Influence of Nanoclay on Thermal Decomposition of Biocomposite Matrix Starch/Carrageenan Blend

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Abstract. The synthetic plastic waste was the big problems for sustainable environmental. Many efforts to solve it by the incineration process and also developing bioplastics. Addition of nanomaterial into bioplastic as the reinforcement can affect their properties. This study aim was to show the influence of nanoclay on the thermal decomposition of the biocomposite matrix starch/carrageenan blend. This experimental research involved addition of nanoclay with concentration of 0%, 2.5%, 5%, 7.5%, and 10% into bioplastic. The casting methods with homogenizer ultrasonic were conducted to obtain biocomposite. The thermal degradation of biocomposite was observed using thermogravimetric analysis. The result indicate that reinforced nanoclay in the biocomposite matrix of starch/carrageenan blend show four phases of decomposition process which are phase I at the temperature until 145°C, phase II at the temperature from 146°C to 340°C, phase III at the temperature from 341°C to 475°C that indicate the transition of biocomposite into the char and phase IV at the temperature from 476°C to 700°C.

Keywords: Biocomposite, nanoclay, starch/carrageenan blend, thermal decomposition

1. Introduction

Plastics are usually synthetic material that derived from petroleum but many are partially natural. They are organic polymers with high molecular mass. The plastic consumption worldwide was 297.5 million tons in 2015 [1] and most of this was convert to the waste. In the landfills, synthetic plastic takes approximately 50 years to completely degraded [2]. Many efforts were conducted to solve the plastic waste problem by incineration of plastic waste and also developing bioplastics. The internal temperature in incineration can reach 1,000°C while burning [3]. Unfortunately, burning of synthetic plastic can release toxic gases like Polychlorinated Biphenyls, Mercury, Furans, Dioxins, hazardous halogens and pollutes air into the atmosphere with results impact in climate change and vegetation, animal and human health and also the environment [4].

One solution to plastic waste problems is developing bioplastic. Bioplastic is made from a natural material which are polysaccharides, proteins, and lipids. Bioplastic has been used in the packaging industry because of its degradable and properties preservative capabilities [5]. Starch is a bioplastic sources material extracted from cassava, potatoes, and taro which are renewable,
inexpensive, and abundant [6]. Cassava starch composed to 12.28% to 27.38% amylose and 72.61% to 87.71% amylopectin. The amylopectin content gives optimum stickiness while the amylose content affects the mechanical properties of bioplastics [7]. The wide application of bioplastic developed from starch has been restricted because of their low strength, elasticity/brittleness, and moisture sensitivity [8], and the poor ability for processing it in common industry [9]. The approachment have been developed to solve this of bioplastic was reinforced it with nanomaterial like chitosan [10], zinc nanoparticle [11], cellulose nanocrystal [12], and nanoclay [13]. Nanoclay has layered silicates that act as the phase reinforcement and have wide surface area leading to the possibility of better interface interaction in the biocomposite. Therefore, this study investigated the effect of nanoclay addition to the thermal degradation of biocomposite matrix starch/carrageenan blend.

2. Method

2.1 Materials

The materials used in this study were a technical grade of kappa-carrageenan, cassava starch, and glycerol. Nanoclay was supplied from Sigma Aldridge, Singapore.

2.2 Biocomposite synthesis

The biocomposite synthesis was adapted from Suryanto et al. [14]. The biocomposite was made from cassava starch, carrageenan, glycerol, and distilled water with composition of 5.0% (wt/v), 5% (wt/v), 1.5% (v/v), 98.5 ml, respectively. The distilled water and glycerol were mixed in the beaker glass while stirrer for 5 min using the magnetic stirrer. Nanoclay (2.5%, 5%, 7.5%, and 10% (wt/wt)) was mixed into the solution then heated until 80°C while stirring for 45 min on the magnetic stirrer. The cassava starch was mixed into the solution then heated until 90°C and stirred for about 15 min. The solution temperature then increased up to 135°C while stirring for 15 min. The Ultrasonic Homogenizer (KG-MT-UPDHM-3N, KGC Indonesia) was applied to the mixed solution for spreading nanoclay in solution uniformly with homogenizer frequency of 20 kHz, ultrasonic power of 300W for 60 min. After the homogenization process, the cassava starch was mixed to the solution at 80°C for 30 min on hot plate magnetic stirrer subsequence by addition of carrageenan 5.0% (wt/v) until forming the gelation solution. The biocomposite solution was cast into the mold and dry it in an oven for four hours at 70°C.

2.3 Thermogravimetric analysis (TGA)

The thermal decomposition of biocomposite was observed using the TGA apparatus (Perkin Elmer). Biocomposite crushed to make a powder and then dried in the electric oven for 2 h at 80°C. Biocomposite powder of 7 mg filled into a porcelain cup then put it in the TGA apparatus. TG scanning was applied in presence air with a debit of 50 ml.min⁻¹ and a heating rate of 10°C.min⁻¹ up to 700°C.

3. Results and Discussion

3.1 The product of biocomposite casting

The image of the biocomposite product obtained by a casting process was shown in Figure 1. The bioplastic made of starch show a transparent clear (Fig. 1A), After addition of nanoclay, the transparency of biocomposite reduced (Fig. 1B to 1D).
3.2 Thermal decomposition analysis

Figure 2 show the weight loss of nanoclay reinforced biocomposite based blend starch/carrageenan after thermal exposure at elevated temperatures (from 25 - 700°C). After decomposition process until 700°C, addition of nanoclay by 0%, 2.5%, 5%, 7.5%, and 10% (w/w) in biocomposite results an increased decomposition residue by 2.2%, 2.2%, 4.1%, 5.8% and 9.9% (wt), respectively.
Figure 2. Thermogravimetric analysis (TGA) of nanoclay reinforced biocomposite based blend starch/carrageenan

Figure 3. Differential thermogravimetric analysis (DTG) of nanoclay reinforced biocomposite based blend starch/carrageenan
After weight loss from Fig. 2, data were differentiated, the results of this analysis were shown in Fig.3 that indicate the rates process of the biocomposite decomposition after exposure with the heat. The increment heating applied to biocomposite until high-temperature results in the breakage of chemical bond into the constituent with released the heat. From the Fig. 3, the process of thermal decomposition can be divided into four phase. Phase I occurred at the temperature until 145°C that indicate the water evaporation process and losses of light volatile bioplastic compound with the weight loss of composite about 7.3-8.7%. Phase III is the main process of decomposition because the highest material lost as much as 61% to 67.5% that indicate the process of bioplastic depolymerization. This phase occurred at the temperature from 146°C to 340°C which is the cassava starch begins to decompose at 300°C [15]; Phase III occurred at the temperature from 341°C to 475°C that indicate the transition of biocomposite into the char. The char is a flammable material with oxygen and volatile matter diffused into the char surface that makes it burns simultaneously. This phase occurs after the volatile matter released and forming carbon with mass loss of about 21%; and Phase IV occurred at the temperature from 476°C to 700°C as horizontal line that indicates all sample have decomposed and result residue or ash about 2.2, 2.2, 4.1, 5.8, and 9.9% for biocomposite with nanoclay addition of 2.5, 5.0, 7.5 and 10%, respectively.

Addition of nanoclay was able to reduce the degraded mass of biocomposite. In phase I and II, nanoclay have a role to reduce the decomposition of volatile mass and at phase III, bioplastic started to decompose at 380°C but after addition of 10% nanoclay, biocomposite was fully decomposed in 397°C, as shown in Fig. 3. The nanoclay addition in biocomposite can enhance the amount of char residue, cause a decrease in the onset temperature decomposition, and decreasing the weight loss rate of the biocomposites. Nanoclay has a function as the thermal barrier layer [3] resulting in a decomposition of biocomposite at a higher temperature.

4. Conclusion

Thermal decomposition of nanoclay reinforced biocomposite starch/carrageenan blend show four phases of decomposition process which are phase I at the temperature until 145°C, phase II at the temperature from 146°C to 340°C, phase III at the temperature from 341°C to 475°C and phase IV at the temperature from 476°C to 700°C. Addition of nanoclay was able to increase the thermal stability of biocomposite.

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