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Evaluation of Bioplastic Developed from Corn Starch and *Euphorbia antiquorum* Latex

R. K. Atchaya [a*], U. Devipriya [a], K. Sreeja [b] and P. Buvanesh [a]

[a] Kongu Engineering College, Perundurai, Erode, Tamil Nadu, India.
[b] Kelappaji College of Agrl. Engg. & Technology, Tavanur, Kerala, India.

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

Traditional plastic materials have a negative environmental impact and one potential strategy to reduce this rising plastic pollution is to use compostable materials like bioplastic. An experiment was conducted at RVS School of Engineering and Technology, Dindigul to synthesize bioplastic from agricultural products like corn starch, latex of *Euphorbia antiquorum* and polyvinyl alcohol (PVA). Two sets of blend bioplastic film samples were prepared using solution casting method; Sample A (corn starch + latex of *Euphorbia antiquorum*) and Sample B (corn starch + latex of *Euphorbia antiquorum* + PVA). Studies on the degradation properties were carried out by solubility, swelling and soil burial test. The biodegradability of the samples was investigated by soil burial test. Based on this study, the Sample A film without PVA was found to be highly biodegradable as compared to Sample B. The solubility and swelling tests were performed using organic solvents; ammonia, acetic acid, methanol and water. The swelling property of Sample B film showed less

**Corresponding author: E-mail: atchayakrishnan26@gmail.com;*

percentage of swelling. The solubility test showed that none of the bioplastic samples were completely soluble in any of the organic solvents. Result of this research work indicated that the bioplastic with incorporation of PVA is a better alternative to conventional plastic films.

Keywords: Bioplastic; Euphorbia antiquorum; corn starch; polyvinyl alcohol; PVA; biodegradability; swelling.

1. INTRODUCTION

Plastics, which are synthetic organic polymers derived from petrochemicals. Plastics take over a century to degrade, causing plastic pollution. Due to their low cost and durability, humans produce a significant amount of plastic. Their chemical structure makes them resistant to natural degradation, taking millions of years to break down. Fossil fuel-based plastics also produce more greenhouse gases compared to bio-based polymers.

Single-use plastics persist in the environment, contributing to a significant carbon footprint and causing harm by leaching into food, disrupting hormones, contaminating the ocean, and threatening marine life and vegetation. Additionally, they hinder rainwater from percolating into deep wells. Dumped plastic waste in water bodies has even altered aquatic ecosystems, becoming a new food source for aquatic animals. This poses a severe environmental tragedy [1].

Traditional plastics are currently under blaze from the public due to their negative impact on the well-being of people and the environment. To keep this market afloat, the industry is searching for new plastics or raw materials. In this context, the key phrases are "bio-based" and "biodegradable" [2]. Biodegradability is defined as the decay of organic material under aerobic or anaerobic conditions by the use of microorganisms to produce CO_2 / methane, water, mineral salts, and biomass [3]. When compared to conventional plastics, bioplastics disintegrate within 20-45 days provided there is sufficient soil moisture, oxygen, and number of microorganisms, which might be encountered in organic landfills or manure [4,5].Biodegradable plastics are developed by formulating natural organic substances such as polysaccharides, proteins, and lipids. Among the above mentioned plastic sources, starch-based bioplastics remain as a promising substitute as they are available in abundant, renewable and sustainable [6]. Biodegradable plastics are obtained from biomass feed stocks which have biodegradation property [7].

Starch is a widely recognized carbohydrate polymer whose plant source is grown in all temperate zone. Corn, wheat, potato, and rice are the world's leading crops, which accounts for 84%, 7%, 4%, and 1% of total production [8]. The thermoplastic starch films made from the starches can display a wide range of chemical, physical, and mechanical properties due to their different film-forming properties [9]. Loose-fill packaging, various types of bags and sacks, flexible and rigid packaging, agriculture and horticulture applications, and hygiene and cosmetics products are all made from starch [7]. The inclusion of plasticizers (like glycerol) during bioplastic processing is preferred to enhance the mechanical properties of bioplastic, particularly the elasticity [10].

Proteins, enzymes, alkaloids, glycosides, cardenolides, terpenoids, furanocoumarins, and starch are just a few of the bioactive substances that can be found in the latex of different plant species. [11]. Different species of the Euphorbiaceae family's latex have been utilized as an impact modifier and secondary plasticizer for polyvinyl chloride (PVC), as adhesive for glass joints, and in paint formulations[12]. The white latex of *E. antiquorum* is a versatile material which offers the potential for creating biodegradable composites and can be used as a biopolymer in the production of bioplastics. Despite being a renewable and entirely biodegradable polymer, starch lacks the mechanical properties necessary to completely replace traditional plastic. By blending starch with synthetic polymers, mechanical qualities can be enhanced. The addition of Polyvinylalcohol (PVA) to starch improves its mechanical properties. [13]. PVA is a widely used thermoplastic polymer that is benign to living tissues, harmless, and nontoxic [14]. Because of its many advantageous qualities, including biocompatibility, nontoxicity, non-carcinogenicity, swelling properties, and bioadhesive characteristics, PVA is employed as a biomaterial in medical devices [15]. Rudresh et al. [16] investigated the influence of thermoplastic polymer on mechanical and thermal properties of hybrid blends.

Polyvinylalcohol (PVA) is a biodegradable polymer which is water soluble and they release their component into cold or warm solution. PVA hydrolyzes quickly and is a bio inert, so protein and cell attachment are confined on the pure substance [17]. The solubility of PVA in water depends on the levels of polymerization and hydrolysis. PVA grades with high degrees of hydrolysis having low solubility in water [18]. Starch or chitosan blend along with PVA macromolecules provides film flexibility; furthermore, it also works on improving water-related properties [19]. Regardless of the fact that starch-based bioplastic films have been the subject of substantial research, starch-based films containing Euphorbia antiquorum latex have not been studied. Hence, an attempt has been made in this study to synthesis bioplastic from corn starch, latex of *Euphorbia antiquorum* and PVA.

2. MATERIALS AND METHODS

An experiment was conducted to prepare bioplastic from agricultural products such as corn starch, latex of *Euphorbia antiquorum* and Polyvinyl alcohol (PVA) at Agricultural practices laboratory, RVS Educational Trust Group of Institutions, Dindigul in 2019. Commercial corn starch (Fig. 1) was purchased from the local grocery market. Latex of *Euphorbia antiquorum* (Fig. 3) was extracted from plants (Fig. 2) obtained in local regions of Dindigul, Tamilnadu. The analytical grade Glycerol and Polyvinyl alcohol was purchased from S. P. R. M. Chemicals. Other chemicals like Methanol, Acetic acid, Ammonia, Sodium meta bisulphate ($Na_2S_2O_5$) were utilized from the laboratory in the Institution.

Fig. 1. Corn starch

Fig. 2. Euphorbia antiquorum

Fig. 3. Latex of *Euphorbia antiquorum*

2.1Treatment Details

Two treatments were followed for preparing bioplastic film.

Sample A: Bioplastic film without PVA (corn starch + latex of *Euphorbia antiquorum*)

Sample B: Bioplastic film with addition of PVA (corn starch + latex of *Euphorbia antiquorum* + Polyvinyl Alcohol)

2.2 Preparation of Bio-plastic Film

2.2.1 Preparation of sample A (Bio-plastic without PVA)

Initially 2.5 g of corn starch was added to 25 ml of distilled water and mixed with 3 ml of 0.1N hydrochloric acid and 2 ml of propane-1, 2, 3-triol (glycerol). About 2 ml latex of *E. antiquorum* was added to this sample. The bioplastic films were prepared by conventional solvent casting method [20]. The mixture was heated carefully for 15 minutes. Enough sodium hydroxide solution was added to neutralize the mixture. Then this sample was poured on a labeled petridish or white tile and spread with glass rod to get an even thickness (Fig. 4). The sample was left for drying in oven at 40°C for 24 hours and taken for further analysis.

Fig. 4. Bio plastic film for drying

Fig. 5. Prepared bioplastic film

2.2.2 Preparation of sample B (Bio-plastic with PVA)

Initially 2.5 g of corn starch was added to 25 ml of distilled water and mixed with 3 ml of 0.1N hydrochloric acid, 2 ml of propane-1, 2, 3-triol (glycerol) and 6ml of PVA. About 2 ml latex of *E. antiquorum* was added to this sample. The mixture was heated carefully for 15 minutes. Enough sodium hydroxide solution was added to neutralize the mixture. Films were prepared by solvent casting method. The mixture was poured onto a labeled petridish or white tile and spread with glass rod to obtain even covering. The sample was left for drying in oven 40°C for 24 hours and taken for further analysis (Fig. 5).

2.3 Testing of Developed Bio-plastic samples

2.3.1 Biodegradability test

Two different trials were carried out for each of sample A and sample B. In trial 1; sample A and sample B were treated with 0.5% $Na_2S_2O_5$. Samples of trial 1 are A1 and B1. In trial 2, sample A and B were kept untreated and they are samples A2 and B2 respectively. Two containers with soil and samples 0.3 g (2 cm x 2 cm) of each treated and untreated bio-plastic samples were taken (Fig. 6). The samples were buried in soil at a depth of 5 cm from the surface. Some water was sprinkled on the soil so that bacterial enzymatic activities could be activated. These samples were kept in container under room temperature for about 10 days and observations were taken at every two days interval. The change in weight before and after burial was measured and compared to determine biodegradability [10]. Each test was done in triplicate in order to ensure the results [21]. The amount of bio degradation occurred was accounted by calculating the weight loss of the bioplastics samples using following equation,

$$\text{Soil degradation (\%)} = \frac{w - w_o}{w_o} \times 100 \qquad (1)$$

Where,

w_o- Initial weight of sample, g
w - Final weight of the sample, g

Fig. 6. Sample prepared for biodegradability test

2.3.2 Swelling test

The swelling test was carried out according to ASTM D570-98 specifications [22]. The samples were initially dried in oven at 50^0C for 30 min and then cooled to room temperature before subjecting to the swelling test. The swelling behaviour of the developed bioplastics was studied by immersing the dried samples in distilled water (solvent 1) and methanol (solvent 2) for about specific time interval of 2 hours (Fig. 7). The samples were taken, blotted with tissue paper to remove excess solvents, and then weighed. The swelling percentage was determined gravimetrically from the weight difference of the sample [23]. The increase in weight of the sample indicated the quantity of water or methanol penetrated into them which give a measure of swelling percentage [21]. The percentage swelling was calculated by using the following equation,

$$\text{Percentage Swelling (\%)} = \frac{w-w_o}{w_o} \times 100 \qquad (2)$$

Where,

w_o- Initial weight of sample (before immersion in solvent), g
w - Final weight of the sample (for a given immersion time), g

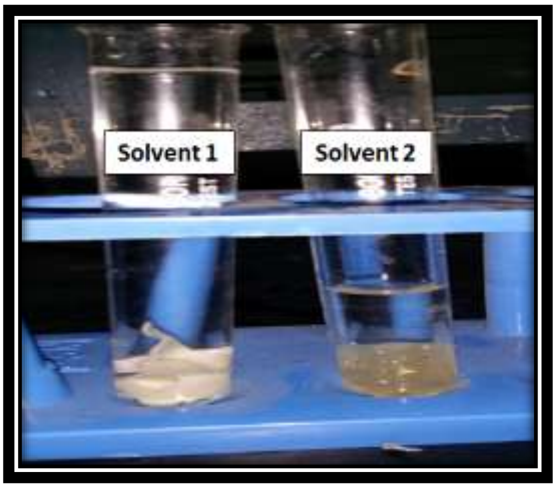

Fig. 7. Swelling test

2.3.3 Solubility test

Three replications of bioplastic samples were prepared and the solubility studies were conducted to check the persistence of these bioplastic materials. The samples of bioplastics taken for conducting the solubility test were A1, B1 (treated with $Na_2S_2O_5$) and A2, B2 (untreated). The samples (2 x 2 cm) treated with $Na_2S_2O_5$ and untreated were immersed in different solvents like ammonia, acetic acid, methanol and water for one hour in separate test tubes (Fig. 8). The solubility of the prepared samples in these solvents was observed and recorded accordingly [21].

3. RESULTS AND DISCUSSION

3.1 Biodegradability Test

The soil burial test for biodegradability of blend bioplastic samples were conducted as per the standard procedure. The samples were weighed at regular intervals and the percentage biodegradation of bioplastic samples were computed. The observations taken are shown in the Table 1. From the results obtained, sample A2 indicated 50% biodegradation and sample B1 showed 36% biodegradation after 10 days. The percentage of biodegradation was observed higher in bioplastic sample A which is untreated and lower in sample B which is treated with $Na_2S_2O_5$.

A reduction in the weight of bioplastic made from corn starch, latex of *Euphorbia antiquorum* and PVA were observed because glycerol was readily soluble in water as well as the addition of PVA to starch might have increased hydrophilic property of starch [24]. In Sample B (PVA + starch), PVA effectively blends with starch, enhancing the polymer's biodegradability [25]. Although Sample B exhibited a longer degradation time compared to Sample A, it still considerably outperformed traditional bioplastics in terms of biodegradability. PVA contributed high strength, chemical and thermal stability to the prepared bioplastic material. The sample treated with $Na_2S_2O_5$ inhibited the growth of microorganisms, resulting in less deterioration than the untreated samples. The starch content was consumed by soil micro-organisms and they cause the biodegradation. The micro-organisms will utilize the bioplastic sample as a carbon source by degrading their polymeric structure.

The soil burial test by Wahyuningtiyas et al. [26] of their bioplastic synthesised from Cassava starch with different proportions of glycerol showed complete degradation after 1 week on sample with starch and glycerol alone. Our bioplastic films using PVA and latex demonstrated a greater ability to withstand biodegradation than those in their study. There is a potential for long-term stability of the product for particular uses, and the addition of PVA may have prevented the premature degradation of bioplastic samples.

3.2 Swelling Test

Table 2 shows the results obtained from swelling test done in bioplastic samples. The swelling percentage of all the bioplastic samples was computed and there were no much change in the integrity of bioplastic when samples soaked in methanol. However, a slight increase in the weight of the bioplastic material when soaked in water for 2 hours was observed as compared to samples soaked in methanol.

The bioplastic sample A exhibited higher percentage of swelling which is 50% when soaked in water. Lower swelling percentage of 20% was observed in bioplastic sample B soaked in methanol. The lower percentage of swelling indicates higher resistant property of bioplastic material which means the capacity to absorb water will be less [21]. Therefore it will be harder for water to penetrate into the bioplastic sample. As per the results obtained (Table 2), less extent of swelling was observed in the prepared bioplastic material soaked in methanol medium, but swells a little higher in water medium.

Some exposed hydroxyl groups of starch not involved in cross-linking with plasticizers, react with water when exposed leading to swelling of the film [27]. This might be the reason for higher swelling of sample A (starch + latex). Similar results were observed by Krishnamurthy and Amritkumar [28] in their study.

3.3 Solubility Test

The solubility of the films is an indicator of the presence of hydrophilic compounds in the film [28]. The results from solubility test indicated that none of the samples were completely soluble in the different media used (ammonia, acetic acid, methanol and water). The natural rubber component of *E. antiquorum*'s latex may have given the produced bioplastic material its non-soluble chain flexibility. All the samples were least affected by the solvents used but got softened in all the solvents. The results were in accordance with the study by Jack et al. [29] and Krishnamurthy and Amritkumar [28]. These are the desired results for preparation of bioplastic based products to compete with the traditionally used plastic.

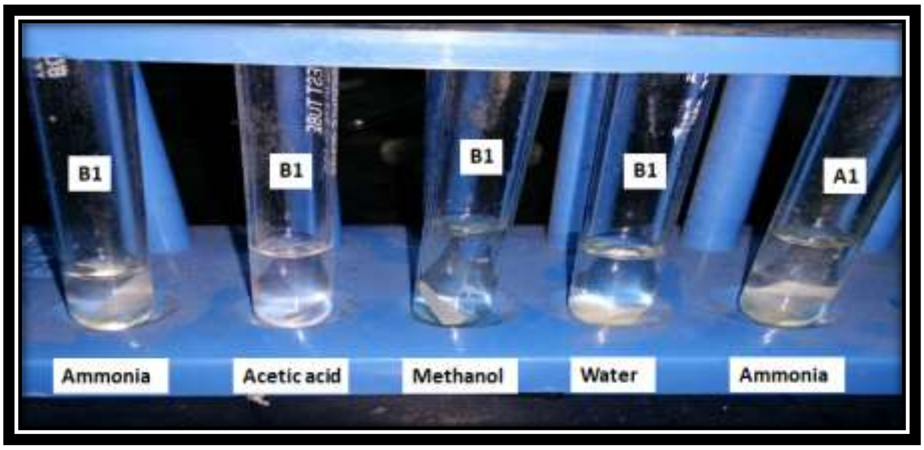

Fig. 8. Solubility test in various solvents

Table 1. Percentage of biodegradation of synthesized bioplastic material

Bioplastic sample	Treatment of samples	Initial weight (g)	Final weight (g)	Percentage of biodegradation, %
Sample A (Corn starch + Latex)	Treated with $Na_2S_2O_5$ (A1)	0.3	0.18	40
	Untreated (A2)	0.3	0.15	50
Sample B (Corn starch + Latex + PVA)	Treated with $Na_2S_2O_5$ (B1)	0.3	0.19	36
	Untreated (B2)	0.3	0.16	46

Table 2. Percentage of swelling of the developed bio plastic samples

Bioplastic sample	Solvent medium	Quantity (ml)	Initial weigh (g)	Final weight (g)	Difference (g)	Percentage of swelling, %
Sample A (Corn starch + Latex)	Water	20	0.3	0.47	0.17	56
	Methanol	5	0.3	0.38	0.08	26
Sample B (Corn starch + Latex + PVA)	Water	20	0.3	0.43	0.13	43
	Methanol	5	0.3	0.36	0.06	20

When comparing the production of this bioplastic to traditional plastic production, there are several key environmental advantages. This bioplastic is manufactured using renewable resources, such as latex, which possesses excellent antifungal and antimicrobial properties, and PVA, which is more easily biodegradable compared to conventional plastics. As a result, the production of this bioplastic requires less energy input and results in a reduced carbon footprint when compared to the production of traditional plastic. This means that the bioplastic production process has a lower overall environmental impact in terms of resource utilization and greenhouse gas emissions compared to traditional plastic production methods.

This study indicated good range of biodegradability in the formulated samples of bioplastic films. Emphasis needs to be given in modifying and optimizing the composition of this product inorder to meet the strength criteria in future studies.

4. CONCLUSION

From this study it is concluded that starch based bio plastic has been successfully synthesized from corn starch, latex of *E. antiquorum* and Polyvinyl alcohol. The current report has made an effort towards the synthesis of natural polymeric material. The bio plastic material prepared could be substantial and the bio degradability was one of the main challenges in developing them. These bioplastic samples with Polyvinyl alcohol have exceptionally high bio degradability property with decent solubility and swelling property which make them as a suitable low cost alternative for the conventional plastic. Furthermore, starch and latex of *E. antiquorum* are cheap and can be easily modified. This means someday it is unnecessary to rely on petroleum to prepare polymers, people may ‘plant’ polymers of suitable performance from the earth and the environmental problems will be no longer as severe as today. It is imperative that in future studies, bioplastic composition needs to be optimized by investigating its strength, toxicity (application in food packaging industry), stability and degradation rate under various environmental conditions over extended periods of time. Future approaches are significant to assess its resilience and potential vulnerabilities.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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