The Chemistry of Plastics

DEEPENING

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TEAM 6
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INTRODUCTION

This deepening is about the chemistry of plastics, with a specific focus on biodegradable plastics and sustainability. The information from this paper was used to choose sustainable and durable properties for Solar Still; a solar-powered desalination device for the Greek refugee camp Moria.

In this document, a variety of topics that are related to plastics and sustainability will be covered. First, some general information about plastics will be provided, such as different types of plastics and the chemical structure of plastics. After that, several types of biodegradable plastics and their properties will be discussed. We will then describe the production process of both synthetic and natural plastics, with a particular focus on the materials that will be used for Solar Still. Then, we will describe the degradation process of plastics, giving the most attention to biodegradability. Finally, the impacts of plastics on public health and the environment will be explored.
CHEMICAL STRUCTURE OF PLASTICS

Plastics are defined as long-chain polymeric molecules that are man-made. Plastics are currently widely used, because of their favorable physical properties, such as their strength, low mass, and water resistance. Furthermore, plastics are very stable and durable (Shah, Hasan, Hameed, & Ahmed, 2008).

Some of the most used plastics are polyethene (PE), polyvinyl chloride (PVC), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), and polyurethane (PU) (Shah et al., 2008). The chemical structures of these polymers are shown in figure 1.

Plastic Types Based on Processing

Thermosets

A thermoset is a polymer that solidifies irreversibly when it is heated. Once such a material has been hardened, it cannot go back to its softer form. These plastics are strong and durable and are used for many different product applications, such as insulation or coating. Some widely used thermoset polymers are polyurethanes, unsaturated polyesters, and epoxies (“American Chemistry Council,” n.d.)

Thermoplastics

Thermoplastic polymers are held together by weak secondary bonding forces. They soften when they are exposed to heat, but return to their original condition when they are cooled back down. This process can be repeated multiple times. Thermoplastics are versatile and offer a wide range of applications, like packaging and siding. Examples of thermoplastics include polyethene (PE), polypropylene (PP), and polyvinyl chloride (PVC) (“American Chemistry Council,” n.d.).
**BIODEGRADABLE PLASTICS**

Biodegradable plastics are designed to become susceptible to microbial attack. This makes them degradable in microbially active environments. Many biodegradable plastics are polyesters. They have this name because they are a chain of esters. They are usually also polyhydroxyalkanoates. Examples of biodegradable plastics that have been manufactured successfully are poly-3-hydroxybutyrate (PHB) and poly-3-hydroxybutyrate-co-3-hydroxyvalerate (PHBV), although many more useful biodegradable plastics exist (Shah et al., 2008). The chemical structures of the aforementioned polyesters are shown in figure 2.

**POLYMER BLENDS**

The conversion of biodegradable plastics into consumer products is not always straightforward. Although they have many advantages, raw biodegradable plastics often lack certain material properties that are required for them to be useful. For instance, they generally have poor water-resistance, poor oxidative stability, and poor bio-resistance (Biressaw & Carriere, 2004).

Therefore, biodegradable plastics are presently not used as homopolymers but are blended with other polymers, which is called polymer blending. By doing this, material properties are enhanced, meaning that the aforementioned shortcomings of raw biopolymers can be overcome (Avella, Martuscelli, & Raimo, 2000; Biressaw & Carriere, 2004). Reasons for polymer blending include:

- Reducing the costs of the plastic
- Achieving specific material properties
- Recycling industrial plastic scraps

**PHB AND POLYETHER BLENDS**

PHB can be blended with aliphatic polyethers, which are materials of methylenic units that are linked by oxygen bridges (Avella et al., 2000):


\[
[-(CH_2)_x-O-]_n \quad \text{Where } x \text{ and } n \text{ are whole numbers}
\]

An important characteristic of polyethers is that they are potentially able to form hydrogen bonds. This is made possible by the presence of paired oxygen in the molecule, which allows for oxygen-donor properties (Avella et al., 2000). Polyethers have weak van der Waals forces because their molecules are only slightly polar. Small changes in chemical structures can thus lead to strong deviations in chemico-physical properties. (Avella et al., 2000)

Because polyethers can have a large range of properties, they can be used to obtain biodegradable polymer blends with a variety of useful characteristics (Avella et al., 2000). A specific beneficial result of PHB blending is a decrease in melting temperature, which makes it possible to process the materials at a lower temperature. However, it is important to consider that this also decreases the temperature range of utilization (Avella et al., 2000).
Examples of polyethers that can be blended with PHB are poly(methylene oxide) (PMO) and poly(ethylene oxide) (PEO). Both polyethers result in strong polymer blends with high melting points (Avella et al., 2000). For our product, we will use PEO, because this blend is more conventional, which means that more research is available about it.

**POLYSTYRENE AND BIODEGRADABLE POLYESTER BLENDS**

Biodegradable polyesters have a high molecular weight. They possess the water-resistant properties of synthetic polymers. Hence, they can be used to develop synthetic materials with improved biodegradability without compromising water resistance and other useful properties. Biodegradable polyesters can be blended with polystyrene (PS). The resulting materials can be injection molded to obtain the desired shape (Biresaw & Carriere, 2004). Three examples of biodegradable polyester blends that have been developed successfully are polycaprolactone (PCL), poly(lactic acid) (PLA), and poly(tetramethylene adipate-co-terephthalate) (EBU). The blending of these materials with PS results in higher stress resistance, except PLA, which has lower stress resistance when the proportion of PS increases (Biresaw & Carriere, 2004). However, the blending of PLA with PS still leads to other enhanced material properties, such as reduced oxidation.

Biresaw & Carriere (2004) have researched the yield stress of biodegradable polyester/PS blends at various weight percentages of PS. A material with high yield stress is considered to be strong and durable. Figure 3 shows a summary graph of their results. It can be seen that pure PLA has a high yield stress. However, combining PS with PLA can be very useful, since PS has other useful properties. A PLA/PS blend with 25 weight % of PS still has high yield stress, while also possessing the beneficial properties of PS.

PLA as an individual molecule is quite resistant to UV-light, but this property can be further enhanced by adding an antimicrobial that is not sensitive to UV aging into the biopolymer matrix. ZnO is very useful for this. This addition also increases antimicrobial effectiveness (Mizielińska et al., 2018).
SYNTHESIS OF PLASTICS

The plastics we use today can be made from both inorganic and organic raw materials. The basic materials needed for the production are extracted from oil, coal, and natural gas, depending on the desired plastic (Shah et al., 2008). The production of plastics happens through several steps and processes. First, plastic polymers are made in polymerization reactions. The created polymers are then processed into finished products, which can be done through a variety of different processing methods. Sometimes, additives are included in the molecule, to introduce or enhance the desired material properties. This can be done during the polymerization or the processing into finished materials (“American Chemistry Council,” n.d.). The different steps of plastic synthesis will be elaborated upon in the upcoming section.

POLYMERIZATION

Plastic polymers are made in polymerization reactions. These reactions are the first step in creating consumer plastics. Polymers are made in reactors, where monomers are linked together to create a long chain. Polymerization processes can be divided into two broad categories: step-growth and chain polymerization (Painter & Coleman, 2009).

STEP-GROWTH POLYMERIZATION

Step-growth polymerization reactions are condensation reactions. This means that they involve the splitting out of a molecule of H₂O (Painter & Coleman, 2009). Figure 4 shows the condensation reaction between ethanol and acetic acid, which is an example of such a reaction.

To create a linear polymer chain, bifunctional molecules, with two reactive end groups, are needed. Otherwise, the reaction ends prematurely, after each functional group has reacted. Step-growth polymerization reactions do not happen all at once; the monomers do not connect all at the same time, but in a step-growth fashion (Painter & Coleman, 2009).

Plastic polymers that are synthesized through step-growth polymerization reactions include polyesters like PET, and polyamides (nylons) (Painter & Coleman, 2009).

CHAIN POLYMERIZATION

Chain polymerization happens through addition reactions. This type of reaction can occur by breaking double or triple bonds in monomers or by breaking up a ring molecule. This polymerization process requires the presence of an active site at the end of a growing polymer chain. Monomers are added to this polymer chain sequentially, which leads to the polymer increasing in molecular weight (Painter & Coleman, 2009).

Chain polymerization happens in three basic steps. The first step is initiation, in which the reaction first gets started. For initiation, the minimum activation energy needs to be reached. After that, propagation occurs, during which the sequential growth of the polymer chain occurs. The process ends with termination when there are no more particles that can interact with each other. The final result of these three steps is a stable polymer chain (Painter & Coleman, 2009).
PROCESSING
Individual polymers can be converted into finished products through a variety of different processing methods (“American Chemistry Council,” n.d.). The most established ones will be discussed in the upcoming section.

EXTRUSION
Extrusion starts by loading plastic materials into a hopper and feeding it into an extruder. This is a cylindrical heated chamber, through which it is moved by a continuously revolving screw. The combination of the mechanical work of the screw and the heat from the extruder wall melts the plastic. This is forced out through a small opening, known as a die, to form the shape of the finished product. This processing method is a continuous process and can be used for thermoplastics. Thermoset elastomers can also be extruded, but this is more difficult because it requires catalysts (“American Chemistry Council,” n.d.).

INJECTION MOLDING
Injection molding also makes use of an extruder. At the end of the extruder, the plastic is forced into a closed cold mold. This needs to be done at high pressure to ensure the mold is completely filled. The plastic then cools to a solid, after which the mold opens and the finished product is ejected. Injection molding can be used to create intricate parts of high quality (“American Chemistry Council,” n.d.). This is the processing method we will use to create the parts of the Solar Still.

BLOW MOLDING
In extrusion blow molding, the die forms a continuous semi-molten tube of plastic material. A chilled mold is clamped around this tube, after which air is blown into it. This conforms the tube to the interior of the mold, creating a hollow plastic product (“American Chemistry Council,” n.d.).

Injection blow molding is the process in which a preform is injection molded. This preform is heated, after which the softened plastic is blown into the final shape in a chilled mold (“American Chemistry Council,” n.d.).

EXPANDED BEAD BLOWING
This process begins by placing a measured volume of plastic beads with a gas dissolved in the plastic into a mold. The closed mold is heated to soften the plastic. Because of the heating, the gas within the beads expands. This results in a fused closed-cell structure of foamed plastic that can conform to the desired shape (“American Chemistry Council,” n.d.).

ROTATIONAL MOLDING
In rotational molding, a mold is mounted on a machine with two axes that rotate simultaneously. A resin is placed within the mold, after which it is heated. The rotation leads to an even distribution of the plastic within the mold. After cooling, this leaves a hollow plastic configuration (“American Chemistry Council,” n.d.).

COMPRESSION MOLDING
The process of compression molding starts with a prepared volume of plastic, that is placed into a mold cavity. After this, a second mold or plug is applied, which is used to squeeze the plastic into the desired shape. Compression molding can be done manually, but it can also be automated. Generally, this method is used to process thermoset plastics (“American Chemistry Council,” n.d.).
CASTING
Casting is one of the few processing methods that does not require high pressure, which makes it favorable for certain situations. Casting begins by adding liquid thermoset plastics into a mold. By doing this, the plastic can be formed into intricate shapes. Casting can be used to create sheets that are several inches thick (“American Chemistry Council,” n.d.).

THERMOFORMING
Thermoforming starts by heating films of thermoplastic polymers, which softens them. After this, the soft film is made to fit a mold. This can be done through pulling by vacuum, pushing by pressure, or by pressing it into the mold with a plug. This process can be automated for high volume production, but it can also be done by hand labor to craft individual items (“American Chemistry Council,” n.d.).

ADDITIVES
Plastics sometimes have the desired properties for a commercial product when they emerge from reactors, but often they do not. Including additives can change basic mechanical, physical, and chemical properties. It can also protect the polymer from degradation or provide special material characteristics. Additives can be incorporated during the manufacturing process, i.e. the polymerization. Sometimes, they can be added after the polymerization, during the processing into finished parts (“American Chemistry Council,” n.d.).

SYNTHETIC PLASTIC PRODUCTION
In our product, we will use two synthetic plastics, polystyrene (PS) and poly(ethylene oxide) PEO, blended with biodegradable polymers. More information about our material choices can be found in the section Our Product. It is important to know how these materials are produced. In this section, the manufacturing process of PS and PEO will be discussed. For the production process of the biodegradable plastics, please refer to the section Bioplastic production.

POLYSTYRENE PRODUCTION
Like other plastic polymers, polystyrene is produced through a polymerization process. In the case of PS, this happens by the vinyl polymerization of styrene monomers, initiated by the presence of free radicals. The polymerization mechanism is shown in figure 5. This can happen through two different processes, which produce different types of PS polymers (“Polystyrene (PS) Production, Price and Market,” n.d.).

5 POLYMERIZATION OF STYRENE INTO POLYSTYRENE (“POLYSTYRENE,” N.D.)
The production of atactic polystyrene happens at a temperature of 90 degrees Celsius. In the polymerization process, the phenyl groups are distributed randomly on both sides of the polymer chain. This prevents the chains from aligning. However, enough regularity is provided to achieve the desired crystallinity (“Polystyrene (PS) Production, Price and Market,” n.d.).

Syndiotactic PS is created by the Ziegler-Natta polymerization process at a temperature of 270 degrees Celsius. In this process, phenyl groups are positioned on the alternate sides of the polymer backbone. The produced syndiotactic PS polymer is highly crystalline (“Polystyrene (PS) Production, Price and Market,” n.d.).

In short, polystyrene is synthesized through the vinyl polymerization of styrene. This can be done in two ways, resulting in the production of either atactic polystyrene or syndiotactic polystyrene.

**POLY(ETHYLENE OXIDE) PRODUCTION**

The polymerization of ethylene oxide (EO) is oxyanionic. This process relies on nucleophiles as initiators. For the synthesis of PEO, EO is added to water or alcohol in the presence of alkaline catalysts. The process of PEO polymerization involves the ring-opening of ethylene oxide (Herzberger et al., 2016). This mechanism is shown in figure 6.

6 RING-OPENING POLYMERIZATION OF EO INTO PEO (EUROPALCSCHES PATENTAMT EUROPEAN PATENT OFFICE, 1986)

**BIOPLASTIC PRODUCTION**

Bioplastics are polymers that are made from natural and renewable resources. This can be from the growth of microorganisms or genetically-engineered plants. These plastics are likely to replace conventional plastics in the future. As oil prices continue to rise, bioplastic production will become cheaper, when compared to traditional plastics (Murariu & Dubois, 2016; Shah et al., 2008).

One of the most widely used bioplastics is polylactic acid (PLA) (Murariu & Dubois, 2016; Shah et al., 2008). In our product, we will use a blend of PLA combined with polystyrene. We will also use poly(3-hydroxybutyrate) (PHB) blended with PEO. This choice will be elaborated upon more in the section Our Product later in the paper. In the upcoming section, the PLA lifecycle and the production process of PHB will be discussed.

**PLA LIFECYCLE**

The production of PLA begins by the fermentation of polysaccharides and sugars, such as glucose and saccharose. These chemicals can be extracted from resources like corn, potatoes, cane molasses, and sugar beets. All of these sources are non-fossil, renewable, and natural (Murariu & Dubois, 2016). With the fermentation process, lactic acid or lactide is obtained. The PLA polymer is then formed by the polymerization of lactic acid monomers, or by the ring-opening polymerization of lactide (Bakibaev et al., 2015; Murariu & Dubois, 2016).
PLA is most often derived from lactic acid, which exists in the form of two isomers: L- and D-lactic acid, as shown in figure 7 (Porter, 2006). The polymerization of lactic acid happens through a condensation reaction, so it is a step-growth polymerization. This reaction is carried out in two stages. First, an oligomer of lactic acid is obtained. After that, the oligomer is polymerized under the influence of a catalyst. In both steps of the polymerization, H₂O (water) is formed (Bakibaev et al., 2015). Both stages of the polymerization of lactic acid are shown in figure 8.

The polymerization of lactic acid usually happens with tin octoate as a catalyst, especially when a high molecular weight is desired. The activation energy that is required for this process, is traditionally achieved under conventional heating. However, Bakibaev et al. (2015) found that the process is much faster when proceeded under microwave irradiation. The synthesis of PLA through lactic acid polycondensation is an equilibrium reaction. In the first step of the reaction, hydrolysis of the ester bonds can lead to difficulties in completely removing water. This limits the maximum molecular weight of the attained PLA, which is a downside to this polymerization method (Porter, 2006).

A second method of obtaining PLA is the ring-opening polymerization (ROP) of the cyclic dimmer lactide. Lactide is a cyclic molecule that consists of two units of lactate acid (“Polylactide – Biologie,” n.d.). This molecule has three stereoisomers: D-lactide, L-lactide, and meso-lactide (Porter, 2006). Their chemical structures are shown in figure 9.

Different microstructures of PLA can be formed through the ROP of lactide, depending on which combination of isomers is used for the synthesis. In contrast with the polymerization of lactic acid, this process is not a condensation polymerization, so the removal of water is not required. Hence, a higher molecular weight can be achieved (Porter, 2006).
The reaction mechanism for the ROP of lactide is shown in figure 10.

![Reaction Mechanism](image)

**10 RING OPENING POLYMERIZATION OF LACTIDE (“POLYLACTIDE – BIOLOGIE,” N.D.)**

The ROP of lactide requires a high temperature for the activation energy to be reached. It can take place at temperatures between 140 and 180 degrees celsius (“Polylactide – Biologie,” n.d.). The synthesis of PLA in this manner happens under influence of a metal catalyst, such as zinc or titanium (“Polylactide – Biologie,” n.d.; Porter, 2006). Tin(II)-2-ethyl hexanoate (Sn(Oct)2) is the most widely used catalyst, because it has good solubility in the monomer melt, results in high reaction rates, and produces high molecular weights (Porter, 2006).

After the synthesis of the raw PLA, the polymer is processed into a finished product. This can be realized with equipment that is similar to that of traditional polymers. The processing of PLA can be done with various methods, including, but not limited to injection molding, compression molding, and extrusion (Murariu & Dubois, 2016).

After the manufactured products have been used, they can be disposed of through composting. The biodegradation of the PLA-based product leads to the polymer being converted back into biomass. The degradation process of plastics, including PLA, will be elaborated upon in a later section. The CO₂ and H₂O that this produces, are used in photosynthesis for the production of polysaccharides and sugars, meaning that the atoms are back in their original chemical form. Thus, the biological cycle of PLA is complete (Murariu & Dubois, 2008, 2016). The complete life cycle of PLA is shown in figure 11.

![Life Cycle of PLA](image)

**11 THE LIFE CYCLE OF PLA (MURARIUI & DUBOIS, 2008)**
**PHB PRODUCTION**

As a polyhydroxyalkanoate (PHA), PHB is formed in the cells of microorganisms, usually in an environment that is unfavorable for the organism cells. The material is used to store carbon and energy when essential nutrient supplies are insufficient (Bonartsev et al., 2007; McAdam, Fournet, McDonald, & Mojicevic, 2020a).

The synthesis of PHB begins with the condensation of two acetyl-CoA molecules into acetoacetyl-CoA. This reaction is reversible and is catalyzed by β-ketothiolase. After this, the Acetoacetyl-CoA is reduced into (R)-3-hydroxybutyryl-CoA by an acetoacetyl-CoA reductase. This molecule is then polymerized into PHB by PHB synthase (McAdam et al., 2020a). The full mechanism of PHB synthesis from Acetyl-Co-A is shown in figure 12.

PHB materials can be extracted from bacterial cells in several different ways. The specific form of PHB that is synthesized depends on the used microorganism and the used extraction method. In this paper, we identify three main routes of synthesizing PHB materials. First of all, this can be done through the ring-opening polymerization of β-butyrolactone. Secondly, natural plants can be used. Lastly, PHB materials can be obtained through material fermentation. This last approach is the most commonly used because it has the highest efficiency (McAdam et al., 2020a).

There are different fermentation processes to obtain PHBs. An overview of these processes is shown in figure 13. They will be elaborated upon in the upcoming section.
The first method is the batch culture process. This is a simple, discontinuous process that is relatively easy to carry out, but it is also associated with low productivity. This is due to the physiological preconditions of the production, which restricts the concentration of nitrogen and carbon sources (McAdam, Fournet, McDonald, & Mojicevic, 2020).

The repeated batch approach has been introduced to reach higher volumetric productivity. This method is preferable over simple batch processes because it has higher efficiency. It also eliminates the time required for the cleaning, refilling, and sterilization of the bioreactor between each individual batch. Thus, the total amount of productive time increases (McAdam et al., 2020).

In fed-batch systems, the addition of the substrate is fed through pulses when the concentration falls below a set minimum value. To have higher productivity than batch culture processes, a proper feeding strategy with optimal feeding rates of carbon and nitrogen sources is required. A challenge associated with this fermentation method is the control over the concentration of the feeding substrate. The fed-batch system can be enhanced by using a two feeding-pulse strategy to obtain the highest volume of PHB concentration (McAdam et al., 2020).

Presently, continuous feeding methods are considered to be the most suitable for PHB production. They operate under controlled conditions, where external factors are kept constant. These methods use a chemostat, with one or multiple stages. Unfortunately, constant conditions are required to generate high active biomass, which results in a small fraction of accumulated material when only one chemostat stage is used. Hence multi-stage fermentation processes with different conditions across the different reactors lead to higher productivity (McAdam et al., 2020).

After PHB synthesis and extraction, the acquired polymers are processed into finished products, which happens through the same methods as traditional polymer processing. After usage, the material is fully biodegradable, which will further discussed in a later section.
DEGRADATION OF PLASTICS
Polymer degradation includes all processes that induce changes in polymer properties caused by bond scission and chemical transformation through chemical, physical or biological reactions (Shah et al., 2008). Polymer degradation can happen in three different ways from a chemical standpoint; it can happen through scission of the main chains, scission of the side chains, and scission of the intersectional chains (Qi, Ren, & Wang, 2017).

There are several different processes through which degradation can happen, the most important of which will be discussed in the upcoming section. Biodegradation will not be covered in this part of the paper, as it will be covered more thoroughly in a later section.

PHOTODEGRADATION
Photodegradation happens through the absorption of high-energy radiation in the ultraviolet part of the spectrum, or other high-energy forms of radiation. This activates electrons, causing them to be more reactive. Electron reactions can lead to different forms of degradation, such as oxidation and cleavage. For polymers to be able to photodegrade, they should absorb light with wavelengths between 295 and 2500 nm. At these wavelengths, tropospheric solar radiation is highly energetic, which is required for electron activation (Nkwachukwu, Chima, Ikenna, & Albert, 2013; Shah et al., 2008).

In photodegradation, UV-light and high-energy radiation are the main active agents. The initiation of the reaction (getting the reaction started) is slow, but propagation (the actual reaction) is quite fast. This degradation process is considered to be environmentally friendly, as long as UV-light is used. Unfortunately, photodegradation is currently still quite costly. Hence, it is not widely used as a waste disposal method at the moment (Shah et al., 2008).

THERMAL DEGRADATION
The thermal degradation of polymers happens as a result of high temperatures. When thermal energy is high, molecular scission can occur, which means that the monomer components of the polymer chain backbone begin to separate. The separated components then start reacting with one another, which causes physical and optical property shifts in the material (Nkwachukwu et al., 2013; Shah et al., 2008).

For thermal degradation, only heat and oxygen are required. The process is very quick and inexpensive. However, the negative environmental impacts, such as high energy usage and carbon dioxide emissions, are considered to be too large. For this reason, thermal degradation is deemed an unacceptable method of degradation (Shah et al., 2008).

CHEMICAL DEGRADATION
When corrosive chemicals, such as ozone or sulfur from agricultural chemicals are brought into contact with the material, chemical degradation may occur. These corrosive chemicals start reacting with the polymer chain, which causes bond breaking or oxidation. Hence, the polymer will begin to degrade into smaller oligomer components (Nkwachukwu et al., 2013).
BIODEGRADATION
The breakdown of organic substances by living organisms, such as bacteria and fungi, is called biodegradation. In wild nature, plastics are biodegraded aerobically. They are biodegraded anaerobically in sediments and landfills. In composites and soil, biodegradation is a combination of aerobic and anaerobic processes (Alshehrei, 2017; Shah et al., 2008).

Microorganisms play a vital role in the process of biodegradation. Many bacteria, fungi, and actinomycetes can degrade plastics. For conventional plastics, this is a very slow process. Biodegradable plastics are specially designed to be more susceptible to this microbial attack, which means that the biodegradation process is much faster for these materials (Alshehrei, 2017).

AEROBIC BIODEGRADATION
Aerobic degradation is the degradation of plastics that generally happens in wild nature, where oxygen is sufficiently available. Aerobic microbes use this oxygen as an electron acceptor, which allows them to break down organic chemicals into smaller organic compounds. This process produces carbon dioxide and water as by-products (Alshehrei, 2017).

The general chemical reaction mechanism of aerobic degradation looks as follows (Alshehrei, 2017):

\[ \text{C plastic} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{C residual} + \text{Biomass} \]

ANAEROBIC BIODEGRADATION
When oxygen is not present, organic contaminants are biodegraded inorganically. Anaerobic bacteria can use different molecules as electron acceptors to break polymers down into smaller compounds, such as nitrate, sulfate, iron, manganese, and carbon dioxide (Alshehrei, 2017).

PROCESS OF BIODEGRADATION
Most biochemical processes take place inside of the cells of microorganisms. However, the polymers cannot be passed directly through microorganisms' outer cell membranes, because plastic polymers are long and non-water soluble. Hence, the polymers must be depolymerized outside the cells for them to be transported into the cell, where the microorganisms use them as a source of carbon and energy. To this end, microbes excrete extracellular enzymes that depolymerize the polymers outside of the cells (Alshehrei, 2017).

The biodegradation of polymers happens according to the following steps:

1. Attachment of the microorganism to the surface of the polymer
2. Microorganism growth and primary degradation
3. Ultimate polymer degradation

If a polymer is hydrophilic, microorganisms can attach to its surface. It is then able to grow, using the polymer as its source of carbon. In the primary degradation stage, the main polymer chain is cleaved by the extracellular enzymes secreted by the organism. This leads to the formation of oligomers, dimers, monomers, and other low-molecular-weight fragments. These compounds are used by the microbes as additional carbon and energy sources (Alshehrei, 2017). The reaction pathways of polymer degradation are shown in figure 14.

[Diagram: Reaction pathways during biodegradation of polymers (Alshehrei, 2017)]
Biodegradation of Synthetic Plastics

The degradation of synthetic plastics is generally a slow process; it can take up to decades for a synthetic polymer to biodegrade fully. The specific mechanism of degradation and the microorganisms involved depends on the specific type of polymer. The majority of our product’s components will be made of a blend of the biodegradable plastic PLA and polystyrene (PS). One component will be made of a PHB and PEO blend, of which PEO is not a natural plastic. Hence, the biodegradation of PS and PEO as individual polymers will be discussed in the upcoming section.

Polystyrene generally has a high molecular weight. As an individual polymer, it is generally not biodegradable at a fast rate. Different types of organisms, such as bacteria and fungi, have been found to be capable of degrading this plastic, but the rate of decomposition is very low. The addition of cellulose and minerals can significantly increase the rate of biodegradation of PS (Alshehrei, 2017).

No research can be found on the biodegradation of poly(ethylene oxide). From this, we can conclude that PEO has very low biodegradability as an individual polymer. This is likely due to the high energy requirement of PEO depolymerization, which is why the degradation is normally a thermal process. After the initial polymerization, the further oxidative degradation of the smaller components requires less high levels of energy (Yang, Heatley, Blease, & Thompson, 1996).

To summarize, neither PS nor PEO has good biodegradability properties when used as an individual polymer. However, biodegradability properties change when a synthetic polymer is combined with a biodegradable one. More information about this can be found in the Degradation of Polymer Blends section.

Biodegradation of Biodegradable Plastics

Biodegradable plastics are designed to be susceptible to microbial attack. This means that they can be degraded quickly by microorganisms in a sustainable way (Alshehrei, 2017; Shah et al., 2008). The specific way in which the biodegradation occurs depends on the type of plastic. Our product will be made of two blends, respectively containing PLA and PHB. Therefore, the biodegradation processes of both plastics will be described in the upcoming section.

PLA Biodegradation

PLA has complete biodegradation, which occurs mainly through the scission of ester bonds. In nature, hydrolytic degradation and photodegradation may also occur. The depolymerization is first induced by a hydrolysis reaction, and it can even fully degrade hydrolytically, but this is a slow process. Hence, microbial degradation is important for efficient degradation in nature (Qi et al., 2017).

The microbial degradation of PLA begins with the excretion of extracellular PLA depolymerase by PLA-degrading microorganisms. This generally needs to be stimulated by some inducers, which usually have L-alanine units that are similar to L-lactic acid units in PLA. The depolymerases attack intramolecular ester links of PLA, causing the polymer chain to break down into smaller oligomers, dimers, and monomers. These smaller compounds enter the microbial membranes, where they are decomposed into carbon dioxide, water, or methane by intercellular enzymes (Qi et al., 2017). Figure 15 on the next page shows the biochemical processes that are involved in PLA degradation.

Multiple types of PLA degrading microbes have been identified. They include actinomycetes, bacteria, and fungi. Actinomycetes are filamentous bacteria that can be mainly found in soil. PLA degraders are all members of the Pseudonocardia family. Compared to actinomycetes, PLA-degrading bacteria are rare in the natural environment, so bacterial degradation of PLA is less...
common, although it does occur. PLA-degrading bacteria are mostly firmicutes and belong to thermophilic bacteria. Most fungi are unable to degrade PLA, but research has found that temperature is a key parameter for fungal degradation of PLA (Qi et al., 2017).

In microbial PLA degradation, PLA-degrading enzymes play a vital role. Most of these enzymes are serine proteases, with proteinase K being the most prominent one. This group of proteases has serine at its active site (Qi et al., 2017).

15 BIOCHEMICAL PROCESSES IN PLA DEGRADATION (QI ET AL., 2017)

**PHB BIODEGRADATION**

PHB can be completely biodegraded to carbon dioxide and water by microorganisms. This can happen through the process of enzyme degradation, or the process of biotic degradation (Bonartsev et al., 2007; dos Santos, Oliveira Dalla Valentina, Hidalgo Schulz, & Tomaz Duarte, 2018).

During enzyme degradation, the long polymeric chain is broken down by enzymes, so that oligomers and monomers are formed. In this process, intra- and extracellular depolymerases are involved. Various microorganisms are able to secrete these enzymes. In general, the optimum pH for the depolymerization is between 7.5 and 9.8 (dos Santos et al., 2018).

Biotic degradation is an irreversible process that involves biological activities. This type of degradation occurs when the polymer and micro-organism are present in the same biologically active environment. The involved micro-organisms use PLA degrading enzymes, that break down the polymer chain into smaller components. Biotic degradation begins with biodeterioration, which
Depolymerization of PHB rarely reaches 100%, because part of the polymer’s carbon becomes embedded in the microbial biomass. The process is affected by the presence of oxygen. In aerobic conditions, CO₂, water, and biomass are produced. In anaerobic conditions, these same molecules are produced, but a lack of oxygen also results in the production of methane (CH₄), which can be damaging to the environment. Hence, biotic degradation of PHB should ideally happen under aerobic conditions (dos Santos et al., 2018).

BIODEGRADATION OF POLYMER BLENDS

The degradation of polymer blends depends on the degradation of their biodegradable components. This initial degradation process breaks the structural integrity of the polymer, which considerably increases the surface area of the components that are more difficult to degrade. Hence, the exposure of the remaining parts of the polymer to microbes and enzymes is enhanced, leading to higher biodegradability of the material as a whole (Shah et al., 2008).

For our product, we use two polymer blends, a blend of PHB and PEO, and a blend of PLA with PS. Both blends involve synthetic polymer and a biodegradable polymer. As described, the fast degradation of PHB and PLA will increase the surface area of their corresponding synthetic polymer, thereby increasing biodegradation. Hence, both polymer blends will be biodegradable at higher rates, making the product environmentally sustainable.

FACTORS INFLUENCING BIODEGRADATION

The process of biodegradation depends on different factors. First of all, polymer characteristics such as molecular weight, the type of functional groups, and its mobility play a role. Furthermore, the type of organism carrying out the degradation, as well as environmental factors must be taken into account (Qi et al., 2017; Shah et al., 2008).

POLYMER CHARACTERISTICS

For a microbial attack to occur, bacteria require the substrate to be assimilated through the cellular membrane. This happens most smoothly when a molecule has high solubility. Hence, if a polymer has functional groups that increase hydrophobicity, this leads to faster degradation. Additionally, larger and heavier molecules are less soluble, which means that polymers with a higher molecular weight are generally less degradable by microorganisms (Alshehrei, 2017; Shah et al., 2008).

Besides solubility, the general structure is an important factor that influences the rate of biodegradation. Some polymer bonds are more difficult to break than others, and the presence of easily breakable bonds leads to faster degradation. In general, esters bonds are broken most easily, followed by ethers and amides respectively. Urethane bonds are more difficult to break (Alshehrei, 2017).

Furthermore, the nature and physical form of the polymer influence biodegradation rates. For example, the plastic can have the form of a film, pellet, or powder. As a rule, substances that are spread out more evenly have higher reaction rates, because this leads to a larger surface area relative to the total volume. Therefore, plastics that are distributed evenly, such as powders, biodegrade the fastest (Alshehrei, 2017).
In short, a polymer has optimal biodegradability when it is highly soluble in water, so when it has hydrophobic functional groups and has a low molecular weight. Biodegradability is also enhanced when the polymer has bonds that are easily breakable and when the plastic is distributed very evenly.

**ORGANISM CHARACTERISTICS**

The degradation ability of the microorganisms that carry out the depolymerization process is very important for biodegradation. Polymers are generally too large to pass through the bacterial membrane. Hence, the organism must have produced extracellular enzymes that are capable to break the large chains down into smaller monomers.

**ENVIRONMENTAL FACTORS**

Like all reactions, biodegradation reactions are most effective under certain circumstances. They all have an optimum temperature and pH-value. Additionally, some microbial degradation mechanisms require external resources, such as water or light. The ideal circumstances are different for every reaction. They depend on the type of polymer, as well as on the microorganism that carries out the degradation (Qi et al., 2017).
Impact of Plastics on the Environment and Public Health

Over the past 50 years, polymers have dramatically increased in production (Nkwachukwu et al., 2013). Unfortunately, the rise in plastic usage leads to several negative effects on public health and the environment. Harmful chemicals are being released during both production and usage, and the manufacturing of plastics requires the use of fossil fuels. Additionally, plastic pollution of the natural environment and oceans is of increasing concern (Jambeck et al., 2015; Nkwachukwu et al., 2013; Ritchie & Roser, n.d.; Shah et al., 2008).

In the upcoming section, the impact of plastics on the environment and public health will be discussed. Both the positive and negative effects of plastic usage and production will be touched upon.

Plastic Production

The environment is negatively impacted by the plastic production process in three important ways. First of all, harmful chemicals are released during plastic manufacturing. Secondly, the production of plastic requires the use of fossil fuels. Lastly, plastic waste is generated throughout the entire production process.

In the upcoming section, the environmental effects of chemical release and fossil fuel usage will be elaborated upon. The effects of plastic waste production will be discussed in a later section.

Release of Chemicals

During the manufacturing process of plastics, several chemicals are released into the environment. This can lead to different problems, depending on the characteristics of the chemical that is released. The most prominent chemicals and their corresponding potential issues will be discussed in the upcoming section.

Chlorofluorocarbons

The production of foamed plastics involves the usage of blowing agents, all of which eventually escape into the air. Among them are chlorofluorocarbons (CFCs), which cause damage to the stratospheric ozone layer (Nkwachukwu et al., 2013; Noakes, 1995).

CFCs are halocarbons, and they have the ability to transport halogens, particularly chlorine, to the height of the ozone layer. Once there, the halocarbon decomposes under the impact of UV radiation. This creates free radical species, which interferes with the balance of the stratospheric ozone layer, potentially causing it to deteriorate (Noakes, 1995).

Dioxins

When manufacturing materials containing chlorine, the production and release of dioxins is unavoidable. These unintentional persistent organic pollutants are formed as a result of incomplete chemical reactions or combustions in thermal processes involving organic matter and chlorine (Nkwachukwu et al., 2013).

Dioxins have a persistent nature, which causes them to accumulate in the environment, where humans are exposed to them. The caused health effects depend on several factors, including the level and duration of exposure, and predispositions of the exposed individual. Possible health effects of dioxins include cancer development, immune system suppression, reproductive complications, and endocrine disruption (Nkwachukwu et al., 2013).
EXTRACTION OF RESOURCES
A large amount of fossil fuels is needed for the production of conventional plastics. It is estimated that around 4 percent of the total global oil production is used as a material for plastic production. During the manufacturing process, an additional 4 percent is used to generate energy. This means that in total, 8 percent of world oil production is used for the production of plastics (“Environmental toll of plastics,” 2020).

This extraction of fossil fuels can lead to problems in the future. The world still depends heavily on them as an energy resource, but fossil fuel reserves are limited. Literature about fossil fuel depletion is contradictory, but the consensus is that fossil fuels will run out at a certain point. This could have a great impact if no sufficient alternative has been found at that time. Hence, fossil fuel usage should be limited (Shafiee & Topal, 2009). For this reason, the heavy oil usage in plastic production should be decreased.

PLASTIC USAGE
Presently, nearly every individual uses plastic in their daily life. This means that people are exposed to chemicals from plastics on a daily basis. For example, almost every adult has measurable amounts of phthalates in their body, and 93 percent of people have detectable levels of BPA in their urine. Exposure to such chemicals can be damaging to individuals’ health, making them more vulnerable to develop a variety of diseases (“Environmental toll of plastics,” 2020).

Some of the prominent chemicals have been shown to affect reproduction and development in both animals and humans. Literature has shown direct links between adverse health outcomes, like increased rates of heart disease and diabetes. Combining this with the fact that over 90 percent of the population has measurable levels of these potentially harmful compounds in their body does raise concerns. However, there is no conclusive research yet that determines the precise health effects related to exposure to plastic compounds (“Environmental toll of plastics,” 2020).

PLASTIC POLLUTION
During all stages of the plastic production process, plastic waste is released. Additionally, every plastic product is a waste product after consumption. It is estimated that about 50% of plastic is used for single-use purposes, meaning that they are disposed of after being used only once (Nkwachukwu et al., 2013).

Most commodity plastics lack biodegradability, meaning that they are very persistent in our environment. Hence, plastic waste materials that are not properly disposed of, are a significant source of environmental pollution. If the situation remains unchanged, the world will have to deal with an enormous environmental accumulation and pollution problem, which would take centuries to solve (Shah et al., 2008).

For this reason, plastic pollution of the natural environment and oceans is of increasing concern (Jambeck et al., 2015; Nkwachukwu et al., 2013; Ritchie & Roser, n.d.). The widespread presence of plastic waste has caused numerous accounts of wildlife becoming entangled in plastics. This entanglement can result in injury, impaired movement, or even death. Additionally, plastic pollution leads to a public health concern for humans, as there is evidence that indicates that toxic chemicals from plastics accumulate in living organisms throughout the nutrient chain (Nkwachukwu et al., 2013).

The upcoming section discusses the effects of plastic pollution. Additionally, different methods of proper waste disposal will be compared.
ENVIRONMENTAL IMPACTS
Plastic pollution of the natural environment is of increasing concern. Not only does it pose a threat to wildlife, it is also potentially harmful fur human health and wellbeing. These negative effects will be elaborated on further in the upcoming section.

Pollutants that are released from burning plastic waste are transported through the air and then end up on landmasses or in bodies of water. Several of these pollutants persist for long periods of time in the environment, where they are often eaten by animals. Annually, over a billion seabirds and fish die from plastic ingestion (“Environmental toll of plastics,” 2020). Larger animals can also get entangled in nets and films, which can cause them to drown or suffocate.

At least 267 different species are known to have suffered from either ingestion or entanglement. It is important to note that the impact of plastic pollution is not limited to the death of one animal. After the animal dies and decomposes, the plastic is released into the environment again, where it will potentially harm another organism (Nkwachukwu et al., 2013).

Plastic ingestion by animals is not only dangerous for the animal itself, it also poses a potential threat for humans. Plastics have a tendency to bioaccumulate through contaminated water and food, which means that they build up in predators at the end of the food chain, which is where humans are. Hence, humans can be exposed indirectly when they consume contaminated fish, meat, or dairy products. This can have many negative effects, such as an increased risk of cancer, reproductive failure, and immune diseases (Nkwachukwu et al., 2013).

Furthermore, plastic bodies in the ocean can serve as a transportation device for smaller organisms. This allows alien species to be introduced to new habitats, which often disrupts the ecosystem and is detrimental for local species (“Environmental toll of plastics,” 2020).

Littering of plastic bags may also lead to clogging of gutters and drains. This can prevent rainwater from leaving cities through underground systems. This has led to severe flooding on several occasions, for example in Mumbai, India in 2005, and Bangladesh in 1988 and 1998. Additionally, the clogging of sewer pipes by plastic bags causes stagnant water, which creates perfect habitats for mosquitos and other parasites. This leads to the potential spread of a large number of diseases, with malaria being the most notable and concerning one (Nkwachukwu et al., 2013).

WASTE MANAGEMENT
A large proportion of plastic pollution is caused by mismanaged waste. Jambeck et al. (2015) define mismanaged waste as “material that is either littered or inadequately disposed of”. This type of waste is not formally managed (Jambeck et al., 2015). In this paper, we identify three important proper waste disposal methods: landfill dumping, incineration, and recycling.

DUMPING IN LANDFILLS
Landfill dumping involves the depositing of waste in layers under the ground (“Waste - The waste dump or landfill,” n.d.). Although dumping waste in assigned landfills is considered to be a proper waste management method, this way of plastic disposal is the least efficient one and has several downsides (“Waste - The waste dump or landfill,” n.d.).

First of all, it takes up large areas of land. Generally, landfill sites cannot be used post-closure due to engineering or health risk reasons. Hence, landfill of waste tends to imply an irrecoverable loss of land. Furthermore, these large areas of waste landfills can cause visual disturbance (Nkwachukwu et al., 2013).
In addition to this, landfill dumping can generate bio-aerosols, odors, and hazardous chemicals. Organic breakdown after landfill disposal of biodegradable waste, including bioplastics, leads to greenhouse gases being released (Nkwachukwu et al., 2013). Furthermore, plastic’s chemicals often sink into the ground around the landfill, causing contamination of groundwater (“Environmental toll of plastics,” 2020).

Because of the aforementioned negative effects of landfill dumping, this waste management method is not considered to be a sustainable solution in the medium to long term (Nkwachukwu et al., 2013).

**Incineration**

In plastic incineration, plastic wastes are burnt. The energy that this produces is then tapped and used for other purposes. The environmental impacts of this waste disposal method include the release of airborne particles and greenhouse gasses. In some circumstances, the energy recovery of waste can lead to increased net CO₂ emissions due to substituted heat and electricity production. For these reasons, incineration activities should have suitable filter systems, so that environmental pollution is minimized (Nkwachukwu et al., 2013).

It is important to note that incineration cannot be done with all products that contain plastics, because this may lead to toxic chemicals being released into the environment. For example, electronic waste contains plastics, but also many harmful substances (Nkwachukwu et al., 2013).

The net societal costs or benefits of incineration depend on the existing alternatives for power generation and waste disposal for the specific polymer. It can be used complementary to other waste disposal methods, as long as environmental precautions are taken (Nkwachukwu et al., 2013).

**Recycling**

Plastic recycling is the reprocessing of used plastics so that they can be reused in new products. This waste management method has potential environmental and economic benefits, although it needs to be carried out in an environmentally sustainable manner (Nkwachukwu et al., 2013).

There are several constraints on the use of recycled plastics. With the exception of recycled PET, they are not used for food packaging due to hygiene standards and concerns about food safety. This is unfortunate because food packaging is one of the largest single markets for plastics (Nkwachukwu et al., 2013).

Another problem that often occurs in plastic recycling is that plastics are often a blend of different polymers, to which a composite may be added. This makes recovery challenging (Nkwachukwu et al., 2013).

For multiple reasons, PET is considered to be a suitable plastic for recycling after usage. First of all, because it is directly suitable for contact with food after recycling. It can also be used for many different applications, and it can easily be converted into PBT, which is also used for a wide variety of purposes (Nkwachukwu et al., 2013).

Wider implementation of plastic recycling is expected to have several effects. These include positive impacts on public health and the environment (Nkwachukwu et al., 2013).

**Positive Effects of Plastics**

“If plastics are made and used responsibly, they can help solve some environmental problems” (“Environmental toll of plastics,” 2020). They are used for many different purposes, some of which have the potential to reduce mankind’s negative influence on the environment.
First of all, plastics can be used to replace other, less efficient, materials. For example, packing beverages in PET rather than glass or metal reduces energy usage by 52 percent, and greenhouse gas emissions by 55 percent (“Environmental toll of plastics,” 2020). Additionally, plastic usage in food packaging can delay food expiration. Thereby, plastics prevent food losses (Nkwachukwu et al., 2013).

Furthermore, plastics are used as a material in wind power rotors, solar panels, and solar water heaters. It is estimated that wind power rotors and solar panels save between 600 and 1,300 million tonnes of CO₂ annually (Nkwachukwu et al., 2013). Solar water heaters can provide up to two-thirds of a household’s yearly demand for hot water, thus reducing energy consumption (“Environmental toll of plastics,” 2020).

In short, plastics can be beneficial for the environment by increasing material efficiency and allowing for green energy production. However, plastic production and usage must be done mindfully, so that its positive effects are not negated by the negative ones.
OUR PRODUCT
Our design consists of several parts, which all require specific material properties. Hence, they will all consist of different polymer blends. When deciding on which material to use, it is important to find a balance between optimal material properties, biodegradability, and cost-efficiency.

BODY
The body of our product will be a hard plastic, which will be either injection molded or blow-molded. It must not deteriorate under ultraviolet light. These basic property requirements apply for all other parts as well.

Considering these requirements, the body could be made out of a blend of polystyrene with a biodegradable polyester. These materials can be injection molded, and have good resistance to water (Biresaw & Carriere, 2004) and ultraviolet light, especially when ZnO is added into the biopolymer matrix (Mizielińska et al., 2018).

As described previously, a blend of PLA with 25 weight % of PS is very strong. Hence, we will make the body out of this blend with ZnO added into the matrix.

STORAGE CONTAINER
The desalinated drinking water will be stored in a storage container. In addition to the aforementioned basic requirements, it needs to be safe to store drinking water in the container without it becoming contaminated.

PLA blends are widely used for food and beverage packaging (Muraru & Dubois, 2016). Thus, they can be used to store drinking water safely. This means that the storage container can consist of the same PLA/PS blend that will be used for the body.

BOILER
The boiler must absorb as much energy from the sun as possible. This is why it will be made of black material. Hence, it is important that the plastic we use can be artificially colored, and that this color does not fade over time.

PS can be artificially colored by creating a copolymer with a photonic crystal (PC). A graphene-based PC (SGPC) immersed in tetrahydrofuran (THF) produces a black color (Dong, Yang, & Weng, 2014). Therefore, we can once again use the aforementioned PLA/PS blend. We will give this the desired black color through copolymerization with SGPC-THF.

The boiler will have to withstand weather conditions such as strong weather conditions and humidity. To maintain the efficiency of the boiler, there will be an additional plastic layer attached to the boiler. This will be made of thin transparent plastic. Transparency is a desired property of this film because the black color of the boiler needs to be visible. The plastic layer must not become opaque through UV-deterioration.

For this, we can use a CO₂-based bioplastic film. Poly(propylene carbonate) (PPA) combined with cellulose acetate (CA) creates a biodegradable film. PPA.CA films show excellent transparency and would hence be a suitable option for our product.
**SEALANT**

The sealant is used to seal the water compartments. This will need to have rubber-like properties.

The modification of biodegradable plastics like PHB can be impacted by using an acrylate rubber, such as poly(butyl acrylate) (PBA). Experiments have shown that the rubber exerts a positive influence on the toughness of the material and gives it properties that are similar to rubber. This effect is especially prominent at temperatures close to, and above room temperature (Avella et al., 2000).

Hence, we will use a blend of PHB with PEO in combination with PBA or another acrylate rubber. This will give the biodegradable material the required properties so that it can be used as a sealant.
CONCLUSION

This paper gave an introduction to the chemistry of plastics, with a particular interest in biodegradable plastics and environmental sustainability. Different aspects of plastic composition, production, degradation, and sustainability were covered.

The information in this deepening provided my team with the knowledge to choose the materials for Solar Still. These choices are argued in the Our Product section of the document. The general goal when deciding on our materials was to create a product that is durable, as well as being socially, economically, and environmentally sustainable.
REFERENCES


