POLYCAPROLACTONE AND ITS USE AS A BIODEGRADABLE TRASH BAG

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Abstract

The Earth is choking from the pollution of man made plastic and the environment is in desperate need of a solution that will aid in the fight against climate change. The emerging research and production of biodegradable polymers offers hope of an environmentally safe alternative that will be able to be used in place of standard plastic. This study aims to strategize a substitute for the linear low-density polyethylene (LLDPE) trash bags using polycaprolactone (PCL), a biodegradable polyester. Specifically, this research investigates PCL's manufacturing capabilities and molecular effectiveness as a LLDPE replacement. These investigations bring into question PCL's capability to be used as a trash bag and feasible modifications of PCL are theorized to mimic the molecular properties of LLDPE.

To examine PCL as a LLDPE substitute, this research study details the molecular properties and material characteristics of both materials and future experimentation. Trash bag manufacturing methods are also described in order to determine the ability for PCL to be a replacement from a production standpoint. There is a probable need for a modification of PCL in order for it to be a feasible alternative and multiple solutions are explored, including a branch addition polymerization synthesis and various polyester blends. This study also gives recommendations to fix grave concerns in regards to biodegradable plastic production. The theory of this eco-friendly alternative presents possible and adequate results as a LLDPE substitute.

Table of Contents

Introduction

Importance of The Study:

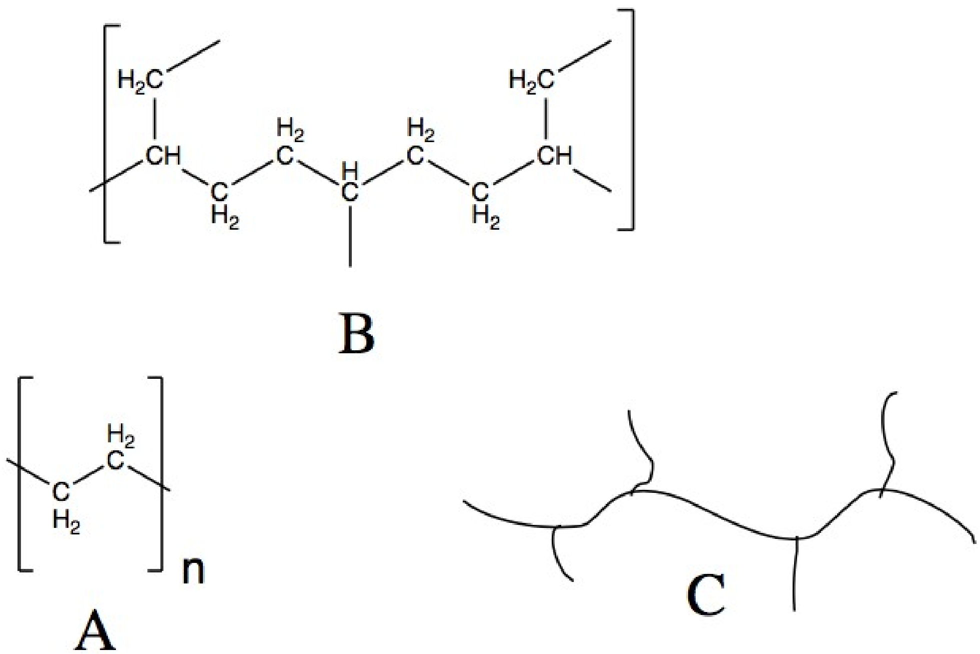
As the global threat of pollution continues, the need to make grave ecological changes to our means of production rises. Humans create a large amount of non-biodegradable waste and a large number of that comes in the form of plastic. This plastic then ends up in landfills or it is incinerated. These plastics are long polymers chains with extremely strong carbon-carbon bonds that cannot be consumed by microorganisms like bacteria and fungi. Most plastics are derived from propylene and can only degrade by UV rays and that require centuries to break down. They are also commonly melted down which in turn releases toxic fumes such as dioxins and polychlorinated biphenyls (BCPs) into the atmosphere that threaten the health of humans, animals and vegetation. These hazardous chemicals are known to produce cancer and introduce reproductive anomalies. In accordance with this issue, the demand for biodegradable plastic is on the rise. The research and experimental formulation to create a biodegradable plastic has skyrocketed and there have been many attempts to create biodegradable plastic in recent years. Plastic such as linear low-density polyethylene is utilized for its lightweight, flexible and strong properties. To find a suitable biodegradable alternative for LLDPE, research and formulation is done to attempt to mimic those same properties.

<u>Diagram 1</u>: LLDPE (Linear Low Density Polyethylene)

Created on CHEMDRAW. A) Polyethylene Unit.

B) LLDPE chemical structure demonstrating branching

C) LLDPE composted of short multiple branches

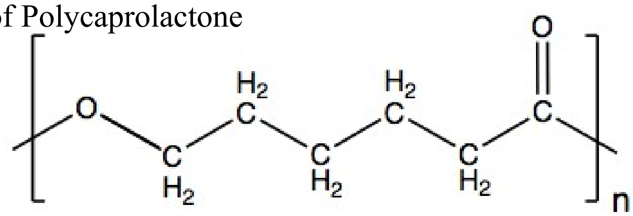


A biodegradable polymer must be able to go under biodegradation. In other words, microorganisms must be able to decompose and break down the plastic into nutrients that do not harm the environment. The research and formulation of such plastics has arisen a number of issues including the shelf life and rate of decomposition. The attempts to create such a plastic have yielded a number of results. Products have been formed that are average non biodegradable plastic with additives such as starch which only partially degrade. Other biodegradable products on the market use peptide bonds as opposed to carbon-carbon bonds which are more readily broken down. Many attempts have given a wide variety of results, but there has been little true success in creating such a plastic that can be an economically efficient alternative. There are biodegradable polymers on the market, but the use of such polymers is limited.

To attempt to find a biodegradable polyester, PCL will be investigated to see if it can be used as an alternative for LLDPE in trash bags.

Diagram 2:

Single Unit of Polycaprolactone



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The average single use LLDPE plastic trash bag can only be decomposed through photodegradation at high temperatures, not through biodegradation. In order to explore alternative materials that can function as single-use trash bags, PCL and it's modifications are investigated to theorize its functionality as a trash bag. Research will help decide whether PCL is a material that could feasibly replace the standard LLDPE single use bag.

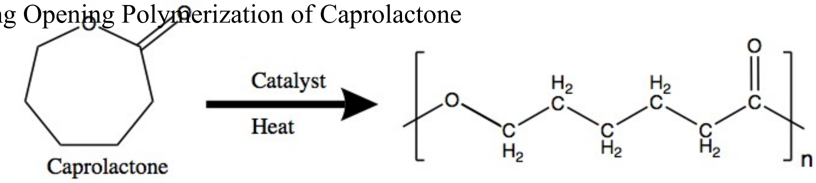
<u>The Characteristics of PCL:</u>

PCL is a synthetic aliphatic polyester. Polyesters are considered biodegradable due to the fact that they are manufactured using esterification which can be chemically reversed via hydrolytic enzymatic action . Polyesters have the potential to be broken down through enzymes secreted by actinomycetes, and fungal strains. Specifically PCL was discovered to be broken down by *Streptomyces thermoviolaceus* subsp. *thermoviolaceus* strain 76T-2, a thermophilic isolate found in the soil. In a simulated environment laboratory study, the microorganisms *Streptomyces thermonitrificans* PDS-1 and *Bacillus licheniformis* HA1 were reported to completely degrade PCL into CO_2 and water through hydrolysis. (1). It was also found that PCL can be broken down by the lipase enzyme from *Lactobacillus brevis*, *Lactobacillus plantarum* which can be found in the ocean. These studies suggest PCL's aptitude for effective biodegradation.

PCL is synthesized by a ring opening polymerization of caprolactone under heating and catalytic conditions. The ring opening polymerization process is favorable in mass production because it can be done in a relatively short time frame and yields a higher molecular weight. PCL has a melting point of 57-60 °C and is a solid polymer with a molecular weight over 20,000. (4,6,7)

Diagram 3

: The Ring Opening Polymerization of Caprolactone



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The Creation of Standard Trash Bags:

To find a material that can be used to create trash bags, it is important to understand how a trash bag is made. The process of manufacturing a standard LLDPE trash bag begins as polyethylene pellets. These pellets are stored in hoopers, which are large containers where they are stored in mass quantities. From the hopper they are sent through an extruder where these pellets are melted to make them more pliable and moldable. This melted plastic is then placed in a die where it is cut like a ring shape where air can be forced through it in order for it to be formed into a thin strong bubble. When the air is removed from the bubble, the material is very thin and can be easily cut into sheets that can be melted together at the seams to give the shape of the trash bag. In order for PCL to be used as an alternative to the LLDPE trash bag, it must be able to undergo similar manufacturing techniques for it to be cost effective and mass produced. (8)

The Ability for PCL to be Used as an LLDPE Trash Bag Replacement

In order for PCL to replace LLDPE in trash bags, it must be able to be similarly manufactured. PCL's manufacturing capabilities rely on the melt strength which is essential for the bubble formation and the creation of thin sheets. PCL has a low melting point of 57-60 °C and LLDPE has a melting point of 105-115 °C. Already PCL requires less heat and therefore is more environmentally friendly in means of production because the melting of the LLDPE requires a larger amount of energy when produced at a large scale compared to PCL.

For PCL to be a feasible alternative to LLDPE, it must have adequate characteristics relating to the functionality of the trash bag. Calculating the mechanical properties a plastic needs to function as a trash bag and comparing them to PCL will show if it can be a LLDPE replacement. Tensile strength and puncture resistance experimentation should be done on both PCL and LLDPE and will show how these materials compare.

Melt Strength:

It is important that PCL has the melt strength to undergo trash bag manufacturing. Melt strength has to do with the melted plastic's ability to undergo tension, in the case, being able to have air forced through it to create the thin sheets. It is important that the melt strength of PCL has the extensional viscosity to undergo these manufacturing techniques and in order see if it has a high enough melt strength an extensional rheometer could be used test the maximum tension that both the melts of LLDPE and PCL can be subjected to without breaking. Melt strength depends on the polymer's ability to resist untangling under strain. To compare the melt strength of these materials, testing of PCL would be compared to LLDPE to show if the melt strength is high enough to undergo similar manufacturing techniques.

Puncture Resistance and Tensile Strength:

In order for PCL to be used as a material for single use trash bags, it must have some of the capabilities of a trash bag. LLDPE is used for trash bags because of its ability to stretch. Therefore, in order for PCL to be used, it must have similar strength and flexibility. To test this, puncture resistance and tensile strength must be analyzed for both

LLDPE and PCL. It's important that a PCL bag has a decent puncture resistance if it's going to function properly. Puncture strength relies on the materials breaking strength and the penetration distance. Material thickness, the rate of penetration, temperature, shape and type of probe must be constant for both tests in order to see how both of these polymers compare. Puncture resistance can be organized on a graph with the load and deflection being analyzed and compared to one another. These tests can be done using equipment like the modular eXpert 5000 or eXpert 7600 single column testing machines that are made for low force testing. Although it's important to see how they compare, it also must be noted what puncture resistance is needed for an effective trash bag. This can be done by using the two bags with the same amount of weight inside and seeing how sharp objects affect the bag.

The strength of the bag is very important. The average single use kitchen trash bag is anywhere from 12-16 gallons and weighs about 22 pounds. A test that should be performed would include different weights of garbage at full capacity to see how they hold up under these conditions. To test how the bags compare to one another tensile test could be performed. These tests test the strength of the polymer and its resistance to breaking under tension. The ASTM D638 is the most common apparatus used in these tests and can generate a strain stress graph. Strain, ε, can be calculated using the following equation, where Δ L gauge length, L_0 is the initial gauge length, and L is the final length of the specimen. The force, σ, can also be measured where F_n is the tensile force and A is the cross-section of the specimen.

Strain Equation:

$$\varepsilon = \frac{\Delta L}{L_0} = \frac{L - L_0}{L_0}$$

Force Equation:

$$\sigma = \frac{F_n}{A}$$

These machines pull on the polymer and can measure the force and speed that these materials break. The force that the polymer can undergo is important for the use of a trash bag. This is tested by increasing the force applied on the material before it breaks. It is important that the thickness, length and temperature of the sample remain constant for these readings.

Issues Using PCL as a Trash Bag:

Research has been done that casts doubt on PCL's ability to undergo trash bag manufacturing. Literature has shown that PCL has a low melt strength. Therefore modifications and blends of PCL should be tested similarly to see if melt strength can be improved. Furthermore, the increased speed of degradation that PCL would experience under these manufacturing conditions raises concern. PCL is very sensitive to high temperatures and moisture, which causes it to degrade very quickly. This has been shown to create difficulties in using PCL in many manufacturing processes such as melt spinning, which the process used to create polyester fibers (4). This has been contested however and under conditions where moisture is carefully controlled, PCL has been described as having "outstanding processability" with little thermal degradation when spun into fibers or blown at 200°C. (6) Regardless, the manufacturing temperature would need to be very precise and in a dry environment, which is so sensitive, it may no longer be feasible.

The structure of PCL, does implicate issues relating to its ability to be used as a trashbag. Aliphatic polyesters have a linear chain configuration. It's structure is weak and has low mechanical properties (1), which theoretically may not yield the necessary tensile strength to be used as a trash bag. In ``Microbial degradation of four biodegradable polymers in soil and compost demonstrating Polycaprolactone as an ideal compostable plastic", Granules of PCL were used to create polymer sheets. These sheets were created by melting the granules in a halogen oven for 20 min at 80 °C for the compost studies. For tensile strength studies, the sheets with a thickness of 0.4–0.5 mm were made by melting 12.5 g of PCL granules in 100 mL dichloromethane and then poured into a levelled glass cast. It was reported in this study that all strips had near identical maximum tensile strength measuring 13.9 ± 0.4 MPa (2). This offers competitive numbers to LLDPE which was reported to have a tensile strength of 8.48 - 26.2 MPa (average of 12.7 MPa) with a thickness of 0.034 mm thickness (3). The PCL sheets were much thicker, which is most likely the reason for these competitive tensile strengths. If the PCL trash bags were made with a 0.034 mm thickness, it can be assumed that that tensile strength would not be able to compete with LLDPE. If the PCL trash bags were made with 0.5 mm thickness, then a significantly larger amount of material would be required to make the trashbag effective and no longer be cost effective.

Modifications of PCL

In regards to PCL, there is a strong possibility based on past experiments and research of its molecular properties, that it cannot compete with LLDPE. A polymer's ability to resist this untangling depends on molecular-weight distribution and molecular branching. Most favorably, Both PCL and LLDPE have short branches which are effective for trash bag usage because the molecular branches do not become so entangled that its tensile strength, puncture resistance and stretch ability is compromised. The issues with standard PCL is due to its low melting point. The melt strength of PCL is the main reason for its unexplored capabilities as a trash bag material. However, there are several modifications that can be made to optimize its conditions for manufacturing.

Adding Side Chains:

One modified PCL possibility would be to add side chains. These branches would be added via a chemical polymerization synthesis. These branches can get caught within one another, making the molecules less able to slide past each other and this theoretically would have positive effects on PCL's melt strength. There are several syntheses to add these branches. For example, an alpha hydrogen on the polycaprolactone chain can be substituted by a longer side chain. Issues may arise with adding to the polymer and changing the molecule in this way may also weaken the tensile strength. Researchers' interest in PCL as a biodegradable polymer are due to its stretchy characteristics, adding these branches may increase its brittleness. Adding side chains may be an important step to increasing melt strength, but it is also crucial that these sidechains don't affect its ability to biodegrade.

Starch/PCL Blends:

A formula used in many products on the biodegradable polymer market is starch polyester blends. Starch has favorable properties in bioplastic application, and PCL and starch have the ability to counterbalance each other's negative effects. Favorably, Starch's low cost is able to make PCL/starch blends more economically feasible as a LLDPE replacement. Furthermore, modified thermoplastic starch (TPS) is extremely biodegradable, and when blended with PCL, will increase the rate of biodegradation. PCL also is able to overcome the high water sensitivity and reduces the rigidity of TPS. These factors aid the blend's water moisture resistance and stretch capability in trash bag applications. In "Polycaprolactone/starch composite: Fabrication, structure, properties, and applications" the Young's Modulus, or the polymers stretching ability increased as the amount of starch in the blend increased. However, this favorable effect was accompanied by a lower tensile strength. The research showed that higher amounts of glycerol, the plasticizer, was able to improve the tensile strength of the blend. TPS/PCL/Glycerol blends for trash bag use have already been created and implemented by The Yukong Company in Korea.

Although starch has potential in blends with biodegradable polyesters, it's low cost and high rate of decomposition have led to unethical and mischaracterized biodegradable products. Due to the lack of government regulation on the definition of biodegradability, corporations exploit the bioplastic emerging market by blending TPS with non biodegradable plastics. These products are only able to partially degrade and this is misleading to consumers wishing to switch to environmentally safe products. Additionally, once the TPS degrades, the reminisce of the traditional plastic are small fragments, which can cause devastating effects. These remnants are known as microplastics and quickly release harmful chemicals into the environment. Microplastics in soil can render agricultural land unusable, contaminate water bodies, and when ingested expose animals to toxins.

PLA/PCL Blends:

Polyester blends have offered good results in a variety of uses. The aliphatic polyester Poly Lactic Acid (PLA) is rigid and has a high tensile strength which is why it has been widely researched. However, PLA is very brittle, and there has been success in blending it with PCL, which is much more flexible. In the study, "Effect of PCL and Compatibility Contents on the Morphology, Crystallization and Mechanical Properties of PLA/PCL Blends", several different blends of PLA and PCL were tested and compared to attempt and increase its melt strength and tensile strength. Melt strength slightly increased, overall the PCL lowered the tensile strength of the PLA. The melt strength detailed didn't increase enough to allow this blend to be used as a trash bag. It's also important to note that these blends were done with the plasticizer, Pluronic. Pluronic f127 has been used medically as an hydrogel scaffold encapsulation system and has been found to have favorable biodegradability (11), therefore is a good plasticiser to be investigated in the future in regards to PCL blends. (5)

PP/PCL Blends:

Another PCL blend that has been researched is PCL and polypropylene (PP). PP has a much more favorable melt strength than PCL, but is less biodegradable. In "Study on Properties of Polymer Blends from Polypropylene with Polycaprolactone and Their

Biodegradability", PP/PCL blends with higher PP content showed a higher Young's Modulus and tensile strength in tensile testing. Higher PCL content showed increased crystallinity in X-ray diffraction experiments, which is associated with higher rate of biodegradation. To combat this oxidized PP was substituted in the blend and was able to increase all of these properties. However this oxidized PP was resistant to enzymatic attack due to its hydrophobic nature, and makes this blend no longer completely biodegradable.

Plasticizers:

Plasticizers as well as other chemicals have been investigated to enhance the thermoplastic and mechanical properties of PCL blends. There are several biodegradable and non toxic plasticizers, such as Pluronic, which should be more widely tested. More commonly, there have been many unethical decisions using plasticisers to create PCL blends. The use of starch in the creation of biodegradables is where the most misinformation can be found. TPS has many advantages in PCL blend application, most notably in its cost reduction, which has caused it to be abused. Many TPS/PCL blends use Glycerol as a plasticizer. Glycerol, is widely used in starch blends due to its high plasticising capacity and thermal stability. Although a non toxic plasticizer, it does pose risks to the blend's ability to biodegrade due to Glycerols antibacterial and antimicrobial properties. In "Processing and characterization of starch/polycaprolactone products" among other research articles have utilized Glycerol. Experiments have shown that 20-25 kg of glycerol is used to produce 100 kg of thermoplastic starch (12) . Therefore, despite any positive results in using starch and glycerol in PCL blends, its uses as a biodegradable environmentally friendly replacement are null. Research has also been done using Urea and Formaldehyde as plasticisers (13). Urea can cause algae to produce domoic acid, a deadly toxin that has been linked to mass animal deaths. Urea is found urine when disposed of properly, is chemically treated before being released into water bodies, but if used in polymers and disposed of as most plastics are, it cannot be used without these adverse effects on the environment. Formaldehyde is highly biodegradable, but is broken down into formic acid and carbon monoxide, which are highly toxic to aquatic life, animals and humans. It is highly concerning that such studies can appear to be conducting ethical research to produce biodegradable plastics while creating an environmentally harmful product as a replacement.

The Future in using PCL and Biodegradable Plastic

The uses of polyesters like PCL offer hope for sustainable polymer substitutes for LLDPE. PCL and modified PCL will undergo melt strength, tensile strength and puncture resistance testing to see how it compares to LLDPE. Manufacturing trials of PCL will be conducted in order to see if it can undergo standard hopper/extruder methods currently used to create standard trash bags. Modifications of PCL are being widely researched to change it’s thermal and mechanical properties for various uses. There are several ways currently being investigated to increase the melt strength in order for it to be used as an LLDPE replacement in trash bags. The creations of these products must be done ethically and transparently. Those who aren’t educated in chemistry and environmental science may believe that biodegradable products using dangerous chemicals are eco friendly. To combat this, there must be government regulation on what can be considered biodegradable. These laws must detail time constraints on its biodegradability, and percentage able to be degraded. The by-products of the biodegradation should be regulated, so only polymers that break down into non toxic constituents can be labeled as a biodegradable plastic. All biodegradable plastics should also undergo non simulated environmental experiments to test biodegradability. Currently most biodegradability research is done in simulated experiments and due to the complexity of nature, biodegradability needs to be tested in multiple natural environments including oceans and landfills. The experimentation of PCL as a trash bag is just a small sect of the future of biodegradable plastics. Humans must internationally agree to increase research and regulation in biodegradable alternatives to plastic to help save the world from its certain demise due to the pollution we've caused.

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