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THE EXTENT OF DEGRADATION OF POLYLACTIDE CHARACTERIZED BY
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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ABSTRACT

The effects of temperature, shear rate and residence time on the degradation of biodegradable polylactide (PLA) were studied using an injection molding machine. The extent of the degradation was characterized by analyzing the optical properties and the change in chemical structure of the processed material. A spectrophotometer was used to quantify the changes in color due to degradation and nuclear magnetic resonance (NMR) spectroscopy was performed on the degraded PLA to determine its chemical structure. Additionally, the tensile modulus of the degraded material was determined using a tensile measurement instrument. The effects of degradation on color were correlated to the chemical structure and the tensile modulus.

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INTRODUCTION

Poly lactide (PLA) is a biodegradable polymer produced from renewable resources such as corn and sugar beets. PLA has excellent mechanical properties making it ideal for packaging purposes. PLA can be made in various forms including and not limited to fibers, films, sheets, and solid objects. This means that PLA products can be produced by all of the major plastics forming processes which include blow molding, extrusion, injection molding, and thermoforming. In short, it is an extremely valuable alternative to petroleum-based polymers. However, a barrier to commercialization of PLA at this time is a severely limited production capacity which results in scarcity in the market and artificially high prices.

PLA is derived from lactic acid, which exists naturally as two enantiomers, L-lactic acid and D-lactic acid. Using either the L or the D forms of lactic acid would cause problems during synthesis of the final product. Lactic acid undergoes a condensation polymerization which forms water as a by-product. Removing the water being formed during polymerization can be difficult. Failure to remove all of the water can limit the maximum molecular weight attained due to the hydrolysis of the ester bonds. To solve this problem a cyclic dimer of lactic acid is used instead of the standard naturally occurring L and D enantiomeric forms.

The cyclic dimer of lactic acid undergoes ring opening polymerization to give Poly(lactic) acid. This form of polymerization is not a condensation reaction, and therefore does not evolve water as a by-product. Instead, ring opening polymerization is an addition polymerization process. The ring opening of cyclic lactic acid is a thermodynamically driven process caused by the relief of angle strain and the subsequent

switching of the E and Z ester conformation upon ring opening. Once the ring is opened, the addition polymerization mechanism works by way of heterolytic carbon-carbon bond cleavage. A ring opened lactic acid molecule contains two free radical electrons on carbon atoms. As another ring opens, the ends of the molecule containing the free radicals forms a carbon-carbon bond with other lactic acid molecules also containing free radicals. This process occurs until there nearly all of the available monomers have reacted. Typical polymerization conditions for PLA is the reaction of lactic acid monomer at 180-210°C and 2-5 hours to reach 95% conversion. The average molecular weight for PLA ranges from 80,000-100,000 g/mol.

The mechanism for degradation of PLA is rather simple. The polymer is aliphatic and intrinsically hydrolysable because it is a polyester. Upon exposure to heat and water, the polymer breaks down into low molecular weight oligomers. Further degradation of PLA occurs by microbial attack on the fragmented chain ends to produce lactic acid and ultimately CO₂ and water.

PLA has a melting point of 177-193°C. The glass transition temperature, or temperature at which the polymer chains begin to gyrate and move and the polymer softens, occurs at 56-58°C. This means that PLA will remain rigid under normal packaging and manufacturing conditions. The thermal expansion coefficient is 126-145µstrain/°C. Finally, the specific heat for the polymer is 1180-1210 J/kgK.

Mechanically, PLA is about as rigid as PET. It has a tensile modulus, the customary measure of stiffness, of 3540-3830 MPa. The ultimate tensile strength for PLA ranges from 48-60 MPa. The ultimate tensile strength is the nominal stress at which a round bar of the material, loaded in tension, separates. Interestingly enough, the

compressive strength of PLA also ranges from 48-60 MPa. The compressive strength measures the force required to deform the polymer in a crushing manner. The next property that is often considered is the flexural strength or modulus of rupture for the polymer. The flexural strength is a measure of the maximum surface stress in a bent beam at the instant of failure. The flexural strength of PLA ranges from 81-99 MPa. PLA can elongate 2-6% before fracture. Finally, in its standard semi-crystalline state, PLA's density ranges from 1.37-1.49 g/cm³.

PLA has many other remarkable properties. Namely, PLA proves to have reasonable chemical resistance to many solvents. It has good resistance to attack by weak acids and bases; however, PLA degrades significantly when exposed to strong acids and bases. PLA is listed as having average resistance to degradation due to organic solvents. However, it has proven to dissolve readily in acetonitrile, toluene, ethyl acetate, acetone, tetrahydrofuran, and methylene chloride. PLA has poor resistance to ultraviolet light and oxidizes readily at 500°C.

While PLA has many excellent physical properties, its distinguishing feature is its sustainability. It takes 20-50% less energy to produce PLA as it does conventional plastics. This means that 2-5 times more PLA can be produced as compared to petrochemical-derived plastics using the same amount of energy. Furthermore, PLA evolves a small amount of CO₂ when it biodegrades in the environment which is actually balanced out by the fact that the feedstock uses the CO₂ for respiration and photosynthesis. This means that PLA leaves a very small CO₂ footprint on the environment. The CO₂ footprint for PLA is 0.3-0.35 kg/kg. For comparison purposes, the CO₂ footprint for polypropylene, a very common packaging material, is 2.69-2.98

kg/kg.

In summation, PLA offers many appealing physical properties which include a naturally soft feel, stain and soil resistance, low smoke generation when burned, excellent dead fold and twist retention, colorability, high tensile modulus, high yield strength, unique properties in its amorphous and semi-crystalline phases, and ultimately its inherent biodegradability and sustainability.

THEORY

Traditionally, as plastics are heated and sheared to the point where they degrade, their viscosity decreases dramatically. However, based on the chemical composition of PLA, it is likely that cross-linking reactions occur between the polymer chains. Cross-linking likely occurs by two possible mechanisms. One possible mechanism for cross-linking occurs by way of polymer chain scission due to excessive heat and shearing. Chain scission forms a reactive carbocation. The carbocation acts as a nucleophile which reacts with a nearby polymer chain, thus connecting the two individual chains. The second proposed mechanism for cross-linking occurs through a process known as transesterification. Transesterification occurs by exchanging an alkoxy group from one polymer chain with one from another polymer chain. Under normal conditions, the lactic acid polymer chains conform to regular helical pattern. A transesterification reaction would link the closely packed helical lactic acid chains to one another. If cross-linking reactions do take place in PLA, the viscosity will increase orders of magnitude when compared with uncross-linked PLA. Cross-linking reactions in PLA would likely be initiated by excessive thermal energy caused by increased temperature or shear rates. If this is the case, further limitations will be placed on the processing conditions when producing PLA parts. This limitation comes in addition to the already limited processing window before degradation occurs.

Saturation of PLA with water is the primary mechanism through which degradation occurs. As mentioned, PLA is naturally hydrophilic due to polar oxygen atoms and –OH groups which terminate the polymer chains. Water acts to break down the polymer chains, as well as provides an environment for which microbes can grow.

The microbes will further break down and degrade PLA by actually consuming the polymer. The duration of PLA's degradation period can be affected by the temperature and relative amount of water present in the polymer during degradation. To increase the amount of water present in PLA, hydrophilic additives could be added. The hydrophilic additives would act to absorb more water from the environment than was possible with PLA's natural hydrophilicity.

This degradation, either through hydrophilic and microbial degradation or degradation from excessive heat and shear, causes PLA to yellow significantly. In fact, the degree of yellowness is proportional to the amount of degradation that the polymer has undergone. This is an important due to the fact that its use is a function of PLA's ease of processability and appeal to consumers. If PLA degrades and yellows too significantly during processing, its use will be limited because it will be unmarketable. Therefore, it is important to establish boundaries or a processing window in which acceptable parts can be produced and sold.

Establishment of this processing window was completed by correlating an exact color measurement to the degree of degradation experienced by the PLA. The model for color measurement was the CIE 1976 color space model whose coordinates are L^* , a^* and b^* . This model was derived from the previous model created by the International Commission on Illumination (CIE) in 1931. Through the study of the perception of color, mathematically defined coordinates of are plotted in 3-space as XYZ components called color spaces.^[4] If the coordinates of L^* , a^* , and b^* were replaced with the XYZ coordinates, a resulting 3-dimensional coordinate system would result where a^* is the measure of green (-a) to red (+a), b^* is a measure of blue (-b) to yellow (+b) and L^* is a

measure of brightness (0-100). From this, a ΔE value can be calculated. It is a color difference index calculated as the square root of the sum of the squares of the color difference of the three dimensions of color space. A ΔE of greater than one can be perceived by the human eye as a change in color. In this way, a specific color identity can be assigned to the degraded PLA parts. Furthermore, this color identity can be used to correlate the amount of degradation of PLA to the perceived color as a visual indicator of the relative mechanical properties of the material at that level of degradation.

EXPERIMENTAL PROCEDURE

Before any testing was performed, an Arburg 270S was used to injection mold samples from NatureWorks® 3051D Polylactide. A single cavity mold with a cold runner was used to mold circular disks. The edge gated 64mm diameter, 1mm thick disks were chosen because they could be easily analyzed with a spectrophotometer. The injection molding process for the disk was generated using a two-stage startup procedure.

After establishing a baseline and allowing it to stabilize, five specimens were collected. The nozzle temperature was then increased from 195°C to 215°C and another five specimens were collected after the process stabilized. This process was repeated to obtain samples for nozzle temperature settings of 235°C, 255°C, and 275°C. After collecting all samples, the temperature was returned to 195°C.

Shear rate was modified next, by modifying the injection rate. The baseline process had an injection rate of 27 cc/s. This was increased to achieve injection rates of 46 cc/s, 64 cc/s, and 82 cc/s. Five samples were collected for each injection rate. Moldflow® analysis was performed to determine the shear rates. The shear rates corresponding with the injection rates are as follows:

| Run | Injection Rate | Shear Rate |
|-----|--------------------|-------------------|
| 1 | 27 cc/s (baseline) | 8230/s (baseline) |
| 2 | 46 cc/s | 16200/s |
| 3 | 64 cc/s | 24960/s |
| 4 | 82 cc/s | 34350/s |

To modify the residence time, cooling time was increased which increased the overall cycle time. The baseline process had a cycle time of 40s. This was increased to 80s, and five specimens were collected after allowing the process to stabilize. This was repeated to achieve cycle times of 120s and 160s.

| Run | Cycle Time | Residence Time |
|------------|-------------------|-----------------------|
| 1 | 40 s (baseline) | 6 min (baseline) |
| 2 | 80 s | 12 min |
| 3 | 120 s | 18 min |
| 4 | 160 s | 24 min |

After all samples were molded, the parts were allowed to normalize for 24 hours.

The color was then measured using a Konica Minolta Spectrophotometer.

Once the color of the degraded samples was measured, Nuclear Magnetic Resonance (NMR) spectroscopy experiments were performed on them. For each processing variable, 0.010 grams of degraded PLA was dissolved in 0.010 L of deuterated tetrahydrofuran (THF). The dissolved samples were tested using a Bruker Advance II-400 MHz NMR spectrometer. The spectra obtained were analyzed and compared to the color data for the respective processing variable.

Finally, the disks were machined on an end mill to form bars that were 64 mm long, 24 mm wide, and 1 mm thick. Each bar was tested on the Instron 4400R Tensile Tester to determine the tensile modulus and elongation relative to the other bars.

RESULTS

Figure 1: Brightness (L) with Respect to Temperature, Residence Time and Shear Rate

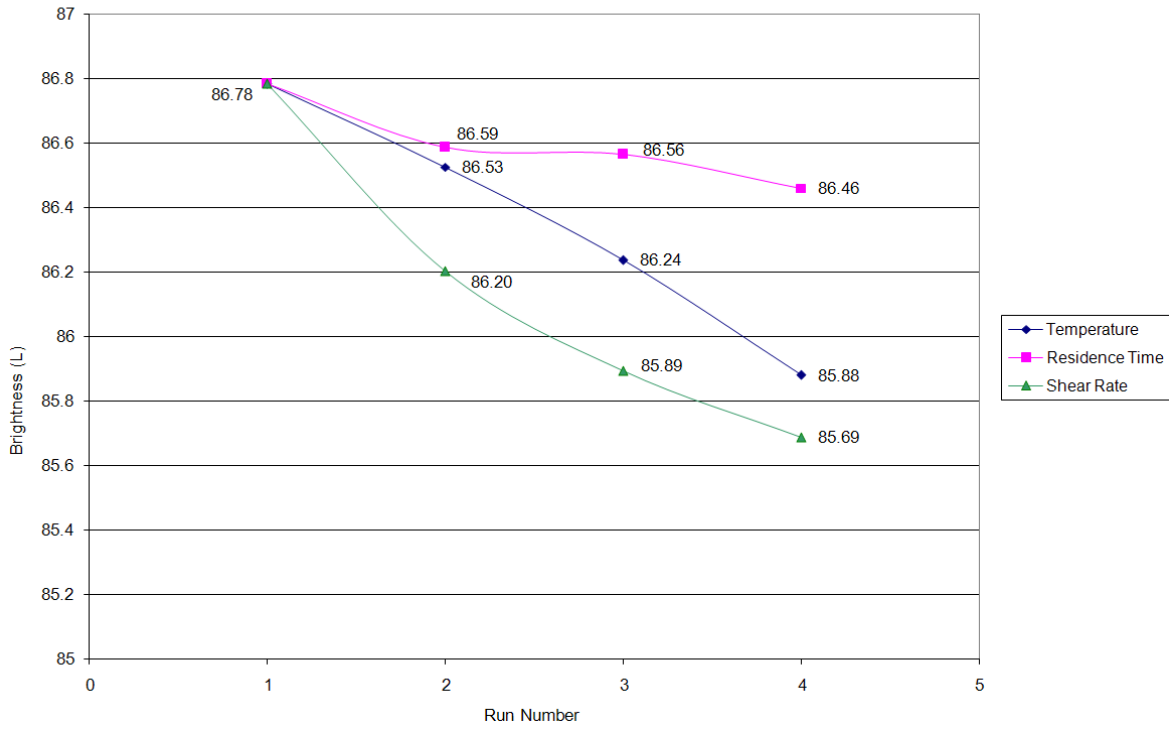


Figure 2: Blue (-b) to Yellow (+b) Shift with Respect to Temperature, Residence Time and Shear Rate

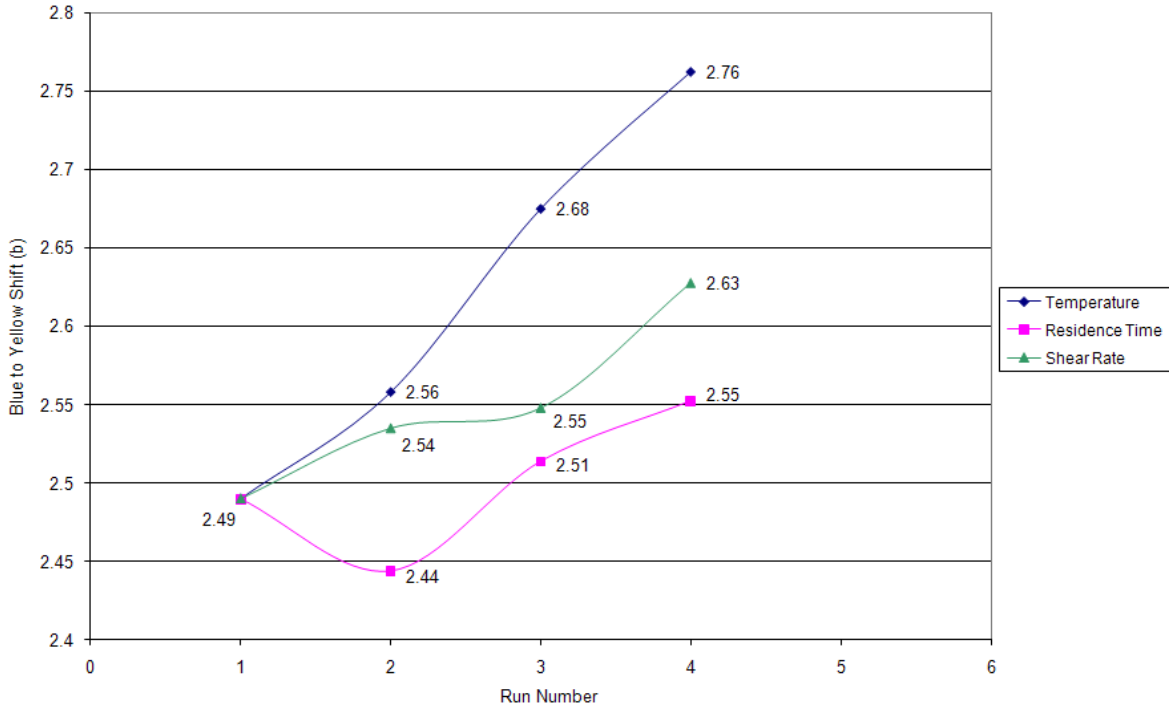
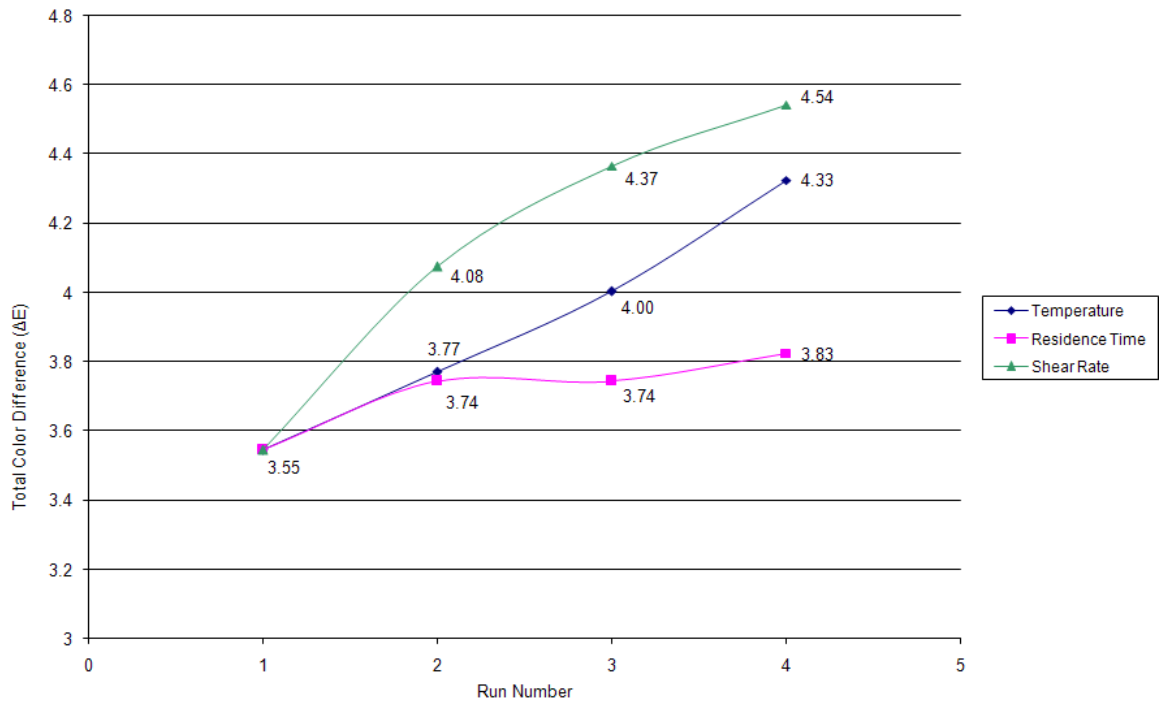


Figure 3: Total Color Difference (ΔE) with Respect to Temperature, Residence Time and Shear Rate



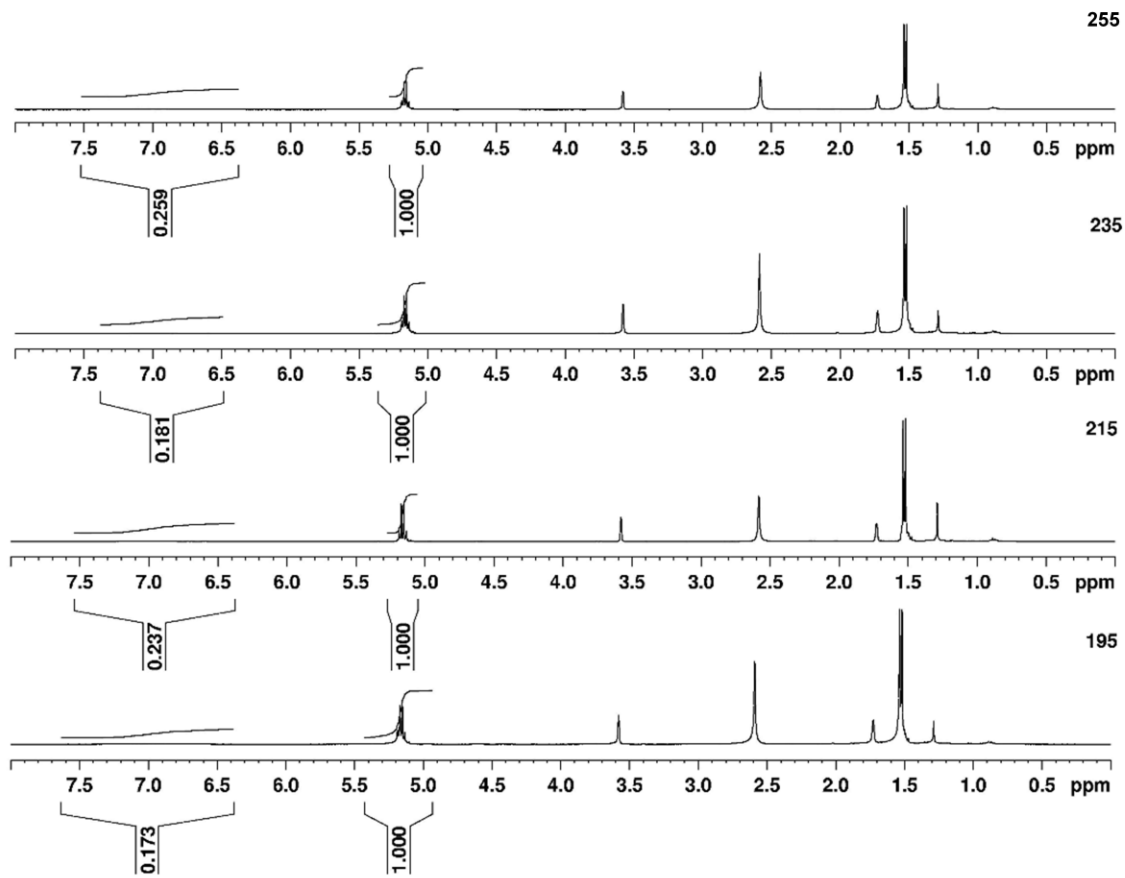


Figure 4: NMR Spectra Comparing the Chemical Changes in Temperature for the PLA Samples.

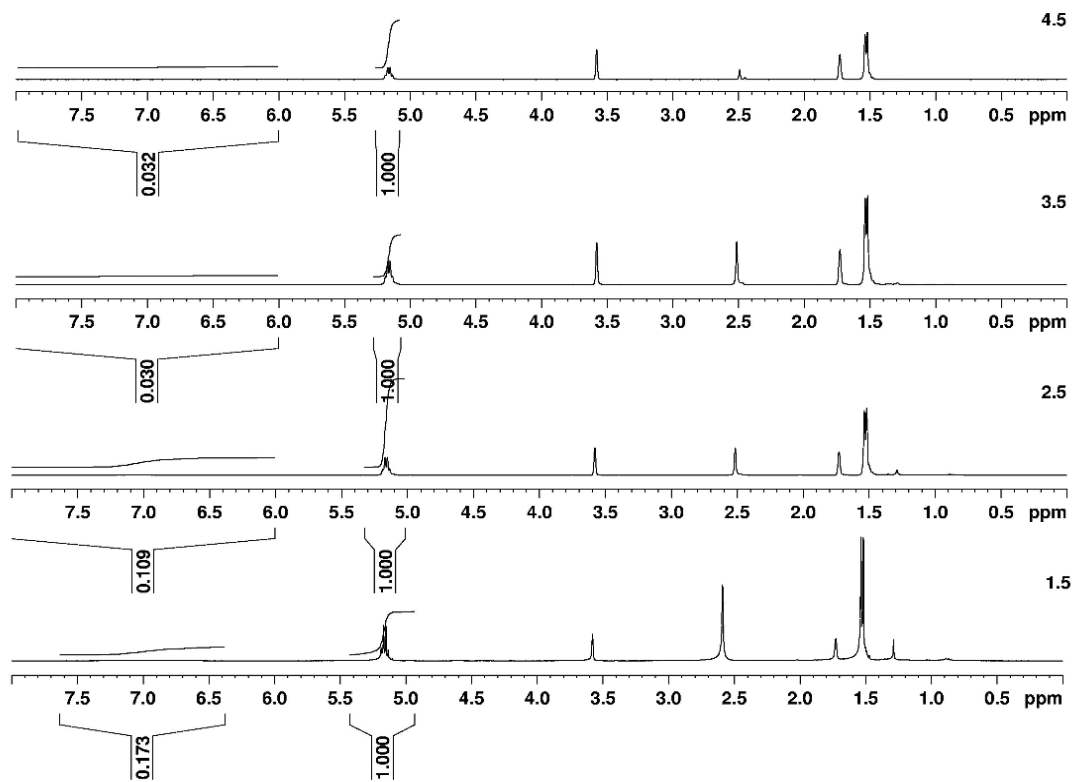


Figure 5: NMR Spectra Comparing the Chemical Changes in Injection Speed for the PLA Samples.

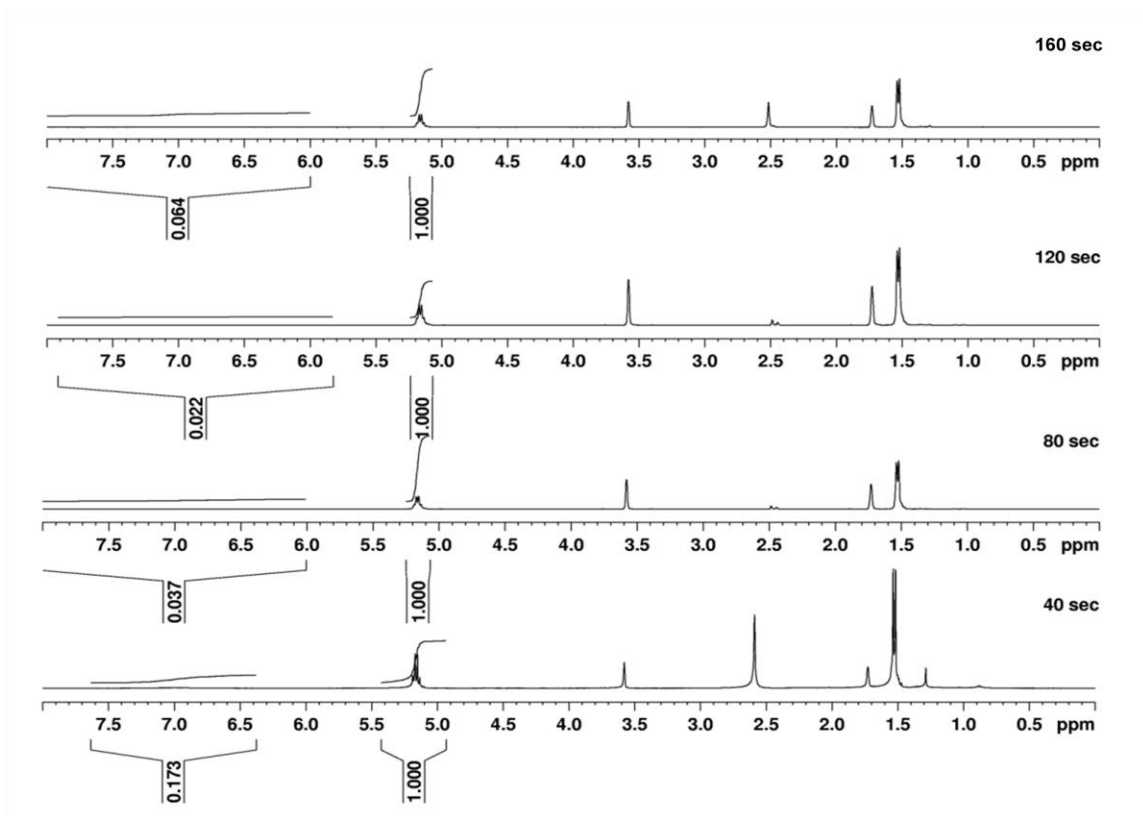


Figure 6: NMR Spectra Comparing the Chemical Changes in Cycle Time for the PLA Samples.

Figure 7: Effects of Temperature on Tensile Modulus

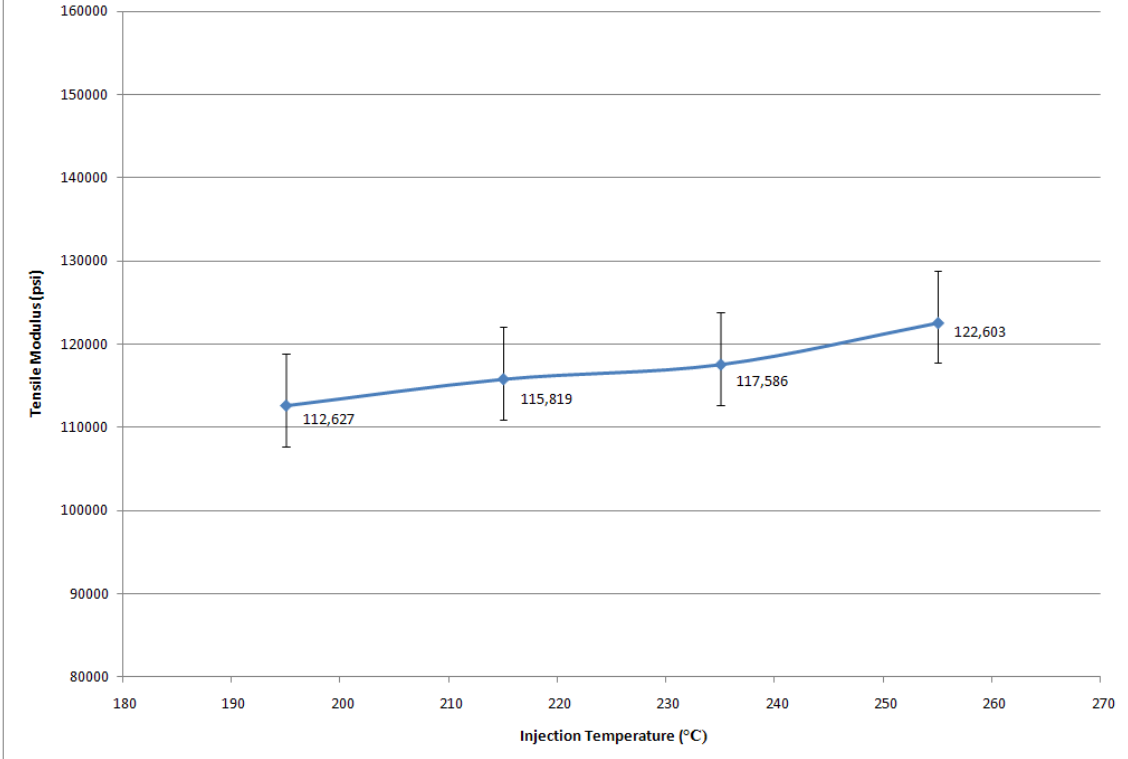


Figure 8: Effects of Injection Speed on Tensile Modulus

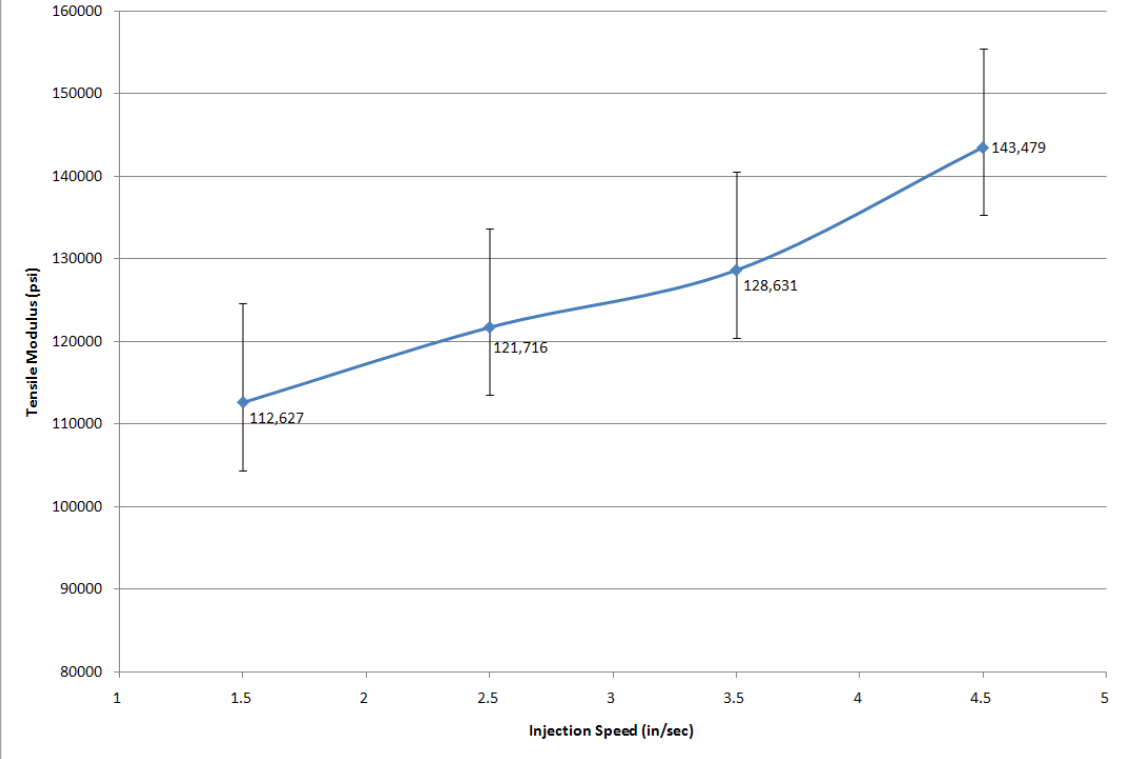
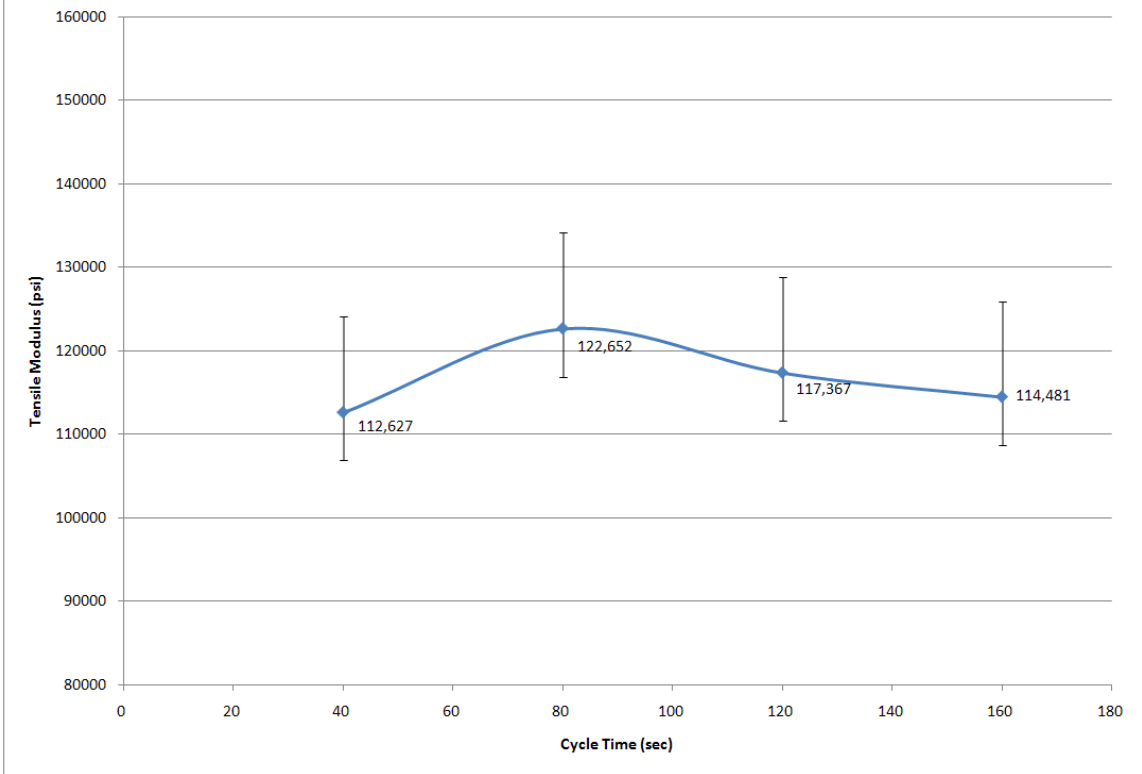


Figure 9: Effects of Cycle Time on Tensile Modulus



DISCUSSION

The injection molded specimens showed slight color shifts after analysis with a spectrophotometer. As temperature, shear rate, and time increased, there was a corresponding decrease in the L value (see figure 1). The b value increased as the test parameters increased (see figure 2). Delta E also increased as the temperature, shear rate, and time increased (see figure 3). This indicates that there was a change in the polymer on a molecular level.

The decrease in L indicates that the brightness of the specimens shifted from slightly more white to slightly more black. The shift was most significant with the increased shear rate.

In all instances, b increased as the test factors were increased. An increase in b indicates that the color shifted to a slightly more yellow state. As molecular chains split due to degradation, the polymer yellows more. The temperature caused the most significant increase in b, with a change of 0.27. This was followed by residence time, which increased 0.14. Cycle time had a slight decrease, before increasing 0.06. For cross-linking to occur in PLA, chain scission must first occur. These results imply that temperature (within the tested range) caused the highest rate of chain scission when increased followed by shear rate, then residence time.

Delta E increased as all test parameters increased, indicating an increase in total color. The most significant change in color was observed when changing shear rate. This was followed by temperature and residence time respectively.

NMR data is interpreted based on the integration of the peaks that correspond to a particular chemical feature on the molecule being tested. See figures 4-6 for the NMR

data. The doublet at 1.53 ppm corresponds to the $-\text{CH}_3$ group, the quartet at 5.15 ppm corresponds to the $-\text{CH}$ group, and the broad peak between 6.5 and 7.5 ppm corresponds to the $-\text{OH}$ group at the chain ends. By standardizing the quartet at 5.15 ppm to have an integration value of 1.000, the relative amount of $-\text{OH}$ groups were determined for the samples.

Increasing the temperature had the largest effect on the shift in yellowness as well as the relative amount of $-\text{OH}$ groups present in the polymer. However, the NMR results for the changes in temperature prove to be inconclusive. The samples molded at 195°C had the fewest $-\text{OH}$ groups. By comparison, the samples molded at 255°C had the most $-\text{OH}$ groups and therefore the most chain ends. However, the results obtained from the samples molded at 215°C and 235°C proved to be questionable. Due to the expense of the deuterated THF, further testing on these samples was unable to be conducted.

Increasing the shear rate had the largest effect on the total color change and the second largest effect on the change in yellowness. The PLA samples that were processed with an injection speed of 27 cc/sec had the most $-\text{OH}$ groups and therefore the most chain ends. The samples processed at 46cc/sec contained the second $-\text{OH}$ groups. The samples processed at 64 cc/sec and 82 cc/sec showed to have essentially no $-\text{OH}$ groups present. Having less $-\text{OH}$ groups present means that there are less chain ends. The reduction in chain ends could be due to cross-linking or lengthening of the chain by reaction at the reactive $-\text{OH}$ chain ends.

The residence time had the least significant effect on the yellowness and total color change. The samples processed with a cycle time of 40 seconds contained the most $-\text{OH}$ groups. The samples processed with times of 80, 120, and 160 seconds contained

essentially no –OH groups.

The tensile modulus (Young's modulus) was measured for the bars of PLA that were machined from the original disks. Injection speed proved to be the variable that had the largest effect on the tensile modulus. On average, the tensile modulus increased from 772 MPa at an injection speed of 27 cc/sec to 990 MPa at an injection speed of 82 cc/sec. See figure 8.

Temperature had the second largest effect on the tensile modulus. The difference in the tensile modulus of the baseline at 195°C and the highest temperature of 255°C was much less than the difference in the minimum and maximum injection speeds. The tensile modulus increased from 772 MPa to 846 MPa. See figure 7.

Residence time had the smallest effect on the tensile modulus. Additionally, there did not appear to be a distinguishable trend for the tensile data obtained from the samples which varied in residence time. See figure 9.

CONCLUSIONS

There did not seem to be a connection between the NMR data and the color data that was obtained. The PLA samples that were degraded at high temperature showed to have the largest degree of yellowness and also the most chain ends. The PLA samples that were subjected to the largest shear rates had the second highest degree of yellowness; however they showed to have the least number of chain ends. Therefore, a direct link between NMR results and yellowness could not be made.

Based on the NMR data alone, distinct conclusions can be drawn. The PLA sample that was tested at 195°C had the fewest chain ends because the sample was not breaking down under excessive heat. At 255°C, the PLA sample had the most chain ends because the heat supplied was enough to break down long polymer chains into smaller ones. At temperatures in excess of 250°C, many organic molecules break down because the thermal energy is enough to break the covalent bonds between the atoms.

The reduction in chain ends for the PLA samples tested at high shear rates and long residence times is likely due to an improved mixing process. An improved mixing process would allow smaller chains to react at chain ends to form larger polymer chains with less chain ends present.

The tensile modulus data showed trends for the PLA samples that varied with temperature and shear rate. The tensile modulus is much lower than it should be due to an improper tensile bar design. However, the data is useful in comparing results relative to the other PLA samples tested.

As the shear rates increased, the tensile modulus increased. This is due to the fact that an increased shear rate increases the number of polymer chains in the direction of

flow.

As the temperature increased, the tensile modulus increased. However, the modulus did not increase as significantly as it did when the shear rate was increased. An increase in temperature caused the polymer to be more brittle and thus have an increased modulus.

This study sought to understand the mechanism for yellowness from a chemical standpoint and to link this yellowness to a degree of degradation that could be observed through a sample's mechanical properties. However, it was proven by this study that the problem of yellowness can not be directly linked to subtle changes in the chemical structure of PLA, as revealed by the NMR results. Furthermore, the mechanical properties of the PLA bars behaved as expected given the processing conditions. The connection between yellowness, degradation, mechanical properties and chemical structure is not well understood. This study ultimately concludes that NMR and mechanical data is simply not enough to understand and predict the complex problem of yellowness and degradation.

REFERENCES

- [1] NatureWorks LLC, *NatureWorks PLA Polymer3051D Injection Molding Process Guide* pp. 1 (2005).
- [2] Y. Durant, Recent Developments on Polylactic Acid, Advanced Polymer Laboratory, U. New Hampshire, 2006.
- [3] J. Hilborn, N. Revagade, B. Gupta, Poly(lactic acid) fiber: An overview. *Prog. Polym. Sci.* 32 (2007) 455-482.
- [4] CIE (1931). *Commission Internationale de l'Eclairage Proceedings*. Cambridge University Press, Cambridge.

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