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Canna Edulis ker. Starch-Based Biodegradable Plastic Materials: Mechanical and Morphological Properties

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Abstract

Bioplastics were produced by mixing starch with carboxymethyl cellulose (CMC) during the manufacturing process. The physical characteristics of the bioplastics were investigated using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). Tensile strength, elongation, and Young's modulus tests were utilized to assess the mechanical characteristics of bioplastics. The bioplastic with the highest tensile strength was BP3 (7.03 ± 0.341 N/mm²), whereas BP0 had a tensile strength of 1.57 ± 0.111 N/m². The addition of CMC increased the viscosity of the solution and, consequently, the strength of the bioplastic. The range of bioplastic hydrophobicity was approximately 128.32% to 323.74%. FTIR, XPS, and XRD indicated that the physical mixing utilized during synthesis did not result in the addition of functional groups other than the native functional groups of the substances since no chemical reaction occurred. The thermal behavior investigation revealed that increasing the amount of CMC added to TPS can increase the presence of O-H functional groups in bioplastics, contributing to an increase in the glass transition temperature. Furthermore, both bioplastics broke down at approximately 250°C.

1 Introduction

Conventional plastics are not completely stable in quality because of the possibility of plastic monomers migrating to the packaged material. Furthermore, the use of single-use plastic in the packaging of horticultural products is one of the factors that contributes to the accumulation of plastic waste [1], [2]. Thermoplastic starch (bioplastic) development is one of the latest solutions available for packaging problems. Starch-based bioplastics have been developed from several kinds of materials, such as tubers [3], [4], legumes [3], [5], cereals [3], [6], agricultural wastes [3], [7], [8], [9], [10], [11], and marine wastes [12], [13], especially in Indonesia, because of the diversity of abundant natural resources. Due to their natural properties, microorganisms can decompose starch-based bioplastics, thereby minimizing single-use plastic packaging pollution [14], [15], [16].

Canna edulis ker. Tubers, as one of the local wisdoms in Indonesia, are a natural source of starch [17], [18]. A high amount of starch with an amylose proportion of 42.40% and an amylopectin proportion of 50.90% showed unique characteristics. The proportion of amylose in tuber starch is much lower than that of amylopectin in many cases, ranging from 15–30% of the total starch [17], [18]. Starch with a high amylose content easily forms a gel due to the easy formation of bonds between starch molecules. Canna edulis starch also has a large granule size of approximately 56 μm [17], which can reduce the energy and time required for gelatinization [19]. These characteristics of Canna edulis starch are desirable for producing biodegradable plastics. On the other hand, starch will more easily bind water, where this condition provides an advantage in the degradation process and weakens the brittleness of the synthesized bioplastic.

The addition of plasticizers and fillers can affect the mechanical properties of starch-based bioplastics [12], [20], [21]. Research has reported that the addition of CMC in the range of 1.25-2.00 g results in an increase in the mechanical properties of tensile strength and elongation compared to those of other treatments [22]. This treatment resulted in high-quality bioplastics that met the Indonesian National Standard (SNI) no. 17557:2011 on the basis of their mechanical properties. This study aimed to observe the mechanical and characterization properties of Bioplastic developed using Canna edulis ker. starch-based plastic compared to conventional plastic to substitute for single-use plastic. Several parameters, including tensile strength, elongation, thickness, biodegradability, and hydrophobicity, were tested and observed via Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and thermal behavior analysis.

2 Materials and methods

2.1 Materials

Canna edulis ker. starch was obtained from the local market (Gresik, Indonesia) under the brand name “Mama Kamu”. The additive materials sorbitol were obtained from Merck Ltd. (Surabaya, Indonesia), and the additive materials carboxymethylcellulose (CMC) and glacial acetic acid were obtained from Sigma–Aldrich Co. Llc. was obtained from commercial trade (Malang, Indonesia).

2.2 Design Experiment

In this study, a bioplastic was created using the CMC composition as a variable that was added independently. There are four different ways to add CMC: no addition (BP0), 1.00 grams (BP1), 2.00 grams (BP2), and 3.00 grams (BP3) in various solutions. Every bioplastic undergoes testing for various physical attributes, such as mechanical properties, thickness, biodegradability and hydrophobicity. The results of the physical tests were analyzed for significant differences through statistical tests to determine the most effective treatment. The best treatment is based on the addition of bioplastic CMC, which has good physical characteristics. Furthermore, additional tests were conducted on the control treatment (BP0) and the optimal treatment using FTIR, XPS, XRD, and DSC-TGA analysis. This study aimed to examine the morphology, crystallinity, and thermal properties of the materials.

2.3 Bioplastic production procedure

The starch from *Canna edulis* ker was weighed at 3.00 grams using an analytical balance (Radwag AS R2 PLUS) and then dissolved in 100 ml of distilled water. The resulting solution was mixed with 1 gram of sorbitol and 1.5 grams of glacial acetic acid. Different bioplastic formulations were developed with additional CMCs according to the experimental design in different solutions. The resulting mixtures were stirred at 80°C for 25 minutes for the homogenization process. The bioplastic solution was molded into a mold and baked in an oven (Memmert Universal Ovens) at 50°C for 24 hours [22].

2.4 Properties and characterization

2.4.1 Mechanical property measurements

The tensile strength test was carried out by preconditioning the samples (BP0–BP3) to be tested in a room with a standard relative humidity temperature (± 23°C) for 24 hours. Then, the sample was cut according to the standard. The tensile strength test was carried out by clamping the two ends of the sample on an MCT-2150 tensile testing machine (Materials Innovation Laboratory, Sepuluh Nopember Institute of Technology, Indonesia). The initial length was subsequently recorded, and the recording ink tip was placed at position 0 on the graph. The start knob was turned on, and the broken sample was pulled by the tool. The tensile strength (F) and length after breaking were subsequently recorded. The tensile strength test was calculated using Eq. 1.

$$TS = \frac{Load\ of\ break}{(Original\ width)\ (Original\ thichness)}$$

1

The elongation measurements were carried out using the same method used for the tensile strength test. Elongation is expressed as a percentage through Eq. 2.

$$\%Elongation = \frac{Elongation\ break - Initial\ length}{Initial\ lenght} x100\%$$

2

2.4.2 Thickness Measurement

The thickness of the Bioplastic was measured by mechanical scanning using a TW-21 (provided by TÔZAI SEIKI CO.LTD.) based on ASTM F2251. Bioplastic samples (BP0–BP3) were cut to dimensions of 20 mm² and placed between the anvil and the spindle of the micrometer, and a force of 0.1 N to 0.2 N was applied. The thickness was measured on the micrometer display. The measurements were repeated at different points across the sample to obtain the thickness uniformity [23].

2.4.3 Biodegradability measurements

Biodegradability was measured using a soil burial test following the methods of [23]. The sample was prepared with dimensions of 2 cm × 6 cm, after which the mass of the sample was weighed. Next, the samples were buried in the soil and allowed to stand for 7 days. After 7 days, the bioplastic was dried in a desiccator for 15 minutes and weighed until a constant weight was obtained. The following equation was used to calculate the biodegradation during the test:

$$\%Weight = \frac{Initial\ weight - Final\ weight}{Initial} x100\%$$

3

2.4.4 Hydrophobicity measurements

Hydrophobicity measurements were carried out following the methods of [24]. The hydrophobicity test was initiated by weighing the initial weight (W_0) of the sample (BP0–BP3). The samples were filled with distilled water and 100 ml of beaker glass, after which the samples were submerged and removed from the beaker glass after 10 minutes. Next, after the sample was soaked, it was weighed (W_1). The sample was reimmersed into a container, lifted every 10 seconds and subsequently weighed. This step was carried out several times until a constant final weight was obtained. The amount of water absorbed by the sample can be calculated using Eq. 4.

$$\%Water\ absorption = \frac{W_1 - W_0}{W_0} x100\%$$

4

2.4.5 Fourier transform infrared spectroscopy analysis

Analysis and characterization of the Bioplastic functional groups were carried out using Fourier Transform Infrared Spectroscopy (FT-IR) [24], [25]. Small pieces of Bioplastic were placed on germanium pieces of an infrared spectrophotometer, and the absorbance was measured at wavelengths ranging from 500 cm-1 to 4000 cm-1. OriginPro 2016 32-bit software was used to plot the data collected from the plotted FTIR analysis. The peaks in the graph represent functional groups in bioplastics based on wavelength values. This method was adapted from [26] with some modifications.

2.4.6 X-ray photoelectron spectroscopy analysis

A K-Alpha X-ray photoelectron spectrometer (JPS-9010TR, JEOL, Japan) was used to conduct X-ray photoelectron spectroscopy (XPS) experiments at room temperature with a monochromatic Al Kα radiation (1486.6 eV) source at 10 kV and 20 mA. A 2 mm by 0.4 mm area of the sample was exposed to an X-ray beam with a 200 mm diameter and a power of 100 W. With a 50-eV pass energy and 0.1 eV resolution, a high-energy photoemission spectrum was obtained. These circumstances resulted in an FWHM for the $Ag_3d_5/2$ line of 0.80 eV [27].

2.4.7 X-ray diffraction (XRD) analysis

Bioplastic samples were dried in a desiccator for 24 hours to remove any leftover moisture. An X-ray diffractometer (D8 Advanced, AXS-Bruker, Germany) was used to assess the crystallinity of the samples with a Cu-Kα radiation (1.5418 Å) source at 40 kV and 40 mA. With a scanning rate of 4°/min, samples were tested in the angular range of 2θ = 10–60° [24], [28].

2.4.8 Thermal property analysis

Bioplastic samples were subjected to thermogravimetric analysis (TGA) using a thermogravimetric analyzer (TG/DTA7300, Seiko Instruments Inc., Chiba, Japan). A platinum crucible containing 5 mg of bioplastic was heated at a rate of 15°C/min from ambient temperature to 550°C. Adaptive carrier A 200

mL/min flow of argon gas was used. A differential scanning calorimetry (DSC) device (X-DSC-7000, Shimadzu, Kyoto, Japan) was used to investigate the melting point (T_m), glass transition temperature (T_g), and cold crystallization temperature (T_c) of the bioplastic. A pan made of aluminum was filled with approximately 5.0 grams of plastic and heated to 110°C from room temperature. Under an atmosphere of argon (Ar), the samples were chilled to 30°C and subsequently heated to 110°C (heating/cooling rate: 10°C/min). DSC thermograms were used to collect the data [29].

2.5 Statistical analysis

The mechanical properties, thickness, biodegradability, and hydrophobicity were tested by taking into account the standard error (SE) and standard deviation (SD) of the average results. These tests were conducted five times. For all the statistical computations, Microsoft Excel (Microsoft Corporation, USA) was utilized. The collected data were subjected to univariate ANOVA ($p < 0.05$), and mean differences were identified using Duncan's multiple range test (DMRT).

3 Results and discussion

3.1 Physical and Mechanical characteristics

The form and color properties of the produced bioplastics were physically analyzed. Table 1 demonstrates that the bioplastics produced with the addition of CMC formulations are transparent to yellowish in color. The polymerization of the utilized ingredients, such as starch and CMC, alters the transparency of the bioplastic [4], [30], [31]. Starch-based bioplastics are typically translucent or slightly opaque due to their inherent composition. In the process of polymerization, monomers—simple molecules—are chemically combined to create more complex polymers. Moreover, the physicochemical properties of TPS can also be affected by the addition of fillers and other additives [30], [31]. Physically, BP2 was more robust and elastic. [1], [32] reported that the addition of more CMC can increase the robustness and elasticity of bioplastics. Conversely, BP3 has a yellowish appearance consistent with previous claims [33] that bioplastics become yellower as more CMC is added.

Table 1
Physical properties of Canna starch-based bioplastics

Formulation	Bioplastic Physical Form	Bioplastic Color
BP0	Thiner, brittle, granules	White, opaque
BP1	Thin, slightly elastic, brittle, white patches	White, transparent
BP2	Thicker, slightly firmer, elastic, smooth surface	Clear, Transparent
BP3	Thicker, slightly brittle, smooth surface, bubbly	Yellowish transparent

The strength of bioplastics can be improved by introducing CMC (carboxymethyl cellulose) during the production process. Additionally, the inclusion of CMC also has a notable influence on the thickness of

the final bioplastic product due to the hydroxyl group present in CMC, which can bind water [12], [30]. Consequently, this hydroxyl group directly impacts the thickness of the bioplastic, which leads to gradual thickening of the solution. However, the addition of additional CMC may lead to slight brittleness in the resulting bioplastic [34]. Therefore, the utilization of CMC serves as a crucial factor both for strengthening bioplastics and determining their overall thickness [1]. Moreover, an increase in the CMC content can lead to a bubbly appearance on the bioplastic surface. The CMC impacts the rheological characteristics of the bioplastic melt. As the material cools and hardens, the gas bubbles stay distributed and create a cellular structure. This cellular arrangement is responsible for the bubbly look on the surface [35].

Tensile strength, elongation, and Young's modulus tests were used to evaluate the mechanical properties of the bioplastics. According to Table 2, the inclusion of CMC resulted in an increase in the tensile strength. The bioplastic with the highest tensile strength was BP3, for which the tensile strength was 7.03 N/mm², whereas the use of BP0 as a control treatment provided a tensile strength of 1.57 N/mm² (Fig. 2). The treatment outcomes satisfied the minimum requirement of SNI no. 17557:2011 at 1,343 N/mm². The addition of CMC, which creates cross-links between polymer molecules, increased the viscosity of the solution and, consequently, the tensile strength of the bioplastics. Bioplastic materials undergo cross-linking, which increases the stiffness, pressure resistance, and strength of the material [6]. The inclusion of CMC also induces hydrogen bonding between hydroxyl (OH) and carboxyl (COOH) groups, increasing the tensile strength of the resultant bioplastic [4], [6], [36].

With the variation in the CMC addition, however, the elongation value is inversely related to the tensile strength. This is due to the combination of starch and CMC, which both contain many hydroxyl groups (OH), which causes the number of hydrogen bonds to increase, thereby increasing the intramolecular forces between chains and decreasing the flexibility of bioplastics [22]. The thickness and compressive strength of plastic are related because thick plastic has stronger material linkages, which causes pressure to build. The test results also revealed that the relationship between elongation and tensile strength is inverse. Due to the presence of hydroxyl groups shared by starch and CMC, which results in greater intramolecular tension between chains, bioplastics are less flexible as a result of enhanced hydrogen bonding [22], [36].

Table 2
Results of the Mechanical Characteristics Test

Formulation	Elongation (%)	Young's Modulus (N/mm^2)	Thickness (mm)
BP0	2.72 ± 0.367^a	8.35 ± 0.676^a	0.0932 ± 0.000^b
BP1	3.80 ± 0.172^b	11.13 ± 0.402^b	0.0873 ± 0.002^a
BP2	3.57 ± 0.172^b	16.12 ± 0.634^d	0.0860 ± 0.001^a
BP3	3.63 ± 0.195^b	14.27 ± 1.095^c	0.0867 ± 0.003^a

Remark

SNI abbreviation for the Indonesian National Standard

3.2 Biodegradability and hydrophobicity analysis

A biodegradability test was also conducted to determine the rate at which soil microorganisms might breakdown bioplastics [24], [25]. The weight of the bioplastics was impacted by the biodegradation process (Table 3). BP3 was biodegraded by 37.26%, while BP2 was biodegraded by approximately 33.81% after 7 days, and BP1 had an average residual weight of 15.70%. The percentage of biodegradation produced in this study over 7 days was consistent with that in previous reports [37], [38], [39], in which bioplastic samples had a residual percentage of 20–30% for one week. The more CMC is added, the easier it is for the soil to decompose bioplastics. The ability of the materials employed to absorb water was similarly correlated with the deterioration of bioplastics [22], [40], [41].

Table 3
Results of Biodegradability and Hydrophobicity Test

Formulation	Biodegradability Percentage (%)	Hydrophobicity Percentage (%)	Source
BP0	9.74 ± 1.452^a	128.32 ± 1.855^a	Based on analysis
BP1	15.70 ± 0.833^b	173.10 ± 10.603^b	
BP2	33.81 ± 1.037^c	297.03 ± 4.702^c	
BP3	37.26 ± 1.650^d	323.74 ± 19.447^d	
-	20–30	-	[41]
-	-	99	SNI no. 17557:2011

The average hydrophobicity of the bioplastic after the addition of CMC ranged from 173.10–323.74% (Table 3). The capacity of the Bioplastic to absorb water increases with the amount of CMC added, decreasing the material's water resistance. CMC was utilized as a filler with hydrophilic characteristics, allowing simple water absorption by the bioplastic produced [12], [22], [42]. In addition, because starch contains more hydroxyl (OH) groups than other materials and is therefore quicker to absorb water, its usage in the production of bioplastics may have an impact on the hydrophobicity process. Hydrophilic canna starch can bind water because of its unique characteristics. The characteristics of canna starch were the reason for the decreased water resistance of the bioplastic [17], [19]. After conducting physical tests on bioplastics, BP3 was identified as the most effective treatment, prompting additional characterization tests with BP0.

3.3 FT-IR analysis

The functional groups of certain chemical compounds were qualitatively examined using an FT-IR spectrophotometer. According to the findings of the FT-IR study (Fig. 3), both Bioplastic BP0 and BP3 exhibited several peaks. These peaks appeared and indicated the presence of various functional groups on bioplastics. There is a peak at 3200–3600 cm^{-1} in the absorption region that is indicative of the O–H stretching vibration of acetic acid. The C-H functional group region is in the absorption range of 2900–3000 cm^{-1} and consists of a stretching vibration of native starch and a C-O functional group at 1000–1300 cm^{-1}. Furthermore, this was confirmed by the formation of characteristic dual peaks at 1076.06 cm^{-1} and 1149.76 cm^{-1} for BP3. The intensity of these dual peaks was greater in the presence of higher amounts of CMC, which represents the stretching vibrations of the C-O bond and C-O-C bond in ethers [12], [32].

The presence of the stretching vibration of the C-O bond and the C-O-C bond in ethers can improve the bioplastic tensile strength due to the polar characteristic of the C-O bond and its dipole moment [26], [43]. The dipole moment increases as the length of the linker increases, increasing the intermolecular pressure between the polymer chains. The information shown above is consistent with research that found O-H, C-H, and C-O functional groups, which are the structures that make up the formulas of materials [22]. This result is in agreement with a previous report on the synthesis of TPS from native starch [24], [44], [45]. There was no evidence of the formation of additional functional groups or the mixing of contaminants during the production of bioplastics. This demonstrates that physical mixing is used during the production of bioplastics.

3.4 XPS analysis

XPS spectra of BP0 and BP3 are presented in Fig. 4. The spectrum shows a wide range of binding energies from 0–1,200 eV. Oxygen, carbon, nitrogen, sodium, and calcium were found in both BP0 and BP3. The increasing amounts of CMC did not affect the composition of the products, despite the increasing intensity. O-H, C-H, and C-O components are present in both samples (Fig. 3a) on their surfaces due to the natural properties of starch, as well as the structural nature of the CMC material [12],

[17], [18], [22]. XPS measurements were performed at certain energy ranges to acquire a more thorough understanding of the surface composition. The results of the wavelength range analysis for oxygen and carbon present on the surface of the bioplastics are depicted in Fig. 3b and Fig. 3c, respectively. It should be noted that each treatment exhibited a slight variation in peak intensity, which was primarily attributed to the minor addition of CMC [22]. This addition, however, does not significantly impact the overall results.

3.7 XRD analysis

The XRD pattern of the bioplastic surface is shown in Fig. 5. The 2θ values reveal that small crystalline peaks emerge for both Bioplastics and remain flat in comparison to the amorphous area. Bioplastics based on starch are more amorphous than starch itself; thus, crystalline materials could be found with low intensity during observation. The crystallinity tends to decrease with increasing CMC. [46] reported that the addition of CMC to thermoplastic starch can decrease the crystallinity intensity due to the large conversion of starch and CMS to the amorphous state. This discovery contrasts sharply with the relatively well-defined crystalline areas typical of untreated starch [31], [36], [47]. Indeed, as a result of the many transformational events that occur during their synthesis, bioplastics derived from starch are more amorphous than their parent material.

Plasticization occurs when starch is exposed to heat and shear pressures, resulting in a derivative substance known as plasticized starch (PS). The breakdown of hydrogen bonding networks and intermolecular tension give starch its more rigid structure, characterizing this phase change [24]. Therefore, the mechanical characteristics of the blends followed a similar pattern to that of pure PS, with the quality first decreasing due to plasticization due to moisture absorption and then increasing due to retrogradation over time [2].

3.8 Thermal Behavior

The thermal properties of bioplastics were investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and the results are shown in Figs. 6a and 6b, respectively. The glass transition temperature (T_g), which is indicated by an abrupt increase in heat flow, may be revealed via DSC. Increased mobility during devitrification causes this increase in heat capacity. When the two DSC plots at BP0 and BP3 are compared (Fig. 5), there is no obvious T_g observable up to 110°C. This difference is caused by an increase in the amount of CMC, which causes an increase in the amount of the amorphous network. The addition of CMC to TPS can enhance the presence of O-H functional groups in bioplastics, hence improving their hydrophilicity [1], [20]. The presence of O-H functional groups in the bioplastic might improve its hydrophilicity, which can contribute to an increase in T_g [13], [48].

The samples were heated at a rate of 15°C/min from room temperature to 550°C, and changes in relative weight were recorded. A minor decrease of several weight percentage points (13%) was observed in the temperature range of 55°C to 230°C. This decrease is produced by the release of water trapped during the synthesis of bioplastics. Both bioplastics degrade at approximately 250°C, during which organic

molecules degrade and volatile organic compounds are released, resulting in a decrease in sample weight. These breakdown temperatures provide important characterization insights into the structure of bioplastics. However, this temperature should not be regarded as critical for application and processing because starch polymerization can begin under pressure at 80°C [49].

4 Conclusion

Bioplastics derived from Canna edulis starch exhibit physical properties similar to those of typical thermoplastic starch products, including white and opaque appearances, as well as elastic physical properties and smooth surface qualities. While the mechanical properties of the two treatments, particularly the tensile strength, fulfill the SNI criteria, the contradiction in the elongation characteristics of the products does not. The addition of CMC to the bioplastic formulation, on the other hand, increases the hydrophilicity of the material, which is consistent with the increase in the intensity of the O-H functional groups shown in the FT-IR and XPS measurements. Bioplastics may be damaged at 250°C, during which the entire material degrades owing to its organic molecular content. Furthermore, the mechanical properties, hydrophobicity, and thermal behavior of bioplastics can be enhanced by altering the properties of canna starch, adding biopolymers, or employing nanocellulose fillers.

Abbreviations

BP0	Bioplastic formula without the addition of CMC
BP1	Bioplastic formula with the addition of 1.00 g of CMC
BP2	Bioplastic formula with the addition of 2.00 g of CMC
BP3	Bioplastic formula with the addition of 3.00 g of CMC
CMC	Carboxymethyl Cellulose
DSC	Differential Scanning Calorimetry
FT-IR	Fourier Transform Infrared Spectroscopy
PS	Plasticized Starch
TGA	Thermogravimetric Analysis
TPS	Thermoplastic Starch
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction

Declarations

Contributions

AAG and AYR conceived the presented idea, wrote and edited the manuscript, developed the theory and performed the formal analysis. Both authors discussed the results and contributed to the final manuscript. YST wrote the original draft. TE provided laboratory resources for this work. RMMNF and KT performed formal testing on the material. SI conducted the material synthesis. AH and SII supported the project administration.

Conflict of interest statement

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

Data availability

The data will be made available upon request.

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Figures

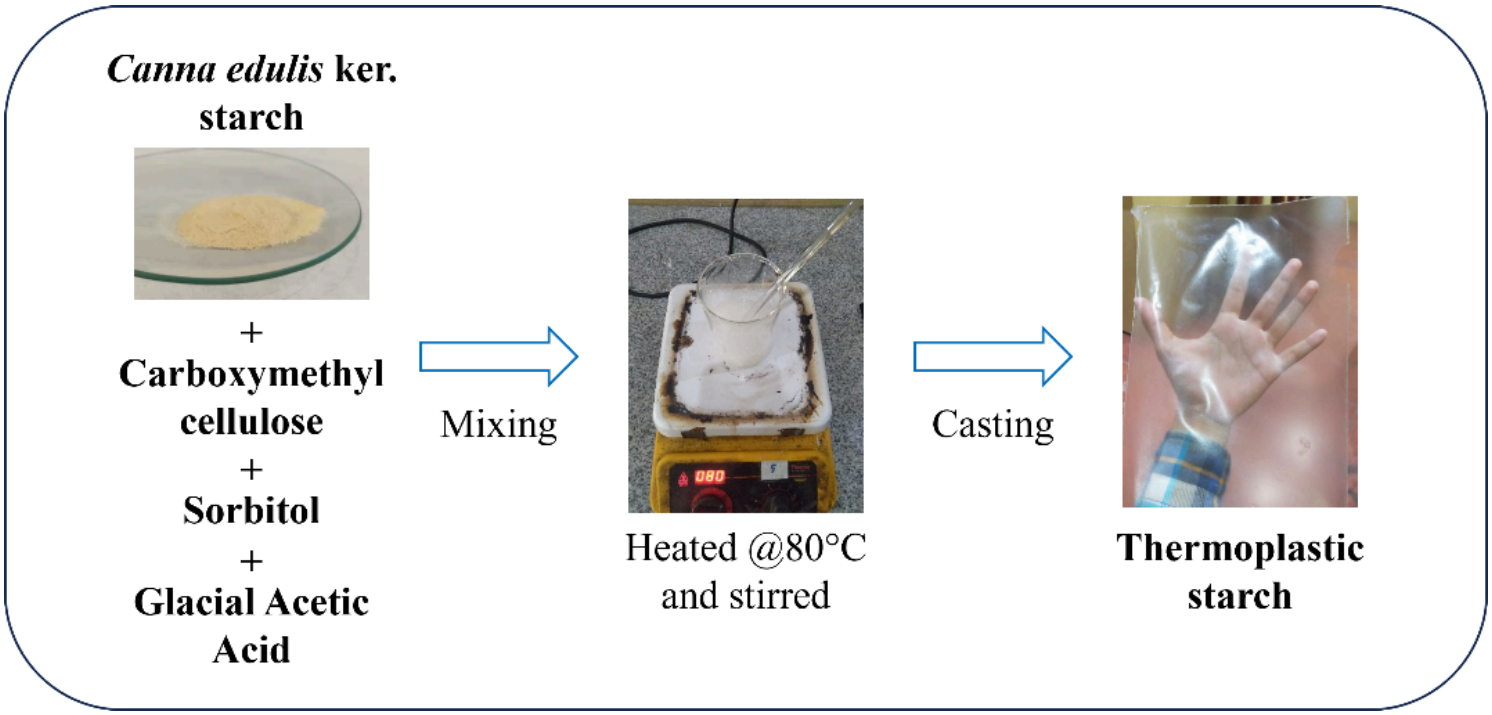


Figure 1

Bioplastic production process

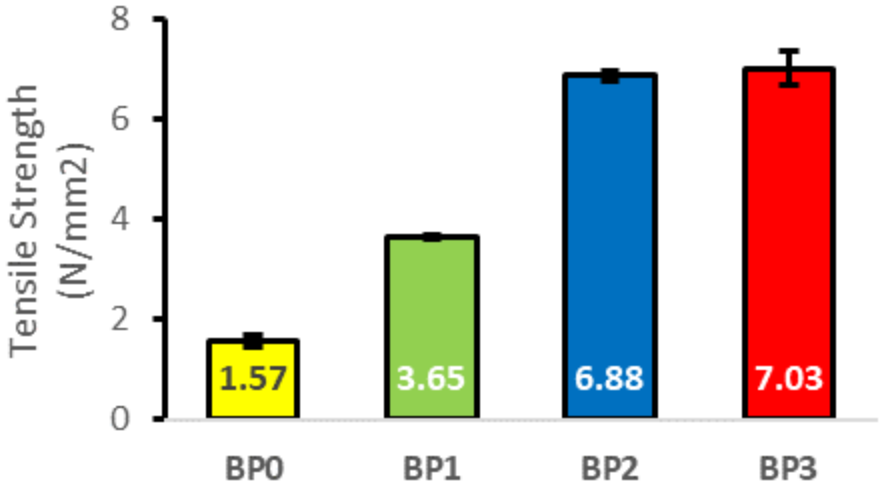


Figure 2

Tensile strength of Canna starch-based bioplastics.

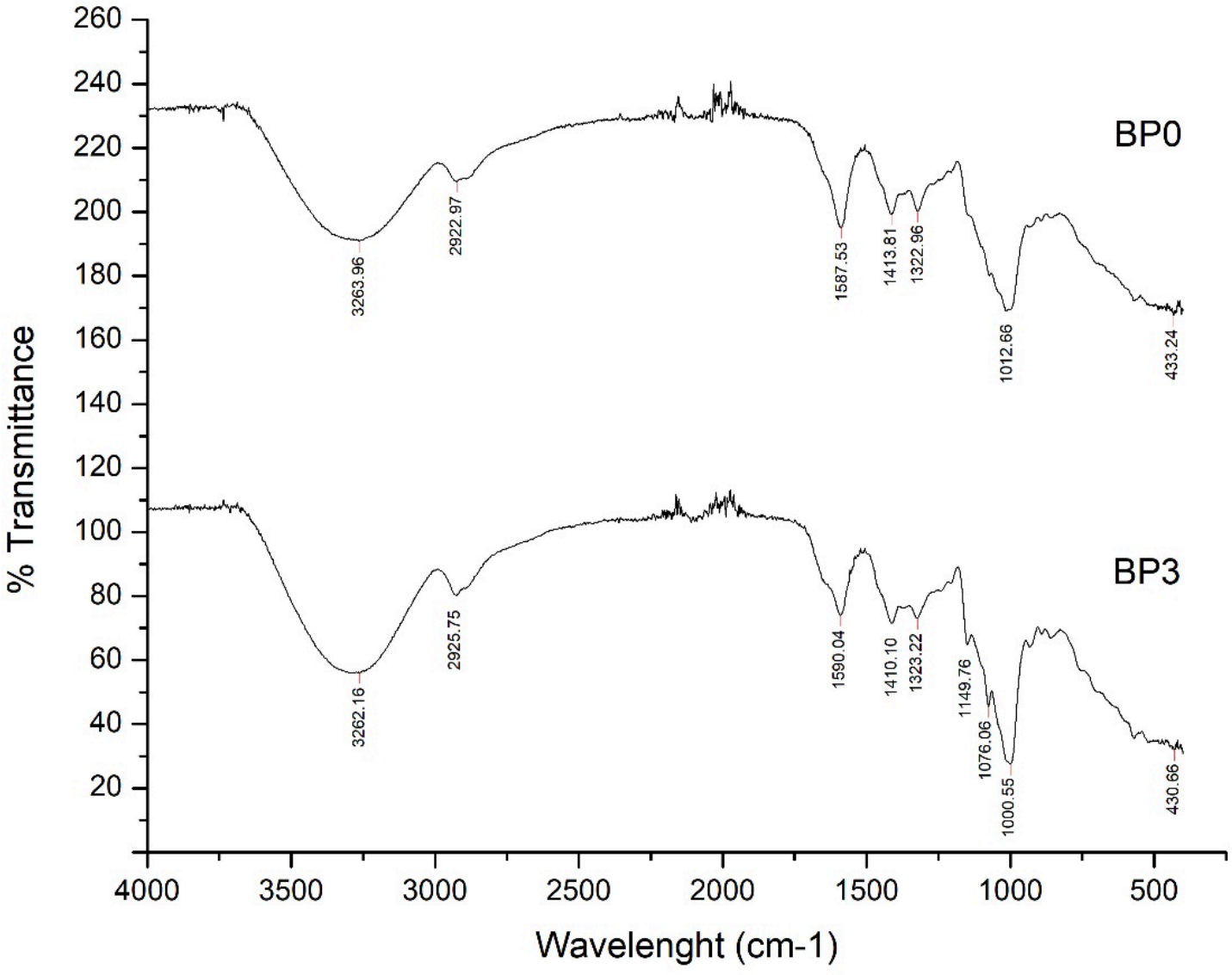


Figure 3

Functional group analysis of Canna starch-based bioplastics.

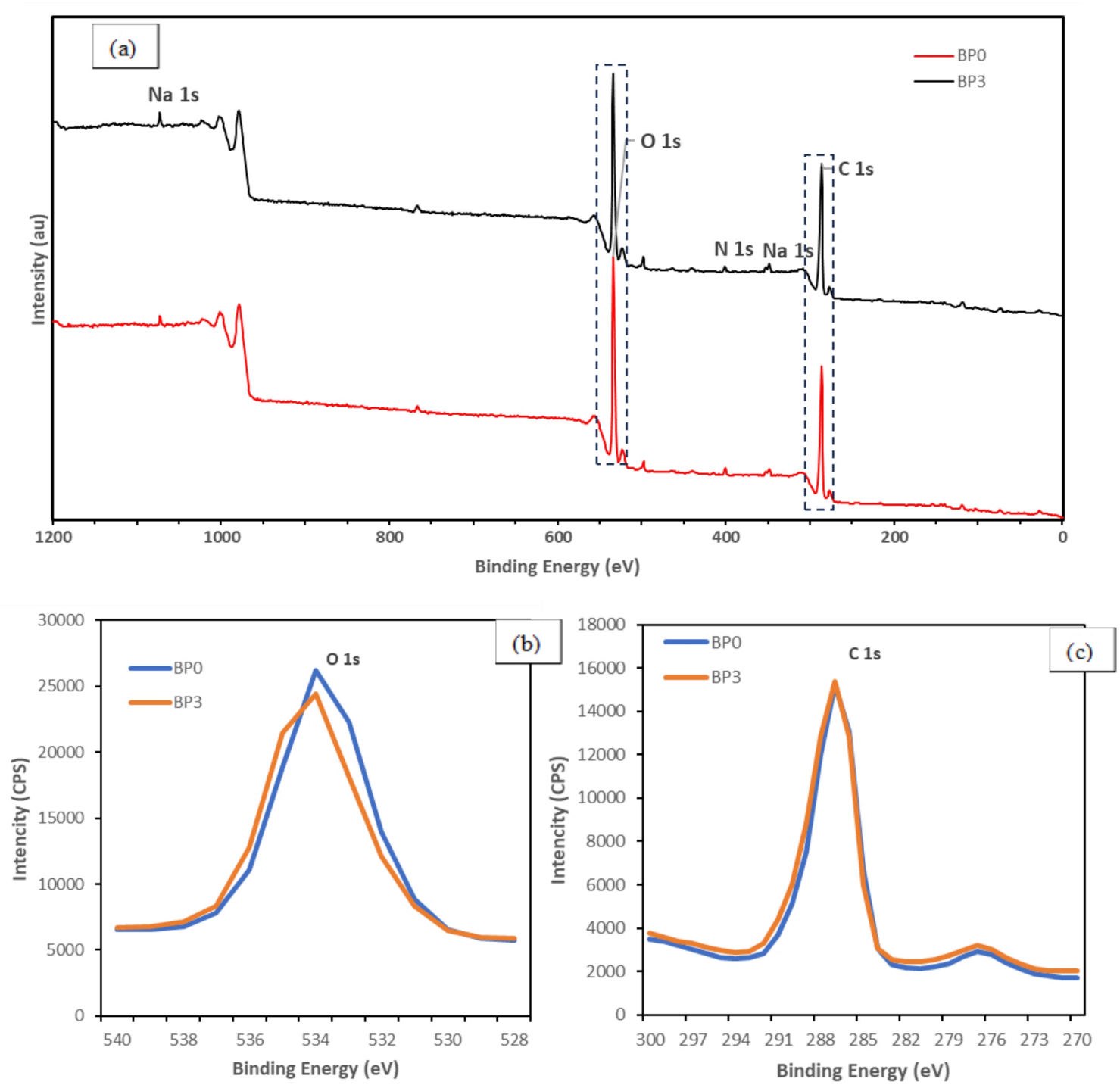


Figure 4

XPS spectra of BP0 and BP3 (a). XPS spectra for oxygen (b) and carbon (c) on the surface of both bioplastics (BP0 and BP3).

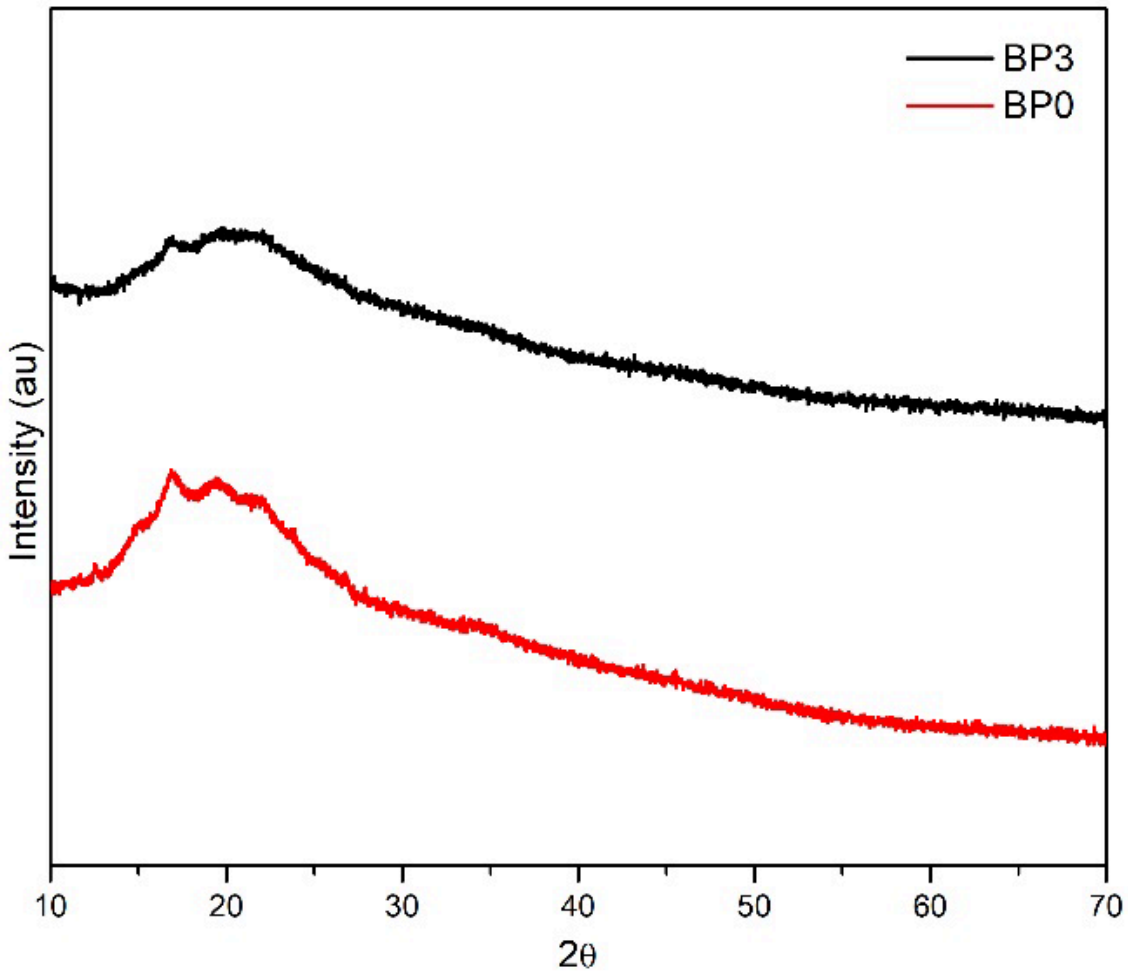


Figure 5

XRD **test results for the bioplastics**

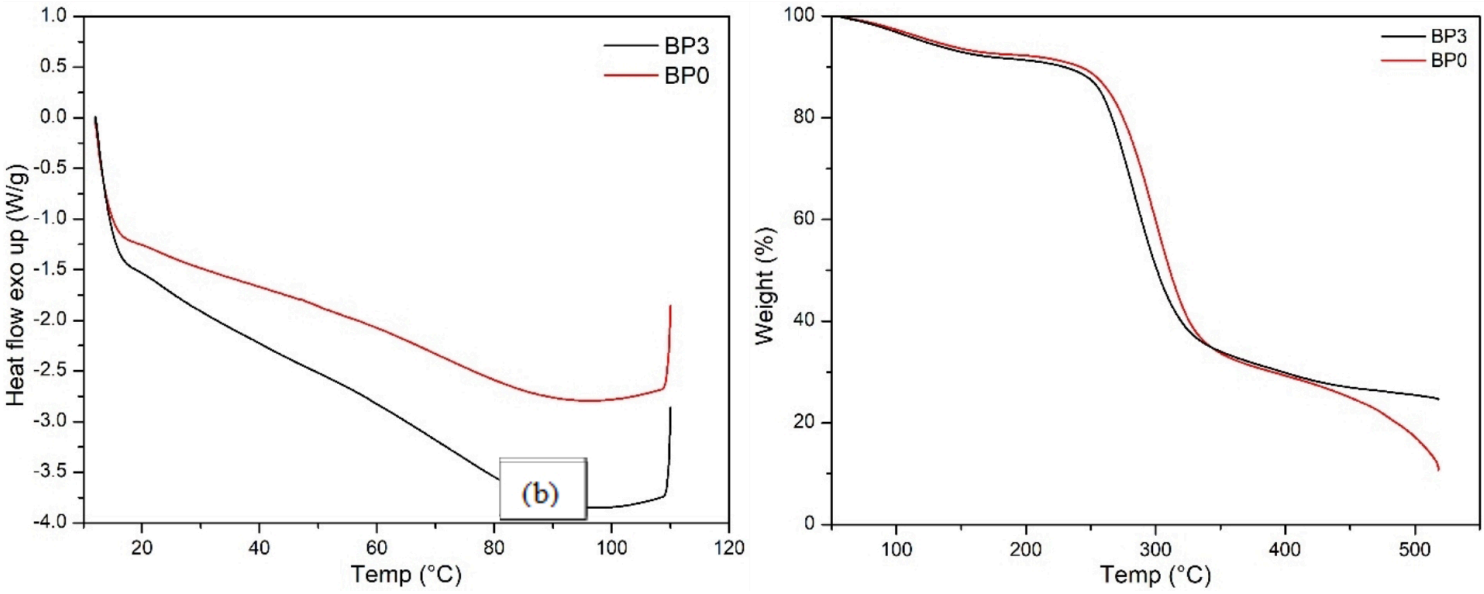


Figure 6

DSC test results (a) and TGA test results (b) for the bioplastics