The Biodegradation of Certified Compostable Laminate Fruit Labels:
In Home Composting Environment

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Abstract

Sinclair International produces certified compostable laminate fruit labels and were interested in the end-of-life period, when disposed of in various settings. The goal of this project was to study and analyze the biodegradation of Sinclair International’s certified compostable labels under home-composting conditions. The labels were sent out to 4 different regions within the United States, including an arid zone (Arizona and New Mexico), mediterranean climate (Atascadero, California), tropical region (Hawaii), and temperate region (Ithaca, New York). The labels were composted for a total of 12 months with samples being collected every 2 months to analyze for possible degradation. The samples were analyzed using three different methods, environmental scanning electron microscopy (ESEM), Fourier transform infrared spectroscopy (FTIR) and Differential scanning calorimetry (DSC) in order to determine if biodegradation had occurred. FTIR analysis was performed on each sample region, showing a decrease in the chemical bonds present over 12 months. ESEM images showed small 5µm-20µm cracks on the 12 month samples that were not present on the undegraded sample. The DSC data did not show any significant change in the glass transition temperature or crystallinity over 12 months. Using these tools, it was found that the labels degraded a small amount over the course of the 12 month period.
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Introduction

Life of Plastics
Plastic production began in the early 1900’s and has exponentially increased over the last hundred years. In the 1950’s plastics became increasingly popular due to its benefits to societal health, safety, and energy [1]. In the past 20 years, plastic production accounts for more than half of the total plastics produced. In 2019 alone, 368 million metric tons were produced as shown in Figure 1 [2]. The problem, however, is that plastic is highly inert and does not readily degrade under natural conditions [3]. Depending on the type of polymer, deterioration of plastics can take tens or even hundreds of years to completely deteriorate [4][5]. Along with this, the disposal of plastics is mainly done in three different ways; discarding, incinerating, or recycling. Before 1980, almost all plastics produced were discarded. Nowadays, 55% of all plastics are discarded with 25% being incinerated and 20% being recycled [5]

![Global Plastic Production 1950-2015](image)

**Figure 1: Global plastic production from 1950-2015 [5].**

Environmental and health consequences
The demand for plastics continues to grow exponentially given its highly sought after characteristics including low cost, convenience, and durability. With plastics high demand and their resistance to erosion, there is an ever growing accumulation of plastics in the environment [6]. Moreover, plastics are often found in unintended places causing damage to those inhabiting the areas. As of recently, there has been a large focus on plastics in aquatic environments due to 10% of all plastics entering the sea. Plastics oftentimes contain additives that are toxic to living organisms and are sometimes consumed, causing digestive problems. Along with this, animals that feed on these organisms are then consuming the plastics themselves, including humans [1].
Potential solutions
When looking into the end of life period of plastics, as stated previously, there are three main ways plastics are treated including discarding, incinerating, or recycling. Included in these treatments is a common phrase: reduce, reuse, recycle. The most effective way to reduce plastic use is to not produce them at all, however, given that we live in a consumer society, the reduction of plastic production is not a promising solution. The next best way to reduce is to utilize reusable items. Along with this, recycling is another strategy that is being implemented, however, most of what is placed in the recycling bin is not recycled due to contamination or it simply not reaching the correct destinations for recycling. Due to these conditions, 91% of all plastics produced do not get recycled [7]. Among small towns, incineration is a process that is widely used, however, there can be an incomplete burning of plastic fragments or microplastics. These microplastics can be toxic and produce pollutants or potential safety problems [8].

An up and coming solution is the use of biodegradable materials. Biodegradable materials are composed of renewable raw materials that can naturally degrade in the environment. They are usually made up of proteins and polysaccharides that are obtained from agricultural, animal, marine or microbial sources [9]. In comparison to plastic’s multiyear degradation period, biodegradable materials can take just weeks to degrade. In a review done in 2020, it was noted that biodegradation of bioplastics in aerobic conditions showed degradation of over 60% in 40% of the experiments evaluated. Of these experiments, degradation periods ranged from days to a year, depending on the environment [10].

Degradation environments
Depending on the environment, the rates of degradation can vary from one setting to another. Numerous strategies have been enacted in order to increase the rate of degradation, mainly in the form of stress/strain, increase in temperature, exposure to UV, humidity, and controlled pH levels [5][11]. The majority of items that are discarded are placed in landfills, and in the case of biodegradable materials, specifically bioplastics, it is a viable option as 90% of the material degrades over 9 days [10][12]. In aquatic environments, the rates of degradation appear to be consistently higher in salt water in comparison to fresh water [10]. Recently, composting has become a prominent way of recycling materials. Composting is the recycling of organic material that can enrich soils and promote plant growth. Compost is the byproduct of a natural process that decomposes organic material at an accelerated rate. Food scraps and garden waste account for over 28 percent of what is thrown away. The food waste we throw away has a negative impact on our environment and requires significant funding to process it. Within the United States alone, 267 million tons of waste were generated in 2017, with two-thirds of it going to landfills and incinerators. On average, it costs roughly $55 per ton to put food scraps in a landfill, costing billions of dollars per year [13].

Project background
Sinclair International manufactures food-safe produce labels for packers and shippers to identify their products. Based out of Fresno, California, their labels comply with the requirements of the Food and Drug Administration and the European Union. Sinclair provided us with three variations of their laminate fruit labels including polyethylene, paper, and their certified compostable label. The composition of their certified compostable laminate label was not
Sinclair’s goal was to see the end of life stage of their labels in various regions under home composting conditions. The labels were sent out to 12 volunteers in 4 different regions including temperate regions, arid zones, tropical regions, and mediterranean climates. The temperate region selected was Ithaca, New York due to its cold winters and mild summers. Arizona and New Mexico were selected for the arid zones because of the year round heat and dryness. Hawaii was used as the tropical zone for its hot and wet climate. Lastly, Atascadero, California was selected as the mediterranean climate for its mild winters and hot summers. Figure 2 displays the locations of the volunteers and where the labels were composted.

Figure 2: Map of the various locations where the labels were composted [14].
How is degradation measured

Biodegradation can be measured using many different tools, the methods used in this experiment were Fourier Transform Infrared Spectroscopy (FTIR), differential scanning calorimetry (DSC), and environmental scanning electron microscope (ESEM). These methods provide qualitative data on the degradation of a sample.

**FTIR**

FTIR uses infrared radiation to excite chemical bonds to determine the type of bond and relative amount of that bond. The type of chemical bond can be determined by the wavenumber (inverse of wavelength) that it absorbs. The amount of infrared radiation that is absorbed indicates the relative amount of that bond. When degradation occurs, bonds are being broken down, so over time the amount of infrared radiation that is absorbed will decrease.

**DSC**

DSC measures the heat flow in a sample to find the glass transition temperature, melting temperature and crystallinity of the material. Bacteria eat away at amorphous regions first so as a material degrades the crystallinity goes up. Higher crystallinity can change the glass transition temperature and melting temperature.

**ESEM**

ESEM uses electrons to image the surface of a sample at much higher magnification than optical microscopes can. The images that are produced are greyscale and can show some depth. Degradation causes surface damage such as cracks or pitting. The images from ESEM can be used in conjunction with other methods to gain a better understanding of the sample.

**Methods**

**Composting**

The samples were put into mesh sleeves with strings tied onto them, shown in Figure 3, so that they would not be lost in the compost piles. Each sleeve contained five samples. The volunteers were sent six sets of sleeves. Every two months the volunteers sent back one set of sleeves. The samples were removed from the sleeves, any large debris was removed with a soft bristle toothbrush, and then they were dried under a heat lamp for 48 hours. The samples were stored in individual plastic containers, shown in Figure 4, until they were analyzed.
Figure 3: Samples in a mesh sleeve with string attached ready for composting.

Figure 4: Samples in labeled individual containers for storage.

**FTIR**
Samples were analyzed utilizing a Jasco 4600 Fourier Transform Infrared Spectroscopy (FTIR). Samples were inserted into the FTIR and analyzed, ensuring that there was minimal contamination by wearing gloves and cleaning with isopropyl alcohol. The FTIR settings were, 32 scans, resolution of 2.0 cm\(^{-1}\), and range of 4,000-400 cm\(^{-1}\). Once the tests were run, the main peaks were identified and labeled. The graphs were then overlaid to compare the undegraded sample to the 12 month samples from each region.
**ESEM**
The fruit labels were examined using a FEI Quanta 200 environmental scanning electron microscope (ESEM) with a conventional tungsten electron filament. Because the samples were nonconductive the ESEM was run in low vacuum mode with a large field detector (LFD). The samples were mounted to 12mm aluminum studs using double sided carbon tape. The samples were mounted with the ink side up. After mounting, compressed air was used to remove any remaining debris on the samples. The images were taken at 500X, 1,000X and 2,000X magnification with a spot size of 4, 20kV beam, and chamber pressure at 100Pa.

**DSC**
The samples were examined using a Mettler Toledo differential scanning calorimeter (DSC) 3+. The samples were cut in half and folded to be put inside aluminum pans. Each sample varied in weight ranging between 7-19 mg. The lid of the pans were punctured to prevent gas build up. The 12 month samples from each region were heated from -60℃ to 180℃ at a rate of 10℃ per minute and held at 180℃ for five minutes to make sure it melted. The undegraded sample was heated twice to see if there was any crystallinity from the manufacturing process. On the second heating the DSC was held at -60℃ for five minutes to make sure the sample was thoroughly cooled. All tests were performed in a nitrogen environment.

**Results and Discussion**

**FTIR**
FTIR was performed on each of Sinclair’s compostable labels including an undegraded sample. All samples from the two month periods were tested and analyzed, however, when looking at the results from period to period, there were minimal changes visible. Figure 5 displays an overlay of an undegraded sample with samples from each of the different regions after 12 months of composting and the intensities of the peaks appear to have minimal differences. During the process of degradation, the amorphous regions degrade first as enzymes within the compost attack the free spaces. When looking at the spectrum, the ester peaks at roughly 1710 cm\(^{-1}\) were the primary focus. This was due to the fact that ester bonds are sensitive to enzyme activity and a reduction in the amplitude of the ester bond peak is an indication that an enzymatic attack is occurring. With these enzymatic attacks occurring, the chains were being broken down and the label was degrading. Figure 6 displays the same graph from Figure 5, just zoomed in on the ester peak at 1710 cm\(^{-1}\). The percent transmittance of the 1710 cm\(^{-1}\) peaks are 19.037, 21.9685, 22.0989, 22.901, and 23.6191 cm\(^{-1}\) for the undegraded label, Ithaca, New York label, Atascadero, California label, Hawaii label, and New Mexico label after 12 months of composting, respectively. From these relative values, the labels that were subjected to 12 months of composting produced consistently higher levels of transmittance in comparison to the undegraded sample. This indicates that degradation has occurred.
Figure 5: FTIR overlay of 12 month composted samples from all regions and an undegraded sample.

Figure 6: FTIR overlay of 12 month composted samples from all regions and an undegraded sample, zoomed in on the 1710 cm\textsuperscript{-1} peak. Legend follows the order of the graphs.
The DSC graph of the undegraded sample, shown in Figure 7, was heated twice. In the heat the sample had a glass transition temperature of -32.08℃ and three endothermic peaks at 66.13℃, 121.50℃, and 144.98℃. The sample had three endothermic peaks because it is made of multiple polymers laminated together. Each polymer can have different melting points. The Integral of the endothermic peaks is the amount of energy per gram that it takes to melt the material which also correlates to the crystallinity of the material. The three endothermic peaks of the undegraded sample have enthalpies of 0.736 J/g, 4.045 J/g, and 2.604 J/g. The second heat of the undegraded sample has a similar glass transition temperature of -33.27℃. Two of the endothermic peaks have disappeared and the third is much smaller with an enthalpy of 1.093 J/g, half of what it was before. The change in melting enthalpy is due to the crystallinity changed when it was cool after the first heat. The higher crystallinity in the first heat comes from mechanical processes such as cooling the label while it is being stretched. After the sample was completely melted it was cooled slowly and solidified with a lower crystallinity.

Figure 7: DSC curve of undegraded sample heat twice from -60℃ to 180℃ at a rate of 10℃ per minute. Tg: -32.08℃ enthalpy: 0.736 J/g, 4.045 J/g, 2.604 J/g.

A 12 month composted sample from each of the four regions were analyzed using the DSC, shown in Figures 8-11. All of the 12 month composted samples have glass transition temperatures between 30-34℃ which is similar to the undegraded sample. The 12 month composted samples have 3 endothermic peaks that occur within five degrees of the undegraded samples peaks. The enthalpy of melting for all the 12 month composted samples is within ±2 J/g of the undegraded samples enthalpy when adjusted for weight. The 12 month composted samples do not show any trends of reduced crystallinity compared to the undegraded sample. It is possible that the changes in crystallinity are too small to detect with this machine.
Figure 8: DSC curve of the 12 month composted New Mexico sample heat from -60°C to 180°C at a rate of 10°C per minute. Tg: -30.80°C enthalpy: 0.465 J/g, 2.051 J/g, 1.284 J/g.

Figure 9: DSC curve of the 12 month composted California sample heat from -60°C to 180°C at a rate of 10°C per minute. Tg: -31.20°C enthalpy: 0.670 J/g, 2.055 J/g, 1.297 J/g.
Figure 10: DSC curve of the 12 month composted Hawaii sample heat from -60°C to 180°C at a rate of 10°C per minute. Tg: -33.54°C Enthalpy: 1.159 J/g, 2.967 J/g, 1.058 J/g.

Figure 11: DSC curve of the 12 month composted New York sample heat from -60°C to 180°C at a rate of 10°C per minute. Tg: -32.26°C Enthalpy: 1.217 J/g, 3.975 J/g, 3.308 J/g.
ESEM
The ESEM images of the undegraded sample at 1,000X magnification in Figure 12 shows a marbling pattern. The marbling pattern goes mostly in one direction which suggests that it was caused by a manufacturing process. The results from the DSC undegraded sample also show evidence of mechanical effect on the sample. The surface of the undegraded sample is uniform. Even at 2,000X magnification there are no signs of degradation, such as cracks or pitting. The white spots on the undegraded sample are most likely bits of debris or texture of the laminated polymers.

Figure 12: undegraded compostable sample at 1,000X (left) and 2,000X (right) magnification 20kV.
The 12 month composted California sample also showed a faint marbling pattern similar to the undegraded sample. Signs of degradation can be seen in the 2,000X magnification image in Figure 13. The white lines in the image are cracks that are about 5-15 µm long. The cracks are in line with the marbling pattern and seem to avoid the darker region. This suggests that the darker regions are more crystalline, therefore harder to degrade. The other 12 month samples have similar signs of degradation. The Hawaii sample has cracks ranging from 5-20 µm long, all going in the same directions.

Figure 13: 12 month composted California sample at 1,000X (left) and 2,000X (right) magnification 20kV

Figure 14: 12 month composted Hawaii Sample at 1,000X (left) and 2,000X (right) magnification 20kV.
The New Mexico sample had a large crack about 1 mm long. There were no other large cracks on the New Mexico sample or the other 12 month samples so it might have been caused by moving around in the compost pile. There are signs of smaller degradation similar to the other sample, in and around the large crack. The white line on the New Mexico and New York samples, seen in Figures 15 and 16, are similar to the one on the other 12 month samples. The FTIR data shows a small decrease in bonds which can be seen in these ESEM images as small cracks. The cracks indicate that a small amount of degradation has occurred to the samples over the 12 month period.

Figure 15: 12 month composted New Mexico sample at 500X magnification 15kV.
Conclusion

With the exponentially increasing plastic production, there is an equally increasing accumulation of plastic waste. To combat this, biodegradable materials are being implemented to aid in reducing plastic waste. The degradation of Sinclair International’s certified compostable laminate fruit labels was characterized and analyzed utilizing FTIR, ESEM and DSC. We were able to find a correlation within each of the characterization techniques that pointed in the same direction. DSC displayed no changes in crystallinity, however, FTIR displayed a decrease in ester bonds present and ESEM showed physically visible cracks. From these characterization techniques, we can conclude that a small amount of degradation occurred to Sinclair International’s certified compostable laminate fruit labels over a 12 month period.
References


