

## The Effect of UV Treatment on the Degradation of Compostable Polylactic Acid

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### Summary

Though many compostable plastics have entered the market, they often require lengthy treatment processes to degrade. Polylactic acid (PLA) has the greatest potential to replace petroleum-based plastics due to its comparable cost with generic plastics. The aims of this study were the following: 1) evaluate the effectiveness of UV treatment on the degradation of PLA; 2) examine the influence of mechanical chopping on its degradation; and 3) propose an economic alternative composting process. PLA samples were treated with UVC light for 30, 60, and 90 minutes. Half of the PLA sample was chopped, and the other half was left unchopped. The extent of PLA degradation was measured using mass loss and molecular weight analyses (i.e., gel permeation chromatography or GPC). After 90 minutes of treatment, the chopped pieces lost 3.95% of their original mass, while the unchopped pieces lost 8.97%. The mass decreased linearly as UV treatment time increased. The PLA average molecular weight decreased from 113,500 g/mol (untreated PLA) to approximately 10,000 g/mol after UV treatment. Based on the experimental results, it was concluded that UV light significantly shortens the time of PLA degradation in comparison to the current process of hydrolysis. However, the results regarding mechanical degradation were inconclusive. As a result of the study, a new process for PLA composting is proposed, which may shorten the current process from days to hours. In this new process, PLA materials would undergo a 3-step continuous process made up of: 1) mechanical chopping, 2) UV treatment, and 3) disposal in a compost facility.

### Introduction

Many compostable plastics have entered the market in an effort to reduce the growing landfill problem. Polymers created from renewable feedstocks have begun to gain popularity with consumers and have the potential to replace petrol-based plastics. However, many so called “compostable” bioplastics require significant energy and time consuming processes to degrade. One possible solution to this problem is treating plastics to accelerate their degradation using various methods, such as UV light to promote photodegradation. This study aims to identify an alternative method to the current hydrolysis method for composting plastics by examining the effectiveness of UV pre-treatment and mechanical chopping on the degradation of polylactic acid (PLA) plastic.

Bio-based plastics are man-made or man-processed organic macromolecules created from biological resources for plastic and fiber applications. Bio-based plastics are facing economic barriers, including the short-term availability of bio-based feedstocks, and the relatively lower material properties of bio-based plastics (1). PLA, a bio-based and compostable plastic, has gained popularity in the market due to its ideal mechanical properties, as well as its comparable cost, for replacing traditional plastics in food applications. PLA is usually created from common starches and is compostable. More specifically, Nature Works LLC uses corn in PLA production.

Degradation is the process by which different factors (e.g., light, thermal, or mechanical) cause deterioration of the properties of a polymer, which results in smaller fragments. The polymer becomes brittle, which limits its lifespan. PLA will not break down in a home composting facility, but it will break down in a typical industrial composting facility (2). PLA can be depolymerized in the presence of water at elevated temperature, which results in poor mechanical properties (3). Currently, PLA is degraded by hydrolysis, a chemical process in which a water molecule is added to a polymer and results in the break down of that polymer, which can take multiple days at very high temperatures.

Photodegradation is the process by which UV light (i.e., wavelengths of 10-400 nm) oxidizes polymeric structure, facilitating mechanical and molecular breakage of a polymer into smaller fragments. The specific type of light used in this experiment is UVC, which has a wavelength of 100-290 nm and is thus the highest energy type of UV light. UVC light is not commonly found in sunlight because the ozone layer of the atmosphere absorbs most UVC light. UVC light is only found in mechanical applications, such as germicidal lamps where the high energy UVC light is used to kill microorganisms. Exposure to UV light causes a breakage of bonds in polymers leading to photo-oxidation (4). Photosensitizers, which are additives used to promote the photodegradation of plastics, are often added to compostable plastics. Some systems can only degrade in the presence of light, but other reactions are self-catalyzing and do not require the presence of light. In contrast, conventional plastics do not undergo oxidation quickly, even at elevated temperatures (5). It is also critical that the degradation mechanism of the plastic does not affect the effectiveness of the plastic as a packaging material (6).

In summary, bioplastics have gained popularity in the market as an environmentally friendly alternative to petroleum-based plastics. Both bio-based and compostable, PLA has emerged as one of the most viable bioplastics, with relatively competitive material properties compared with traditional plastics. However, a large obstacle to the adoption of bioplastics is their inability to degrade in landfills. Bioplastics require extensive energy-consuming processes, such as hydrolysis, to degrade. Hence, it is important to understand degradation mechanisms so the correct pretreatment can be used to improve their eco-friendliness. In an attempt to identify a more effective disposal technique for PLA, two

different methods were examined in this study that could potentially enhance the degradation of PLA, namely UV treatment and mechanical chopping. It was hypothesized that while both methods will enhance the degradation of PLA, UV treatment will be more effective at breaking down the PLA polymers. It is also anticipated that the effects observed with mechanical chopping followed by UV treatment will enhance the degradation of PLA to a greater extent than UV treatment alone.

## Results

In this experiment, the effects of UV exposure and mechanical chopping on the degradation of PLA were monitored. PLA samples were first treated with UV light for different lengths of time (i.e., 0, 30, 60, and 90 minutes). Half of the samples were then mechanically chopped and half were left unchopped. The effects of UV exposure and mechanical degradation were measured visually, by mass loss, and by gel permeation chromatography (GPC). GPC was used to determine the average molecular weight of the samples following UV treatment to determine the relationship between PLA degradation and the UV treatment durations. During GPC, a sample of the solution is injected into a column chromatograph. Under high pressure, some polymer chains are forced into the pores of porous beads while others pass by these gel beads. A low molecular weight polymer will easily be forced into the pores of the beads and travel a distance equal to hundreds of times of the actual column length. Therefore, it takes a longer period of time for the low molecular weight polymer to pass through the column. A high molecular weight polymer cannot fit into the pores and can only pass directly to exit the column, so it takes a shorter amount of time for the high molecular weight polymer to pass through the column. Degradation is naturally non-uniform within a piece of plastic (i.e., not all parts of the PLA have degraded to the same extent). As a result, the molecular weight distribution is a bell curve determined by GPC testing, which represents the range of molecular weights within the same PLA sample. The beginning of the bell curve represents the time at which the highest molecular weight polymer chains within the PLA sample exit the column. The end of the curve represents the time at which the lowest molecular weight polymer chains within the same PLA sample exit the column. By analyzing these curves, an average molecular weight for each sample can be calculated, allowing for comparisons of the average polymer size of each sample relative to each other.

### UV treatment of PLA leads to noticeable, visual changes

Over the span of UV treatment, there was significantly increased discoloration in the PLA. Furthermore, the PLA became more brittle over time. Specifically, the PLA turned more yellowish-brown in color, and it became so brittle that pieces of PLA broke off when touched. Before treatment, the PLA was a clear, flexible polymer. Following treatment, the PLA became very brittle and discolored.

UV treatment of PLA leads to a significant decrease in mass

The mass of the PLA (in grams) was recorded (Table 1) in 30 minute intervals for total treatment durations of 30, 60, and 90 minutes. The percentage of mass loss of both the unchopped and chopped PLA samples increased linearly as UV treatment time increased (Table 2). The unchopped film lost 8.97% of its mass after 90 minutes (Table 2). The chopped pieces lost 3.95% of their mass after 90 minutes (Table 2). In summary, the unchopped pieces lost twice the amount of mass as the chopped film.

		Duration of UV Treatment (min)			
Sample Condition	Testing Condition (min)	0	30	60	90
Chopped Pieces	0	0.2701	0.2700	0.2700	0.2701
	30	0.2503	0.2465		
	60	0.2714	0.2679	0.2648	
	90	0.2660	0.2625	0.2597	0.2555
Unchopped Film	0	0.2463	0.2465	0.2463	0.2462
	30	0.2676	0.2593		
	60	0.2804	0.2740	0.2680	
	90	0.2810	0.2733	0.2653	0.2558

Table 1: The Mass of PLA During UV Treatment. The masses of PLA following different UV treatment times.

		Duration of UV Treatment (min)			
Sample Condition	Testing Condition (min)	0	30	60	90
Chopped Pieces	0	0.00%	-0.04%	-0.04%	0.00%
	30	0.00%	-1.52%		
	60	0.00%	-1.29%	-2.43%	
	90	0.00%	-1.32%	-2.37%	-3.95%
Unchopped Film	0	0.00%	0.08%	0.00%	-0.04%
	30	0.00%	-3.10%		
	60	0.00%	-2.28%	-4.42%	
	90	0.00%	-2.74%	-5.59%	-8.97%

Table 2: The Percentage of Mass Loss of PLA During UV Treatment. Mass loss data following different UV treatment conditions.

PLA polymer length decreases with UV treatment over time

Among the unchopped samples, the untreated PLA had the highest average molecular weight followed by the 30 minute unchopped, the 90 minute unchopped, and the 60 minute unchopped samples (Figure 1a). Among the chopped samples, the untreated PLA (i.e., control) had the highest average molecular weight (i.e., least time in column) followed by the 30 minute chopped, 60 minute chopped, and the 90 minute chopped samples (Figure 1b). The 30 minute unchopped sample had a higher average molecular weight than the 30 minute chopped sample, but both samples had lower average molecular weights in comparison to the control (Figure 2). The 60 minute chopped sample had a higher average molecular weight than the 60 minute unchopped sample, but both samples had lower average molecular weights in comparison to the control (Figure 2). The 90 minute chopped sample had a higher average molecular weight than the 90 minute unchopped sample, but both samples had lower average molecular weights in comparison to the control (Figure 2).

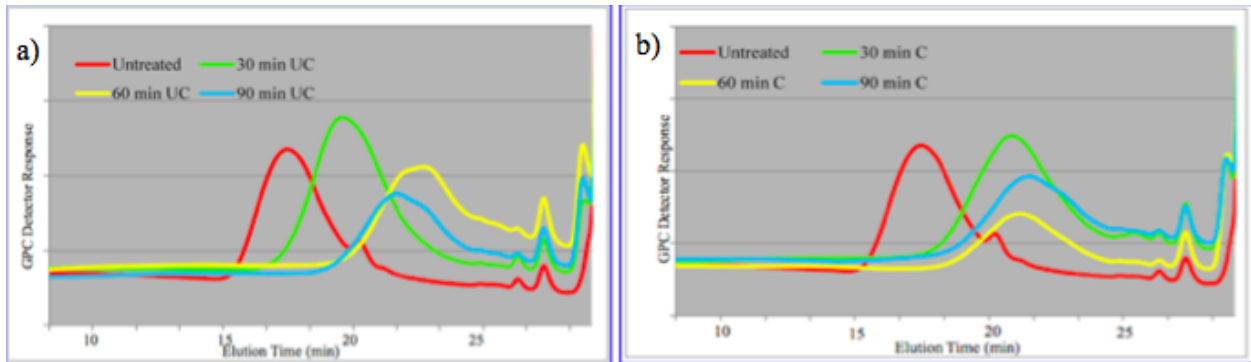


Figure 1: GPC Results of UV Treated PLA. GPC results showing the molecular weight distributions of a) unchopped (UC) and b) chopped PLA (C) samples at different UV treated conditions.

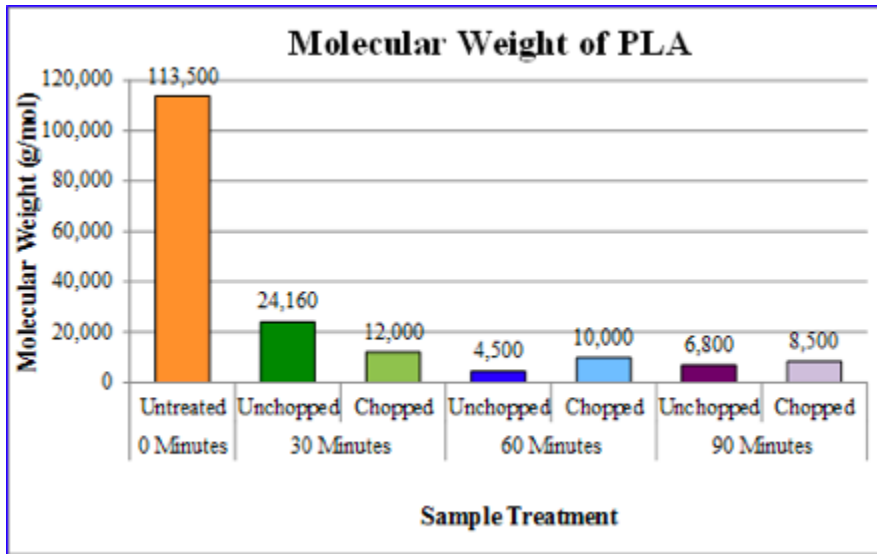


Figure 2: Estimated Average Molecular Weight of UV Treated PLA. A summary of the GPC results of the average molecular weight of PLA samples following various UV treatment durations.

## Discussion

The quantitative data was made up of two parts: mass loss and molecular weight. The masses of the PLA samples (both unchopped and chopped) decreased almost linearly as treatment time increased (Table 1). The unchopped film lost 8.97% of its mass after 90 minutes (Table 2). The chopped pieces lost 3.95% of their mass after 90 minutes (Table 2). The masses of the unchopped PLA samples were all less than the masses of the chopped PLA samples. UV treatment resulted in mass loss likely because plasticizers and other chemicals that were originally present in the plastic (to make the PLA stronger, sturdier, etc.) were released and evaporated. Furthermore, when UV light degrades polymers into small oligomers, the oligomers can evaporate if the oligomers have degraded to an extent where they have extremely small molecular weights, which results in mass loss. The reason that the unchopped film lost approximately twice the amount of mass as the chopped pieces at the same UV treatment condition is likely due to the direct exposure of the entire surface of the unchopped film to the UV light. During treatment, the chopped PLA pieces were stacked on top of each other. Therefore, the top layer may have shielded the bottom layers from the UV light, resulting in less mass loss (i.e., only the chopped pieces on the top received direct UV light versus the entire surface of the unchopped film receiving direct UV treatment).

As shown in Figure 2, the molecular weights of all the treated samples were degraded to an average molecular weight less than 25% of the original molecular weight (113,500 g/mol). It is clear that the UVC treatment can shorten the degradation time from days, which is the duration of current hydrolysis processes, to hours. In general, the optimum UV treatment time appears to be 60 minutes since there is no significant further degradation observed between 60 and 90 minutes based upon the GPC data (Figure 2).

Although the mass reduction continued after 60 minutes of UV treatment, the molecular weight stopped decreasing after 60 minutes for the unchopped sample. This discrepancy may be explained by the fact that the mass reduction of the polymer is not only attributed to degradation but also to the evaporation of plasticizers and additives. Therefore, the mass loss may be attributed to plasticizers and additives continually evaporating, while the PLA itself stopped degrading. Furthermore, the molecular weight increase from 60 to 90 minutes of the unchopped sample may have been caused by crosslinking. Because commercial plastics include many kinds of additives to stabilize their materials, too much exposure to UVC light can cause other kinds of secondary reactions from the additives, including the introduction of free radicals. Those reactions may be different from the polymer main chain scission. The GPC experiments should be repeated in the future to confirm that the small increase in molecular weight was due to crosslinking, not simply experimental variation. Mechanical chopping did not accelerate PLA degradation significantly based upon the GPC data (Figure 2). However, further investigation is required to understand these inconclusive results.

Furthermore, because only 3 to 5 mg of the UV-treated PLA was used for GPC, the location of the PLA could have been altered—meaning that some of the chopped PLA used for GPC received more direct UV treatment than others (e.g., on the top of the pile versus the bottom), resulting in variations within the molecular weight results. As UV treatment time increased, molecular weight decreased with the exception of the 60 minute unchopped sample, which had a molecular weight of 4,500 g/mol in comparison to the 90 minute unchopped and chopped samples (6,800 and 8,500 g/mol, respectively). To clarify these results, the experiment should be repeated to further confirm this finding.

The experimental results from this study may have the potential to enhance the effective degradation of many compostable plastics. Specifically, as shown in Figure 3, an alternative 3 step continuous process consisting of 1) mechanical chopping, 2) UV treatment, and 3) disposal in a compost facility, may be implemented in the future. This may allow for the shortening of current PLA composting processes from days, even weeks, to hours. Furthermore, the PLA may no longer need to be heated to high temperatures for long periods of time, resulting in reduced energy consumption and, possibly, even reduced cost. While the process described above requires further investigation to confirm the possible benefits mentioned, the initial results from this study are promising.

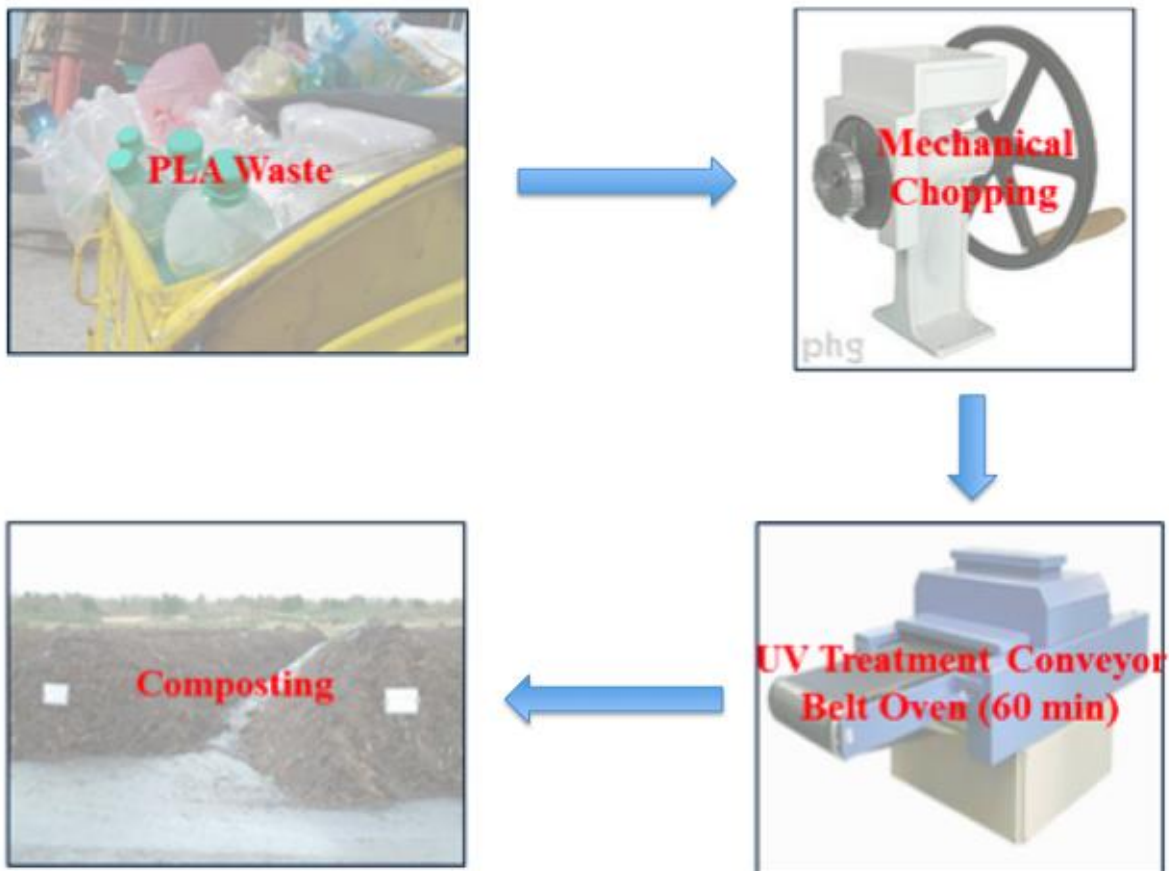


Figure 3: An Alternative Composting Process of PLA. A proposed alternative composting process flow chart with the aim of shortening composting time.

During the preparation of the PLA samples, a few pieces of the chopped PLA fell out of the aluminum trays. This likely had no effect on the results. However, preventing electric static charge must be considered so the chopped pieces of PLA do not stick together and form a small stack. Furthermore, the UV Chamber had to be stopped every 30 minutes for 5 minutes in order to prevent overheating. This may have affected the results because it prevented a consistent UV treatment. The chopped PLA would also be spread out in the tray to prevent varied UV treatment within the same sample. In the GPC testing, although an unchopped, untreated PLA sample was tested, the chopped, untreated PLA was not tested. Though it is unlikely that simply chopping the PLA without any UV treatment would lead to a significant molecular weight reduction, this is an important control that should be included in future GPC studies. The mass loss results demonstrated that chopping the PLA does not result in a decrease in mass over time, but the lack of this control in the GPC experiment could affect the interpretation of these results. Additionally, in the future, more trials should be run to confirm the findings, as only one trial was conducted in this experiment.

The information gathered from this study can be used to enhance effective degradation of many “compostable” plastics. UV treatment significantly degrades PLA and can be used to speed up decomposition in industrial composting sites from the current duration of days or weeks to hours, as compared to the current hydrolysis method. Throughout this experiment, many different processes used to measure the properties of polymers were explored, such as GPC. In the future, more trials should be run to validate the findings of the study. Though the results from this mechanical chopping experiment were inconclusive, it would be extremely interesting to test the effectiveness of mechanical degradation in large quantities of UV-treated PLA. Furthermore, in the future, it would be interesting to soak the UV-treated PLA in water to further degrade the PLA. The water might dissolve degraded oligomers and thus contribute to further mass loss.

With zero-carbon life cycles, and their ability to degrade in compost facilities, bioplastics are an eco-friendly alternative to conventional plastics. However, many challenges still face the bioplastic industry regarding degradation. Bioplastics cannot degrade in landfills and require energy and time-consuming processes, such as hydrolysis. While the current process of hydrolysis leads to a 93% reduction in the molecular weight of PLA in 9 days (at 69°C), UVC light can degrade PLA to the extent of a 96% reduction in molecular weight in 60 minutes. This method has the potential to significantly speed up the degradation of PLA and, overall, make the degradation process much more efficient.



## Methods

During experimentation, the NatureWorks PLA bag (PLA Flat Bag with 1" Lip & Tape 5.5" x 8") was cut into ten 6 cm by 6 cm squares. Half of the PLA squares were chopped into small pieces (i.e., mechanical degradation) and half were left whole. The PLA (both chopped and unchopped) was placed in small aluminum trays into a UVC Chamber (Jelight UVO Cleaner Model 42 – Tray size: 15 cm x 15cm x 2.5 cm) for 30, 60, and 90 minutes at the UMass Food Science Department (Figure 4). In 30 minute intervals, the PLA was taken out to be massed and observed visually. At the end of the total treatment time, the treated PLA was sent to the UMass Polymer Science Department for GPC testing.



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