Mechanical properties of starch-based biocomposite: The effect of acidic atmosphere treatment

Y A Setyamarsa¹, H Suryanto¹,²*, D Kustono¹, A. Aminnudin¹, A Suyetno¹, D L Edy¹, Y R A Pradana¹, D Z Lubis¹, R D Bintara¹
¹Department of Mechanical Engineering, Faculty of Engineering, Universitas Negeri Malang
Semarang 5 Malang, East Java, Indonesia
*E-mail: heru.suryanto.ft@um.ac.id
²Centre of Advanced Material for Renewable Energy (CAMRY), Universitas Negeri Malang
Semarang 5 Malang, East Java, Indonesia

Abstract. The objective of this study was to obtain the mechanical properties of starch-based biocomposites after treated in an acidic atmosphere. The research applied the tapioca starch, glycerol, distillate water, and nanoclay as biocomposite raw materials. Starch-based biocomposite was made by casting method. Acid sources for acidic atmosphere treatment were acetic acid with various pH of 1, 3, and 5 with exposure time for 4 hours. Characterization of biocomposite was conducted using tensile test, SEM and FTIR analysis. The acidic atmosphere treatment results decreasing both in the tensile strength and modulus in higher acidic atmosphere. The tensile test of biocomposite treated by the acidic atmosphere with acidic source pH 5 has an optimum modulus of 36.9 MPa and tensile strength of 9.1 MPa. The functional group of biocomposite changed after treatment in wavenumber of 2358 cm⁻¹.

Keywords: acidic atmosphere, FTIR, mechanical properties, starch-based biocomposite,

1. Introduction
In recent years, the awareness of sustainable environmental brings effort to develop biodegradable materials from renewable resources to replace petroleum-based polymer materials, especially to reduce the use of plastic packaging in the food packaging applications. Estimated 5.4 million tons of plastic wastes produced in Indonesia, every year [1]. In landfills, recycling of synthetic polymer waste is difficult or prohibited due to contamination. It is the sources problems for the environment so that the Indonesia government plan for reducing and recycling the waste till 70% by 2025 [2]. The green material such as biocomposite contributes to the preservation of the environment.

The cassava starch as a degradable polymer material has ability to replace the synthetic polymer because it’s abundantly available, but it has a challenge in increasing the mechanical properties and reducing moisture absorption [3]. The hydrophilic property of starch-based biocomposite causes easily absorb the water from the atmosphere and changes biocomposite properties.
Generally, food safety and freshness are considered as the important parameters for the food consumers. Efforts to maintain this parameter include the use of quality packaging material. Food spoilage can modify the atmosphere surrounding the product. Modified atmosphere packaging is the use of plastic covering fresh produce in the change of the surrounding atmosphere of the product [4]. It is used to maintain the quality and extend the shelf-life of the food product [5]. Storage time caused a gradual rise in meat pH [6]. The pH variability of the product can modify the product atmosphere. Long storage of the food products can make microbial spoilage due to pH change in the local microenvironment that surrounds the packed food items [7]. So, this study aims to determine the influence of acidic atmosphere on the mechanical properties and functional groups of biocomposites.

2. Methods

2.1 Material
The cassava starch and glycerol (98%) in the technical grade were purchased from Malang (CV. Makmur Sejati), East Java, Indonesia. The nanoclay as biocomposite reinforcement and acetic acid as acidic atmosphere sources were supplied from the Sigma Aldrich, Singapore.

2.2 Synthesis biocomposite
Starch-based biocomposite was produced according to Suryanto et al. [8], with containing a matrix of tapioca starch 5% (b/v), reinforcement of nanoclay 5% (b/b), plasticizer of glycerol 1.5% (v/v), and distillate water of 100 ml. All materials were entered in a beaker glass then mixed and stirred on a magnetic stirrer at 900 rpm for 30 min. The mixed solution was homogenized using an ultrasonic homogenizer at 300W and 20 kHz for 60 min. The homogenized solution was slowly heated to 120 °C then cast into the mould and dried in the oven for 4 h at 100 °C. Starch-based biocomposite film product kept in a dry room.

2.3 Acidic atmosphere treatment
Acidic atmosphere treatment of starch-based biocomposite film was conducted in a room with a schematic, as shown in Figure 1. The starch-based biocomposite film with area 60x60 mm² was hung in a room treatment that fulfilled by acidic air from the acid chamber (25°C). The air was flew using a fan from inlet to surface of acetic acid solution (with various pH) to fill the treatment room. This process was conducted for 4 hours.

![Figure 1. Schematic process for the acidic atmosphere treatment of starch-based biocomposite film](image-url)
2.4 Mechanical properties analysis
Mechanical properties were evaluated by a tensile test performed using an ASTM standard (D882-02) with film dimension of 60 mm x 5 mm in a tensile tester (Techno tensile tester, Indonesia). Starch-based biocomposite film was clamped and pulled with a rate of 0.025 mm s\(^{-1}\) until breaks [9]. Tensile strength was calculated, dividing the maximum load by the original minimum cross-sectional area of the specimen. All specimens were evaluated in triplicate. The film fracture morphology was observed by scanning electron microscope (SEM).

2.5 FTIR analysis
The spectrum of functional group in the starch-based biocomposite film was recorded in the spectrometer (FTIR, Prestige-21, Shimadzu) with the range from 4000 to 400 cm\(^{-1}\) by a resolution of 2 cm\(^{-1}\).

3. Result and discussion
3.1 Starch-based biocomposite film product
Biocomposite resulted from the casting method is as shown in Figure 2. Observation using an optical camera show that biocomposite has color little bit opaque, slippery and transparent, flexure texture. The physical feature of nanoclay reinforced biocomposite was affected by the concentration of starch, glycerol, nanoclay, and also homogenizing and drying process. The ultrasonic homogenization duration causes uniform dispersion of nanoclay into matrix and makes a better structure of biocomposite by intercalation and exfoliation of nanoclay in biocomposite structure [9].

![Figure 2. Starch-based biocomposite film product: a) Product in mould, b) After drying and releasing from the mould](image)

3.2 Tensile strength properties
Mechanical properties of materials represent the ability of any material to receive the load until broken. The tensile strength of biocomposite material is influenced by some factors such as uniformity dispersion of reinforcement into a matrix, compatibility of reinforcement with a matrix
material, the ratio of reinforcement content to a matrix in the composite materials [10]. The tensile test of biocomposite results in a curve of load vs elongation, as shown in Figure 3. Percent elongation at break represents the value of the maximum extension of biocomposite film at the specimen breakpoint after pulling, dividing to the initial gage length. It shows that the treatment using pH 1 and pH 3 can increase the elongation of biocomposite. It means biocomposite is more plastic compare than the control. After analysis, the mechanical properties of biocomposite are shown in Figure 4. Tensile test results indicate that the control specimen, treatment with pH 1, pH 3, and pH 5 have the tensile strength of 8.56 MPa, 6.26 MPa, 8.46 MPa, and 9.10 MPa, respectively. Tensile test results also indicate that the control specimen, treatment with pH 1, pH 3, and pH 5 have the elastic modulus of 31.8 MPa, 15.5 MPa, 26.45 MPa, and 36.9 MPa, respectively. Other research shows that the tensile strength of cassava starch bioplastic is range from 1.85 ± 0.34 MPa to 6.06 ± 1.04 MPa [11]. Higher tensile strength indicates acidic atmosphere make biocomposite films has stronger interactions between plasticizer and biopolymer that induce an increase of macromolecular mobility and also the adsorption and intercalation of glycerol into clays.

Figure 3. Tensile test graph of biocomposite film after treated in various acidic atmosphere

Effect of acidic air treatment on biocomposite film observed by SEM is shown in Figure 5. Morphology of biocomposite film is not porous, and it looks smoother, no cracks or air bubbles. By using SEM, the morphology of the resulting biocomposite film, there is an agglomeration of nanoclay that indicating that the homogenizing process is not optimal yet. Lower pH of acidic treatment shows the morphology of fracture of tensile test specimen become smooth (Figure. 5b, 5c) that indicate the properties of biocomposite after treatment becomes brittle. On the treatment of acidic atmosphere with pH 5 (Figure 5d), the morphology of fracture shows the ripped into a matrix that indicates good macromolecular bonding, approved by the higher elastic modulus of the specimen (Figure 4).
Figure 4. Mechanical properties (tensile strength and elastic modulus) of biocomposite film after treated in various acidic atmosphere

| Acid Sources | Tensile Strength (MPa) | Modulus (GPa) |
|--------------|------------------------|---------------|
| control      | 8.58                   | 6.26          |
| pH 1         | 31.8                   | 15.5          |
| pH 3         | 26.45                  | 8.46          |
| pH 5         | 36.9                   | 9.1           |

Figure 5. SEM analysis of biocomposite film after treated in acidic atmosphere: a) control; treated by acid source with b) pH 1, c) pH 3, d) pH 5 for 4 h
3.3 FTIR analysis

Analysis of the functional group was conducted using FTIR with results, as shown in Figure 6. FTIR analysis shows the presence of acid causes the breakdown of amylopectin branching chains of α-1,6 glycosidic groups in bioplastic samples and leaves a helical linear chain in the α-1,6 glycosidic and acid chains also play a role in the loss of C≡N cyanide function in bioplastic samples and leave a helical linear chain in the α-1.6 glycosidic, and acid chains also play a role in the loss of C≡N cyanide function in wavenumber of 2358 cm\(^{-1}\). The effect of the acid, which makes the function of the cyanide hydrolyzed and lost to gas [12]. Acidic atmosphere treatment in the bioplastic influences the smoothing spectra of OH functions in the region of 3639 cm\(^{-1}\). It is suggested that there is an esterification process caused by acidic atmosphere treatment that modifying starch-based biocomposite through changing the –OH group to –OR ester group. The replacement –OH group into –OR ester group in starch able to separate the active compound with chiral molecular structure [13]. After decreasing pH (pH 1 and pH 3), the acid reacted with starch can be considered as the internal or co-plasticizer that make higher elongation [14].

![FTIR analysis](image)

**Figure 6.** Functional group analysis of biocomposite film after treated in various acidic atmosphere

4. Conclusion

Based on the analysis, it can be concluded that the exposure of acidic air at pH 5 into the starch-based biocomposite is able to change the structure and increase the tensile strength of the biocomposite. Exposure to acidic atmosphere cause nitrile functional group in wavenumber of 2358 cm\(^{-1}\) was eliminated.

5. References

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