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Corn Starch as Eco-friendly Bioplastic and the Thermodynamic and Kinetic Analysis

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ABSTRACT

The study's goal is to prepare bioplastic by corn starch environmentally favorable. Corn Water, gelatin, glycerin, a food coloring coconut oil, and cotton were used to make bioplastic. The data demonstrate that bioplastic is biodegradable, with an average weight loss of 57.9%. It was partially soluble in ethanol and water but totally soluble in HCl. Swelling test showed no change when immersed in chloroform, but a slight change in water. It degrades more quickly as temperatures rise. The thermodynamic parameters results that the activation energy ΔE_a was 36.5 $Jmol^{-1}$, the positive values of Gibbs energy, entropy ΔS had suggesting non-spontaneous and less organized structure behavior and a negative ΔH value indicating exothermic nature.The rate of kinetic rises as the starch concentration increased. The manufactured bioplastic possesses features such as minimum swelling and is insoluble in water. Corn starch will be making it commercially feasible and a renewable resource.

Keywords: Corn starch, Bioplastic, Biodegradation, Kinetic, Thermodynamic.

INTRODUCTION

Polyvinyl chloride (PVC) was combined with *C. reinhardtian* extracts (0-75% yield) to produce bioplastic sheets. The 50% algal extract/PVC blend had the best mechanical qualities, with a tensile stress of 9.41 MPa and a 2% elongation rate. Chloroform extracts of *C. reinhardtian* had considerable antibacterial action against bacteria and fungi, with the maximum inhibition (31±0.28mm) against *Staphylococcus aureus*. This work suggests that *C. reinhardtian*-based biodegradable antimicrobial bioplastics could be environmentally acceptable alternatives to traditional plastics. Chemical discharge from plastic products causes the accumulation of harmful compounds in wildlife, with humans being a primary concern[1,2]. Because of the environmental damage caused by plastics, there is an urgent need for appropriate green alternatives[3-5]. Except for composting, food waste is deemed undesirable. Shrimp peels, orange peels, and leftover ground coffee are some of the various food wastes being transformed into bioplastic[6]. Cornstarch (CS), for example, can be one of the most effectively which raw ingredients because of its low cost and availability[7]. According to[8], corn is grown and harvested in several parts of Malaysia. In 2018, the cultivated area for maize in Malaysia was roughly 11,713 hectares, with an annual production of approximately 84,170 tones. Starch also includes a lengthy chain of two glucose units joined together, known as polymerized amylopectin or amylose. Furthermore, starch-based bioplastics can serve as thermoplastics, exhibiting improved thermal and mechanical properties. Create bioplastic from corn starch through gelatinization and investigate its properties. Unlike previous investigations, the study examined and compared new bioplastic formulations with varied maize starch-to-glycerol ratios of 1:0.5, 1:1, 2:1, and 2:2, referred to as Sets A, B, C, and D. The Fourier Transformation Infrared Spectroscopy study revealed that all manufactured cornstarch-based bioplastic samples included the four primary plastic functional groups, indicating that they were classified as polyester, Because bioplastic can break down naturally by ethanol created by bacteria in soils through anaerobic processes, it has the potential to be utilized as a fertilizer coating to reduce fertilizer release rate in areas with heavy rainfall[9]. Although most biodegradable plastics produce lower carbon dioxide emissions than conventional alternatives, there are genuine concerns that the global bio-economy's development may contribute to increased deforestation if the problem is not addressed effectively. Which has a negative impact on water supply and soil erosion. As a result, the creation of bioplastics from waste materials is becoming more relevant to the current scenario[10-11]. This research seeks to create biodegradable cornstarch-based bioplastic using gelatinization in a simple, eco-friendly, and environmentally beneficial manner. Corn starch is chosen because it is readily available in commercial packaging materials at a low cost, and it contains more amylose than other starch sources, resulting in a more stable decomposition temperature. Several characterization investigations were done, which included biodegradation, solubility, swelling, SEM, kinetic, and thermodynamic analysis.

MATERIALS AND METHODS

Materials

The material used in this work was corn starch powder (CS). It was purchased from local market in Shorura city Najran Saudi Arabia. Gelatin, glycerol, ethanol, chloroform, nitric acid all chemicals are acquired from Sigma-Aldrich.

Preparation of bioplastic films

Corn starch powder was purchased from a neighborhood grocery in Shorura City, Najran, Saudi Arabia. The bioplastic film was created by adding 500 mL of water, 25 g of corn starch powder, 8 g of gelatin, glycerin, coconut oil, and food coloring to provide a subtle green tint for the bioplastic beaker. One gram of cotton was added to the solution before pouring it into a mold. The bioplastic sheet was molded and air-dried for three days after being sprayed with calcium chloride on both sides. The bioplastic sheet was gently removed from the mold after the specified time. To understand bioplastic behavior and applicability for certain applications, a detailed evaluation of their mechanical, chemical, and physical properties is necessary. In addition to examining kinetic and thermodynamic parameters, various tests were carried out to confirm the sustainability and usefulness of the bioplastic, abbreviated as CS bioplastic[12].

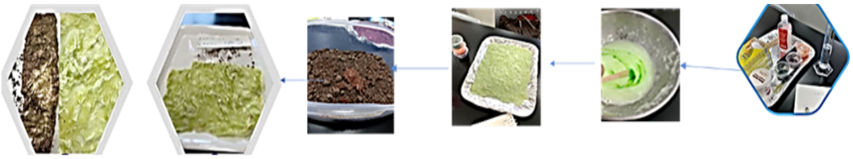

Fig. 1. Preparation steps of Bioplastic in Science and Art Faculty of Shrouraa Laboratory-Najran University-Kingdom of Saudi Arabia

Biodegradability

A pre-weighed piece of bioplastic was sliced into 3 x 3 cm pieces, and its initial weight was measured before being buried 5 cm deep in soil. Water was sprinkled on the soil to increase bacterial enzyme activity. These samples were stored for approximately 14 days, and the morphological structure and weight change of the bioplastic sample were determined. The rate of degradation is calculated based on observed changes, and the time required for significant degradation every day for 14 days at various temperatures ranging from

20 to 25 degrees Celsius is calculated based on the observed changes and the time required for significant degradation to occur. Following this, the weight of the bioplastic decreased, and its final mass after disintegration was determined[13]. The biodegradability material and results were calculated using equation no (1) also plotting weight loss and percentage weight loss versus time(days) figures of straight line obtained.

$$\text{Degradation }\% = \frac{W_2 - W_1}{W_1}100 \qquad (1)$$

Where W_i and W_f are the initial and final weights of a bioplastic sample respectively.

Swelling properties

A swelling study is often performed to examine whether or not the generated material retains the qualities that existed when it was developed during the preparation process. On day one, the samples were weighed after being cut into 15x15 mm pieces and kept at room temperature (23±2°C). The samples were run on a medium containing various solvents, such as chloroform and water. After that, they were periodically removed and weighed again (W_2). The outcomes were Measurements for bioplastic composition were taken three times[14]. Equation 2 was used to determine the amount of water absorbed.

$$\text{Swelling }\% = \frac{W_2 - W_1}{W_1}\times 100 \qquad (2)$$

Solubility

Water solubility was assessed using previously cut and weighed samples of 15x15 mm bioplastic. Following the initial weighing, these samples were immersed in a test tube containing 6 mL of solvents (distilled water, ethanol, and hydrochloric acid) and kept at 25°C. To determine the material's chemical resistance or susceptibility to various solvents, the observed changes in the bioplastic's features after exposure to these solvents were noted and investigated. The final dry weight (W_f) of the bioplastic was determined[15]. Equation 3 was used to estimate the solubility.

$$\text{Solubility }\% = \frac{W_i - w_f}{W_i}\times 100 \qquad (3)$$

Scanning electron microscopy (SEM)

The surface morphology of the bioplastic was investigated with a scanning electron microscope. The samples were attached to an aluminum basis using conductive carbon adhesive tape. The samples were then coated with a gold coating using a crack, apparatus before being placed in a metal holder with double-sided sticky tape to avoid static charge buildup and improve micrograph quality. The working distance of the microscope was 10 mm, and the acceleration voltage was set at 20 kV.

Kinetic study of biodegradation of orange bioplastic

To determine the equilibrium period and kinetic reaction that happened. The biodegradation of (CS) bioplastic took anywhere from one to twenty days. The biodegradation kinetics were calculated using two alternative kinetic models: pseudo-first-order and pseudo-second-order and figures plotted between $\text{Ln}[\alpha]_t$ versus time for first order degradation kinetic also plotting was between 1/t versus time to obtain straight line with slope of $-k_1$ and k_2 for both pseudo first and second order reactions. The equations used to calculate degradation kinetic for both first and second order were as follows:

The equations used to calculate:

First order reaction $\ln[\alpha]_t = -kt + \ln[\alpha]_0$ (4)

Second order reaction

$$\frac{1}{\alpha_t} = k_2 t + \frac{1}{\alpha_0} \qquad (5)$$

Thermodynamic parameters of biodegradation

The thermodynamic properties of the various bioplastics used provide information about the process's workability or spontaneity under various operating settings. The following equation, based on the calculation of the activation energy related to the macroscopic decomposition kinetics and the thermodynamic parameters of the biodegradation of CS, would thus be used to determine the enthalpy change, which represents the total energy consumed by the material for its conversion into the various fractions or products, such as fuel, gas, and coal[16].The equation of the Arrhenius method can be obtained by using the logarithm of Eq. 6. plot lnK vs. (1/T) results in a straight line (slope) to determine the value of activation energy E_a In order to determine the suited n value in the active combustion stage.

$$l\mathrm{nK} = \frac{\mathrm{E_a}}{\mathrm{RT}} + \ln \mathrm{A} \tag{6}$$

$$\Delta H = E_a + RT \tag{7}$$

Where K is constant rate=$d\alpha/dt$, R is constant gas (8.314 J•K•mol^{-1}), E is activation energy, and T is a different temperatures in kelven, A is the pre-exponential factor. While the Gibbs free energy and the entropy of the process is calculated by:

$$\Delta G = -RT\ln K\alpha \tag{8}$$

Finally, the entropy (ΔS) indicates the degree of disorder of the material, which is expressed as:

$$\Delta S = \frac{\Delta H - \Delta G}{T_{max}} \tag{9}$$

Where K equilibrium constant = $\alpha t/\alpha 0$, T_{max} the maximum temperature of bioplastic degradation.

RESULTS AND DISCUSSION

The soil burial test results demonstrate the material's eco-friendliness and degradation profile in the soil environment. Bioplastic samples took 20 days to decompose in soil conditions. Every day, the bioplastic was weighed and examined to monitor its breakdown. The degradation rate was a quantitative assessment of the material's breakdown. The solubility of bioplastic in water demonstrates the bioplastic's ability to totally degrade in water over a short period of time, reducing the risk of water pollution.

SEM Analysis

The SEM analysis revealed particle structure and geometric variances in the surface morphology of the bio-based material. The surface of Fig. 2 is rough and uneven, with some fibers in the mixture; also, the size and form of the bioplastic particles vary. The particles' shapes vary, appearing as uneven pores that are either smooth or severely irregular. As a result, it is obvious that the presence of different polymers in the film altered the shape of the particles. Despite its rough surface, the CS-based material appears homogeneous at magnifications greater than 200 mm, indicating that the particles were evenly spread throughout the composite film material, resulting in more stable structures. These spherical inclusions are characterized as the starch percentage of the blend mix, spread in a continuous

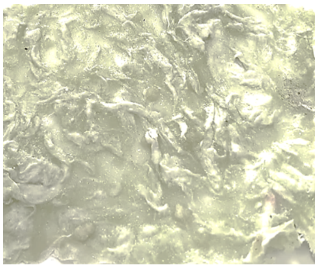

Fig. 2. SEM surface micrographs of bio plastic of corn starch

Biodegradability

The bioplastic's gradual loss of weight and stability, as demonstrated in Table 1 and Fig. 3(a), (b) of weight loss and percentage weight loss with time obtained from the results of kinetic degradation suggests a considerable degradation rate over time, stressing the material's susceptibility to environmental impacts in soil. The breakdown rate gradually increased, reaching 57.9% on day 14, indicating complete degradation and removal of the bioplastic. These findings suggest that bioplastic degrades swiftly in the soil environment, disappearing entirely within the 20-day test period. Weight was monitored at various time intervals. The degradation rate gradually increases over time, resulting in consistent weight loss. The decreased weight and increased disintegration rate indicate a steady loss of bioplastic integrity.The material is very susceptible to degradation, with complete breakdown by day 14 suggesting rapid and severe weakening. The degradation rate was a quantifiable measure of the material's breakdown. The bioplastic's gradual decline in weight and stability, as shown in Table 1, indicates a significant breakdown rate over time, emphasizing the material's susceptibility to environmental elements in soil.

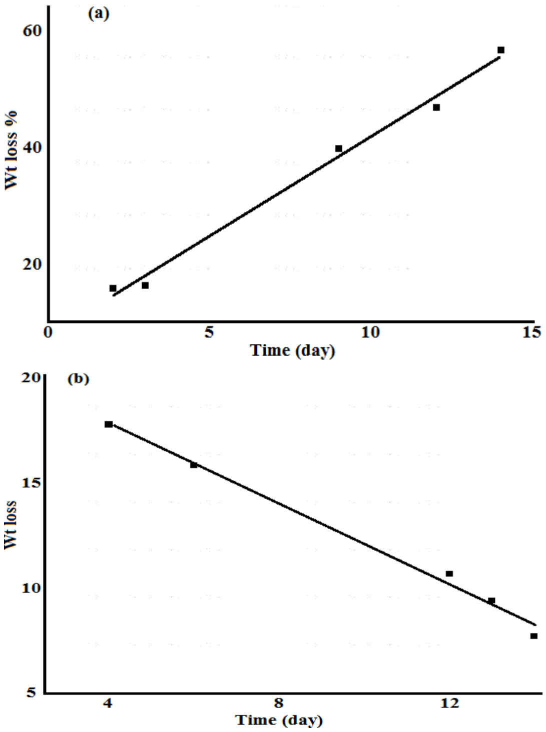

Fig. 3. Biodegradability of bioplastic produced from corn starch(a) % weight loss (b) weight loss with days

Table 1: Weight loss and percentage weight loss of bioplastic produced from corn starch with days

Temperature°C	W_t.% with respect to initial weight 17.85	(W_2) with respect to initial weight 17.85	Time (day)
20	0	0	0
21	15.9	2.85	1
23	15	2.69	2
24	12.5	2.24	3
25	14.6	2.61	4
23	39.9	7.138	7
25	46.9	8.38	8
20	57.9	10.19	14

Solubility Test

Solubility is the primary attribute used to determine whether a synthetic bioplastic material is sustainable or not. If the bioplastic material has low or nil engorgement, it can be called an outstanding material with stability. Table 2 reveals that the bioplastic is somewhat soluble in ethanol and water and totally soluble in hydrochloric acid, indicating that the bioplastic material generated is stable. Immersion of bioplastic samples in water for a period of time to assess material degradation while at room temperature aids in the development of alternative degradable bioplastics with environmentally favorable features.

Table 2: Solubility test results for bioplastic

Solvents used	insoluble	Partially	Completely
Water	-	Yes	-
Ethyl alcohol	-	Yes	-
Hydrochloric acid	-	-	Yes

Swelling test

The findings of the swelling test are provided below. Table 3 demonstrates that when the bioplastic is soaked in water as a medium, its weight increases somewhat, which is a desired result because most additives are manufactured using organic solvents; this will undoubtedly aid in the stabilization of product synthesis and development. does not change much when exposed to chloroform.

Table 3: Swelling of bioplastics by different solvents

Sample No	Solvent	Difference the sample weight in (g)	Final weight	Initial weight of	100%
1	Water	0.596	2.301	1.705	34%
2	Chloroform	0.24	1.942	1.702	14%

Wight losses at different temperatures

The temperature was monitored every day for 14 days while the bioplastic was biodegrading in the buried experiment, and Fig. 4 displays the temperature fluctuation curve over time. The temperature curve indicates an initial temperature of 20°C. As a result, circumstances that promote successful CS biodegradation include a constant temperature of more than 20°C rising to 25°C.[17]

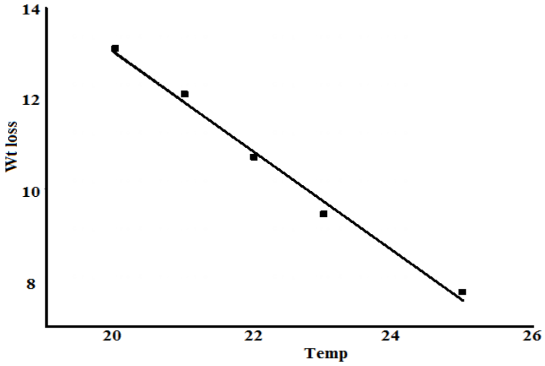

Fig. 4. Weight loss of corn starch bio plastic at different temperatures

Kinetic study of biodegradation of orange bioplastic

The biodegradation kinetics of the produced plastic were investigated for first- and second-order processes, as depicted in Fig. 5(a) and (b) for first and second pseudo-order degradation. The reaction rate of the biodegradation kinetics of orange bioplastic in agricultural soil can be monitored. Table 5 calculates the reaction rate coefficients for each degrading medium, highlighting many aspects that can be drawn from the reaction kinetic results. First, the reaction rate coefficient (k_r) for the plastic's biodegradation process rose as the starch concentration grew. The bioplastic decomposed in the soil with a k value of -0.03741day^{-1} and a second-order constant of 0.0035. According to first-order reaction kinetics, the degradation of starch into a complex starch material (composed of many substances) produces straight lines. A single-phase biodegradation process is indicated by a logarithm value that is more inclined to a straight line. This suggests that the plastic degraded and decomposed before forming a microcrystalline complex that stabilized[18-19].

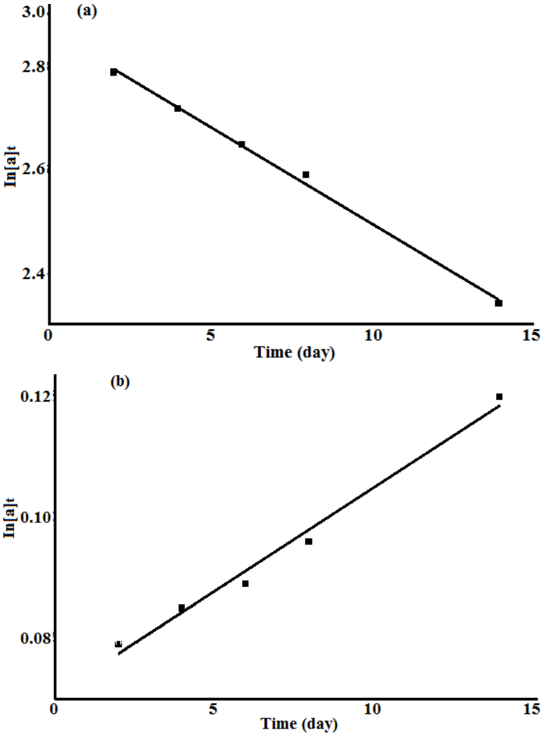

Fig. 5. Kinetic of degradation of bioplastic produced from corn starch with days (a) Pseudo first (b) Pseudo second

Table 5. Kinetic study of bioplastic degradation rate

Pseudo second order reaction			Pseudo First order reaction		
$1/[\alpha]_0$	K_2	R^2	$\ln[\alpha]_0$	R^2	-k
0.073	0.0035	0.97	2.87	0.99	-0.03741

Thermodynamic parameters of biodegradation

Table 6 displays the calculated thermodynamic parameters (ΔH, ΔS, and ΔG) based on kinetic data for both plastic samples. The negative value of ΔH indicates that the thermal decomposition of polymers is exothermic, requiring significant energy. The entropy change was 0.58 JK^{-1} mol^{-1} as temperature increased, demonstrating a gradual transition from more structured to less organized systems. Positive ΔS values suggest that the development of the activated complex leads to an increase in entropy, indicating a "less organized" structure of the substance, as entropy is typically used to evaluate unpredictability. Positive ΔG values indicate a non-spontaneous reaction, similar to the deterioration process. Furthermore, the free energy has a similar value at different heating rates, ranging from 26.796, 83.874, and 153.609 J mol^{-1} as temperature increases. Arrhenius defined activation energy as the minimum energy required to start a chemical reaction (combustion). Bioplastic can generate energy (heat) in two ways: thermochemically and biochemically, or biologically[20]. The maximum R^2 value ensures optimal curve determination for all examined decomposition levels. The activation energy and pre-exponential factor for each active combustion stage were calculated from the end plot's related slope (-E/R) and interceptions (ln(A). Table 1 displays the results of the Arrhenius technique on the final graph.

Table 6: Thermodynamic parameters

ΔS Jmol^{-1}k^{-1}	Temperature(k)	ΔG Jmol^{-1}	R^2	ΔE Jmol^{-1}	ΔH Jmol^{-1}
	293	31.68	0.99	36	-20.57
1.28	296	41.55			
	298	42.86			

CONCLUSION

The goal of this research is to attempt to synthesize and analyze bioplastics derived from natural sources. The method involves making bioplastic from corn starch. Glycerol, gelatin, and sodium hydroxide were to be mixed with orange pastes in a beaker to make bioplastic. Following mixing and drying, the bioplastic was removed from the petri dish. Several tests were conducted to establish the physical properties, including biodegradability, solubility, swelling, moisture content, electron-scanning microscopy, kinetic and thermodynamic parameters. The breakdown rate was 57.9% after 14 days, which was tolerable and acceptable; bioplastics were partially soluble in ethanol, and in water, and completely soluble in HCl. The result of swelling was not much change when soaked in chloroform. A slight increase in weight was observed when bioplastic was soaked in water. According to the moisture test results, the average percentage of weight loss orange was 10% in chloroform, while the average percentage of weight loss for orange in water was 25%. The activation energy was 36, which is the minimum energy required to activate a chemical reaction. The thermodynamic parameters for biodegradation showed positive ΔG values of 31.68, 41.55, and 42.85J mol^{-1}, indicating non-spontaneous behavior, a negative ΔH value of -36 J mol^{-1}, indicating exothermic nature, and a positive ΔS value, indicating less ordered structure. the kinetic reaction rate coefficient (k_r) for the biodegradation process of the plastic became high, as increasing the starch content leads to increased biodegradation. The k_r value for the bioplastic that degraded in the soil is -0.03741 day^{-1}, and the value of the second-order constant is 0.0035. This means that the plastic broke down and decomposed, then formed a microcrystalline complex and stabilized. Future prospects: Despite prior attempts to employ sugar or starch, the development of biobased polymers from agro-based industrial leftovers, particularly corn starch , has advanced significantly. Bio polyester-based polymers can be utilized as feedstock for a variety of applications. This will improve the value proposition for agro-industries by reusing fruit waste and reducing the demand for food feedstock for biobased plastic production. Nonetheless, new bioresources are continually being sought for the development of innovative biobased polymers. The most recent research may pave the way for the development of new biobased polymers. Food packaging materials have a shorter shelf life and can biodegrade in 3 months, making them excellent for industrial packaging. Approximately 30% of all food produced is wasted, the majority of which occurs in supermarkets during high sales seasons. Using biodegradable/biobased plastics to increase the shelf life of consumable products can significantly minimize food waste. Using biobased materials can minimize food waste by 10%, outweighing the extra land needed for dumping during the recycling process. Using these processes to transform agricultural waste into biobased polymers has huge economic implications for this century. Recommendation for researchers to do extra research in order to develop the project of producing bioplastic from waste vegetables and fruits, as well as to uncover some other natural additives that will offer our plastic greater attributes.

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Declaration of competing interest

The authors declare that they have no known competing financial or personal interests that could have influenced the work reported in this paper.

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