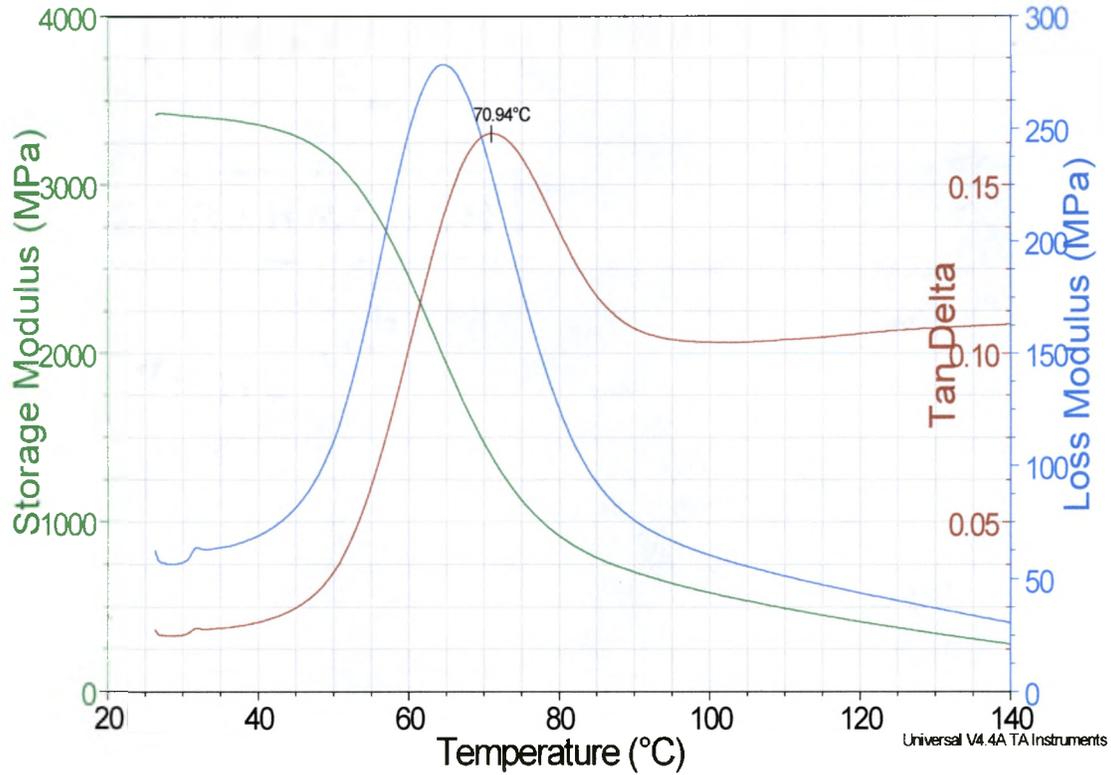


Figure 19. DMA Analysis of Nanoclay Composite. Notice an improvement in storage modulus over time.

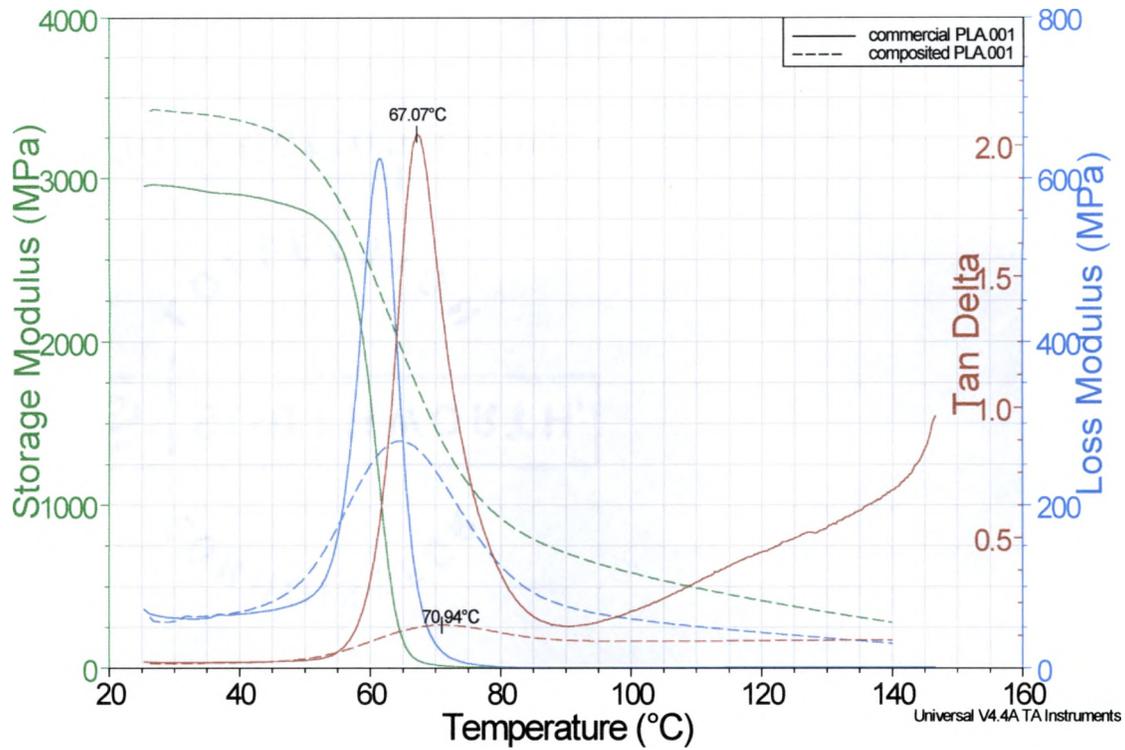


Figure 20. DMA Analysis of Both Commercial PLA (solid) and the Nanocomposite PLA (dashed). Notice the increase in storage modulus, but decrease in loss modulus.

CHAPTER 4

CONCLUSIONS

Initially the challenge of this research was polymerizing neat dimer to high molecular weight. Once the experimental procedure was modified to eliminate any laboratory atmosphere contamination, it was found that the catalyst concentration present in solution was the cause of the previously low molecular weights. Once the proper dilution was used, 96.6% of the theoretically calculated value of 200,000 g/mol was obtained. This was sufficient to continue the project by adding the organoclay to improve the thermal and mechanical properties of the neat polymer.

The first sets of polymerizations with the nanoclay were incomplete based simply on visual analysis. Several either did not polymerize or had a large percentage of crystallized monomer inside the reaction vial. It was determined that the silane-treated clay was not exfoliating properly, thereby yielding poor polymers.

The clay was changed to the TEQ/ODA sample without silane treatment. This was initially done with the intent to limit possible variables with the clay by using a simple clay/quaternary ammonium treatment. When these samples were still incomplete it was determined that excess catalyst may be required. The two proposed mechanisms of catalysis were one involving ring opening, and one involving initiation by hydroxyl groups. The proposed method to exfoliate the clay platelets was to grow the chains directly off of the clay surface. At this point excess catalyst was introduced as a variable

to determine whether the presence of the organoclay facilitated a higher concentration of catalyst in the polymerization system. Once a set of samples was run with catalyst as a variable, 40,000:1 *versus* 10,000:1, it was shown that the higher catalyst concentration did yield a better polymer.

The overwhelming obstacle to the formation of high molecular weight nanoclay composites was the presence of water within the clay galleries. It was determined that the decrease of water in the clay from 1.25% by weight to 0.70% by weight accounts for a 41.7% by weight increase in molecular weight. A large molecular weight increase was observed after the excess drying of the clay, from ~40,000 g/mol to ~80,000 g/mol, which is consistent with the calculated error from the water. This excess water likely both, catalysed ring opening and hydrolyzed the growing polymer chains hindering their growth and the subsequent overall molecular weight. It has also been shown that excess tin (II) octoate catalyst is needed in the presence of water to facilitate formation of large compounds. The water present in solution can also explain the need for excess catalyst in the nanocomposite compared to the neat polymer. High molecular weight polylactic acid nanocomposites can be polymerized only in a highly moisture-free environment.

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VITA

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