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Utilization of Banana Peels as Biopolymer Nanocomposites: A Preliminary Study on the Addition of Electrochemically Exfoliated Graphene

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ABSTRACT

Banana peel is an organic waste that contains starch and is widely available in the environment. It is biodegradable and is a potential material for sustainable biopolymer application. Yet the mechanical properties are still limited. Therefore, in this study, we tried to overcome those weaknesses by adding electrochemically exfoliated graphene (ECG) nanoplatelets, enhancing the banana peel biopolymer properties. By incorporating 4 wt% graphene into banana peel starch films, we obtained a considerable improvement in mechanical properties, with Young's modulus and tensile strength increasing to 135.02 MPa (from 23.13 MPa) and 3.74 MPa (from 2.07 MPa), respectively. Furthermore, the modified biopolymer exhibited a good water contact angle from 44.95° to 50.27°. The biopolymers retained their biodegradability, decomposing into small sizes after 6 days in the soil. This study demonstrates the feasibility of enhancing biopolymer mechanical properties and maintaining the biodegradability and eco-friendly biopolymer of the banana peel, by using ECG nanoplatelets.

Keywords: *Electrochemically exfoliated graphene, banana peel starch, tensile strength, contact angle, biodegradability.*

1. Introduction

Plastic is used almost everywhere for various purposes in daily life. Plastic is cheap, readily available, durable, and versatile, but it is difficult to degrade in the environment [1]. Approximately 8.3 billion metric tons of plastic have been created to date, while around 6.3 thousand metric tons of plastic waste have been generated. Only 9% of this plastic waste is recycled, 12% is incinerated, and the remaining 79% accumulates in landfills or the environment [2]. It is estimated that by 2050, as much as 12 thousand metric tons of plastic waste will accumulate in landfills or the open environment [3]. Conventional petroleum-based plastics do not degrade quickly in the environment and their production requires a significant amount of energy. Burning plastic waste produces carbon dioxide and other toxic gases that pollute the air. In large quantities, non-biodegradable plastics also end up in the oceans. The marine environment triggers the disintegration of these plastics and creates microplastics that contaminate seawater. These microplastic fragments are hazardous to aquatic ecosystems as they contain toxic compounds, such as polychlorinated biphenyls/dichlorodiphenyltrichloroethane, and can easily be mistaken for food by marine creatures. Humans are exposed to plastic particles through seafood, freshwater, and air [4–6], which can cause various health problems such as toxicity or pathogenic diseases [7]. Additionally, another global concern is the high carbon footprint of petroleum-based plastics. The continuously rising prices of non-renewable crude oil drive researchers to seek suitable alternatives [8], the best of which is biopolymers, an environmentally friendly and harmless alternative [9].

As an alternative to these sources, biomass consisting of abundant and renewable carbon sources can be used to produce degradable materials. Degradable materials have a special environmental advantage [10]. Polysaccharides, the most abundant macromolecules in flora and fauna, are one of the most suitable raw materials for biopolymers in the form of starch, which is not only renewable and sustainable but also abundant and inexpensive. Starch also has beneficial thermoplastic properties and can naturally degrade [11]. Starch primarily consists of two types of glucose macromolecules, namely amylose and amylopectin [12]. However, the functional and structural differences between them are distinct [13]. The field of biopolymer research is relatively new, so research is still lacking. Agricultural waste can be used as an alternative cheap and renewable raw material [14].

Bananas are one of Indonesia's leading fruit commodities. Banana production reached 8.74 million tons in 2021 and has tended to increase over the past ten years [15]. Some industries in this country use bananas as raw materials, such as banana cakes, banana chips, fried bananas, and many more. These industries leave behind banana peels that will become waste. Large amounts of organic wet waste can harm the environment and pose a threat to human health. Banana peels contain a high starch content, approximately 18.5% [16]. The aging of banana peels will increase glucose levels. In each case, if the peel is too ripe, the starch will be converted into glucose, while the least ripe peel will become too hard despite having a high starch content [17]. Therefore, banana peels can be an alternative material for biopolymer production. However, films made from native starch tend to be brittle, have high water affinity, and are also not heat-resistant. Additional natural materials commonly referred to as fillers are needed to modify and enhance the film's properties.

Graphene is one potential filler that can be added to improve the properties of biopolymers. A study has been conducted to observe the effect of adding glycerol as a plasticizer, nano clay (NC), and graphene oxide (GO) as nanofillers to films made from banana stems. NC and GO can increase tensile strength but not elasticity. The film's contact angle also increased [18]. However, there is still not much research on biopolymers derived from banana peels with the addition of graphene nanofillers. Therefore, this study aims to synthesize biodegradable materials from banana peels with the addition of graphene nanofillers and to study the effect of graphene addition on the characteristics of banana peel biopolymers. The observed characteristics include chemical, physical, and mechanical properties. In addition, this study will also study the maximum water absorption and thermal properties of the biopolymer. This research also aims to demonstrate that biopolymer films from organic waste have the potential to become an alternative resource in the role of conventional plastic such as for food packaging, compostable utensils and containers, electronic device casings applications, reduce the amount of organic waste, and contribute to waste recycling management in Indonesia.

2. Materials and Methods

2.1. Materials

The commercial banana and cassava peel powders were supplied by Dz Herbal (Bandung, Indonesia). The glycerol, distilled water, and acetic acid 25 % were purchased from local stores. All chemicals and reagents were used without further purification. Ammonium sulfate was obtained from Merck. Graphite rods were obtained from the unused commercial Zn – C battery.

2.2. Preparation of electrochemical graphene (ECG)

The synthesis of ECG was carried out using the electrochemical exfoliation method. The graphite rods were washed and rinsed with distilled water, removing the contaminants. Ammonium sulfate 6.6 g was dissolved in 500 mL of distilled water using a magnetic stirrer and then sonicated for 10 minutes, used as an electrolyte. In brief, about 6 cm of the graphite rods were immersed in ammonium sulfate electrolyte and exfoliated at a constant DC voltage of 10V for 10 minutes. The obtained dispersion is a suspension consisting of two layers, where the top layer is a thin gray layer, which indicates a bilayer, and the bottom layer is a darker color, indicating a multilayer. Next, the suspension was stirred thoroughly and washed with alcohol for one hour.

2.3. Preparation of banana peel starch

The banana peel powders were immersed in distilled water and filtered. The dispersion was left overnight to obtain the banana peel (BP) starch sediment. After that, the as-prepared sediments were dried and ground to become BP starch powders as shown in Fig.1. This powder, along with cassava peel powder, was later used as the biopolymer material.

2.4. Synthesis of BP-ECG biopolymers

BP starch-ECG biopolymers were prepared

using the solution casting method. First, 2 g of BP starch and 4 g cassava peel (CP) powders were mixed with 1 g glycerol and 0.3 g of acetic acid 2.5%, then dispersed in 100 mL of distilled water in a beaker. The ECG suspension in different concentrations of starch emulsion (2, 4, 6, and 8 wt%) was added to the solution under continuous stirring. The mixture was heated using a hotplate magnetic stirrer at 75°C for 30 minutes to form a uniform paste. The paste was cooled down at room temperature, poured into a silicone mold with dimensions of 18 cm x 13 cm x 1 cm, and dried in the oven at 50°C. The resulting biopolymer film has a thickness of ± 4 mm, which was measured with a micrometer screw gauge.

2.5. Characterizations

2D-FTIR absorbance patterns of starch-based and BP-ECG films were conducted using a PerkinElmer Spotlight 400. The dried film was directly examined over wavelength range of 400 – 4000 cm^{-1}.

Scanning electron microscopy (SEM) images of starch-based and BP-ECG films were captured by Hitachi FLEXSEM 100 performing at an accelerated voltage of 20 kV, and were used to observe the morphology of graphene starch composite. The specimens were examined using sputter-coating with the thickness of the gold layer of about 3.5 nm.

The tensile properties of the samples were characterized using an Imada tensile strength tester with a load capacity of 50 N. The dimensions and tests of the samples were according to ASTM D882-92.

The water contact angle measurements of the samples were conducted using an Endoscope Magnifier Camera with a recording speed of 30 frames/second, using 1 ml of deionized water as a liquid dropper.

The degradability of biopolymers was tested by the soil burial method. Rectangle strips of 4 cm x 1 cm were cut from the films for testing. The samples were buried in the soil with a pH of 7 as measured by a digital soil tester, at a depth of 3 cm for 6 days. The images of the samples were captured after a certain time.

3. Results and discussion

3.1. Structure and Morphology

The underlying interactions between banana peel starch (BP) and biopolymer banana peel starch and electrochemical graphene (BP-ECG) were investigated by the evident shifts of the characteristic peak using FTIR analysis. Based on Fig. 2, both BP and BP-ECG are rich in hydroxyl groups (OH), exciting in broad peaks 3600 – 3000 cm^{-1}. The distinguished absorption peak showed BP at 2926.99 cm-1 in the C- H stretching region, which witnessed a red shift to the left of 1 cm^{-1} in BP-ECG. This was followed by a more noticeable –COOH bond at BP-ECG film with a frequency of 1735.07 cm^{-1} revealing that graphene arising strong intermolecular or intramolecular interactions. Graphene can disperse in water-based media, creating oxygen-containing surface functional groups that enhance interactions between the host matrix and graphene through covalent and non-covalent bonds [19].

The fractured surfaces of BP starch and BP-ECG films were investigated by SEM, as shown in Fig.3. The pristine BP starch film exhibited a smooth, cracked surface and a huge cavity. For BP-ECG films, the fracture surface has an irregular texture and the graphene was found dispersed uniformly beneath the starch matrix (Fig. 3b) [20]. The roughness of the fractured surfaces increased considerably with graphene grains shown arranged horizontally aligned in the film matrix. Adding ECG fills voids, densifies the structure, and improves the mechanical properties of banana peel starch-based biocomposites.

3.2. Mechanical Properties

The mechanical properties of BP and BP-ECG biopolymer with typical stress–strain curves

Fig. 1- BP-starch production process.

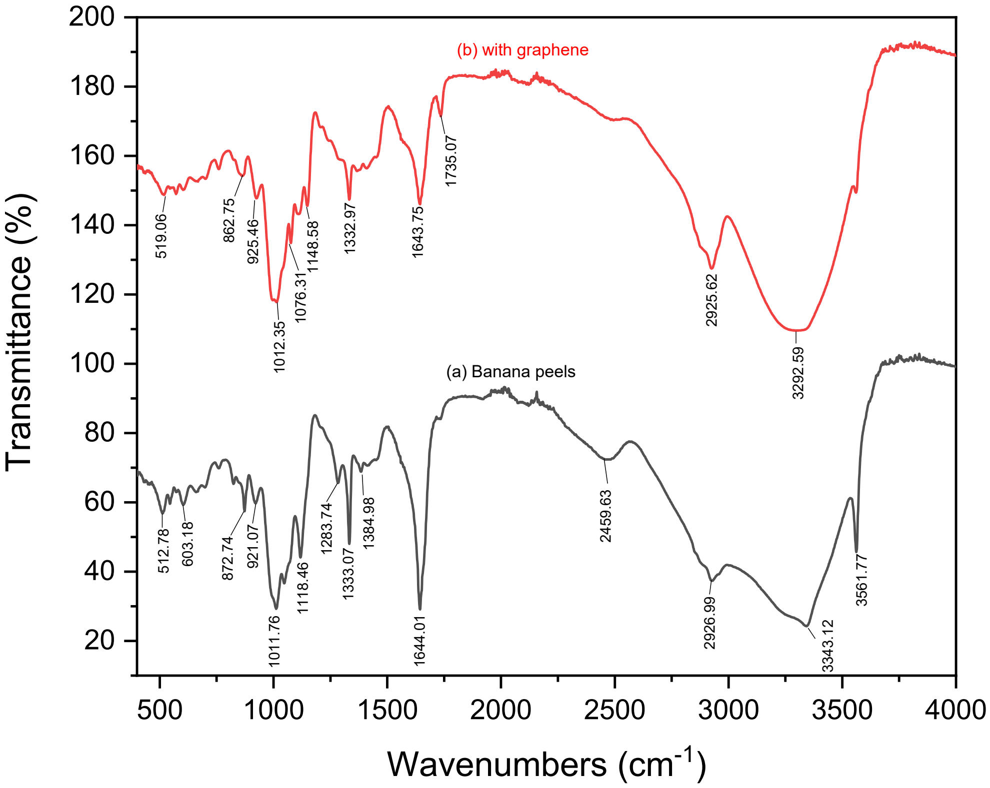

Fig. 2- The FTIR spectra of biopolymers (a) BP (b) BP with graphene.

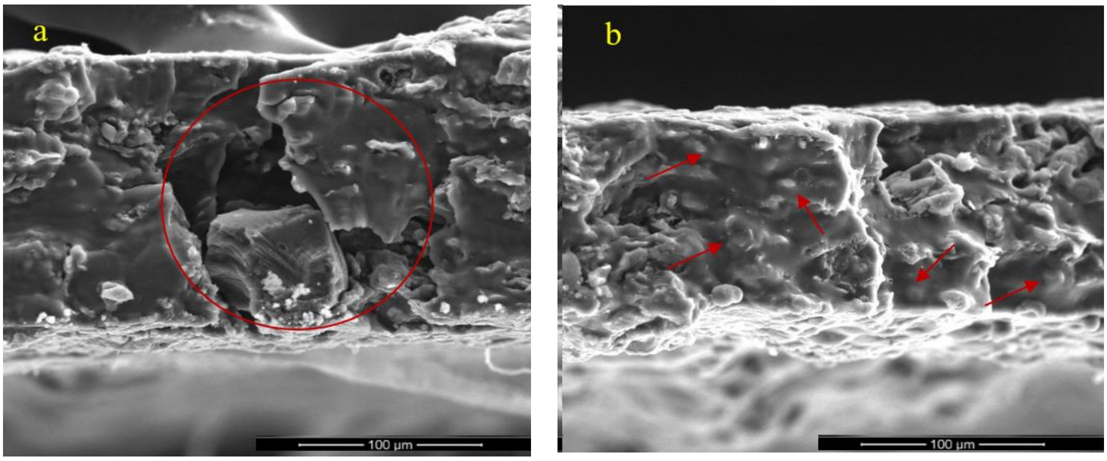

Fig. 3- SEM images of BP (a) and BP-ECG films (b).

are shown in Fig.4. With the addition of ECG nanoplatelets the tensile strength of biopolymer films was improved with the loading of ECG up to 4 wt%. This can be attributed to the inherent mechanical properties of ECG. The sample without the addition of graphene (the black curve) has the lowest performance in terms of strength and strain, failing at around 0.09% strain and 2 MPa. When the biopolymer film is subjected to tension, the strain can be transferred from the BP starch matrix to ECG nanoplatelets through interfacial shear. As the modulus of graphene is larger than the BP starch, much larger stress can be sustained, so that Young's modulus is greatly improved.

Fig.5 clearly illustrates that incorporating ECG nanosheets into banana peel starch enhances strong interfacial bonding, and significantly improves the tensile properties. The addition of ECG significantly pushed up the tensile strength of banana peel biopolymers, reaching the highest level of 3.74 MPa for a sample with 4 wt% graphene content. The enhancement of tensile strength can be attributed to the strong interfacial interaction between ECG and BP starch in the biocomposites matrix. Similar trends have been observed in previous studies on other starch-based materials and polymers, where the addition of graphene nanoplatelets significantly boosted tensile strength. This difference was also marked by a noticeable improvement in stiffness as illustrated by the increase of the Young's modulus. As depicted in Fig. 4b, Young's modulus increases with the addition of ECG, with 4 wt% graphene content in biocomposites having the highest value of 135.02 MPa. The trend of Young's modulus value is directly proportional to the tensile strength value and inversely proportional to the elongation value. The elongation break is the maximum stretch of the biocomposites before it breaks. This can be used as a standard of plastic quality. A larger elongation value indicated poor plastic quality [21]. Figure 4c shows that with the increase of ECG content, the elongation values were decreased with the lowest value of 2.77 %. It can be clarified that the presence of ECG as a filler, internally disrupts hydrogen bonds, leading to the breakdown of the polymer chain [22]. Based on the observed phenomena, it can be seen that adding graphene can increase the tensile strength and Young's modulus values up to a certain maximum value. Then the value decreases as the graphene content increases. Graphene distribution is one possible reason for such behavior, as the uniformity of graphene throughout the biocomposite matrix is crucial. Thus, at high concentrations, the graphene tends to agglomerate and accumulate in several areas of the biocomposite matrix [23].

3.3. Water Resistance

Creating biopolymers that are suitable for their functional applications such as packaging, electronics, or even biomedical devices, enhancing the water resistance properties of starch-based biopolymers is essential. The water contact angle of BP and BP-ECG films are shown in Fig. 6. The pristine BP film exhibited a contact angle of 44.95°, indicating its hydrophilic nature, induced by the presence of free hydroxyl groups in its structure. The contact angle increased with increasing ECG loading, reaching a maximum of 50.7° when 4 wt% ECG nanoplatelets were introduced in the matrix.

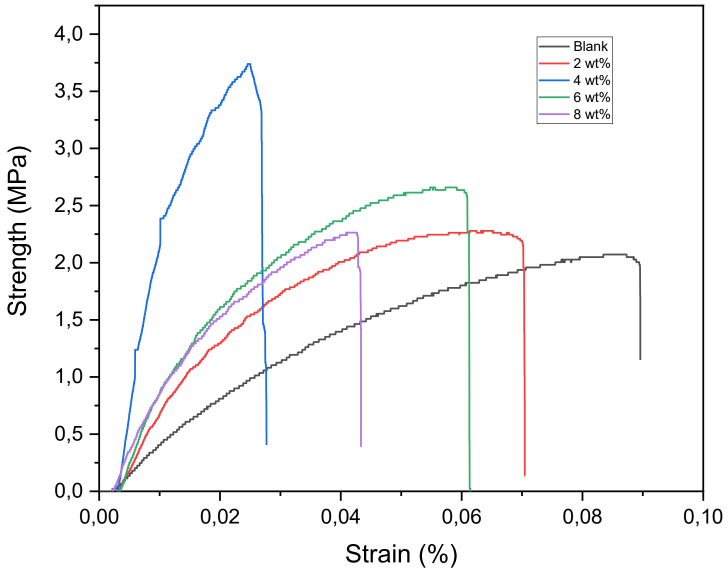

Fig. 4- Stress-strain curves of BP starch and BP-ECG biopolymers with different ECG filler loading.

As demonstrated by FTIR, the polar groups on the surface of graphene could effectively react with the hydroxyl groups of starch, thus inhibiting the interactions between water molecules and starch.

3.4. Soil degradability

Biodegradable materials can break down naturally in the environment, reducing waste and pollution. The nanofillers can enhance the physical properties of materials, but also disrupt biodegradability [24]. The soil burial test was used to observe the biodegradable characteristics of BP starch and BP-ECG nanocomposite films with varying filler contents. Fig.7 displays images of BP

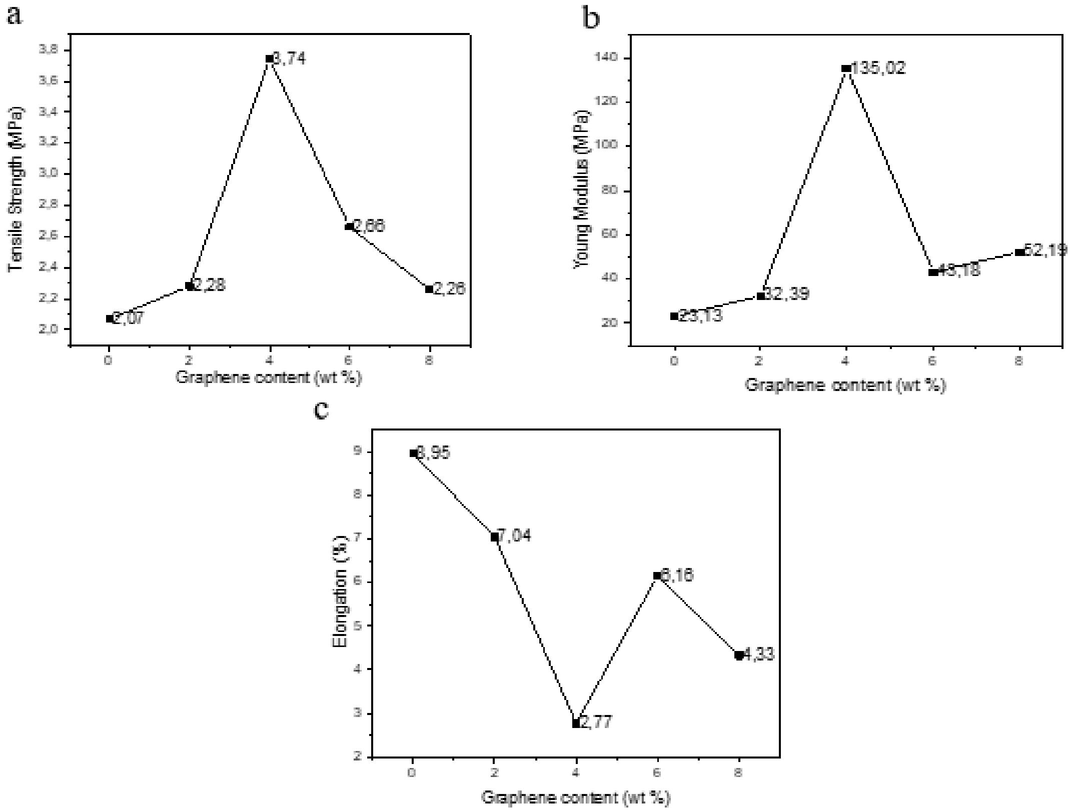

Fig. 5- Effect of graphene content on tensile strength (a), Young’s modulus (b) and elongation (c).

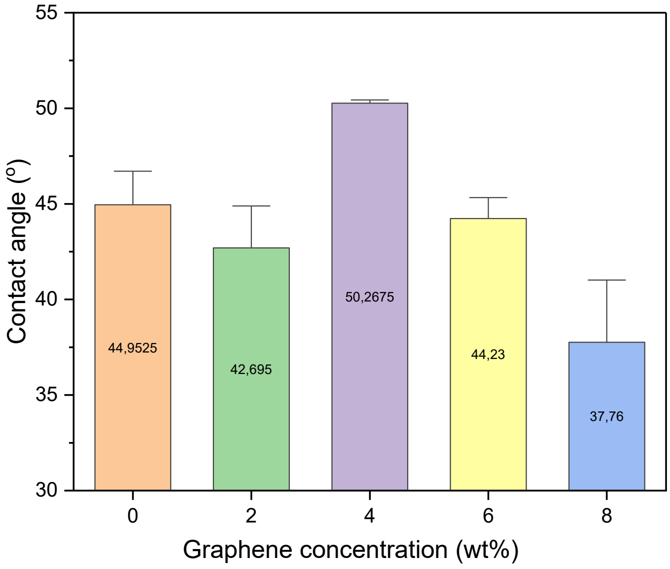

Fig. 6- Water contact angle of BP starch and BP-ECG biopolymers with different filler loading.

Fig. 7- Soil burial test of BP starch and BP-ECG biopolymers with different filler loading.

starch and BP-ECG films that have been buried in soil for 6 days. After 2 days, the films started to degrade, indicated by a shrinking of the film size. After 6 days, the films break down into small pieces. This can be caused by the interfacial interaction between BP starch and ECG were disrupted by soil moisture and biological activity [25].

4. Summary

In this study, we successfully developed biodegradable banana peel (BP) starch biopolymer reinforced with electrochemically exfoliated graphene (ECG)nanoplatelets using a solution-casting method. The structural and morphological observations confirmed the uniform dispersion within the starch matrix, showing the formation of hydrogen bonds with starch chains. This interaction improved the mechanical properties and water contact angle of the biopolymers.

The BP-ECG biopolymer exhibits a promising combination of high-strength and eco-friendly biopolymer. The successful incorporation of ECG nanoplatelets into BP starch matrices improves biopolymer properties while preserving biodegradability, leading to a sustainable replacement for many conventional plastics.

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