Influence of exposure time of acidic air on structure and strength of starch-nanoclay biocomposite

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Abstract. The aim of this study was to determine the influence of acidic air on the strength and structure of starch-based biocomposites. Materials used for making biocomposite samples are tapioca starch, glycerol, distillate water, and nanoclay. Biocomposite synthesis uses a casting method. Treatment of acid-base air on biocomposite samples using acetic acids with a pH of 5 and exposure time for 2, 4 and 6 hours. After treatment, samples characterized using a tensile test and XRD analysis. The results show that the acidic air treatment affects the tensile strength of bioplastic samples. The tensile test results showed that the acidic air treatment of pH 5 for 4 hour results an optimum tensile strength of 9.1 MPa. The phase characterization using XRD showed that biocomposite samples with acidic air treatment indicate the highest intensity at a diffraction angle of 20.04°.

1. Introduction

Plastic is a polymer used as the raw materials in packaging technology. Every year, Indonesia wastes the plastic approximately 14% total production of solid waste, as much as 5.4 million tons [1]. It produced from 384 cities as much as 80,235 tons/day and by 2020, it will increase five times [2]. This waste causes ecology problems because of non-renewable and degradability problem at a short time in a landfill. For these reasons, the government targets to reduce and recycle the waste up to 70% by 2025 [3]. It is important to develop biodegradable material to reduce this problem. The environmentally friendly nature of biocomposite contributes a lot to the preservation of the environment.

Starch is the natural polymer materials that potential for replacing the synthetic polymer. In Indonesia, the cassava starch as a degradable polymer material is enormous because cassava production is the third-largest product in the world reached 26 million tons [4]. Besides the advantage in abundant availability, however, cassava starch absorbs the moisture highly and has low mechanical properties [5]. The hydrophilicity of biocomposite film makes it easy to absorb hydro material from the atmosphere. So, it able to change the properties of the biocomposite film.

Modified atmosphere packaging is commonly used in the food industry to maintain the quality and extend the shelf-life of the food product. There are three gases used modified atmosphere, i.e. nitrogen, carbon dioxide, and oxygen [6]. The modified atmosphere also conducted from the variability of pH of the product. The pH of the packaged items is prone to change upon long storage or microbial spoilage of the packed food products (e.g. fish, meat, and fresh sausages) due to pH change in the local...
microenvironment that surrounds the packed food items [7]. The main requirement for preparing biocomposite films is safety and avoids toxicity issues that may result from the degradation of the film during the application period. So, this study purpose of determining the effect of acidic air on the strength and structure of starch-based biocomposites.

2. Methods

2.1. Material
The tapioca starch in technical grade was bought from Malang, East Java, Indonesia. The Sigma Aldrich, Singapore provided nanoclay as reinforcement. Acid solution used acetic acid (Sigma Aldrich). Glycerol in technical grade was supplied by CV. Makmur Sejati, Malang.

2.2. Sintesis Biocomposite
Synthesis of biocomposite was referred to Suryanto et al. (2016) [8]. The composition of raw materials are tapioca starch 5% (b/v), glycerol 1.5% (v/v), nanoclay 5% (b/b), distillate water 100 ml. The material mixed and stirred at 900 rpm for 30 min. Sonication was conducted to the solution for 60 min. at frequency of 20 kHz and power of 300W. Then, the solution was heated until 70°C (15 min.) then 90°C (15 min), and 120°C (15 min). After that, the hot solution cast into mold 12.5 cm x 17 cm and dried in the oven for 4 h at 100°C. Synthesis product kept in a desiccator.

2.3. Acidic air treatment
A schematic treatment of biocomposite in the acidic air was shown in Figure 1. The biocomposite film (60x60 mm²) which hung in the treatment area was flowed using acidic air. Source of acidic air is the air from the outside chamber (25°C) blown from inlet using a fan to surface of acetic acid solution (pH.5) and flow to fill the treatment chamber. The process was conducted for the various durations of 2, 4, and 6 hours.

![Figure 1. Schematic treatment of starch biocomposite with acidic air](image)

2.4. Tensile test
Tensile testing applied a standard (ASTM D882-02) with specimen dimension of 60 mm x 5 mm. Test conducted using tensile test equipment (Techno tensile tester, Indonesia) with a maximum load of 50N. Biocomposite was clamped with a distance of 50 mm and pulled with a maximum speed of 0.025 mm.s⁻¹. In this tensile test, the specimen was drawn until it breaks [4].

2.5. XRD analyze
The biocomposite structure was scanned using XRD analyzer (PanAnalytical X’Pert Pro) at CuKα radiation (λ = 1.54Å), 30 mA, 40 kV, in the room temperature. Biocomposite film had a dimension of 10x10 mm² in the area and 200 μm in thickness. The scanning step was done at a rate of 0.02°/scanning at range from 10° to 60°.
3. Results and Discussion

3.1. Biocomposite synthesis results
Syntesis of biocomposite used the casting method and the results were observed using an optical camera, and scanning electron microscope have flexure texture, slippery and transparent clear with little bit opaque, as shown in Figure 2.

The forms of biocomposite with nanoclay reinforcement were influenced by some factors which sonication process, the concentration of nanoclay, cassava starch, glycerol concentration, and drying methods. The ultrasonic homogenization duration makes nanoclay dispersion uniform in the matrix, so biocomposite becomes homogeneous [4]. Additional reinforcement like nanoclay in bioplastic was able to change the structure of bioplastic. The concentration of nanoclay influenced intercalation and exfoliation in the biocomposite structure.

![Figure 2. Cassava starch-based biocomposite with glycerol plasticizer](image)

3.2. Tensile strength properties
The ultimate tensile strength of biocomposites is an important properties which have a main role in the application. The tensile strength of biocomposite material is affected by some factors such as uniformity in reinforcement distribution in the matrix, composition ratio of the matrix materials to reinforcement in a composite materials, compatibility of reinforcement with matrix material [9].

![Figure 3. Tensile strength of biocomposite film after treated in acidic air](image)

The tensile strength of biocomposite film was shown in Figure 3. Tensile strength test results indicate that untreated biocomposite film has a tensile strength of 8.56 MPa. Duration of acid air exposure for 2 hours caused a tensile strength of 7.23 MPa. Increasing the duration of acid air exposure for 4 hours and 6 hours produces higher tensile strength than untreated samples, reaching 9.1 MPa and 8.9 MPa,
respectively. Comparing to accelerated weathering treatment of bioplastic, accelerated weathering using artificial light cause the tensile and impact strength slowly decreased caused of increase of water sorption capacity [10]. In the acidic air treatment for 2 hours, starch-based biocomposite was modified through changing the –OH group to –OR ester group. This esterification process makes properties change of starch-based biocomposite. Charmi and Sruti (2017) show that replacing –OH group to –OR ester group in starch able to separate the active compound with chiral molecular structure [11]. After increasing duration time (4 hours and 6 hours), the acid reacted with starch can be considered as the internal or co-plasticizer [12]. The combination of acetic acid and glycerol produces cellulose acetate, which increases the compressive strength of bioplastic [11].

3.3. XRD (X-Ray Diffraction)
Structure analysis using XRD result in some peaks appear at diffractogram, as shown in Figure 4.

![Diffractogram of biocomposite after treated in acidic air](image)

**Figure 4.** Diffractogram of biocomposite after treated in acidic air

The XRD analysis results showed that the longer the acid air treatment, the higher the diffraction peak and intensity obtained were 18.28°, 19.18°, and 18.32° for a treatment duration of 2 hours, 4 hours, and 6 hours, respectively. Nanoclay-reinforcement biocomposite that exposure by acidic air treatment does not show amylose characteristics. Amylose peaks are located at the peaks of 20.04°, 22.50°, and 24.03°. These peaks are associated with the crystalline plane of (0 0 4), (2 2 0), and (1 3 0), respectively [13]. The diffraction analysis indicates tapioca starch undergoes a crystallization process into crystal structures of types a, b and c. In this case, type c is a mixture of crystal structures of type a and type b. Both of shifting in diffraction peaks and decreasing in intensity show indication exfoliated structure [4,14] that causing better properties of starch-based biocomposite.

4. Conclusion
Influence of Exposure Time of Acidic Air on Structure and Strength of Starch-Nanoclay Biocomposite have been investigated. Based on the analysis, it can be concluded that the acidic air treatment affects the tensile strength and structure of bioplastic samples. 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 and results in optimum tensile strength of 9.1 MPa in treatment for 4 hours.
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