

BIODEGRADABLE PLASTICS – A BOON TO THE DEGRADING ENVIRONMENT

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ABSTRACT

Plastic is the most convenient material man has ever discovered due to its relative cheapness, ease of manufacture, versatility, and imperviousness to water. Plastics are used from paper clips to spaceships, and displaced materials such as wood, metal, bones and horns, stone, leather, paper, even ceramics in most of their former uses. But plastic seemed to create a drastic effect. Because it is composed of chemicals (petroleum-based) it takes too long to degrade (considerably non-biodegradable) and improper disposal has led to waste problems and pollution thus destructing our environment. A solution can be achieved by the use of the bioplastics. Bioplastics are just like plastics, but instead of non-renewable petroleum as source, it uses organic sources like plant sources (corn starch, soybean oil, hemp oil, etc.) and microbial sources. They can be made by using plant sugar conversion, fermentation and cultivation. Unlike petro plastics they are biodegradable when disposed properly thus reducing waste production and environmental pollution.

KEYWORDS: Plastics, Drastic effect, Non – biodegradable, Environmental Pollution and Bioplastics.

INTRODUCTION

A plastic material is any of a wide range of synthetic or semi-synthetic organic solids used in the manufacture of industrial products. Plastics are typically polymers of high molecular mass, and may contain other substances to improve performance and/or reduce production costs. Monomers of plastic are either natural or synthetic organic compounds. The first man-made plastic was created by Alexander Parkes who publicly demonstrated it at the 1862 Great International Exhibition in London. The material called Parkesine was an organic material derived from cellulose that once heated could be molded, and retained its shape when cooled.

Bioplastics are a form of plastics derived from renewable biomass sources, such as vegetable oil, corn starch, pea starch, or microbiota, rather than fossil-fuel plastics which are derived from petroleum. Some, but not all, bioplastics are designed to biodegrade. Constituting about 50 percent of the bioplastics market, thermoplastic starch, such as Plastarch Material, currently represents the most important and widely used bioplastic. Pure starch possesses the characteristic of being able to absorb humidity, and is thus being used for the production of drug capsules in the pharmaceutical sector. Flexibiliser and plasticiser such as sorbitol and glycerine are added so the starch can also be processed thermo-plastically. By varying the amounts of these additives, the characteristic of the material can be tailored to specific needs (also called "thermo-plastical starch"). Simple starch plastic can be made at home shown by this method. Cellulose bioplastics are mainly the cellulose esters (cellulose acetate, nitrocellulose...) and their derivatives (celluloid). The aliphatic biopolyesters are mainly polyhydroxyalkanoates (PHAs) like the poly-3-hydroxybutyrate (PHB), polyhydroxyvalerate (PHV) and polyhydroxyhexanoate PHH [1].

Biodegradable packaging and biodegradable bags take much less time to break down after being discarded, if they haven't been recycled. What this means is that it gets absorbed in the earth, and there will no longer be tons of plastic dominating our landfills. Biodegradable plastics are made from biomass, which is a completely renewable resource. It is an organic compound, which breaks down. There is plenty of it around the globe. Biomass includes trees, plants, grass, and all organic materials that decompose. Biodegradable plastics are much better for the environment, because there is no harm done to the earth when recovering fossil fuels. Also, in this process there are very few greenhouse gas and harmful carbon emissions. Biodegradable plastics need less than half the energy to produce than their non-biodegradable counterparts. This means that it is possible to make twice the amount of biodegradable packaging and biodegradable bags using the same amount of energy. They are created from materials that are fully biodegradable. This means that they can break down much faster and recycling them takes less energy. They can re-use more efficiently, which gives them a clear advantage. Traditional plastics are full of harmful by-products and chemicals, which are released during their breakdown process.

Biodegradable plastics are completely safe and do not have any chemicals or toxins as they harmlessly break down and get absorbed into the earth. Such advantages of bioplastics are of extreme importance, as the toxic plastic load on the earth is growing and at this rate will cause a whole range of problems for future.

Biopolymers are polymers produced by living organisms. Since they are polymers, Biopolymers contain monomeric units that are covalently bonded to form larger structures. There are three main classes of biopolymers based on the differing monomeric units used and the structure of the biopolymer formed. Polynucleotides long polymers which are composed of 13 or more nucleotide monomers, Polypeptides short polymers of amino acids, and Polysaccharides which are often linear bonded polymeric carbohydrate structures.

Chitin ($C_8H_{13}O_5N$)_n is a long-chain polymer of a *N*-acetylglucosamine, a derivative of glucose, and is found in many places throughout the natural world. It is in the exoskeletons of arthropods such as crustaceans (e.g., crabs, lobsters and shrimps) and insects, the radulas of mollusks, and the beaks of cephalopods, including squid and octopuses. In terms of structure, chitin may be compared to the polysaccharide cellulose and, in terms of function, to the protein keratin. Chitin has also proven useful for several medical and industrial purposes (Figure 1).

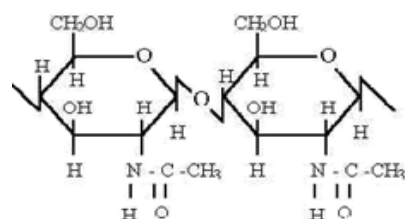


Figure 1. Chitin (chemical name: poly acetyl amino glucose).
Molecular Formula: $[C_8H_{13}O_5N]_n$
Molecular Weight: $[203.19]_n$

This product is chiefly used in waste water treatment for decreasing heavy metal ion in environment pollution control; it is also used in making chitosan and glucosamine series chemicals. As the research results during recently several decades chitin can be used in light industry. In pharmaceutical, cosmetic and agriculture, it was found that chitin is a chemical with good prospects. White to light yellow flake, it is cellulose like biological polymer soluble in concentrated hydrochloric acid, sulfuric acid and glacial acetic acid, but insoluble in water, dilute acid, alkali and organic solvents [2].

Chemists love to play with molecules. They did not spare chitin, the polymer either and made chitosan. The term chitosan is used when chitin could be dissolved in weak acid. When chitin is heated in a strong solution of sodium hydroxide (>40%) at high temperature (90-120°C), chitosan is formed. This harsh treatment removes acetylic grouping on the amine radicals to a product (chitosan) that could be dissolved. It is said that at least 65% of the acetylic groups should be removed on each monomeric chitin to obtain the ability of being put in solution. The degree of

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deacetylation will vary according to the duration, the temperature and the concentration of the sodium hydroxide. Medical grade micronized chitosan is biodegradable, non-allergic, haemostatic, non-toxic and wound healing accelerator. Chitosan films are flexible, tough, transparent, clear and oxygen permeable with good tensile strength. They could be used to make single and biopolymer membranes, non woven fabrics and sponges for surgical applications. It is resistant to alkali, digestive enzymes and urine and can also be cross linked [3].

Increased and indiscriminate use of plastic packaging films, which are petroleum based, has led to ecological problems due to their total non-biodegradability. Continuous use of plastics in any form or shape has to be restricted and may even be gradually abandoned to protect and conserve ecology. Such awareness, of late by one and all, has led to a paradigm shift to look for packaging films and processes that are biodegradable and therefore, compatible with the environment. Such an approach also leads to natural resource conservation with an underpinning on a pollution-free environment. Thus, the concept of biodegradability enjoys both user-friendly and eco-friendly attributes, and the raw materials are essentially derived from either replenishable agricultural feed stocks (cellulose, starch, and proteins) or marine food processing industry wastes (chitin/chitosan). Their total biodegradation to environmentally friendly benign products (CO₂, H₂O/quality compost) is the turning point that needs to be capitalized upon. Polymer cross-linking and graft copolymerization of natural polymers with synthetic monomers are other alternative approaches of value to using biodegradable packaging films. Although complete replacement for synthetic plastics may be impossible to achieve and perhaps even unnecessary, at least for a few specific applications, our attention and efforts are required in the days to come. Though expensive, biopackaging meets tomorrow's need for packaging, especially for a few value added products. It offers an attractive route to waste management, as well. Nonetheless, everyone desires a clean, pollution-free environment in the future.

The use of renewable products to produce valuable and biologically sustainable materials and to minimise waste is a challenge for current research and development. Crustacean processing produces about 40% of shell waste. The global annual production of shell waste from crustacean processing is estimated to be 1.44 million metric tons dry weight. Since biodegradation of this waste is very slow, accumulation of large quantities has become a major concern in the seafood processing industry. The use of this waste for renewable products such as biopolymers is a dual-purpose opportunity. Chitin is a natural biopolymer with a chemical structure similar to that of cellulose and is a major component of the exoskeleton of invertebrates. Therefore, crustacean waste is ideal as raw material for chitin production. The extracted chitin can be used to produce chitin-derived products, such as chitosans, chito-oligosaccharides and glucosamine, but also for bioplastic production. The interest to use chitinous products in foods and pharmaceuticals is increasing due to their broad range of industrial applications.

Today, several companies are producing chitin and chitosan products on a commercial scale; the majority are located in Japan, where more than 100 billion tons of chitosan are manufactured each year from the shells of crabs and shrimps, an amount that account for ~90% of the global chitosan market (approximately four trillion yen). Keeping the importance of chitin and chitosan in mind, an attempt has been made on the extraction of chitin from the shell and operculum of *Nerita crepidularia* and conversion of chitin into chitosan through deacetylation. The chitin was prepared from shell and operculum of *N. crepidularia* (by demineralization and deproteination) and chitosan by the deacetylation of chitin. The yield of chitin and chitosan was found to be 23.91 and 35.43% and 31.14 and 44.29%. The FT - IR spectrum of chitin and chitosan was also confirming the presence of chitin and chitosan in the shell and operculum of *N. crepidularia*. The results of the present study pave the way and provide the baseline information for the utilization of chitin and chitosan in the development of drugs, "artificial skin" as in Japan and in food industries apart from opening in avenue of research to the future researchers [4].

The aim of this paper is to define optimal conditions for the extraction of chitin from shrimp shells. The kinetics of both demineralization and deproteination with, in the latter case, the role of temperature are studied. The characterization of the residual calcium and protein contents, the molecular weights, and degrees of acetylation (DA) allows us to propose the optimal conditions as follows. The demineralization is completely achieved within 15 min at ambient temperature in an excess

of HCl 0.25 M (with a solid-to-liquid ratio of about 1/40 (w/v)). The deproteination is conveniently obtained in NaOH 1 M within 24 hr at a temperature close to 70° C with no incidence on the molecular weight or the DA. In these conditions, the residual content of calcium in chitin is below 0.01%, and the DA is almost 95 %. Thus the study is mainly focused on developing biodegradable bioplastic which is environmental friendly, from the material waste of prawn shells followed by extraction of biopolymers like chitin and chitosan by different methods like decolorizing, deproteination, demineralization and deacetylation. Later observation of antibacterial effect of chitosan towards *bacillus spp* and *kelbsiella spp* and analysis of chitin and chitosan by Fourier transform infrared spectroscopy was undertaken. As a final step Extraction of starch from potatoes to be used in developing bioplastics was also attempted.

MATERIALS AND METHODS

Materials Required

1. Prawn shells
2. Potatoes
3. Homogenizer
4. Oven
5. Water Bath
6. Centrifuge
7. Conical Flask
8. Beakers
9. Dessicator
10. Distilled water
11. Pipettes
12. Measuring Cylinder
13. Incubator
14. Autoclave
15. Sterile Petri plates

Purification of Chitin - Decolourization

1. Prawn shells
2. 0.5% potassium permanganate
3. oxalic acid
4. sunlight

Method

Prawn shells are homogenized in a homogenizer. 50g of prawn shells was soaked in 240ml of 0.5% potassium permanganate and 10ml oxalic acid for 24 hours. It was washed it with tap water and dried in sunlight for 3 days. Decolorized chitin was obtained (Figure 2).



Figure 2. Prawn Shells

Deproteinzation

1. Prawn shells
2. Sodium Hydroxide
3. Water Bath
4. Bowl
5. Homogenizer

Method

Prawn shells are homogenized in homogenizer. 10% Sodium hydroxide solution was prepared. 50g of chitin was taken in a beaker. 250 ml of 10% Sodium hydroxide was added to 50 gm chitin. It was kept in water bath at 100°C for 1hour. It was then cooled and washed with water until it was neutral.

Demineralization

1. Extracted chitin
2. 0.1M HCl
3. Beaker
4. Water bath

Method

250ml of 0.1M HCl was added to 50g of deproteinized chitin. It was kept in water bath at 100°C for 30 minutes. It was cooled and washed with distilled water until it becomes neutral. Chitin from the prawn shell was thus purified and dried at room temperature (Figures 3 & 4).



Figure 3. Deproteinization & Demineralization



Figure 4. Chitin

Preparation of Chitosan - Deacetalization

1. Chitin
2. 50% Sodium hydroxide
3. Beaker
4. Water bath
5. Centrifuge

Method

250ml of 50% Sodium hydroxide was added to 50g of purified chitin. It was kept in water bath at 100°C for 1 hour. It was washed with water until it becomes neutral. It was then centrifuged at 1000 rpm and the extracted chitosan was confirmed by FTIR.

Preparation of Bioplastic from Chitosan

1. Chitosan
2. Distilled water
3. Acetic acid
4. Glycerol
5. Bunsen burner

Method

100ml of distilled water is taken in a 250ml beaker. 50g of chitosan was added to 100ml of distilled water and was subjected to boiling temperature. The solution was stirred well until chitosan completely dissolves. 7ml of chitosan was mixed with 3.5ml of acetic acid and 3.5ml of glycerol. The mixture was boiled at 280°C in oven for 2 min at every half an hour for 4 times. The mixture was poured onto a flat slab and was kept in room temperature for 24 hours. Bioplastic formation was observed.

Antimicrobial activity of chitosan against bacteria Muller Hinton agar (hi-media)

Materials Required

1. Petri plates
2. Sterile swab
3. *Bacillus* culture
4. *Klebsiella* culture
5. Chitosan

Method

Sterile Muller Hinton Agar plates were prepared. 1 plate was swabbed with *Bacillus spp* and 1 plate with *Klebsiella spp* and 1 plate was kept as control. Using well puncture 2 wells were made in each plates and chitosan was added. The plates were incubated at 37°C for 24 hours. After incubation it was checked for zone of inhibition.

Isolation of starch from potatoes

Materials required

1. Potatoes
2. Knife
3. Beakers
4. Conical flask
5. Screeners
6. Dessicator
7. Bunsen burner
8. 1% HCl
9. 2% sodium meta bisulphate solution
10. Distilled water

Method

50g of potatoes are coarsely cleaned for removal of soil. The skin was peeled and the potato was mashed till the cells are disrupted. 50g mashed potatoes was soaked in 100ml of distilled water and was left for 2 hours. The supernatant was filtered using screens. 10 ml of 1% HCl was then added and heated for 10 minutes. Using screens, the clumps formed in the starch solution were filtered. The solution was dried in dessicator until the water was evaporated. White powdered starch was collected.

Biochemical tests for starch

Materials required

1. Starch
2. Iodine
3. Conical flask
4. Burette

Method

Starch extracted from potato is tested using iodine solution. Iodine solution is taken in burette and titrated against starch solution. Blue colour appearance in the solution confirms the presence of starch.

Bioplastic preparation from starch

Materials required

1. Starch
2. 1% glycerol
3. Acetic acid
4. Distilled water
5. Beaker
6. Bunsen burner
7. Flat slab

Method

2.5g starch was taken and mixed with 25ml of distilled water, 3ml of 0.1M acetic acid and 2ml of glycerol. The mixture was heated under Bunsen burner until the starch was completely dissolved. The acidity of the solution was checked and 0.1M sodium hydroxide was added till the

mixture was neutral. The mixture was poured onto a flat slab and allowed to cool. After 24 hour, a thin transparent sheet was formed.

Degradation of Bioplastic

Material Required

1. Soil
2. Bioplastic

Method

Soil is collected from a place where plastic is dumped. Bioplastics was buried in the soil collected. The degradation was observed for every 6 days. The Physical and Chemical Properties of Plastic was confirmed by Water Test, Copper Wire Test, Acetone Test and Heat Test.

RESULTS AND DISCUSSION

Pure chitin was obtained by 3 methods like decolourization, deprotonization, and demineralization. Chitin presence was confirmed by FTIR analysis. The absorption bands were observed at wavelength $>3000\text{ cm}^{-1}$, where the peak shows chitin presence. The absorption bands at wave length 1000 cm^{-1} , 1500 cm^{-1} conforms the removal of proteins and minerals (Figure 5). The chitosan was purified by dissolving 10g in 500ml of acetic acid 1% (W/V) and then filtered using filter paper and then polymers were precipitated by adding sodium hydroxide 4% and is washed with ethanol. The dried powder was used for bioplastic preparation. Chitosan presences was confirmed by FTIR analysis and the absorption bands were observed at wavelength $>2500\text{ cm}^{-1}$ to 3500 cm^{-1} , where the peak conforms the chitosan presence (Figure 6).

The absorption bands at wave length 1000 cm^{-1} , 1500 cm^{-1} shows the deacetylization, that is removal of acetyl groups from chitin. Physical and chemical properties of bioplastics were observed by 4 tests. Water test done revealed the density range of plastic and bioplastic sank in the water. Bioplastic from prawn shells and potato starch has high density than water (Figures 7 & 8). Copper wire test confirmed the presence of chlorine in bioplastic from prawn shells. Orange flame indicated the presence of chlorine. The bioplastic produced from chitosan of the prawn shells on treating with acetone, was found to have a soft and sticky texture which can be easily scraped. This indicates the structure of the polymer chains that makes up the plastic which changed. Heat test revealed the sample to have a soft texture (Table 1).

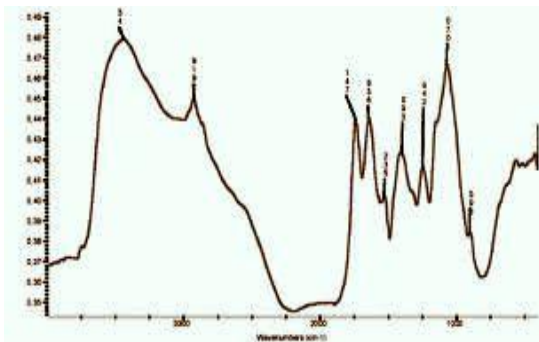


Figure 5. FTIR for Chitin

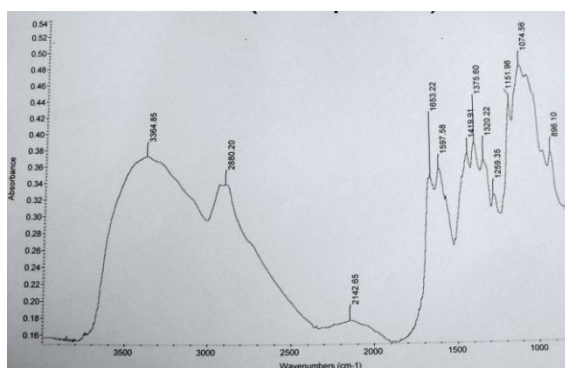


Figure 6. FTIR for chitosan



Figure 7. Bioplastic from Prawn Shells



Figure 8. Bioplastic from Starch

Table 1. Physical and Chemical Properties of Bioplastics

S. No.	Name	Properties	Water test	Copper test	Acetone Test	Heat Test
1.	Sample 1	Moisture proof, transparent, flexible, soften if heated.	Sinks in water	orange flame	Soft and sticky	Soften
2.	Sample 2	Brittle, water soluble, glossy.	Sinks in water	Orange flame	melts	soften

SUMMARY AND CONCLUSION

The new environmental regulation and growing environmental awareness through out the world has triggered a search for new products and process that are compactable with the environment. Plastics are made of straight long chain polymers or line of smaller molecules that are known as monomers. Bioplastics are a form of plastics derived from renewable biomass sources, such as vegetable oil, corn starch, pea starch, or microbiota, rather than fossil-fuel plastics which are derived from petroleum. Extracting biopolymer like chitin and chitosan from prawn shells is utilized for developing biodegradable bioplastic. Chitin is a long chain biopolymer made of *N*-acetylglucosamine which is insoluble in water. Deacetylation of chitin with 50% sodium hydroxide form chitosan. Chitosan is made of D-glucosamine, solubilized in water used to develop bioplastic. Trichloroacetic acid and glycerol is used as plasticizers. Thus Biodegradable plastics were created from materials that are fully biodegradable. This means that they can break down much faster and recycling them takes less energy. This study promises the making of Biodegradable plastics using material waste of prawn shells and also potato starch and is thus environmental friendly and cost effective.

REFERENCES

1. Pradip Kumar Dutta, Joydeep Dutta, V S and Tripathi, Chitin and Chitosan: Chemistry, Properties, and Applications, Journal of Scientific and Industrial Research, 2004, 63, 20-30.
2. Goosen, M.F.A., Application of Chitin and Chitosan, 1997, 98 (12), 297-305.
3. Aline Percot, Christophe Viton, and Alain Domard, Application of chitin and chitosan of functional materials; organo and water soluble chitosan derivative and *N*-acetyl-d-glucosamine. Journal of Industrial Science and Technology, Japan, 2003, 34 (1), 23 - 25.
4. C. Bastioli, M. Versari, - Novamont Spa, Bioplastic from starch: an economically and environmentally sustainable reality. Journal of Ecology, 2009, 45 (4), s56 - 60.