Photooxidation of Biopolymers

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Abstract: The lack of degradation of plastic products have imposed problems in the preservation of natural environments and their ecosystems through plastic accumulation. This collection of plastics promotes toxin exposure to wildlife, finding its way into the food chain, affecting both land and marine ecosystems. The project goal is to understand the degradation mechanisms of biodegradable materials and other comparable materials through UV radiation testing. Polylactide (PLA) films and polycarbonate (PC) films will be compared for their relative deterioration from constant UV radiation in a Q-U-V accelerated weather tester for 28 days. Five 3” by 5” samples of 14 mil thick and 16 mil thick PLA films along with 15 mil thick PC films were prepared for ultraviolet exposure. Mechanical and microstructural property changes will be monitored by tensile testing using ASTM D882 procedure, differential scanning calorimetry, and FT-infrared spectroscopy. Based on preliminary observations, there are no signs suggesting PLA will degrade to a greater extent than PC.

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1. Introduction

It is important to understand the full range of materials that can be used in the materials engineering community. The increased interest to understand the degradation of biopolymers stems for the rise in accessibility of products and the wide range of applications plastics in general contribute to contribute to. From transportation vehicles, telecommunications devices, biomedical devices, fashion, clothing, food accessibility, and packing plastics have a major influence. Over 98% of the plastics produced are synthetic polymers and derived from petroleum base resources. Some motivation to find alternatives to oil-based plastics is that oil is a finite resources and oil mining has a harsh impact on the ecosystems in which takes place in. Synthetic polymers lead to solid waste that can wind up in unwanted places. It has been estimated by that about 10 million metric tons of plastic waste enter the ocean from 192 coastal countries bordered by Atlantic, Pacific, and Indian Oceans as well as the Mediterranean and Black seas. It is also estimated that the amount of plastic waste that will enter these countries with increase by one order of magnitude.[1] Many plastics are promoted as being inert to biological systems, but many times plastics are made with plasticizers that can cause organ disfunction. Materials such as Polycarbonate have bisphenol A which is know to affect the endocrine system.[2] It has also been estimated that 100,000 marine animals and 1-2 million birds are killed from synthetic polymer waste.[1]

There has been a rise in the interest to provide replacements to polymeric materials derived from traditional nonrenewable resources to more innovative materials like biopolymers. These polymers are made to degrade more readily in order to help reduce their impact on natural environments. More accurately biodegradable polymers are defined as polymers that undergo chemical conversion of the carbon in the polymer sample to carbon dioxide or methane, water and residue.[3] Theses biodegradable materials can be made from bio-based materials or petroleum. Although still attractive alternatives, petroleum-based biopolymers are less favorable because of their sourcing and contribution of green-house gases. The applications of biopolymers range from being packaging, medical devices, 3-D printing, to agricultural applications and more. Their degradation, however, can be defined differently by many different ASTM and ISO standards that explore the amount of disintegration that occurs under composting condition over an allotted time. Some biopolymers degrade with the assistance of microorganisms like fungi, bacteria, or enzymes. A non-biological forms of degradation cause deterioration to biopolymers through physical action like hydrolysis, or photooxidation, especially if a material has been improperly disposed of. There are very specific ways to cause optimal biodegradation but there are many products such as plastic bottles, films, and other waste that fails to make it to the proper end of life process. It is reported by Laura Parker from National Geographic that only about 9% of the plastic produced yearly ends up in the proper waste stream or recycled.[4] This leaves many plastics in unwanted places for extended periods of time because of their ear resistance and durablitly. It is interesting to understand the mechanism of comparable materials that photo degrade and how physical alterations can affect mechanical properties. A change in these properties can showcase weather or not there is any benefit to employing biodegradable materials, especially if they are not recycled or properly reused through proper waste streams and end of life cycles. Photodegradable plastics can be thought of as polymers that breakdown in the presence of ultraviolet (UV) radiation. There are many ways to accelerate this process like adding fillers such as $CaSO_4$ to PLA.[5] For now we only will deal with general polylactic acid transparent films as well as unfilled transparent polycarbonate films.

1.1 Polylactic acid photooxidation

Poly lactic acid is an aliphatic polyester with beneficial properties such as high mechanical strength, excellent for thermo, biocompatibility, and being renewably sourced. Some of the downsides are that PLA is inherently brittle, has low water vapor barrier properties, and low thermal capacities. Chemical structure of PLA is ($C_3H_4O_2$) and is a polyester that can take on two forms known as *L and D.* Poly-*L*-lactide is the more abundant form of PLA and is known for degrading under compost conditions. PLA is derived from renewable sources such as corn, sugar, and rice. In the united states it is primarily made of corn. Corn is first made into glucose and later to lactic acid via bacterial processes. Lactic acid is then fermented to lactide and then goes through a ring opening polymerization.[3] A PLA molecule is shown in Figure 1.

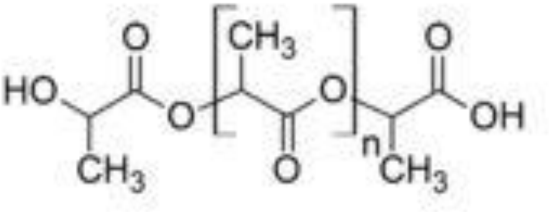

Figure 1. A polylactic acid molecule showing the simplest form of the polymer.

It has been shown that the photooxidation of PLA follows a mechanism now as the Norrish reaction in which the absorption of ultraviolet A and ultraviolet B rays initiate degradation in the presence of oxygen. The irradiation of light with wavelengths above

300 nm and less than about 415 nm causes a tertiary carbon of the ester functional group in PLA to radicalize. This compound is then reacted with oxygen gas to form a peroxy radical and as hydrogen is removed from the PLA chain there is a hydroperoxide formed. This metastable molecule undergoes a chain reaction by β-scission. β-scission can be defined as the splitting of a carbon-carbon bond in a hydrocarbon backbone chain to form a olefin and a free radical. There is a series of possible products from the mechanism. It would be ideal to try and search for these using FTIR spectroscopy, but it has been found that these molecules shown in figure 2.[5] can be found using size-exclusion chromatography.

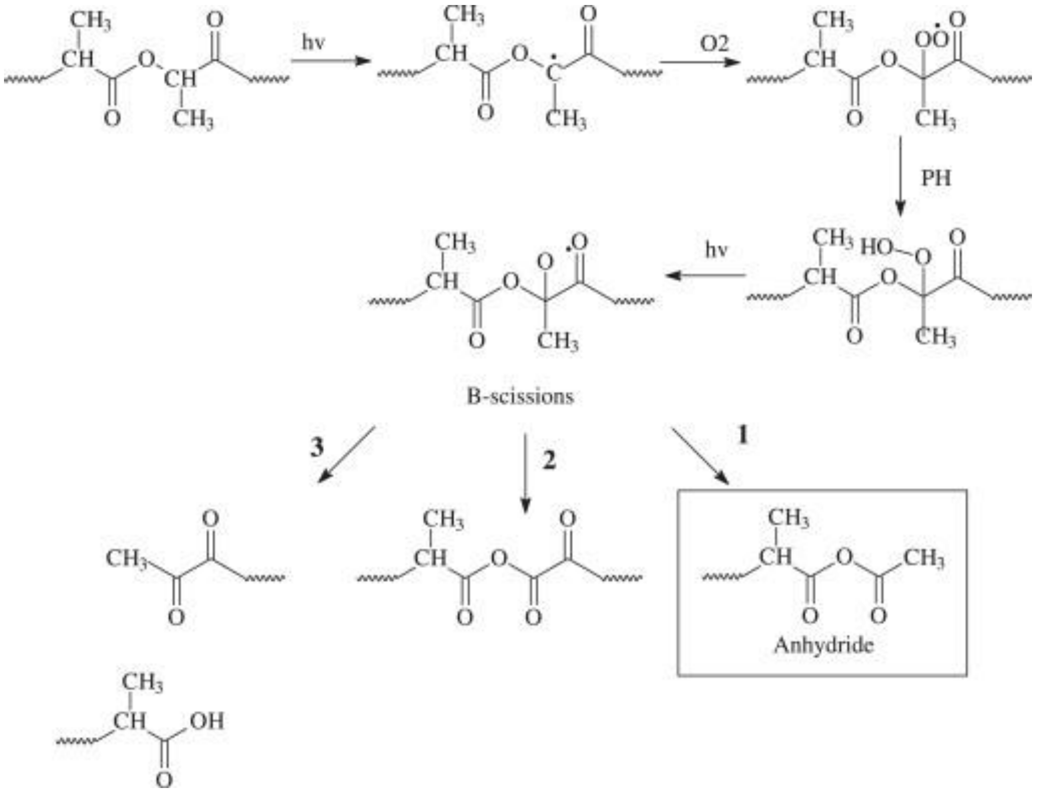

Figure 2. The photooxidation mechanism of PLA through the Norrish reaction.[5]

1.2 Polycarbonate photooxidation

Polycarbonate is a material know to be used ubiquitously used for a variety of applications including safety visors, water bottles, baby bottles, and lenses for glasses. It can also be used for other one time use plastics for packaging. Polycarbonate (PC) is a tough thermoplastic and is one of the top produced engineering resin due to a wide thermal capability. Another key characteristic of PC is that it is transparent, and has good impact resistance. PC is produced by the reaction of bisphenol A and $COCl_2$. It was also found that there is a decrease in mechanical properties due to the exposure of PC samples to UV radiation. An operation that helps determine this is micro-hardness testing with Vickers indentations. It was also found to correlate to a change in the glass transition temperature and confirmed using AMF nanoscale thermal analysis. The glass transition temperature was found to increase to 143 ˚C after just 10 days (225 hours) of UV exposure.[6] There has been studies that have dedicated to the photooxidation of PC and have found that the mechanism of the degradation can be summarized by Figure 3. The process can be broken down into the absorption of light energy by the chromomorphic funtional groups, characterized by their conjugated carbon-carbon double bonds. This promotes the formation of a radical and the abstraction of a hydrogen atom. A peroxy radical is formed from the reation with oxygen or a crosslinking occurs. A more stable route is the formation of a teritary radical where the also known as an isomerization. The peroxides formed in the reaction then go through β-scission to split the main backbone. This can form a variety of products that include ketones, carboxylic acids, and esters. The mechanism can be seen in Figure 3 which shows the breakdown from polycarbonate to smaller molecules.

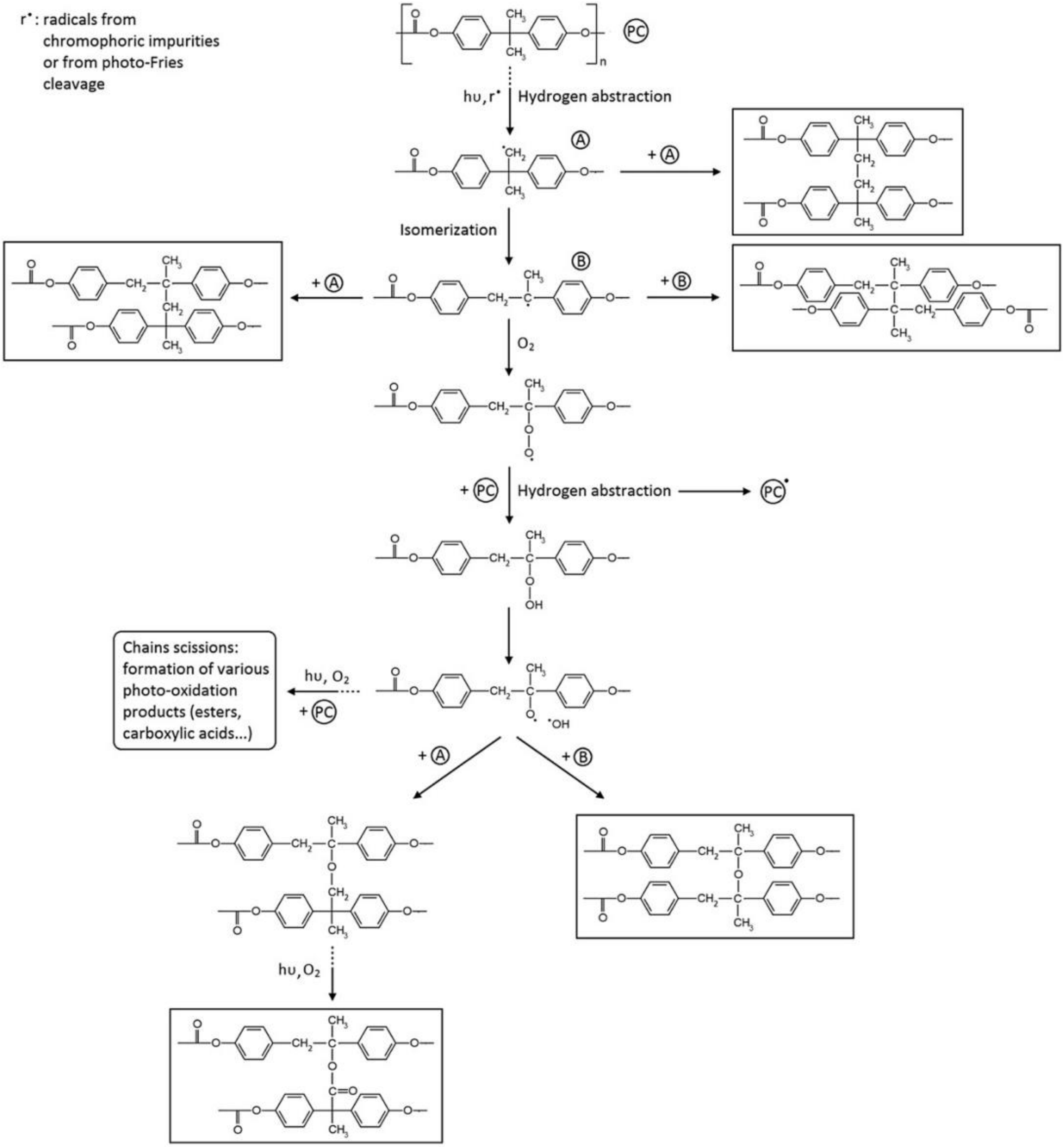

Figure 3. The mechanism of polycarbonate photooxidation into estes, carboxylics acids, and ketones.[6]

2. Testing and equipment

2.1 Methods

The objective of the project was to try and find evidence of photooxidation and to understand the degradation of PLA alongside a comparable material such as Polycarbonate. Samples were prepared and exposed to UV radiation for 21 days and were then characterized using FT-Infrared spectroscopy, Differential scanning calorimetry, and tensile test in accordance to ASTM D882-18.

2.2 Materials

PLA films were provided by *good natured* Products Inc. of Canada. The samples were acquired in small sheets of 5”x 12” with different thickness. Films were 0.014” and 0.016” think samples and were to be sectioned later into smaller specimen of 3”x 5”. These samples are also referred to as the 14 mil and 16 mil PLA samples, respectively. A separate order was made for polycarbonate films of similar thickness from ePlastics online marketplace. An order for 0.015” thick PC was made but was found to be of 0.012” thickness when delivered. This film was also cut down into 3”x 5” samples to be places in testing chamber.

2.3 Equipment

2.3.1 Q-U-V Accelerated Weather Tester

Q-U-V Accelerated Weather Tester was used to irradiate samples for extend periods. The most settings on the Q-U-V were left untouched and it was important to have the heater dial, highlight as the know in red, shown in figure 4 on the lowest setting. The light here would occasionally turn on and off, but the temperature was found to stay consistent inside the testing apparatus. The internal temperature was monitored throughout the test periods and was found to be in the range of about 49˚C - 52˚C and read off the integrated Q-U-V thermometer. To avoid any exposure to the UV radiation, the lid was kept down and anytime the chamber was opened the main power was switched off. As soon as any samples were checked on or removed the lid was closed and only after was the main power switched back on. This was done to avoid promoting degradation that is associated with elevated temperatures. The samples were kept inside for a maximum of 21 days and a minimum of 7 days with almost constant UV radiation exposure. A film was kept as a reference of both types of polymer. Samples were placed in appropriate sample holders with transparent film held by the small aluminum frame and ring as in figure 5.

Figure 4. Q-U-V Accelerated Weather tested with the heater know highlighted.

Figure 5. Samples placed inside the Q-U-V in a manner as to block as much radiation as possible.

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier Transform Infrared Spectroscopy (FTIR) used for the analysis of the PLA and PC samples was the Jasco FTIR-4600 (Figure 6). FTIR is an analytic technique used to identify polymetric, organic and sometimes inorganic materials. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties. A change in the characteristic pattern of absorption bands indicates the presence of contamination or a change in the composition of the material. If problems with the product are identified by visual inspection, the origin is typically determined by FTIR microanalysis. This technique is useful for analyzing the chemical composition of smaller particles, typically 10 -50 microns, as well as larger areas on the surface. FTIR spectroscopy is used to identify and characterize unknown materials, identify contamination on or in a material, additives after extraction from a polymer matrix, Identify oxidation, decomposition, or uncured monomers in failure analysis investigations. The FTIR was calibrated with air. Standard settings were used and unchanged from previous trials.

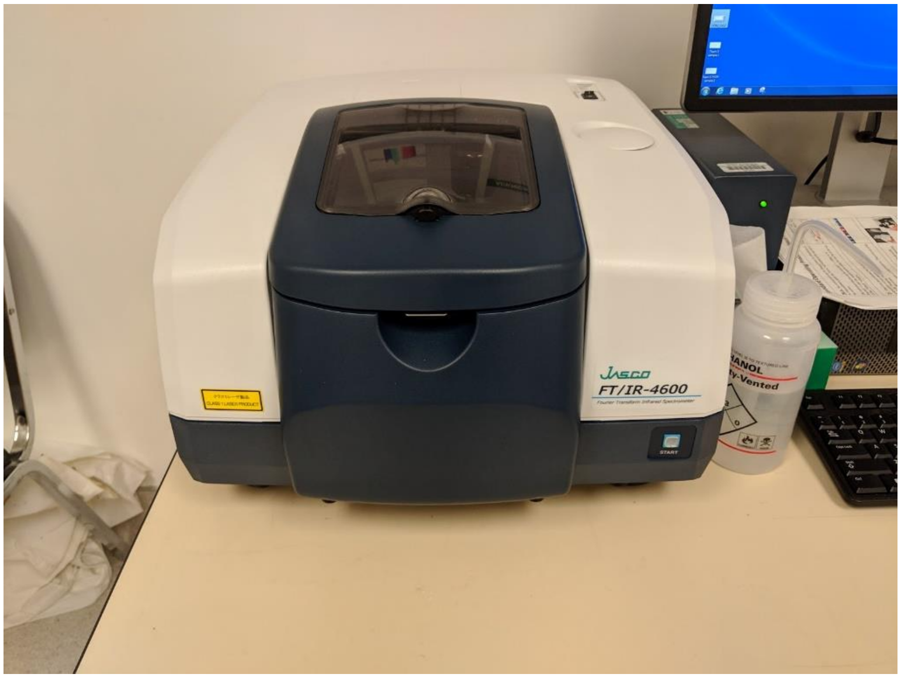

Figure 6: Jasco FTIR-4600 used for the microanalysis of PVDF sample.

Figure 7: DSC3+ machine made by Mettler Toledo. The sample is put inside a crucible which is put on the stage at the left. The liquid nitrogen cooling inlet can be seen on the right.

2.3.3 Differential Scanning Calorimetry (DSC)

Two separate DSC scans were taken for the analysis of PLA and PC. Both polymers went through one complete heating and cooling cycle. Only the results from the proper run with a cooling rate will be evaluated. The samples was measured to be about 4.00 mg to 5.00 mg by use of a scale, and it was analyzed in the Cal Poly MATE Department laboratory with the DSC3+, Mettler Toledo (Figure 7), in a two-segment process. The samples were very difficult to get a precise reading so two measurements were taken and then averaged. The sample and reference were weighed on the FA2004 Electronic Balance located in the same laboratory. A constant ramp rate of 10 °C/ minute was maintained for the initial heating of the sample, and a rate of 10 °C/ minute was used as the cooling rate of the sample for the second segment of the DSC scan. The system was allowed time to equilibrate at 25 °C for approximately 10 minutes prior to any temperature ramping. Once the temperature was equilibrated, the PLA sample was heated from 25 °C to 200 °C, then cooled back to 25 °C. Liquid nitrogen was used for cooling of the system. In a similar fashion, the PC samples were heated from 25°C to 300 °C and back down.

2.3.4 Instron Tensile Tester

Instron tensile tester machine was used in conjunction with Blue Hill data collection software to tensile test samples in accordance with ASTM D882. D8882 provides properties of thin plastic sheeting and was done for samples of both PLA an PC. Samples were cut from 3”x 5” sheets into 5 strips of uniform width and thickness. Samples were of 0.4” wide and 5” long. The at least one inch was left on the top and bottom in order to ensure a 3” gauge length for every sample. The tests were done between 3 and 5 times depending on the quality of the strips cut. The strips were prepared by first measuring the samples to be cut, marking them with thin permanent marker, and sliced using a box cutter guided by a straight edge. Only samples that had no nicks or tears along the edges were chosen to be tested. The speed of testing was found to be 0.3”/min and 1.5”/min for polylactic acid samples of both thicknesses and polycarbonate, respectively.[7] These values were found using the percent elongation at break from CES software for general purpose PLA and unfilled PC in level eco design database in the materials universe.[8] Data were logged and compared for the most consistent and useable test results. Samples were loaded into the Instron by making sure the edges were touching the inner most part of the grips. Sandpaper was also placed in between the grips to help try and reduce slippage during testing.

3. Results

3.1 FTIR spectra

3.1.1 Polycarbonate spectra

Polycarbonate films were tested using FTIR spectroscopy to examine to see if and microstructural changes would occur and be noticeable by finding changes in the spectra. In figure 8, we see the spectra for the reference PC sample and it is almost exactly the same for the spectra of the sample that was exposed to UV for 21 days in figure 9. The peaks that are seen are at 1770 cm^{-1} due to the carbon-oxygen double bond of carbonyls, 1500 cm^{-1} of the benzene rings, 1220 cm^{-1} from the oxygen-carbon-oxygen asymmetric stretching, 1190 cm^{-1} carbon-oxygen backbone stretching, and 840 cm^{-1} of the para-substitutions on the benzene ring.

3.1.2 Polylactic acid spectra

The FTIR spectra of the PLA samples was also taken. The major peaks found are at 3000 cm^{-1} of the doublet aldehyde, 1750 cm^{-1} of the carbon-oxygen double bond of the carbonyl, 1450 cm^{-1} of the carbon-hydrogen bonds in the methyl groups, and 1100 cm^{-1} due to the oxygen-carbon-oxygen ester backbone. The spectra shown in figure 8 shows the results for a sample that was exposed to 7 days of exposure. This was compared to previous work with PLA and was found to make the spectra of pure PLA with no UV exposure.[9] The region that is circled on the two spectra is the only difference found which is not enough evidence to say conclusively that photodegradation can be detected using FTIR in such a short period of irradiation in PLA neither PC.

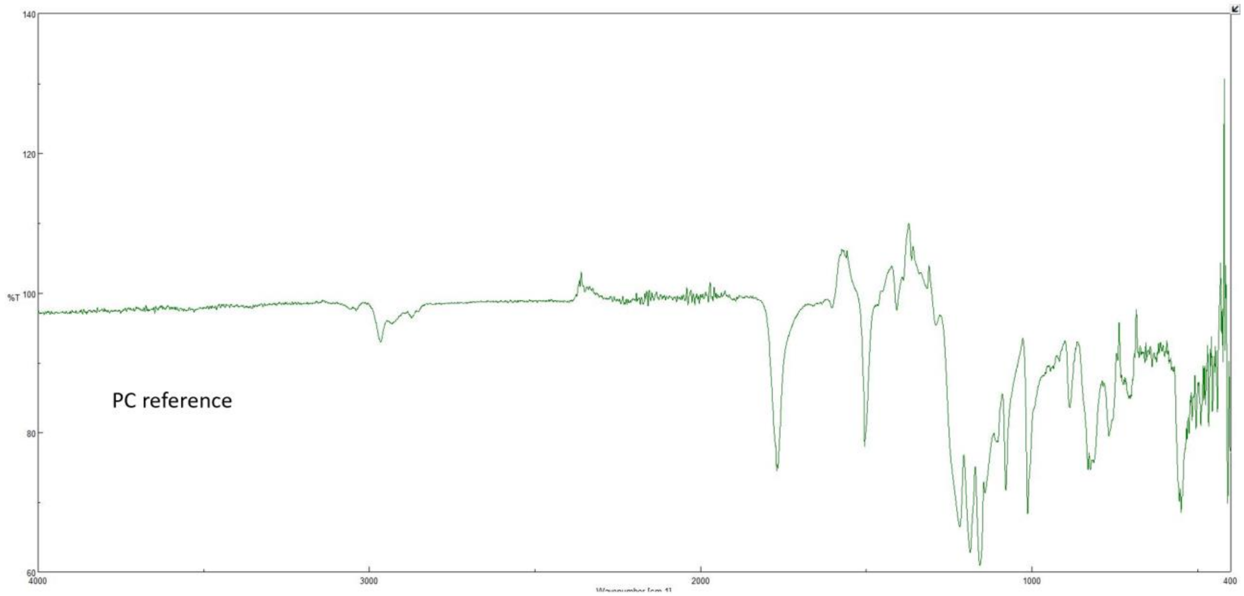

Figure 8. Shows the FTIR spectra of the PC sample not exposed to UV radiation.

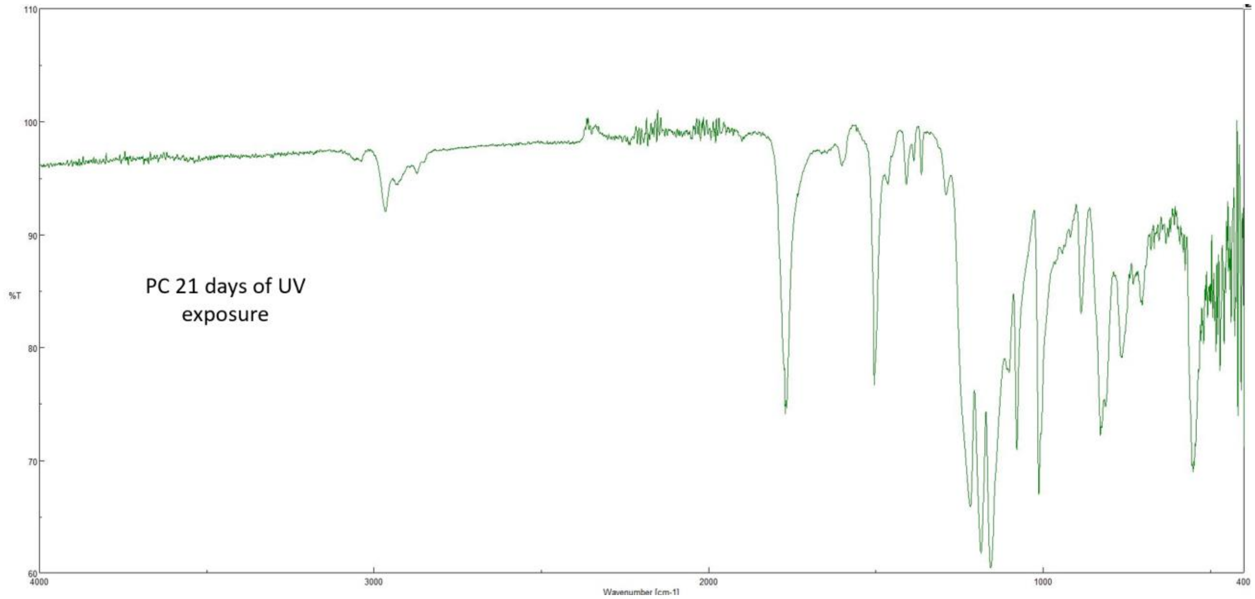

Figure 9. Shows the FTIR spectra of the PC sample exposed to 21 days of ultraviolet radiation.

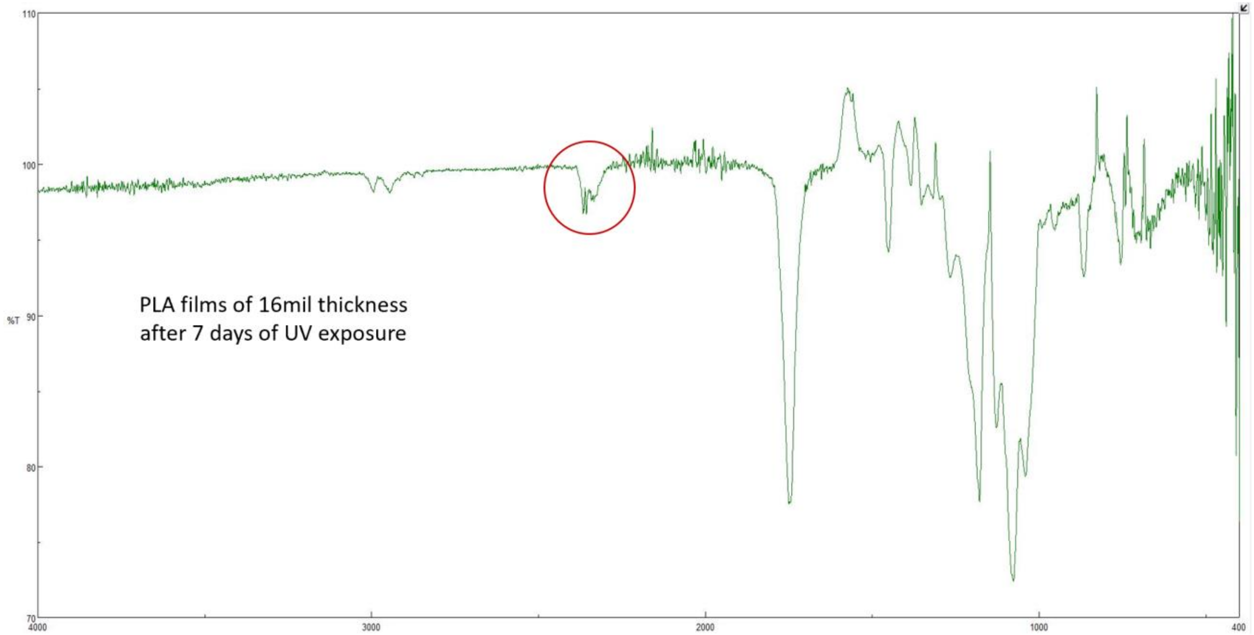

Figure 10. Shows the FTIR spectra of the PLA sample exposed to 7 days of ultraviolet radiation. The peaks circled highlight the most notable difference in the spectra with more UV exposure.

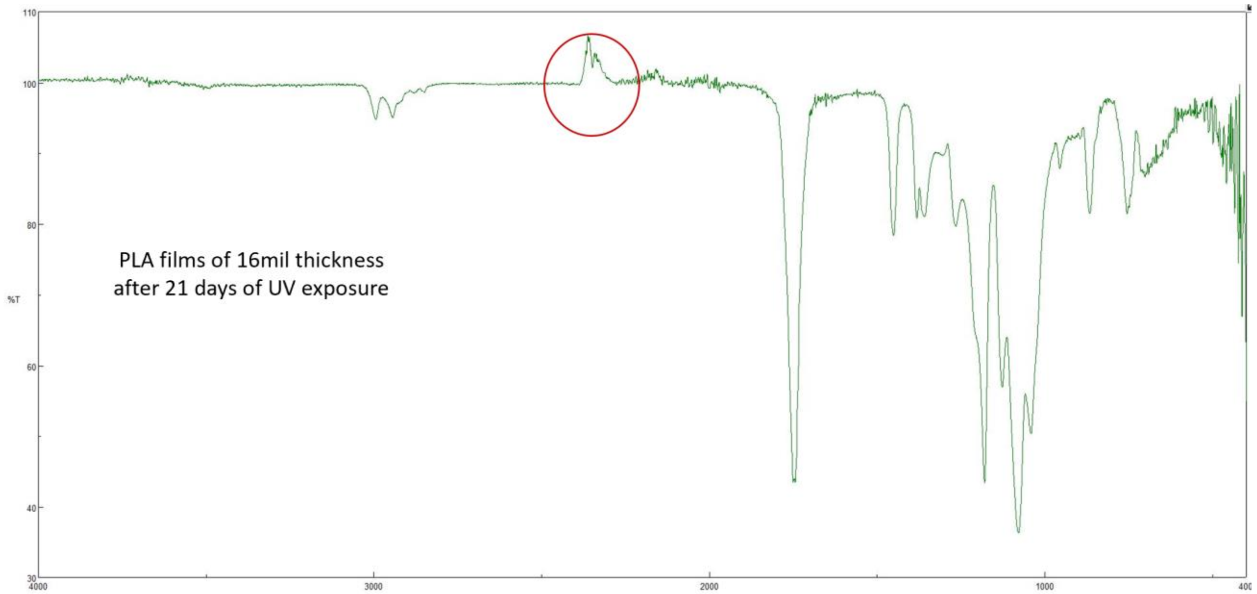

Figure 11. Shows the FTIR spectra of the PLA sample exposed to 21 days of ultraviolet radiation. The peaks circled highlight the most notable difference in the spectra with less UV exposure.

3.2 DSC results

The DSC scans for the 16 mil PLA film are shown in figure 12. The critical temperatures were found using the endotherm peaks. The glass transition temperature was found to be 61˚C – 63˚C for the PLA sample and is associated with the first peak on the heating segment. Crystallization temperature was found to be about 129˚C for both the reference sample and the PLA sample exposed to UV for 21 days. Lastly the melting point was 151˚C for both the samples.

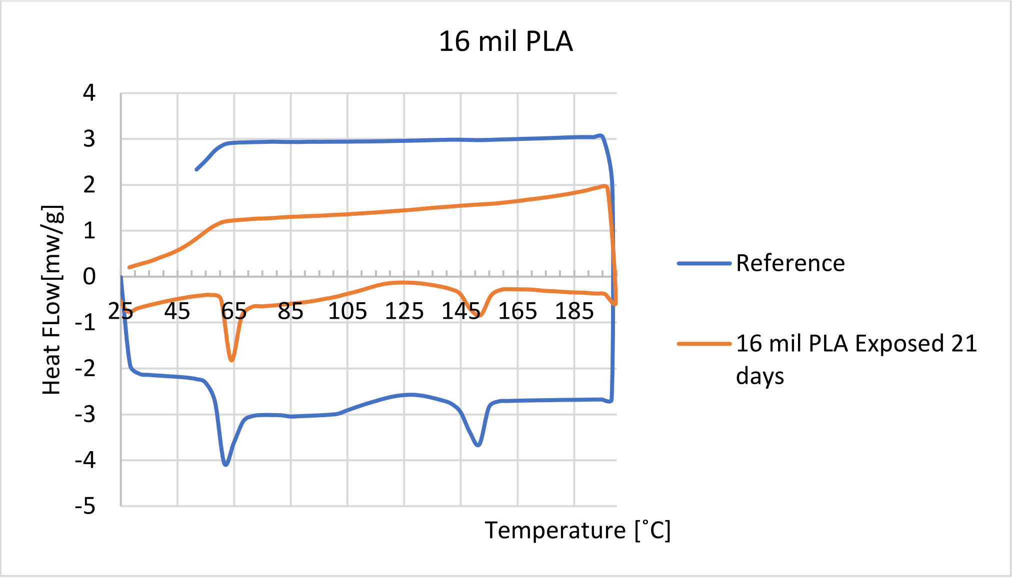

Figure 12. DSC scans comparing the critical temperatures for a 16 mil PLA reference sample and one exposed 21 days to UV.

The DSC scan was also taken for PC reference sample and for a sample that had been exposed for 21 days. What we see is a peak associated with the materials glass transition temperature at 155 ˚C. The DSC scan for the reference sample was omitted due to its faulty data and unrecognizable critical temperatures. Figure 13 shows the T_g found at the dashed circle.

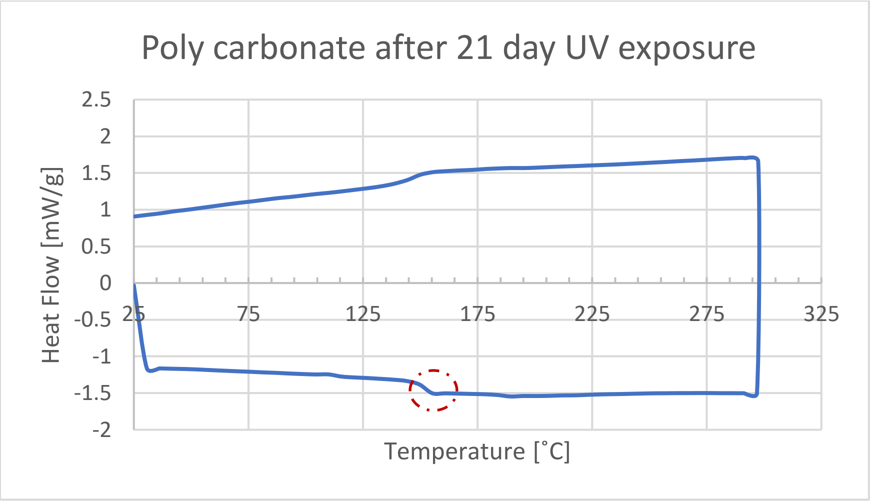

Figure 13. The DSC plot of PC exposed to ultraviolet radiation for 21 days and the T_g=155˚C is marked in the dashed circle.

3.3 Tensile test results

The mechanical properties of the samples were monitored by doing a tensile test following the ASTM standard D882. Five tensile specimens were cut from each sample, but it was important that only samples with no edge defects or nicks were used. For the PLA films of 16 mil there were only two samples that gave relevant data and since not enough test were taken that data was omitted. The stress-strain curves were plotted for PC and PLA of 14mil and shown in figure 14 and figure 15, respectively. These graphs were done by averaging the stress and strain for each sample set of substantial size.

The yield strength for both the PC reference sample and the PC sample that was exposed to ultraviolet light for 21 days showed very similar yield strengths at 44 MPa and 45 MPa. These values were much lower than expected from literature of 63 MPa. The elastic modulus for the unexposed sample was 610 MPa and the UV exposed sample has an elastic modulus of 890 MPa. These values were less than half of the expected moduli of 2300 MPa. These tensile tests did not show conclusive evidence that photodegradation can be detected for the PC samples through tensile testing of polymer thin sheets.

The PLA samples were also tested and averaged to make a stress-strain plot up to the yield point. Data in plastic region was not used because some samples were fracturing in a brittle manner near the ends of the gauges and showing no plastic region. Some samples were found to be too tightly loaded and also helped promote brittle failure. Many tests experienced slipping during some point of the test. Some adhesives that were used as place holder for cutting also caused problems. The adhesive acted as a lubricant in which the sample used to slide in between the grips and the adhesive also interfered by leaving small pieces of polymer in between the grips after tests. This cause unwanted test conditions and made for many specimens. The PLA reference sample had an average yield strength of 37 MPa and the UV irradiated sampled had a slightly lower average yield strength of 34 MPa. Bothe yield strengths failed to match with values expected of 55 MPa. The elastic modulus of the reference sample was found to be 1100 MPa and slightly lower for the UV exposed sample at 1070 MPa. Although there are slight decreases in both mechanical properties there is not enough evidence to state that the tensile tests were performed in a way the photodegradation of the PC and PLA samples was explicitly detected.

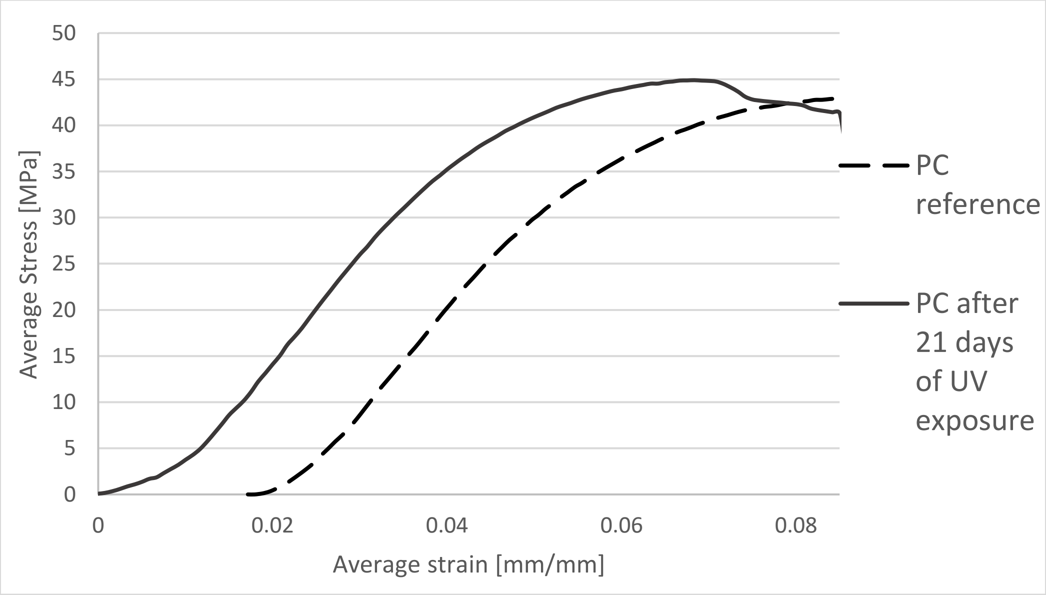

Figure 14. The average stress-strain curve for PC samples.

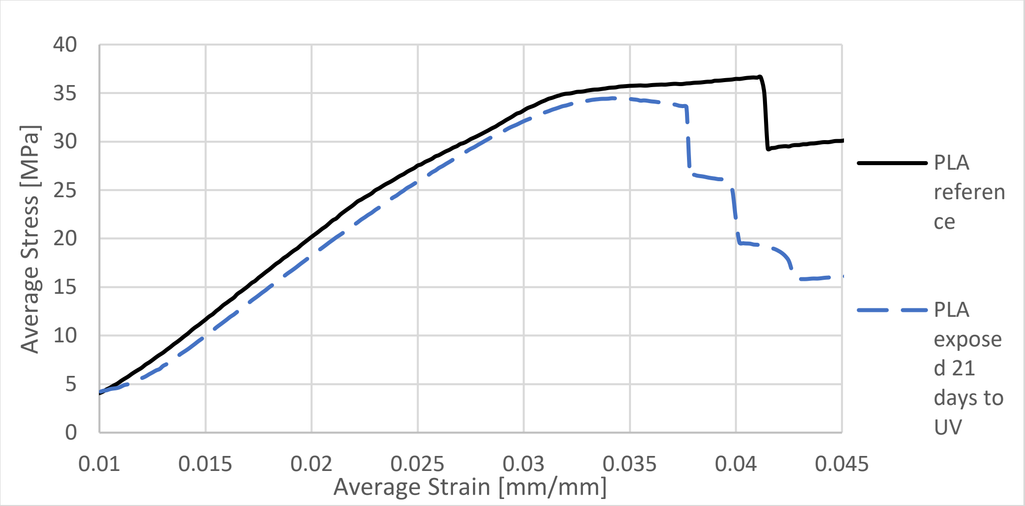

Figure 15. Average Stress-strain plot of PLA 14 mil thickness.

4. Conclusions and future works

4.1 Conclusions

UV degradation was not detected by the FTIR spectral scan of PLA films and PC films. The samples that had been tested showed identical spectra for PC films. Spectra of the PLA films showed only one small change in the which was not significant enough to attribute with any functional group.

The differential scanning calorimetry was useful in finding the critical temperatures of the PLA samples. These temperatures had no alteration even after exposure to UV for 21 days. There was still no conclusive evidence to show that DSC scans can confirm the physical changes caused by photo oxidation of the polymers.

Tensile testing yielded stress-strain plots for the PC films and PLA films from the averages. The yield stresses were found to be below 50% of what was expected for PC but found to have data similar for both reference and UV exposed samples. PLA samples showed slight decrease in yield strength and elastic modulus but was not enough to conclude that the difference was due to the UV radiation breaking down the polymer samples.

4.2 Future works and suggestions

For future works there some recommendations and things that should be tried differently to have some success in detecting photo oxidation of biodegradable polymers and other polymers. In this study, only a small amount PLA films were acquired due to the high prices and extremely excessive roll sizes. I would suggest if only a few samples are able to be acquired then they should all be left in the Q-U-V accelerated weather tester for extended periods of time longer that a minimum of 2 months with the heater on at a higher temperature if FTIR, DSC, and tensile testing is used again. A higher temperature may help accelerate the time in which data can be used to characterize the effects of light exposure. Tensile test strips should be prepared with the greatest of care so that there are no edge defects that affect the test results. I would suggest using a straight edge or square to get best results. For other testing methods, the time to detect the degradation could be much less depending on the sensitivity of the technique. It has been shown that photodegradation can be detected within 10 days of UV exposure in PLA samples. The key is to use the correct means of testing such as AMF thermal analysis. Other tests that can be used to help highlight the effects on the mechanical properties is hardness testing. Lastly, SEM is very delicate and costly process that requires a lot of time and practice to image nonconductive polymers and analyzed those images, especially when the samples are transparent. SEM should be used only after other testing has shown enough data to declare the presence of UV induces photodegradation.

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