Investigation on mechanical properties of biodegradable polymers

Veeresh Kumar G B1*, Krishna Kanth V1,2, Pramod R3

1 Mechanical Engineering Department, National Institute of Technology-Andhra Pradesh, Tadepalligudem, West Godavari district, Andhra Pradesh State, India.
2 Mechanical Engineering Department, Raghu Institute of Technology, Visakhapatnam, Andhra Pradesh, India.
3 Mechanical Engineering Department, Amrita School of Engineering, Bengaluru, Amrita Vishwa Vidyapeetham, India.

*Corresponding author’s e-mail: veereshkumargb@nitandhra.ac.in

Abstract. Bioplastics are plastics made out of biomass such as sugarcane, corn etc. These compounds are getting more attention to conserve fossil fuels, reduce plastic waste, and reduce CO2 emissions. These substances are being increasingly spotlighted as means to save fossil fuels, plastic wastes and reducing CO2 emission. Biodegradability of these bioplastics have been extensively publicized in the society and demand for packaging is quickly increasing among the food industry and retailers’ at large scale. The plastics which are currently available in market are very dangerous as it is non biodegradable. Hence, it is the order of the day that the biodegradable plastics should be produced at large scale and used to replace non-biodegradable plastics. The present article emphasis all these points regarding their applications, types, production, challenges, fermentation, sustainability, process development and use of cheap substrates for bioplastics production. The latter section of the project endeavours to educate a novel method in the production of biopolymers using Gelatin. Dissimilarities in parameters like plasticizer, polymers, hydrolysis and curing times were extensively tested and the optimum combination was obtained.

Keywords: Bioplastics, Gelatin, Biopolymers, Biodegradability, Mechanical Characterization.

1. Introduction
The standardised method for manufacturing starch-based bioplastics, according to the Royal Society of Chemistry, entails hydrolysis of the starch using an acid. [1] Abdolreza et al. (2010) identified the physiological, rheological, and thermal properties of acid hydrolyzed starch in their paper, demonstrating that the amylose content rises at first, but then decreases due to persistent hydrolysis.[2] KarntaratWuttisela et al. (2008) made similar points, emphasising that the amylose content was responsible for the starch's plastic growth. Plasticizers were used to improve the bioplastic samples' mouldability and flexibility. [3] J. Zhou (2008) debated the effects of common types of plasticizers and their effects on a variety of bioplastic film properties such as water vapor permeability, elongation, and tensile strength. [4] Y. Chen et al. (2019) addressed bioplastics applications, especially...
in the packaging industry, where bio-based polymers were used as a factor in food packaging and various techniques for enhancing barrier properties, mechanical properties, and permeability values of multi-layered bio-based plastics were discussed. K. Kanimozi (2014) [5] explored the research and characterisation of bio-plastic formation and identified the study of bioplastic formation and their composition using FTIR spectroscopy in different phases.

Two different types of technologies were developed for the fabrication of bioplastics from starch and agrowaste. The first technology is the direct transformation of inedible agrowaste into bioplastics and the second technology is elastomerization of agrowaste into robust bioelastomers. The first technology utilizes an organic acid to convert the cellulosic agrowaste into amorphous plastic[6]. Later, the acid may be recycled in a closed system of production. The second technology utilizes micronized agrowaste powder with starch dispersed in Silicone (Si) based polymer precursor to produce bioelastomers containing less than 50% by weight vegetable-based ingredient. Typical agrowaste products that may be used were parsley and cacao pod husks, spinach stems, rice hulls, orange peels, starch, and oat hulls. Bioplastic is a type of plastic manufactured primarily from sustainable biomass sources such as fermented sucrose (which is altered to form polylactide), gelatin, vegetable oil, corn starch, pea starch, or cellulose. The plant material needed to make bioplastic can be grown continuously. In contrast, petrochemical-based polymers will eventually run out (i.e. our current rate of use exceeds the time taken for petrochemicals to form). [7] Additionally, many Bioplastic products are biodegradable which means they can be easily broken down into the CO₂ and water by microorganisms. Some may be put into an industrial composting method and will break down by a amount of 90% less than six months. If prepared with a corn-starch biopolymer, the molecules gradually absorb water and will swell up, triggering them to break apart into tiny fragments that bacteria can digest easily.

The actual state of bioplastics and their prospects, since large-scale manufacturing in industries is prohibitively expensive, they have not been commonly used. Bioplastics manufacturing was dominated in the twentieth century by countries such as Western Europe, North America, Japan, and others, and it is expected that by 2013, Brazil will be among the world's leading bioplastics producers. By 2013, Japan's bioplastics production may be many times higher than 178000 metric tonnes, and China has planned to produce 100,000 metric tonnes of bioplastics at the same time [8]. In Southeast Asian countries, the bioplastics industry is also in its early stages. According to research conducted by the BCC, the bioplastics industry valuation reached 541 million pounds in 2007 and is expected to hit 1.2 billion pounds by 2012. Several varieties of biodegradable plastics, such as resins, polylactic acid, polyesters, and others, accounted for nearly 90% of bioplastics production in 2008. Nondegradable plastics may be replaced by environmentally friendly biodegradable plastics. The use of bioplastics would reduce CO₂ emissions associated with nondegradable plastics. One of the main concerns is that bioplastics could wreak havoc on current recycling systems. The cost of producing bioplastics is currently too high, and this is one of the major issues facing bioplastics growth. The main aim of this work is to develop biodegradable plastics and test for its physical, mechanical and biodegradability properties.

2. Methodology

The preparation methodology are being discussed in (6-10) and in this work studies the gelatin based bio degradable polymer. Partially hydrolyzed collagen derived from the skin, bones, and connective tissues of animals such as domesticated beef, chicken, pigs, and fish produces gelatin, which is a combination of peptides and proteins. [11] The natural molecular bonds between individual collagen strands are broken down during hydrolysis, allowing them to rearrange more easily. Its chemical structure resembles that of its parent collagen in several ways. Cattle bones and pig skin are often used to make photographic and medicinal gelatin. The polypeptide chain of gelatin contains proline, hydroxyproline, and glycine. The amino acid glycine is responsible for the chain's tight packaging. [12] The presence of proline causes the conformation to be limited. This is crucial for gelatin's gelation properties. Gelatin dissolves easily in hot water and sets to a gel when cooled. However, it does not
dissolve well when applied directly to cold water. [13] Many polar solvents are also soluble in gelatin. Shampoos, skin masks, and other cosmetics contain gelatin; fruit gelatin and puddings (such as Jell-O) contain gelatin; candies, marshmallows, cookies, ice cream, and yoghurts contain gelatin; photographic film contains gelatin; and vitamins contain gelatin as a coloring and as tablets contain gelatin.

The process starts with heating 125ml water to 80°C, at this stage gelatin is added of 24g and need to stir the solution at 1200 rpm using magnetic stirrer, until it becomes a clear solution. The solution has to be maintained 80°C and further a 5g of glycerine is added. Using the magnetic stirrer mix the solution at a rate of 1000rpm until it starts foaming and gradually decreases the speed of the sitter to avoid further foaming of the solution. This solution with minimum foam has to be poured in the mould and allows it to cool at room temperature. The stages of procedure and cured bioplastic can be observed in the below Figure 1.

Figures 1 (a,b,c): shows the preparation of bio degradable polymer
3. Experimentation
Experimental investigations are carried out in order to estimate the behavior of gelatin based biodegradable polymer. The American Society of the International Association for Testing and Materials (ASTM) is an international standards body that was established in 1898 as the American Society of the International Association for Testing and Materials. Other standards organisations such as the BSI (1901), IEC (1906), DIN (1917), ANSI (1918), AFNOR (1926), and ISO (1927) were established before it (1947). ASTM standard of various test are tabulated in the table 1.

| Test                  | ASTM Standards | Specimen Sizes |
|-----------------------|----------------|----------------|
| Water Absorption      | D570-98        | 40mm X 40mm    |
| Tensile Strength      | D882-02        | 100mm X 25mm   |
| Shore Hardness Test   | D2240-00       | 20mm X 20mm    |

Biodegradable tests
As environmental concerns have grown in importance on a national and global scale, further attempts have been made to save our capital. Sustainable products are becoming increasingly important in industry. As a result, it is important that students understand the significance of these content. Biodegradable polymers are among such material. For an undergraduate materials laboratory course, a laboratory technique for testing polymer biodegradability was created. Students may obtain a thorough understanding of plastics by testing their biodegradability. Biodegradable testing as part of a programme promotes constructive learning through hands-on testing and allows students to partake in lifelong learning and keep up with new content. This paper outlines a study that looked at the biodegradability of biodegradable plastics by tracking carbon dioxide levels and physical property degradation. A low-cost approach for determining biodegradability is also defined. The surface of the cured polymer is studied using SEM analysis.

4. Results and Discussions

4.1 Water absorption
The water absorption was determined using ASTM D570-98. The initial weight of dried sheets was by weighing them before placing them in a bath of purified water at room temperature. After 24 determined hours, the sheets were removed, the water on their surface was cleaned off, and the sheets were weighed again. The following equation was used to calculate the average of five replicates:

\[
\text{Water absorption percentage (\%) = \left( \frac{W_i - W_f}{W_f} \right) \times 100\%}
\]

Where \(W_i\) is the original weight (g) before water immersion and \(W_f\) is the final weight (g) after water immersion. The average water absorption rate observed is 21.23%. This value is comparatively a better one in comparison with cassava and corn starch bio degradable polymers. The test results are showed in the Figure 2.
Figure 2: shows the comparison of water absorption test of Gelatin, Cassava and Corn Starch based polymer. Ref (14-17)

4.2 Tensile Test

Tensile testing is fundamental test in which material sample is subjected to controlled tension until breakdown of the sample. In this test the specimen of given standards is subjected to axial load until it gets fractured or get broken. The elongation of the specimen for different loads is noted down and plotted in a graph elongation vs. load. For engineering applications of different materials these results are used. In material specifications tensile strength is one of the important specifications and is often compared with that of the other newly developed materials. Tensile properties are used to see the behaviour of the material under uniaxial loading. Tensile test is performed on Universal Testing Machine. The below Figure 3 represents a graph of tensile strength and also comparisons are made with others.

Figure 3: Shows the compares the tensile strength of Gelatin, Corn, Potato, Cassava based polymers. Ref (14-17)

Gelatin based biodegradable polymer shows potential values of tensile strength when comparing with corn, potato and cassava. So gelatin based polymers can be adopted and can be replaced the above three polymers. The below Figure 4 graph shows the comparison of young’s modulus in MPa.
Figure 4: Compares the young’s modulus of Gelatin, Corn, Potato and Cassava. Ref (14-17)

As the volume of bioplastic used increased, the percentage of elongation at break increased as well. This is due to the bioplastic's flexibility, which is due to the large level of starch and glycerol it contains. The Figure 5 shows the elongation of gelatin bioplastic and also compares with other bioplastics.

Figure 5: Shows the Elongation of Gelatin, Corn, Potato and Cassava during tensile test. Ref (14-17)

The added tensile force to the specimen is gradually raised. Under the impact of this tensile force, the specimen elongates at the same time. It is obvious that the specimen is being worked on. Up to the point of rupture, the average energy consumed per unit volume of the specimen. At split, the tensile energy is 0.38J.

4.3 Shore hardness test

This indentation test procedure uses a regular indenter to determine the hardness of a rubber specimen. Several rubber hardness measuring scales are referred to by ASTM D2240-00 (A, B, C, D, DO, O, OO, and M). It’s used to test the indentation hardness of elastomers, thermoplastic elastomers, vulcanized
rubber, cellular, gel-like, and composite materials. The procedure entails indenting the specimen with a hardened steel indenter with precise geometry and force, according to the chosen measurement scale. The indenter tip displacement is used to calculate the material's hardness. The displacement data is converted into a hardness number, which is limited to a range of 0 to 100, using a mathematical relationship. The fig 6 represents the test rig and the two most widely used scales are A and D.

![Figure 6: illustrates the experimental setup](image)

This study observed an average shore hardness value of 48.44DM and resulting in very good hardness value. The temperature at which a polymer transforms from a hard glassy material to a soft rubbery material is known as the glass transition temperature. The glass transition temperature does not apply to pure crystalline polymers; the glass transition temperature only applies to amorphous polymers. Amorphous polymers have no melting point; instead, they have a glass transition temperature. Most polymers, on the other hand, have both amorphous and crystalline forms. This ensures that certain polymers have both a melting and a glass transition temperature. The melting temperature is higher than the glass transition temperature. Since different polymers have different glass transition temperatures, certain polymers are better suited for some applications than others. The average glass transition temperature (TG) is 98° degrees Celsius, with a melting point of 120° degrees Celsius.

4.4 Biodegradability tests

To assess the biodegradability of this polymer, conducted Acid test, alkaline test and solubility test and the result are tabulated. Sulphuric acid and Acetic acid were used as the acid test solvents; the Sulphuric acid was a heavy acid, while the Acetic acid was a mild acid. The bioplastic is then put in the beaker with 0.5 M of both acids in 400ml. Check the time it takes for the bioplastics to become completely soluble in strong and weak acids after they appear to dissolve in acids. The aim of the alkaline test was to determine the length of time that the bioplastic is completely soluble in alkaline. Sodium hydroxide was used as the alkaline test solvent, and the NaOH was a solid alkaline. Take 400ml of 0.5 M NaOH, then put the bioplastic in the beaker. As the bioplastic begins to dissolve in alkaline, determine how long it would take for the bioplastic to become completely soluble in NaOH. Water is used as the solubility measure solvent. We take 400 mL deionized water and put the bioplastics in a beaker; the bioplastics begin to dissolve; now verify the time it takes for the bioplastics to completely dissolve in water.
Table 2: The test results of biodegradability.

| S.No | Test                      | Solvent                | Duration of time to completely dissolve |
|------|---------------------------|------------------------|----------------------------------------|
| 1    | ACID TEST METHOD          | SULPHURIC ACID         | 70 Minutes                              |
|      | (Strong Acid Test)        |                        |                                        |
| 2    | ACETIC ACID               | ACETIC ACID            | 175 Minutes                             |
|      | (Weak Acid Test)          |                        |                                        |
| 3    | ALKALINE TEST             | SODIUM HYDROXIDE       | 90 Minutes                              |
| 4    | SOLUBILITY TEST           | DEIONIZED WATER        | 490 Minutes                             |

And finally, flammability test is also conducted to estimate the time taken to convert the polymer into ash. Current test was performed only to verify the biodegradability of bioplastics. Bioplastics become ashes if it is biodegradable. It is the easiest and quickest test to find biodegradability of bioplastics. The flame measurement is carried out in the presence of vapor. Bunsen burners are used to burn the bioplastics. Indirect heat is applied, and bioplastic starts burning without catching fire. The average time taken to burnout the sample is 20 minutes. The results of the biodegradability test are recorded and tabulated in the Table 2. Further SEM analysis is carried out to observe the surface defects and foreign inclusions in the polymer.

**Figure 7:** shows the surface of the Gelatin polymer at magnification rate of 1000 (left), 2000 (right)

**Figure 8:** shows the surface of the Gelatin polymer at magnification rate of 3000
In the Figure 7 and 8, the SEM analysis, revealed that the solution prepared is mixed well and no agglomerations are found. Surface is almost plain because of constant cooling rate. Other surface defects like porosity and cavities are not found like in the resin based polymers. Traces of dust inclusions are found on the specimen,might be during the pouring of the solution and curing the solution.

5. Conclusions
1. Gelatin plastic has much less water absorption than other bioplastics.
2. Theyoung’s modulus and tensile strength of gelatin bioplastic is comparatively better.
3. Some Low density plastics (with Young’s modulus between 110MPa to 450MPa) can be replaced with Gelatin.
4. Spoons, Food wrapping covers can be replaced with Gelatin bioplastic.
5. Obtained bioplastic is biodegradable and Non-toxic.

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