Chapter I

INTRODUCTION

A. Background of the Study

Plastics are carbon-based polymers and we make them mostly from petroleum. With the discovery of plastics, life became much more convenient because it is used to make a wide array of useful materials. But these plastics are so durable that it will take many centuries for these plastics to completely degrade while other plastics will last forever. Discarded plastics are also a big cause of pollution and because of that, plastics make our environment a much less attractive place (Atienza, 2009).

Getting rid of plastics is extremely difficult. Burning these plastics gives off harmful chemicals such as dioxins that could contribute to Global Warming. Recycling these plastics is also difficult because there are many different kinds of plastics and each has to be recycled by a different process. Though these plastics are considered to be one of the greatest innovations ever, they are also imposing a great havoc to the environment, the wildlife and the general public (Woodford, 2008). For this reason, this study aims to develop a biomass-based plastic from the natural polysaccharides of seaweeds.

Biomass-based plastics or bioplastics are a form of plastics derived from renewable biomass resources like vegetable oil or corn starch rather than the conventional plastics which are made from petroleum. Their advantages are innumerable and one is their capability to biodegrade naturally within a short period of time only (Sweeney, 2008).

Seaweeds are best known for the natural polysaccharides that can be extracted from them which are widely used particularly in the fields of food technology, biotechnology, microbiology and even medicine but not yet in the plastic industry. Some of these polysaccharides are Floridean starch, agar and alginate (Montaño, 2010). Since they are renewable biomass resources and are polymers made from sugars which contain carbon, they could be used to create a bioplastic.

In this study, the natural polysaccharides from selected Philippine marine seaweeds will be utilized to develop a biodegradable and high-quality bioplastic.

B. Statement of the Problem

This study will be geared with the development of a bioplastic using different combinations of natural polysaccharides from seaweeds. It aims to make a good, environment-friendly, inexpensive and toxic-free bioplastic from selected Philippine marine seaweeds. It aims to create a biodegradable bioplastic and a bioplastic that will match the quality in terms of tensile strength and chemical resistance of many conventional plastics being used today. Specifically, it will aim to answer the following questions:

1. Will there be significant differences in the amount degraded of the bioplastics when they are put in the following substrates for 180 days?
   a. compost soil
   b. loam soil
   c. freshwater
   d. saltwater
   e. activated sludge

2. Will there be significant differences in the percent weight loss of the bioplastics when they are put in the following substrates for 180 days?
   a. compost soil
   b. loam soil
   c. freshwater
   d. saltwater
   e. activated sludge
3. Will there be a significant difference in the tensile strength of the bioplastics?
4. Will there be significant differences in the amount corroded of the bioplastics when the following chemicals are dropped onto the surface of the bioplastics and polyethylene plastics?
   a. hydrochloric acid
   b. sulfuric acid
   c. sodium hydroxide
   d. potassium hydroxide
5. Will there be significant differences in the zone of corrosion of the bioplastics when the following chemicals are dropped onto the surface of the bioplastics and polyethylene plastics?
   a. hydrochloric acid
   b. sulfuric acid
   c. sodium hydroxide
   d. potassium hydroxide

C. Statement of the Hypotheses

The following hypotheses were drawn from the problems:

H_{o1}: There will be no significant differences in the amount degraded of the bioplastics when the bioplastics are put in the following substrates.

a. compost soil
b. loam soil
c. freshwater
d. saltwater
e. activated sludge

H_{a1}: There will be significant differences in the amount degraded of the bioplastics when the bioplastics are put in the following substrates.

a. compost soil
b. loam soil
c. freshwater
d. saltwater
e. activated sludge

H_{o2}: There will be no significant differences in the percent weight loss of the bioplastics when the bioplastics are put in the following substrates.

a. compost soil
b. loam soil
c. freshwater
d. saltwater
e. activated sludge

H_{a2}: There will be significant differences in the percent weight loss of the bioplastics when the bioplastics are put in the following substrates.

a. compost soil
b. loam soil
c. freshwater
d. saltwater
e. activated sludge

H_{o3}: There will be no significant difference in the tensile strength of the bioplastics.

H_{a3}: There will be a significant difference in the tensile strength of the bioplastics.

H_{o4}: There will be no significant differences in the amount corroded of the bioplastics when the following chemicals are dropped onto the surface of the bioplastics and polyethylene plastics.

a. hydrochloric acid
b. sulfuric acid
c. sodium hydroxide
d. potassium hydroxide

H_{a4}: There will be significant differences in the amount corroded of the bioplastics when the following chemicals are dropped onto the surface of the bioplastics and polyethylene plastics.

a. hydrochloric acid
b. sulfuric acid
c. sodium hydroxide
d. potassium hydroxide

H_{o5}: There will be no significant differences in the zone of corrosion of the bioplastics when the following chemicals are dropped onto the surface of the bioplastics and polyethylene plastics.

a. hydrochloric acid
b. sulfuric acid
c. sodium hydroxide
d. potassium hydroxide

H_{a5}: There will be significant differences in the zone of corrosion of the bioplastics when the following chemicals are dropped onto the surface of the bioplastics and polyethylene plastics.

a. hydrochloric acid
b. sulfuric acid
c. sodium hydroxide
d. potassium hydroxide

D. Significance of the Study

Worldwide, about a million tons of petroleum-based plastics per year are being produced and used. To make these plastics, about seven million barrels of oil per day are being consumed (Sweeney, 2008). Now, imagine that number dropping to zero! With the help of bioplastics, one day, that might be a reality.

With this research, the conventional petroleum-based commercial plastics will soon be replaced by these bioplastics made from seaweeds. An advantage of this is that, they will not fill up the landfills because they are biodegradable and just for months, disposed bioplastics are completely gone unlike petroleum-based plastics which takes about many centuries.

Since another use of seaweeds will be discovered again, the seaweed industry specifically in the Philippines might rise at an increased rate causing the economy to boom. The seaweed stock will not be endangered since these seaweeds can grow at a very fast rate so depleted stocks can be replaced, too.

This research will also be significant to the whole scientific community since it would provide added information about how to make a good, environment-friendly, inexpensive and toxic-free bioplastic from seaweeds.

This research can also serve as a springboard for future researches who want to develop safe and cost effective bioplastics.

E. Scope and Limitations of the Study

This study will only focus on the development of a biodegradable and high-quality bioplastic using natural polysaccharides from selected Philippine marine seaweeds. This includes the harvesting of seaweeds from the field, extraction of the natural polysaccharides, making of the bioplastics, testing the biodegradability, tensile strength and general chemical resistance, gathering and analysis of data and finally, arriving at the conclusions. Most of the materials will be borrowed from the Marine Science Institute of the University of the Philippines-Diliman Campus and from the Philippine Science High School-Cagayan Valley Campus. It will take a week to finish the extraction of the polysaccharides and the making of the bioplastics since there are parts where drying is needed. A span of 180 days will be given for the biodegradability test in which the bioplastics will be put in different types of substrates to measure their biodegradability in varying conditions. Another couple of days will be allotted for the tensile strength and general chemical resistance tests. For the general chemical resistance test, the bioplastics will not be the only kind of plastic to be tested; polyethylene plastics, too, so that results from the bioplastics and from the conventional plastics can be compared. One-Way Analysis of Variance (ANOVA) will be the primary statistical tool to be used in analyzing the data gathered. The research will not be further extended on the massive production of the bioplastics for commercial use but this might also be possible.

F. Definition of Terms

Agar. A phycocolloid of repeating galactose units that can be extracted from red seaweeds. This will be used as a polymer in making the bioplastic.

Alginate. A phycocolloid of repeating mannuronic acid and guluronic acid units that can be extracted from brown seaweeds. This will be used as a polymer in making the bioplastic.

Amount Corroded. A quantity that can be defined as the amount of weight that is lost due to the corrosion brought about by a corrosive chemical.

$$\text{amount corroded} = \text{initial weight} - \text{final weight}$$

Amount Degraded. A quantity that can be defined as the amount of weight that is lost due to the natural biodegradation of the bioplastic.

$$\text{amount degraded} = \text{initial weight} - \text{final weight}$$

Biodegradability. It tells whether a material will degrade 60% of its total mass in 180 days only when immersed in substrates that promotes biodegradation. It is one of the properties of the bioplastic which will be determined.

Bioplastic. A plastic made up of natural biomass sources such as corn starch or vegetable oil.

Casting Compounds. Materials used to give hardness, durability and strength to materials like plastics. This will be used to give hard plastic-like properties to the bioplastic.

Floridean Starch. The main energy storage facilities for red and green seaweeds. This will be used as a polymer for the bioplastic.

General Chemical Resistance. It tells the set of chemicals a material can resist from the deterioration of its fundamental properties and to the chemicals that deteriorates its fundamental properties. It is one of the properties of the bioplastic which will be determined.

Glycerol. An organic substance having the formula, $C_3H_8O_3$, which is used as a plasticizer. This will be used as the main plasticizer of the bioplastic.

Graduated Cylinder. A device that measures the volume of liquids and solutions. This will be used in measuring the volumes of the chemicals to be used in making the bioplastics and the corrosive chemicals.

Instron Machine. A device that measures the tensile strength of a material by generating a force vs. elongation curve. This will be used to measure the tensile strength of the bioplastics.

One-Way Analysis of Variance. A statistical tool that is used to find for significant differences between and among the data gathered. This will be the main statistical tool to be used in this study.

Percent Weight Loss. A quantity that can be defined as the percentage loss in the weights of the bioplastics due to the effect of aerobic biodegradation or the enzymatic action of microorganisms.

percent weight loss = [(final weight – initial weight) / final weight] * 100%

Plaster of Paris. This will be used as the main casting compound of the bioplastic.

Plasticizers. Materials used to give elasticity, flexibility and strength to materials like plastics. This will be used to give soft plastic-like properties to the bioplastic.

Seaweeds. Multi-cellular algae that contain phycocolloids and polysaccharides which can be used as potential polymers for making bioplastics. This is where the Floridean starch, agar and alginate will be extracted.

Tensile Strength. It tells the maximum stress that a material can withstand while being pulled or stretched to the point that it breaks. It is one of the properties of the bioplastic which will be determined.

Vernier Caliper. A device that measures the dimensions of length of small objects. This will be used in the measurement of the sides of the bioplastics and the zone of corrosion.

Weighing Scale. A device that measures the mass of objects. This will be used in the measurement of the masses of the ingredients used to make the bioplastics and the initial, dry and final weights of the bioplastics to be tested.

Zone of Corrosion. A quantity that can be defined as the region that deteriorated due to the effect of the corrosive chemicals that have been dropped on the surface of the material.

Chapter II

REVIEW OF RELATED LITERATURE AND STUDIES

A. Marine Seaweed

A.1. Description

Seaweeds or marine benthic algae are multi-cellular and eukaryotic organisms that dwell primarily in brackish water and sea. They are divided into three groups according to their color – brown, red and green seaweeds. Seaweeds are considered as protists and not plants because they lack the true roots, leaves and stems found in plants (Campbell & Reece, 2008).

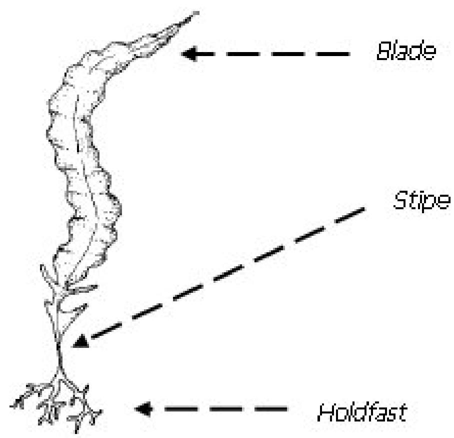

Fig.2.1. Anatomy of a Typical Marine Seaweed

The main body of the seaweed is called thallus. Seaweeds have leafy structures that are called blades. Blades do not contain veins and so, they are not considered as true leaves. Blades are large because they are the main site of photosynthesis. The stem-like structure is called the stipe. The stipe lacks the specialized tissues found in true plants and the stipe provides support for the seaweed. The root-like structure is called holdfast.

The holdfast anchors the seaweed to the bottom and unlike plant roots, the holdfast do not absorb nutrients and water (Miller & Levine, 2006).

A.2. Growth, Development and Reproduction

In most seaweeds, specialized cells are produced during sexual reproduction. When two of these cells join, a new cell is formed that grows into a new alga. Others reproduce asexually by dividing into two or more parts. Each part then grows into a new alga. Vegetative reproduction occurs in algae that have seed-like cells called spores. Once set free, the spores grow into new algae wherever they settle (The New Book of Knowledge, 2006).

A.3. Common Marine Seaweeds in the Philippines

A.3.i. *Gelidium*

Gelidium is a genus of red seaweeds and its species are highly branched. The branches may vary from cylindrical to compressed ones. Colors range from red to purple to green-black. Small, thick-walled, wiry rhizoidal filaments can be found in the subcortical and outer tissue of the medulla and this anatomical feature is used to distinguish them from other red seaweeds (Monterey Bay Aquarium Research Institute, 2010).

Fig.2.2. A Typical Structure of a *Gelidium* Seaweed

Gelidium is primarily utilized for its natural gums like agar. In many parts of Asia, this seaweed is being used a delicacy (Komarow, 1999).

A.3.ii. *Gracilaria*

Gracilaria is a genus of red seaweeds and it is characterized for its thin, solid and cylindrical branches and to its short pointed tips. It is typically red or pink in color. Branching is variable and the branches may reach up to the third level forming a bush-like appearance (Preskitt, 2010).

Fig.2.3. A Typical Structure of a *Gracilaria* Seaweed

Gracilaria is being cultivated for its natural gums like agar. In the Philippines, it is the primary source for gulaman. In many Asian countries like Japan and China, it is considered as a great delicacy (Montaño, 2010).

A.3.iii. *Laminaria*

Laminaria is a genus of brown seaweeds which is characterized by its compressed or cylindrical stipe and blades. The stipe and blades can be hollow or solid. They also have long, large and leathery laminae. Colors may range from golden yellow to dark brown (BayScience Foundation Inc., 2009).

Fig.2.4. A Typical Structure of a *Laminaria* Seaweed

Laminaria is widely cultivated for its high content of alginic acid and mannitol. Its organic content is primarily used as a fertilizer (Montaño, 2010).

B. Natural Polysaccharides in Marine Seaweeds

B.1. Description

Phycocolloids are polysaccharides of high molecular weight that are composed mainly of simple sugars. The term phycocolloid is used to describe a certain colloid that is derived from seaweed. Up to present research, only polysaccharides extracted from marine red and brown algae, such as agar, carrageenan, and alginate contain economic and commercial significance. They are important for the fact that these polysaccharides exhibit high molecular weights, high viscosity and excellent gelling, stabilizing and emulsifying properties. They are all water-soluble and are extracted with hot water or alkaline solution (Peck, 2010).

B.2. Common Polysaccharides in Marine Seaweeds

B.2.i. Floridean Starch

Floridean starch is a special type of starch that is primarily found in red seaweeds but it can also be found in green ones. It acts as the major cellular storage units of molecules and energy in these organisms. This type of starch is said to be three-dimensional in structure and the polysaccharide is sulfated. Floridean starch is found in the cytoplasm of the cell unlike true starch which is found in the chloroplast. To extract Floridean starch, one usually boils the seaweed in water until particles settle at the bottom. The particles will be collected and dried (Montaño, 2010).

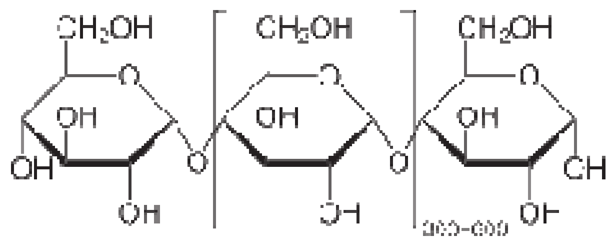

Fig.2.5. The Chemical Structure of Floridean Starch

B.2.ii. Agar

Agar is a cell wall constituent of red algae. It is a natural polymer made from repeating units of galactose. It is an odorless, slightly transparent and sugar-reactive substance which takes the form of a gel. Unlike gelatin which is a protein-based gel derived from animals, agar is a polysaccharide extracted primarily from red seaweeds (Guiry, 2010).

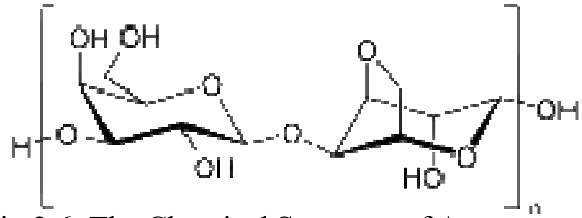

Fig.2.6. The Chemical Structure of Agar

To extract agar, the red seaweed will be cooked in 5% NaOH solution for an hour. It will be washed with running water and will be soaked in 750 mL of 0.5% HOAc solution for an hour. It will be washed again and will be soaked in one liter of boiling water. It will be blended and will be filtered in a filter bomb. The filtrate will be collected and will be put in a freezer overnight. The following day, the gel will be thawed and the agar wafer will be dried (Montaño, 2010).

B.2.iii. Alginate

Alginate is a cell wall constituent of brown algae. It is a natural polymer made from repeating units of mannuronic acid and guluronic acid. It is an odorless, slightly transparent and viscous gum which takes the form of a liquid gel. It has a hydrophilic nature that makes alginate capable of absorbing water much greater than its weight (Guiry, 2010).

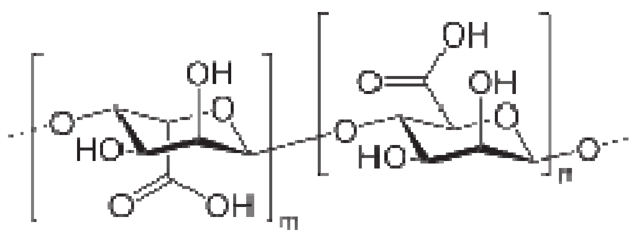

Fig.2.7. The Chemical Structure of Alginate

To extract alginate, the brown seaweed will be soaked in 0.1 M HCl solution overnight. The seaweed will then be washed in one liter of 1% Na_2CO_3 solution. It will be blended and filtered in a filter bomb. The filtrate will be collected and will be precipitated with IsprOH (three times the volume of the filtrate). It will be dried and grinded (Montaño, 2010).

B.3. Uses and Importance

These polysaccharides from seaweeds particularly agar and alginate are widely used particularly in the fields of food technology, biotechnology, microbiology and medicine. Their water absorbent capacities are used as thickening, emulsifying and stabilizing agents in confectionaries and pastries like ice creams and jelly-aces. Agar is used in gel electrophoresis and as a growth medium for microorganisms. Alginate is used in making fibers for band aids and fireproof outfits. Floridean starch is still being researched for its probable applications in the industry (Montaño, 2010).

C. Bioplastics

C.1. Description

Biomass-based plastics or simply bioplastics are a form of plastics that are made from pure renewable biomass resources such as corn starch or vegetable oil (Sweeney, 2008). Some common types of bioplastics are made from starch, polylactide acid and poly-3-hydroxybutyrate but through continuous research and development, other natural polymers can also be used (Bioplastics24, 2007). Most bioplastics are being engineered to biodegrade naturally and with the help of the enzymatic actions of microorganisms. They can be composted and will decay into substances that blend harmlessly with the soil (Woodford, 2008).

Bioplastics are commonly made from water mixed with natural polymer(s), plasticizers like sorbitol and glycerol and some other additives such as casting compounds and food colorings. The mixture will be continuously stirred and heated until a clear gel is formed. The gel will be poured over a mold and will be dried for a day. There is no recommended proportion of the substances in the mixture because varying amounts of the substances will create different properties, too but it is recommended to test whether the proportion you made satisfies the desired characteristics you wanted (Sweeney, 2008).

C.2. Advantages and Importance

These bioplastics are believed to answer the big problem about plastic waste disposal. They are convenient to use since they are almost similar to those of conventional plastics: the only difference is that most bioplastics are biodegradable. They are free from any allergens or toxins that can harm us particularly our health. They are easy to recycle since less energy is required to recycle them. Petroleum stocks will not be depleted since bioplastics are derived from renewable biomass resources. The advantages of using bioplastics are innumerable but most of all, these bioplastics help promote a greener and better living on the planet (Valdez, 2010).

D. Methods of Evaluating the Effectiveness of Bioplastics

D.1. Biodegradability

According to the American Society for Testing Materials (2010), for a bioplastic to be defined as biodegradable, it should meet the following specifications:

1. the material has to degrade at least 60% of its total mass within 180 days only;
2. the material has to disintegrate into very small pieces;
3. the residue has to contain certain specified limits of heavy metals and other contaminants.

Usually, the bioplastics are immersed in different substrates for 180 days. Some common substrates used in testing biodegradability are loam soil, compost soil, freshwater, saltwater and activated sludge (Biyo & Temelo, 2008). From time to time, the carbon dioxide released or the dry weights of the bioplastics will be monitored. A curve will result from the data gathered. After 180 days, the residue will be collected for analysis of its contents. When the bioplastic had successfully met the specifications designated by ASTM, the bioplastic is now considered to be biodegradable (Stevens, 2010).

D.2. Tensile Strength

Tensile strength is the maximum stress that a material can withstand while being pulled or stretched to the point that it breaks (Arevalo & Distefano, 2010). It is also the maximum load that a material can support without fracture when being stretched, divided by the original cross-sectional area of the material. In the SI system, the unit of tensile strength is the pascal (Pa), defined as one newton per square meter (N/m^2) (Encyclopædia Britannica, 2010).

To measure tensile strength, a machine called Instron is used. A gradually increasing force is applied to the material and the Instron machine will generate a force vs. elongation curve that can be used to obtain a complete tensile strength profile of the material (Instron, 2010).

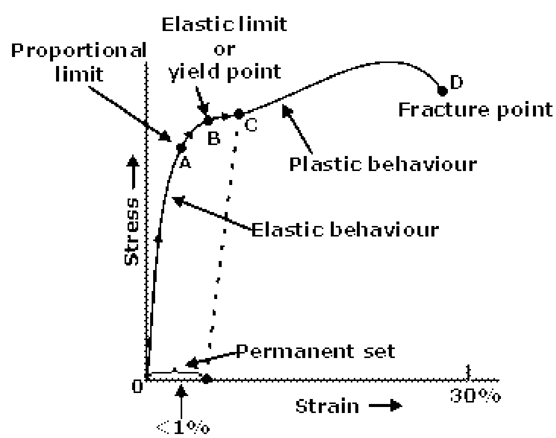

Fig.2.8. A Typical Force vs. Elongation Curve

In the linear part of the graph or the elastic region, the material obeys the Hooke's Law in which the material can be obtained in its original dimensions when the forces are removed. In the curve part or the plastic region, the material no longer obeys Hooke's Law and when forces are removed, the material has already incurred permanent deformations. At the end of the graph, the material is already fractured or broken (Giancoli, 1998).

To get the tensile strength of the material, the force that caused the fracture will be divided by the original total cross-sectional area of the material. Usually, elastic and ductile materials will undergo significant deformations before a complete failure occurs while hard and brittle ones will have little or no deformation (Kopeliovich, 2009).

Table 2.1 shows the standard tensile strengths of some common conventional plastics that are in use today (Dotmar Engineering Plastic Products, 2008).

Table 2.1. Tensile Strength (MPa) of Dotmar Engineering Thermoplastics

Product Name	Plastic Type	Tensile Strength (MPa)
Celazole PBI	PBI Polybenzimidazole	140
Ketron PEEK-CA30	PEEK Polyetheretherketone	130
Torlon 4203 & 4503	PAI Polyamide-imide	120
Ketron PEEK-1000	PEEK Polyetheretherketone	110
PEI-1000	PEI Polyetherimide	105
Ertalon 66GF-30	Nylon	100
Ertalon 4.6	Nylon	100
Torlon 5530	PAI Polyamide-imide	95
Nylatron GS	Nylon	92
Ertalyte	PETP Polyester	90
Ketron PEEK-GF30	PEEK Polyetheretherketone	90
Ertalon 66SA	Nylon	90
Ertalon 6PLA	Nylon	85
Ertalon 6XAU+	Nylon	83
Nylatron MC901	Nylon	81
Torlon 4301 & 4501	PAI Polyamide-imide	80
PSU-1000	PSU Polysulphone	80

Nylatron GSM	Nylon	78
Ertalyte TX	PETP Polyester	76
Ertalon 6SA	Nylon	76
PPSU-1000	PPSU Polyphenylenesulphone	76
Ketron PEEK-HPV	PEEK Polyetheretherketone	75
Techtron HPV PPS	PPS Polyphenylene Sulphide	75
Ertalon LFX	Nylon	70
Ertacetal C	Acetal	68
Nylatron 703XL	Nylon	66
Safeguard Hardcoat XX	PC Polycarbonate	65
Safeguard	PC Polycarbonate	65
Trovidur EN PVC	PVC Polyvinylchloride	55
PVDF 1000	PVDF Polyviylidenefluoride	50
Tetco V	PTFE Polytetrafluoroethylene	36
Polystone 500	PE Polyethylene	28
Tetron S	PTFE Polytetrafluoroethylene	28
Polystone PP	PP Polypropylene	26
Tetron HG	PTFE Polytetrafluoroethylene	25
Polystone 300	PE Polyethylene	23
Tetron B	PTFE Polytetrafluoroethylene	23
Polystone 7000	PE Polyethylene	20
Polystone Ezyslide 78	PE Polyethylene	20
Polystone Ultra	PE Polyethylene	20
Polystone M-Slide	PE Polyethylene	20
Polystone 7000SR	PE Polyethylene	20
Polystone 8000+	PE Polyethylene	19
Polystone M-Flametech AST	PE Polyethylene	18
Tetron C	PTFE Polytetrafluoroethylene	17.6
Tetron G	PTFE Polytetrafluoroethylene	17
Tetron GR	PTFE Polytetrafluoroethylene	16.5
Tetron LG	PTFE Polytetrafluoroethylene	11.7
Playtec	PE Polyethylene	

D.3. General Chemical Resistance

Materials are being tested first before they are being sold in the market. This is being done so that the strengths and weaknesses of the materials can be determined for further improvisation of its quality. One of the properties being verified is the general chemical resistance which refers to chemicals that it can resist from deterioration and to the chemicals that destroy its fundamental properties (Pella, 2010).

Corrosion is defined as the deterioration of the essential properties of a material which takes place when the material is exposed to chemicals that could cause corrosion. Some common examples are rusting iron nails and tarnishing silver plates. Chemicals that could corrosion are called corrosive chemicals. Strong acids like hydrochloric acid and sulfuric acid and strong bases such as sodium hydroxide and potassium hydroxide are some typical examples of corrosive chemicals (Tatum & Harris, 2010).

When testing for the general chemical resistance of a material particularly a plastic, thin strips of it are cut and initially weighed and some corrosive chemicals are dropped onto the surface of the material. After some couple of minutes, the plastic strips will be weighed again. A circle will result from the corrosion. The diameter of the circle will be measured and the area of the circle or the zone of corrosion can now be calculated. It is recommended that the zone of corrosion occupies only a small area (Division of Alabama Specialty Products, Inc., 2011).