RESEARCH ARTICLE

PRODUCTION OF BIODEGRADABLE PLASTICS BY USING OF STARCH (TAPIOCA & CASSAVA)

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ABSTRACT

From this experimental work provide the good quality of biodegradable plastics and avoided the Environmental pollution compare to other synthetic plastic products. In this method we can used Modified starch (tapioca & cassava) was prepared from the reaction between starch and maleic anhydride using sodium hydroxide as catalyst and water as solvent. After the reaction finished, the product was neutralized with hydrochloric acid solution. Plastic sheets can be prepared from the modified starch by casting. Preliminary studies on characteristics and some properties of these plastic sheets were done using several techniques. It was found that the amount of maleic anhydride plays an important role in changing the chemical structures of the modified starch and the characteristics of the plastic sheets whereas the reaction time does not affect them. The plastic sheets are fully biodegradable. They are insoluble in typical solvents such as chloroform or in acidic solution at both room and elevated temperatures while they are soluble in hot basic solution. It was also found that modified starch-based plastic sheets have lower glass transition temperatures, lower melting points, higher moisture absorption and higher hardness than unmodified starch-based plastic sheets.

INTRODUCTION

Nowadays, plastic consumption is increasing rapidly. This is because plastics can be used in many applications such as packaging, automobile parts, etc. The need for such large quantities of conventional plastics and their dominance over other materials is due to their excellent “long life” properties. However, plastics cannot be degraded by natural processes in a short period of time; therefore, they are left as ‘plastic waste’, causing environmental problems. Methods normally used to destroy other types of waste such as burning and burying are not suitable for plastic destruction. Degradation at high temperature, such as in pyrolysis (burning) tends to cause emission of toxic fumes. Plastic accumulation in the environment thus creates tremendous problems for the world, presently and in the future. Environmental problems caused by plastics include changes to the carbon dioxide cycle, problems in composting, and increased toxic emissions. When some types of plastics are burnt, they can release dangerous gases to the atmosphere while burying plastics in soil cannot destroy plastics because they are not biodegradable. Alternative methods to solve this problem have been studied. One method that has been developed is to replace commonly used plastics prepared from synthetic polymers with biodegradable plastics prepared from natural polymers.

Cassava (Manihot esculenta Crantz), also known as mandioca, is a starchy root belonging to the Euphorbiaceae family and is one of the most important energy sources for tropical area of the world. Although cassava thrives in fertile soil, its comparative advantage to other more profitable crops is their ability to grow in acidic soils of low fertility, with sporadic rainfall or long periods of drought. A widely used natural polymer is starch because it is abundant and inexpensive. Since its molecules are closely packed due to its structural regularity and tightly bonded by hydrogen bonds, its melting point is above its decomposition temperature. This causes difficulty in preparation of plastic directly from starch. Besides, many properties of the resulting plastic are not suitable for many applications in which synthetic polymers are normally used. Consequently, most of the research has been concentrated on blending or copolymerizing starch with synthetic polymers. Since 1970, there has been a tendency to produce and apply biodegradable polyethylene (BDPE), which is not harmful to soil or the environment [1,2]. Polyethylene manufacturers add anti-oxidants to the resin because it’s inherently unstable, especially when exposed to ultraviolet (UV) light and hard weathering [3,4,5]. The polymer chain is cleaved and oxidized via free radical formation due to the highly unsaturated carbon bonding in its molecules. So, it could be degraded in this way but usually the oxidant lasts as little as one year [4, 6].

Magnitude Of The Problem

India is an agriculture country, it contain total forest & agriculture land of 1004540 km². In that 1750.25 lakh ha amount of land become polluted (in the year of 1984), but only 247.84 lakh ha of land treated. Still 1502.41 lakh ha of area are remaining. CHENNAI: On Independence Day, the Marina was declared plastic-free no longer are disposable cups, plates, bags or even water sachets allowed on the 4.5 km stretch beginning from the light house to the Anna memorial.

And it’s a problem facing countries across the world: each year, an estimated 500 billion to 1 trillion plastic bags are consumed worldwide, which is about over one million a
minute and most of them end up in the dustbin in a few minutes. Closer home, every Nilgiris supermarket outlet in the city receives an average of 15,000 plastic bags a month. And bookstores in Chennai give out about 30,000 plastic bags a month. To conclude, it is a mistake to focus on finding ways to make products easier to throw away in the name of helping the environment. Biodegradable plastics are exciting and useful materials, but they should only be used when they have a concrete benefit for a specific product. The best way to help save the planet is to save energy and improve ways of recycling and recovering all plastics.

Some Of The Bio-Degradable Plastics

While aromatic polyesters are almost totally resistant towards microbial attack, most aliphatic polyesters are biodegradable due to their potentially hydrolysable ester bonds:

Naturally Produced

- Polyhydroxyalkanoates (PHAs) like the Poly-3-hydroxybutyrate (PHB),
- Polyhydroxyvalerate (PHV) and Polyhydroxyhexanate (PHH).

Renewable Resources: Polyactic Acid (Pla)

Synthetic

- Polybutylene succinate (PBS), Polycaprolactone (PCL)…
- Polyamphidrites
- Polyvinyl alcohol
- Most of starch derivatives
- Cellulose esters like cellulose acetate and nitro cellulose and their derivatives (celluloid)
- Enhanced biodegradable plastics with additives

Starch Molecular Structure

Biodiversity And Occurrence Of Polymer-Degrading Microorganisms

Biodiversity and occurrence of polymer-degrading microorganisms vary depending on the environment, such as soil, sea, compost, activated sludge, etc. It is necessary to investigate the distribution and population of polymer-degrading microorganisms in various ecosystems. Generally, the adherence of microorganisms on the surface of plastics followed by the colonization of the exposed surface is the major mechanisms involved in the microbial degradation of plastics. The enzymatic degradation of plastics by hydrolysis is a two-step process: first, the enzyme binds to the polymer substrate then subsequently catalysis a hydrolytic cleavage. Polymers are degraded into low molecular weight, dimers and monomers and finally mineralized to CO2 and H2O.

Factors Affecting The Biodegradability Of Plastics

The properties of plastics are associated with their biodegradability. Both the chemical and physical properties of plastics influence the mechanism of biodegradation. The surface conditions (surface area, hydrophilic, and hydrophobic properties), the first order structures (chemical structure, molecular weight and molecular weight distribution) and the high order structures (glass transition temperature, melting temperature, modulus of elasticity, crystallinity and crystal structure) of polymers play important roles in the biodegradation processes.

The crystalline part of the polymers is more resistant than the amorphous region. The rate of degradation of PLA decreases with an increase in crystallinity of the polymer. As shown in, the melting temperature (Tm) of polymers has a strong effect on the enzymatic degradation of polymers. In general, Tm is represented by the following formula:

\[
Tm = \frac{H}{S}
\]

Where \( H \) was the change of enthalpy in melting and \( S \) is the change of entropy in melting. It is well known that the interactions among polymer chains mainly affect the \( H \) value and that the internal rotation energies corresponding to the

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyester</td>
<td>(-O-(\text{CH}_2)_n-CO-(\text{CH}_2)_m-CO-)</td>
<td>60</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>(-O-(\text{CH}_2)_n-CO-O-(\text{CH}_2)_m-CO-)</td>
<td>65</td>
</tr>
<tr>
<td>Polyurethane</td>
<td>(-NH-(\text{CH}_2)_n-NH-CO-O-(\text{CH}_2)_m-CO-)</td>
<td>180</td>
</tr>
<tr>
<td>Polyamide</td>
<td>(-NH-(\text{CH}_2)_n-NH-CO-(\text{CH}_2)_m-CO-)</td>
<td>240</td>
</tr>
<tr>
<td>Polyamide</td>
<td>(-NH-(\text{CH}_2)_n-NH-CO-(\text{CH}_2)_m-CO-)</td>
<td>265</td>
</tr>
</tbody>
</table>
rigidity (the flexibility) of the polymer molecule remarkably affect the $\Delta S$ value.

**Chemical formulas of aliphatic polyester, polycarbonate, polyurethanes and polyamides with their (tm) s.**

**Production Of Biodegradable Starch From Modified Cassava Starch**

A simpler and cheaper method for modifying starch based on the following reactions was attempted in this research. Furthermore, preliminary studies on the possibility to form plastic from the modified starch and some properties of the obtained plastic were investigated.

$$\text{Starch} - \text{OH} + \text{OH}^- \xrightarrow{\text{yields}} S\text{tarch} - \text{O}^- + \text{H}_2\text{O}$$

$$\text{Starch-O}^- + \text{RC-OCR} \rightarrow \text{Starch-OCR} + \text{RCOO}^-$$

**MATERIALS AND METHODS**

**Materials Required**

Cassava starch, Maleic anhydride (MA), Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Ethanol, Methanol, Toluene, Chloroform, Xylene, Acetone, Sulfuric acid, Tetrahydrofuran (THF), and Petroleum ethers.

**Modification of Cassava Starch**

Cassava starch was dried in a vacuum oven at 80°C overnight and it was left to cool down in a desiccator. The dried starch (15 wt % of water) was slowly added into a beaker containing aq. NaOH solution at 50°C

$$(\text{NaOH: MA}) = 2.2:1$$

After the mixture was homogenous, MA was slowly added to the mixture. The reaction time was maintained as desired. After that, the product was neutralized by aq. HCl solution. The amounts of MA used were 25%, 50% and 75% of MA acidic groups in molar proportion to hydroxyl groups of starch. The reaction times used were 2, 4 and 6 hours.

Characterization of Modified Starch

Two portions were taken from the modified starch mixture. One portion was poured into ethanol. The precipitate was recovered, washed with ethanol and dried in a vacuum oven. The other portion was dried in a vacuum oven without precipitation from ethanol. Both portions were then characterized by IR spectroscopy.

**Preparation of Sheet Samples from Modified Starch by Casting**

The modified starch mixtures obtained from 1 were poured into plastic moulds. The samples were left to dry at room temperature. After drying, the samples were soaked in 75 % ethanol for 10 minutes and then they were left to dry at room temperature. Sheet samples were obtained.

**Solubility Test**

The sheet samples were cut into small pieces of 0.5 g. They were put into 10 ml test tubes containing 3 ml of a solvent. The solubility of the samples was observed at both room and elevated temperatures.

**Moisture Absorption**

The samples with moisture content were dried in a desiccator until their weights became constant ($W_0$). These samples were then placed in normal atmosphere for 24 hours. After that, the samples were weighed ($W_1$) % moisture absorption, ($%M$) can be calculated from the following equation:

$$%M = \frac{(W_1-W_0)}{W_0} \times 100$$

**Thermal Analysis**

Thermal properties of the sheet samples were studied by differential scanning calorimetry (DSC) using differential scanning calorimeter with a temperature range of 25-200°C and a heating rate of 10°C/min.

**Hardness Test**

Hardness of the samples was determined.

**Biodegradability Test**

Biodegradability test was done based on the soil burial method. Samples were dried in desiccator until their weights became constant ($W_2$). These samples were then buried in soil for 1 month. After that, the samples were dried in a desiccator until their weights became constant ($W_3$). % weight loss, ($%W$) can be calculated from the following equation:

$$%W = \frac{(W_2 - W_3)}{W_2} \times 100$$

**RESULTS AND DISCUSSION**

All modified starch mixtures obtained after neutralization with HCl solution were slightly viscous liquids. The colour of the mixtures prepared with MA 75% at every reaction time was slightly yellow whereas the colour of mixtures prepared with MA 25% and 50% at every reaction time was creamy white. The FT-IR spectroscopic results indicate that the amount of MA has a significant effect on the chemical structures of the modified starches. The broad peak at a wavenumber range of 3200-3600 cm$^{-1}$ corresponds to OH stretching. It can be seen that as the amount of MA increases, this peak split into two peaks. This indicates two types of OH stretching which are from OH groups and COOH groups. All modified starches show broad peaks at a wavenumber range of 1560-1610 cm$^{-1}$ which corresponds to COO of ester groups. The intensity of this peak increases with increasing amounts of MA. However, it is clearly seen in the FT-IR spectrum of modified starch with MA 75% that this broad peak actually splits. This indicates the presence of COO$^-$. The peaks at wavenumber around 870 cm$^{-1}$ in the FT-IR spectra of the modified starches...
Cassava starch can be modified by using maleic anhydride as modifier, sodium hydroxide as catalyst and water as solvent at 50°C. The plastic sheets can be formed from the modified starches by casting. When the amount of maleic anhydride used for modification increases, the difference between the chemical structures of unmodified and modified starches increases. The flexibility of the plastic sheets increases and the toughness of the plastic sheets decreases with increasing the amount of maleic anhydride. However, the reaction time does not affect either the chemical structures of the modified starches or the characteristics of the resulting plastic sheets. The results suggest that a reaction time of 2 hours is suitable for the modification process. It was found that plastic sheets are fully Furthermore, it was found that the sheet samples cast from modified starch mixtures prepared with the same amount of MA but different reaction times have the same characteristics. This also demonstrates that the reaction time has no effect on the chemical structure of the modified starches. Since the reaction time has no effect on the chemical structures of the modified starch, this suggests that a reaction time of 2 hours should be used if this process is applied in industry. Therefore, some further properties of sheet samples prepared using a reaction time of 2 hours were studied.

**CONCLUSION**

**Reference**


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