

Properties enhancement of cassava starch based bioplastics with addition of graphene oxide

A Amri, L Ekawati, S Herman, S R Yenti, Zultiniar, Y Aziz, S P Utami and Bahrudin

Department of Chemical Engineering, Universitas Riau, Pekanbaru, Indonesia

E-mail: amun.amri@eng.unri.ac.id

Abstrak. The properties of cassava starch based bioplastic have been successfully enhanced by addition of graphene oxide (GO) filler. The composite was synthesized via starch intercalation method using glycerol plasticizer with variation of 5 – 15 % v/v GO filler and mixing time of 30 and 60 minutes. The effects of GO content and the mixing time to the mechanical, water uptake and biodegradation were studied. The synthesis of GO and its integration in the bioplastic composite were also elucidated. The increasing of the GO content and mixing time improved the mechanical properties of composite mainly due to of good homogeneity among the constituents in the composite as indicated by scanning electron microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy. The bioplastic produced using 15% of GO and 60 minutes mixing time had the highest mechanical properties with tensile strength of 3,92 Mpa, elongation of 13,22% and modulus young of 29,66 MPa. The water uptake and biodegradation increased as the increase of GO content and decreased as the increase of the mixing time. Graphene oxide is the promising filler for further development of cassava starch based bioplastics.

1. Introduction

The industrial development which is accompanied by the increase in the number of inhabitants, will increase the consumption of natural resources and energy. It causes the creation of several problems including the buildup of waste in large numbers. One of the industrial products has penetrated all the aspects of life is plastic. Plastic is more acceptable, besides due to of its price aspect, plastic is also considered superior to other media such as metal or glass due to of its nature (lighter and not easy to break). Each passing year, the production of the plastic world reached 100 million tons per year [1]. In Indonesia the plastic consumption growth reached 6-7% per year [2, 3]. Significant improvement against the production and consumption causes buildup of plastic wastes.

Conventional plastics is made from petroleum which is limited natural resources (unrenewable) [4]. In addition, the petroleum plastic is difficult to be decomposed by the microorganisms leading to the environmental pollution [5]. It gives an overview of the potential development of biodegradable plastic as substitute of conventional plastic [1]. Biodegradable plastic or often called with bioplastic, it is plastic that can be used like as conventional plastic and has an ability easily to be degraded by microorganisms such as fungi and bacteria [6]. Raw materials used in making of bioplastic filmed are renewable and biodegradable materials such as starch, vegetable oils, and microbiota [7]. The potential of starch derived from cassava or better known as the cassava (*Manihot Esculenta Crantz*) as an environmentally friendly plastic materials are very promising. It contains around 90% of the cassava



starch with other small content such as lipids, proteins and fibres [8]. Generally, the bioplastic from starch cassava has the nature of transparency and a good tensile strength [9].

Even though it has many advantages, the bioplastics still have drawbacks compared to the conventional plastics, namely in term of mechanical properties which is easily to torn and not as strong as conventional plastic. One of the strategies way for improving the mechanical properties of bioplastic is the filler addition in bioplastic matrix. One of the filler which can potentially be added into bioplastic is graphene oxide (GO). GO is one layer of oxidized graphite obtained via chemical synthesis or through others graphite oxidation methods. There are many advantages of the use of GO as filler including it is easily to dissolve in matrix of bioplastic, it has high surface area and biocompatibility, and it still inherit the graphene characters, i.e. strong and flexible [10]. Based on the nature of the cassava starch and the graphene oxide, it is predicted the combination of these materials can produce bioplastic with better properties. To the best our knowledge, no research like this has ever been made.

This work tries to understand the influence of graphene oxide addition to the properties of cassava starch based bioplastic. The main result showed that the addition of graphene oxide and the mixing time improved the mechanical properties of produced bioplastic. The water uptake and biodegradation increased as the increasing of GO content and decreased as the increasing of the mixing time. Graphene oxide is a promising filler for further development of cassava starch based bioplastics.

2. Experimental

2.1 Sintesis of graphene oxide.

Graphene oxide was synthesized using Hummer's method, it has been reported elsewhere [11]. The graphite powder (1 g) was stirred with 23 ml of H_2SO_4 , 0.5 grams of NaNO_3 and 3 grams of KMnO_4 in a beaker glass in an ice bath container with the temperature was kept below 20°C until homogen. The solution was then stirred at a temperature of 40°C in a heat bath. After 14 hours of stirring, the solution was moved to the ice bath and as many as 50 ml of H_2O were added gradually into the aqueous solution with the temperature maintained under 90°C . The solution was then heated at a temperature of 50°C and stirred for 1 hour. Afterthat 150 ml of H_2O were added into solution, and as much as 5 ml of H_2O_2 was added into the solution and stirred for 30 minutes [11].

The phase separation of graphene oxide solution used filter paper and was washed with H_2O repeatedly up to neutral pH was approached. The deposit of graphene oxide was heated at a temperature 80°C using oven for 4 hours, so it gained a solid graphite oxide. Then graphite oxide mixed with H_2O using ultrasonic dispersion to peel layers to form the graphene oxide dispersed in solution [11, 12].

2.2 Sintesis of bioplastic

The manufacturing of bioplastic was carried out using solution intercalation method. Tapioca flour (10 g) were dissolved into the 100 ml aquadest and heated at 60°C while stirring for a while. The glycerol (as plasticizer) and graphene oxide corresponded to variable (0%, 5%, 10%, 15%) were then mixed with the tapioca solution and stirred with a stirring time variation (30 minutes and 60 minutes). A homogeneous solution was then poured into the glass mold and dried during 3 days in room temperature [13]. The produced bioplastic was separated from the mold and the characterizations were performed.

2.3 Chracterizations

The identification of the produced graphene oxide used via X-ray diffractometer (XRD) and scanning electron microscopy (SEM) evaluated using JSM-6390A SEM. Furthermore, the mechanical properties (tensile strength, elongation, and elasticity modulus) and surface morphology of bioplastic samples, biodegradation test and the resilience of water test (swelling test) were also investigated. The cristalline phase identification of the produced graphene oxide was carried out using Bruker - D822 X-

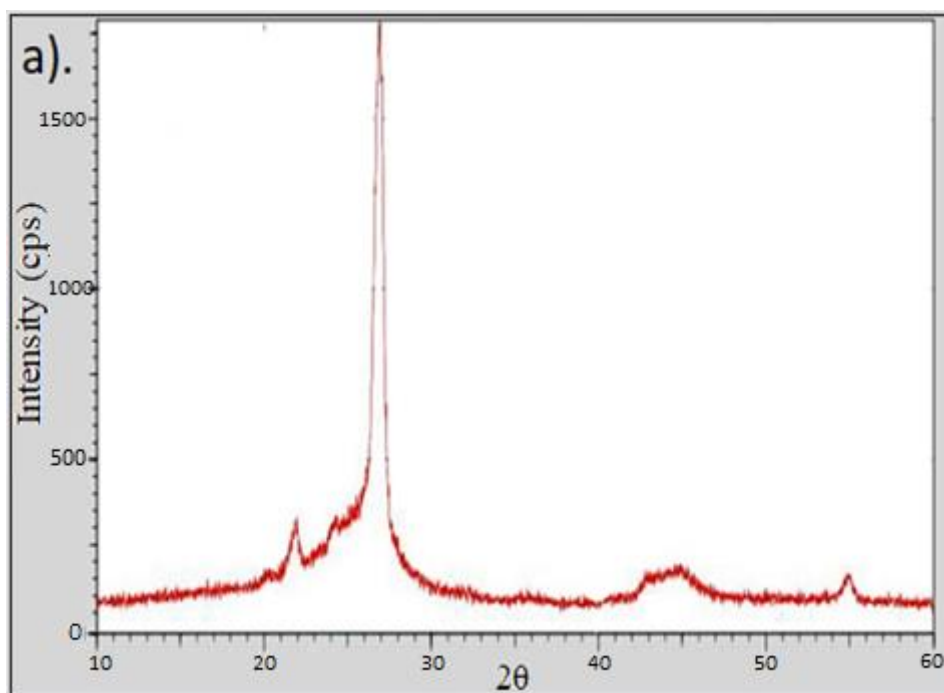
Ray Diffraction with Cu K α radiation. The mechanical properties were performed via ASTM D822-02 using RG 3010 tensile test equipment with specimen size of 100 mm x 15 mm. The rate of biodegradation was carried out by burying the samples in the soil and measured their each mass in a week. The swelling test was carried out by cutting the samples in size of 2cm x 2 cm then was soaked in water with controlling of weight.

3. Result and discussion

3.1. Characterizations of graphene oxide (GO)

The XRD patterns of the produced graphene oxide obtained via Hummers method were shown in Figure 1.(a,b). Figure 1.(a) shows the XRD pattern of the raw graphite before the process, while Fig. 3.1.(b) shows the produced graphene oxide synthesized via Hummer method. From Fig. (a), it can be seen that the graphite has a diffraction peak at 26.60° and it is in accordance with which has been reported by many researchers [14, 15, 17]. After the oxidation, this peak disappears and new peak appears at 2 θ of around 10° (Fig. 3.1.b). It has been reported by many researchers that the diffraction peak at GO lies at 9.10 [18], 10.3 0 [19] and 10.5 0 [20].

Figure 2 shown SEM micrograph image of raw graphite used, while Figure 3 shown the SEM image of the produced graphene oxide after the synthesis process. The morphology of raw graphite consists of very dense stacks of graphene, while after being oxidized and passing through the peeling stages the piles appear more loosely as seen in Figure 3. This occurs because the SO₄⁻ ions penetrate on the interlayer of graphite and break the Van der Waals bonds [21]. The sonification may cause the oxidized graphite to exfoliate further. The addition of water and oxygen molecules in between the layers causes the spacing between d-spacing layers of graphite to become large (Shen et al, 2010). This is supported by XRD data analysis from the raw graphite showing d-spacing of 0,35 nm while the produced graphene oxide having d-spacing of 0,71 nm. Similar case was also reported by Spyrou and Rudolf (2012) with d-spacing of 0.35 nm and 0.68 nm for their graphene and graphene oxide,



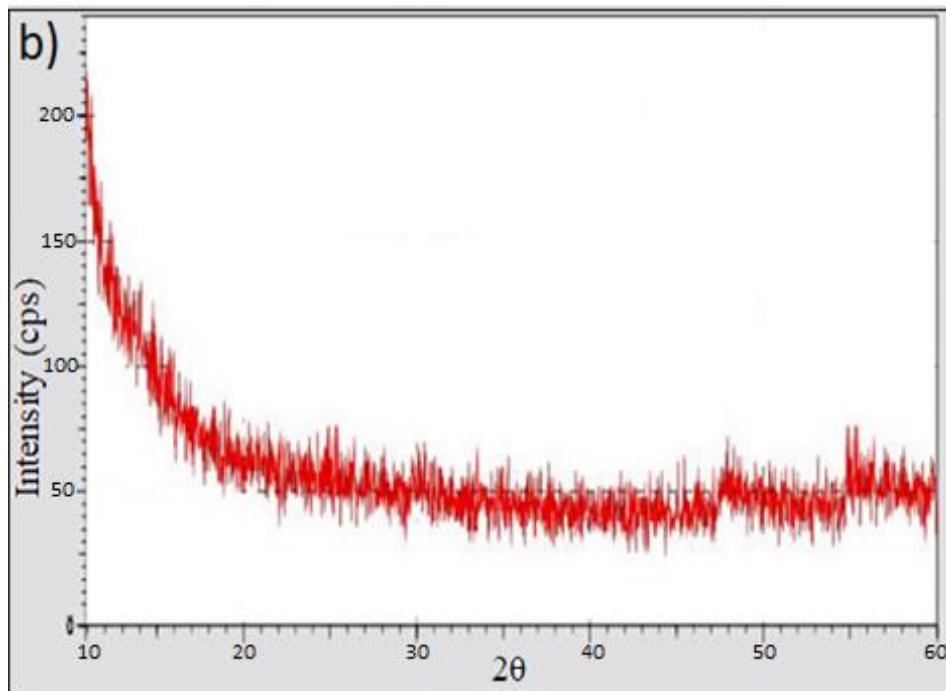


Figure 1. XRD pattern of (a). Graphite before process and (b) produced graphene oxide

respectively [22]. These XRD and SEM analyses confirm the formation of graphene oxide performed in the synthesis process [23].

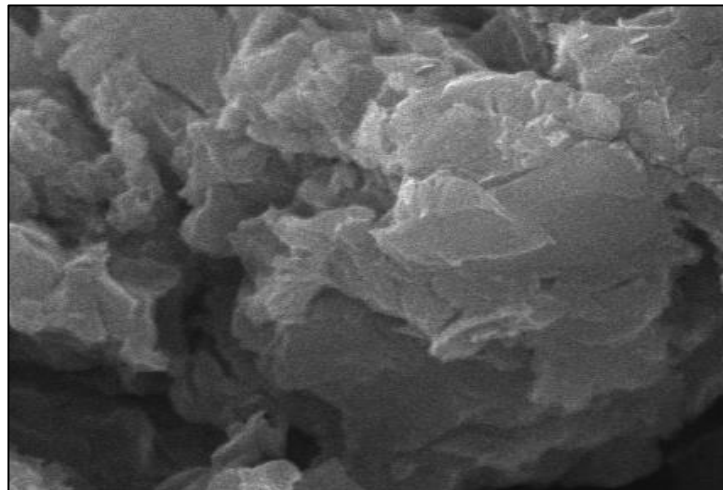


Figure 2. SEM image of the raw graphite used (2000x)

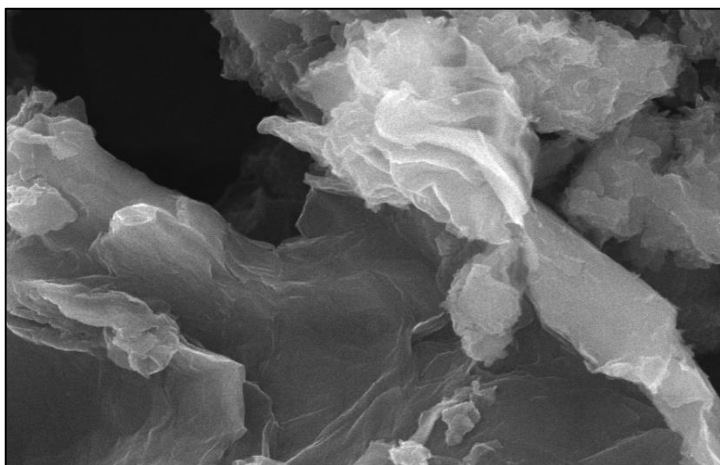


Figure 3. SEM image of produced graphene oxide (2000x)

3.2. Characterizations of bioplastic – graphene oxide composites

3.2.1. Mechanical properties of composites

The tensile tests applied to the samples based on the standard of ASTM D882-92 using the Universal Testing Machine (UTM) were presented in Table 1 and Figure 4 - 6. From Table 1 and Figure 4, it can be seen that the higher the graphene oxide concentration, the higher tensile strength and Young modulus will be, while the elongations decrease. The similar trend is also showed by the increase of the stirring time. This phenomenon indicated that there is a strong influence of graphene oxide to the composite matrix. The highest mechanical properties is exhibited by sample synthesized by using graphene oxide as much as 15% with 60 minutes stirring time, namely tensile strength of 3.92 Mpa elongation value of 13.22 Mpa and young modulus value of 29.66 Mpa.

Table 1. The mechanical properties of bioplastic – graphene oxide composites

Concentration of GO	Time (minutes)	Sample	Tensile Strenght (Mpa)	Elongation (%)	Young modulus (Mpa)
0%	30	1	1,38	28,09	4,88
	60	2	2,25	25,03	9,00
5%	30	3	2,55	20,62	12,36
	60	4	2,65	18,90	13,99
10%	30	5	2,74	15,35	17,88
	60	6	2,84	14,96	19,00
15%	30	7	3,63	13,45	26,95
	60	8	3,92	13,22	29,66

The increase in tensile strength due to the addition of graphene oxide is caused by the strong interaction between the bioplastic compiler molecules with graphene oxide layers. In more detail, it is associated with the interaction between the hydroxyl (OH) group, either from the bioplastic matrix or from the graphene oxide to form oxygen bridge [24]. The stirring time affects the process of mixing between the composite matrix and the filler graphene oxide. This stirring time correspond to the filler particles distribution in the matrix cavity. The longer the stirring time (60 min.), the more GO particles

will spread evenly within the matrix of bioplastic. As the result, the better mechanical properties of bioplastic will be gained.

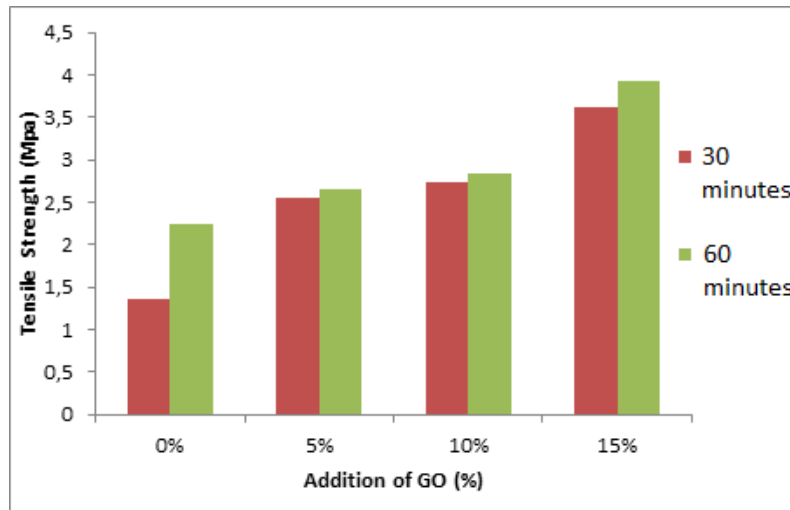


Figure 4. The effects of GO addition and stirring time to the tensile strength

Figure 4 shown the influence of graphene oxide addition and mixing time against the elongation. The percentages of elongation decrease with the increasing of the GO percentages and the increase of mixing time. Elongation is the maximum change of bioplastic length before breaking up when it gets a tensile load. The higher the elongation value, the lower the quality of bioplastic will be. The decrease of elongation is because the filler will reduce hydrogen bonds internally so that there is weakening of the polymer chain before breaking up [25].

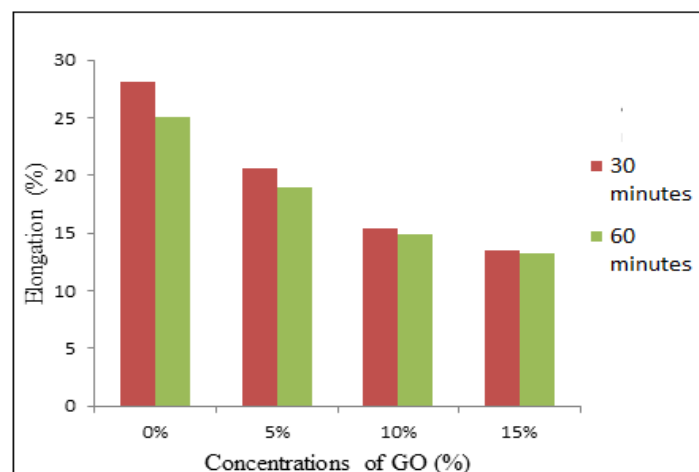


Figure 5. The effects of GO addition and stirring time to the Elongation

The influence of GO addition and mixing time of composites against the Young's modulus can be seen in Figure 6. Young's modulus can be said to be a measure of the stiffness of a material. It can be seen the Young's modulus increase significantly as the increase of GO concentration and mixing time. This confirms good integration of GO into the bioplastic matrix which enlarges the flexibility

level of bioplastic composites. The bioplastic synthesized using GO addition of 15% and mixing time of 60 minutes shows the highest Young's modulus of 29.66 Mpa.

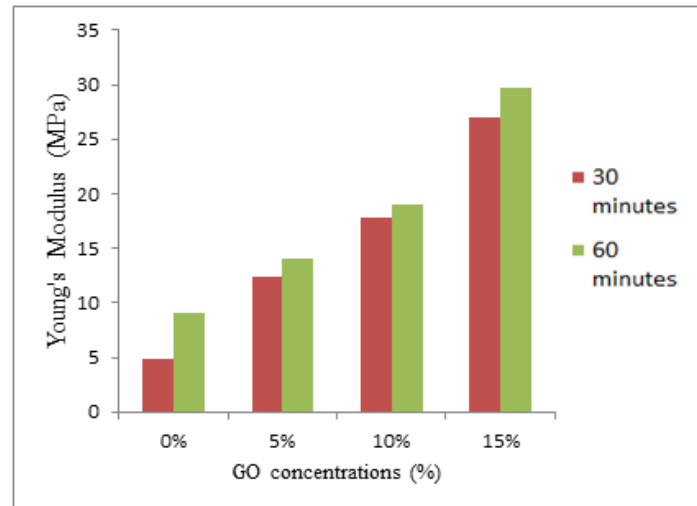
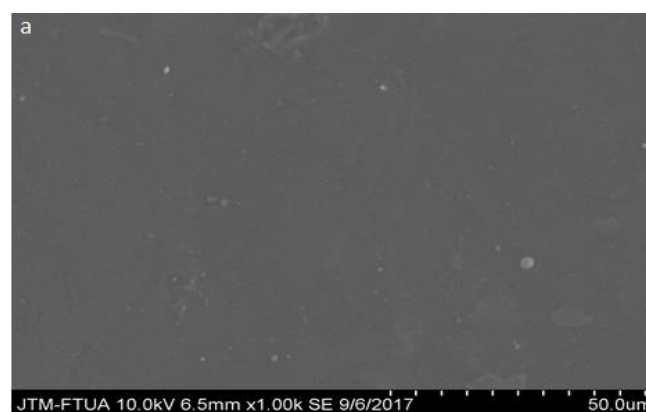


Figure 6. The influence of GO addition and mixing time to the Young's Modulus

3.2.2. Morphology of composites

Figure 7 shows the morphology surface of bioplastic synthesized by various of GO addition (%) and mixing time (t) investigated by scanning electron microscopy (SEM). It can be seen that the surface of composites is relatively smooth with some blemishes when they were stirred for 60 minutes, either with or without GO addition (Figure 7.a-b). It indicated that the GO filler is capable to have good interaction in the composites, and the bioplastic itself (without GO) also contributes to the formation of blemishes. However, when the composites was mixed at a lower stringing time (30 minutes), the surface is relatively inhomogen (Figure 7.d) compared to a longer stirring time. It can be concluded that the stirring time greatly affects the homogeneity of the sample.



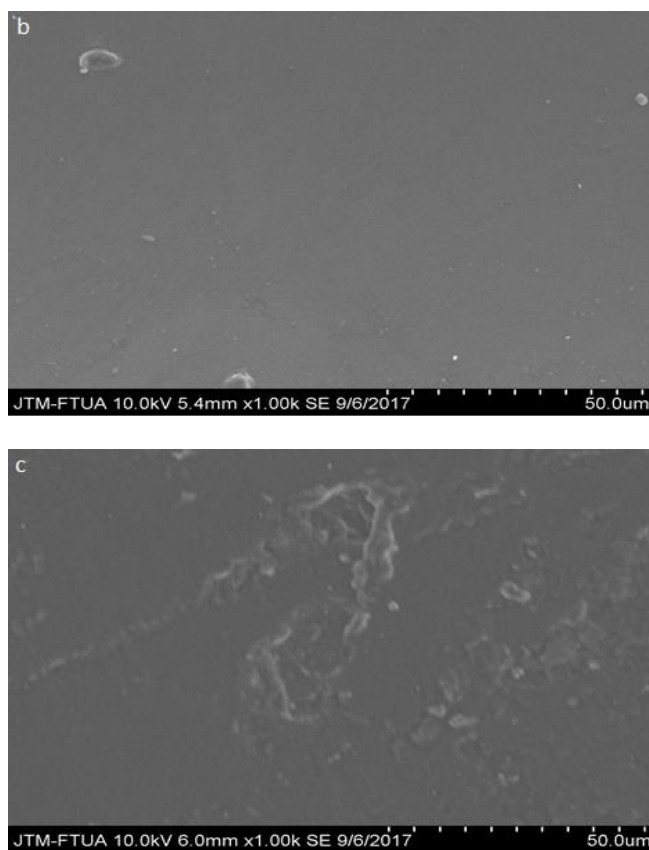


Figure 7. SEM micrograph of bioplastic composites (a) 0% GO, $t = 60$ min, (b) 15% GO, $t = 60$ min, (c) 15% GO, $t = 30$ min.

3.2.3 FTIR Spectra of bioplastic-graphene oxide composites

FTIR analysis is useful to look at the presence of functional groups in bioplastics, graphene oxide and composites as well as their behavior when the variables are changed. The FTIR spectra of bioplastics, graphene oxide and their composites are presented in Fig. 3.8. It can be seen that the FTIR spectrum of graphene oxide consists of some functional groups formed during the synthesis process. The oxygen functional group peak appears strongly at wavenumber around of $3200\text{--}3300\text{ cm}^{-1}$ indicating that the presence of an O-H bond from water molecules and hydroxyl functional groups in the graphene oxide solution. There is also a vibration at the wavenumber of 2850 cm^{-1} corresponding to the presence of the C-H bond. The presence of vibrations around the wavenumber $1540\text{--}1640\text{ cm}^{-1}$ corresponds to the C=O bonds associated with the presence of carboxyl groups at the edges of the graphene oxide layer. In addition, there is a vibration around the wavenumber around of 1200 cm^{-1} corresponding to the presence of the C-O bond. The presence of a C-O group signifies the success of the graphite oxidation process and it also indicates that graphene oxide has a hydrophilic property [14].

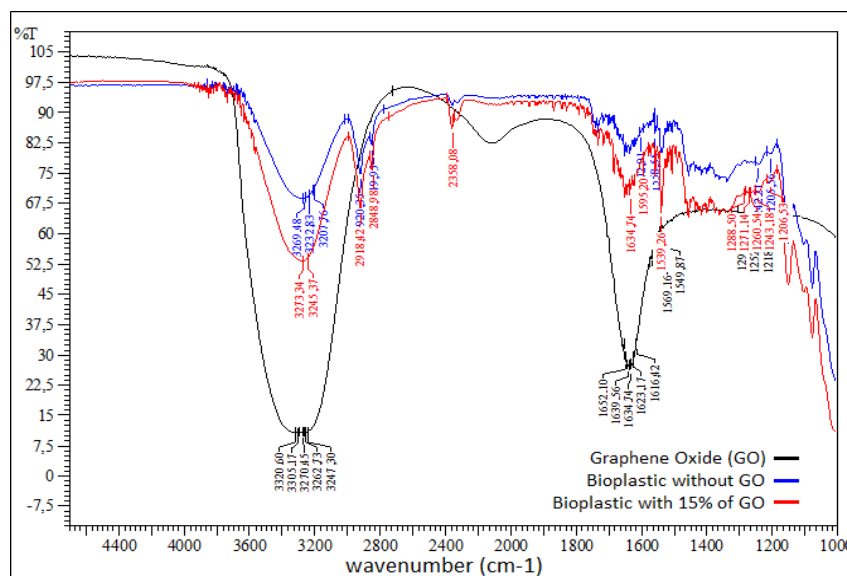


Figure 8. FTIR spectra of graphene oxide, Bioplastic and Bioplastic – GO composites

Figure 8 also describe the FTIR spectrum for bioplastic without graphene oxide addition. It can be seen that generally the bioplastic FTIR spectrum pattern has lower intensity of absorption especially for O-H, C-H and C=O bonds compared with the FTIR spectrum of GO. The oxygen bond is probably derived from the bonds between the starch, glycerol and water. When the bioplastic is added with the graphene oxide, the O-H bond is strengthened due to of hydroxy functional groups from GO increasing the hydrophilic properties of bioplastics. Furthermore, there is a change in the bioplastic structure in the wavelength range 2853-2962 cm^{-1} where there is an increase in the C-H grade in bioplastic by the addition of GO. The similar case with the vibrations in the range around of 1600 cm^{-1} . The vibrations at around 1200 cm^{-1} in the FTIR spectrum of composite indicate an interaction between the bioplastic matrix and GO that creates both intermolecular and intramolecular hydrogen bonds.

3.2.4 Interaction mechanism in composite

The bioplastic composite synthesized consisted of the starch as the matrix and the constituent fillers. The starch is composed of amylose and amylopectin. Basically the heated starch granules will break when it reaches the gelatination temperature (75°C). The heat energy will cause the hydrogen bond to break and the water molecules come into the starch granules. The process of entering the water into the starch will cause the granules to expand and eventually break resulting the cavities in the starch structure and cause the amylose and amylopectin to diffuse out of the granules [5,13].

The composite process begins by mixing the cracked starch granules with glycerol plasticizer and graphene oxide filler. At first, the glycerol molecule will enlarge the formed cavity so that the matrix becomes more elastic which affects the elongation value. Furthermore, the graphene oxide will fill the cavities to form a more dense and strengthening the mechanical properties of bioplastics. It is estimated that the hydroxyl groups from the starch, glycerol and graphene oxide interact each other forming the oxygen bridge and water byproducts. The interaction mechanism in the formation of bioplastic - graphene oxide composites is outlined in Figure 9.

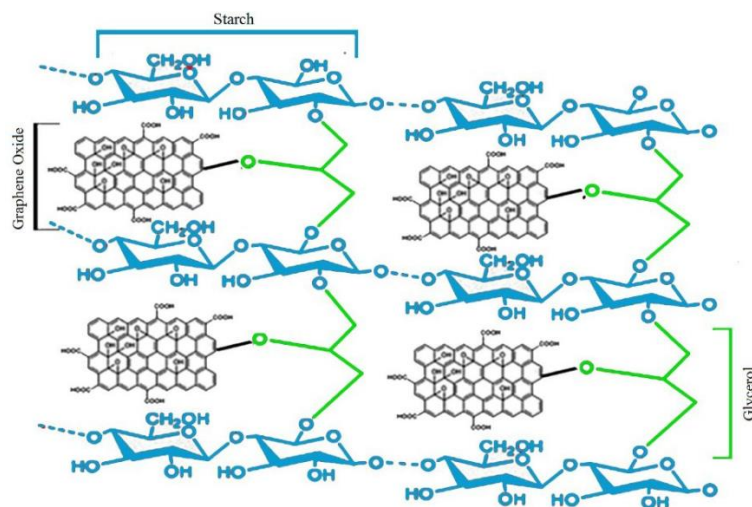


Figure 9. Interaction mechanism in bioplastic-GO composites

3.2.5. Water uptake

The water uptake is the ability of bioplastic absorb water. Bioplastic has good water resistance if it has small percentage of water uptake. Figure 10 shows the water uptake of bioplastic synthesized using various GO addition and mixing time. It can be seen that the water uptake increase monotonically as the increase of GO addition. Darni and Herti [26], stated that the water resistance properties of a molecule depended on the nature of the molecule. In this case, the ingredients of starch and glycerol used are hydrophilic, while the GO is also hydrophilic. Therefore, the addition of GO in bioplastic certainly enhances the ability of bioplastic to absorb the water due to the nature of hydrophilic GO [22]. However, it is different with the mixing time where a longer mixing time (60 minutes) has lower water uptake compared to the mixing time of 30 minutes. It could be attributed to the completeness of reaction between the starch, glycerol and GO resulting H_2O as elucidated in previous section. The longer mixing time then more complete the reaction and more water will be resulted. Eventually, this will disemboque to the water saturated condition which decrease the ability of composites to receive water from external.

The highest water uptake is showed by the sample synthesized using GO addition of 15% and the stirring time of 30 minutes, with the percentage of absorbed water of 30.77%.

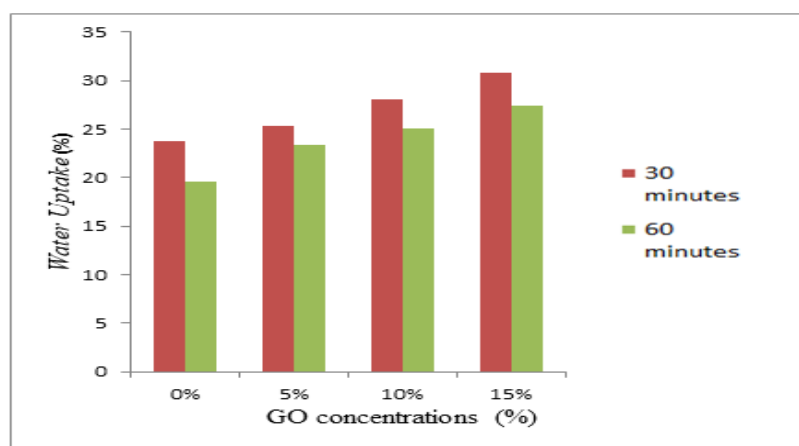


Figure 10. The effect of GO addition and mixing time toward the water uptake

3.2.6. The degradation test of bioplastic – GO composites

Biodegradation test aims to find out how long the bioplastic to be broken down in the environment. Figure 11 shows the results of the composites biodegradation test. It can be seen that more the GO added, more the rate of mass will be reducing. This is related to the hydrophilic properties of GO that improves the hydrophilic properties of composite making the bioplastic more easily degraded [12, 26]. According to Wypich [27], water can break down the structure of the material and help the activation of biology (microbial) during the biodegradation process.

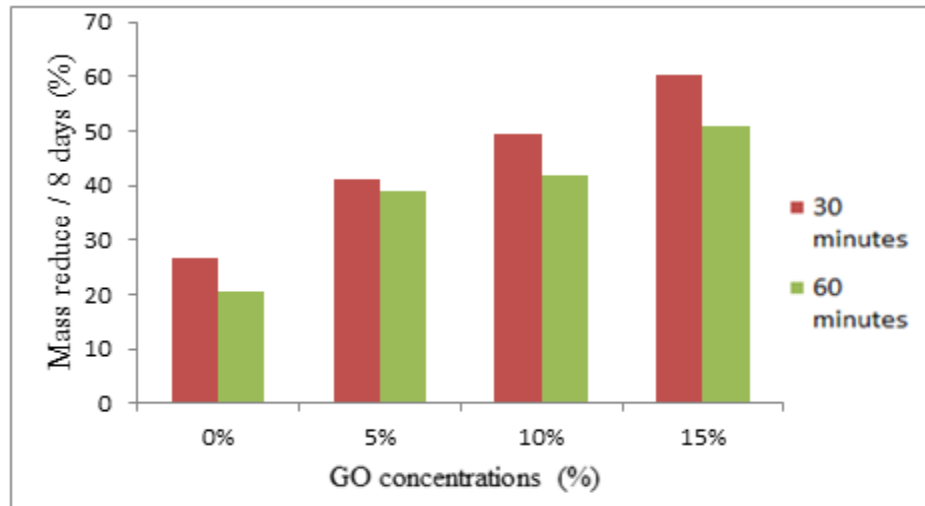


Figure 11. The biodegradation test of bioplastic – GO composites.

Base on Fig. 3.11, it can be seen that the mixing time also influence the rate of biodegradation. The shorter mixing time (30 minutes) has the higher of biodegradation rate. This may be due in the shorter mixing, the interactions among the constituent has not occurred completely yet and there is an empty space between matrix and GO filler forming the intramolekul hydrogen bonds with the water.

4. Conclusions

The graphene oxide filler has been successfully synthesized and integrated in the cassava starch based bioplastics forming the bioplastic-graphene oxide composites. The addition of graphene oxide with various concentrations improved the mechanical properties of bioplastic composites. The more graphene oxide and mixing time the more tensile strength and Young's modulus and the less elongation would be. This was be attributed to the homogeneity of components in the composite as indicated by SEM micrograph images and the FTIR spectra. The estimation of interactions mechanism in the formation of bioplastic - graphene oxide composites was proposed. The water uptake increased as the increase of GO addition and decreased with the longer mixing time attributed to the completeness of interactions among the components. The more GO added, more the biodegradation rate will be. This was atributted to the hydrophilic properties of GO. However, the shorter mixing time, the higher of biodegradation rate due to of empty space in composites as conducive site for biodegradation activities.

Acknowledgment

We gratefully acknowledges to Kemenristek-dikti via PUPT research grant 2017.

References

- [1] Setiawan H, Lutfi M and Masuroh 2014 Optimasi plastik biodegradable berbahan jelarut (*Marantha Arundinaceae L*) dengan variasi LLDPE untuk meningkatkan karakteristik mekanik *Jurnal Keteknikan Pertanian Tropis Dan Biosistem* Vol 2 124-130

- [2] Supriadi A 2016 Inaplas soroti manajemen sampah dan pengelolaan dana plastik. CNN Indonesia. http://www.cnnindonesia.com/ekonomi / 2016022_2123332-92-112525/inaplas-sorot - manajemen-sampah-dan- pengelolaan- dana-plastik / Accessed 10 April 2017
- [3] LIPI 2016 Indonesia penghasil sampah plastik kedua terbesar di dunia. <http://lipi.go.id/lipimedia/konsumsi-plastik-indonesia-tertinggi-kedua-di dunia/ 15182> Accessed 10 April 2017
- [4] Atifah N 2010 *Pemanfaatan hidrolisat pati sagu sebagai sumber karbon pada produksi bioplastik polihidroksialkanoat secara fed-batch oleh Ralstonia Eutropha*. Tesis Institut Pertanian Bogor.
- [5] Marbun S 2012 Sintesis bioplastik dari pati ubi jalar menggunakan penguat logam Zn dan penguat alami selulosa. *Skripsi Fakultas Teknik*. Universitas Indonesia, Jakarta.
- [6] Avella M 2009 Eco-challenges of bio-based polymer composites *Mater.* **2** 911-925.
- [7] Stevens E S 2002 *Green Plastic: An Introduction to the New Science of Biodegradable Plastic* (New Jersey: University Press)
- [8] Liu Q 2005 *Food Carbohydrates*. 978-0-203-48528-6.
- [9] Arrieta A A, Piedad F G, Samith E M and Robin Z 2011 Electrically conductive bioplastics from cassava starch *J. Brazilian Chem. Soc.* **22** (6) 1170–1176
- [10] Rahman M M, Jiang Z T, Yin C Y, Amri A, Chuah L S, Goh B M, Wood B J, Mondinos N, Altarawneh M and Dlugogorski B Z 2016 Structural thermal stability of graphene oxide-doped copper-cobalt oxide coatings as a solar selective surface *J. Mater. Sci. Technol.* **32** (11) 1179-1191
- [11] Rafitasari Y, Suhendar H, Imano N, Luciana F, Radean H and Santoso I Sintesis graphene oxide dan reduced graphene oxide *Prosiding Seminar Fisika FMIPA*. Universitas Gadjah Mada, Yogyakarta.
- [12] Widjaja H, Jiang Z T, Altarawneh M, Yin C Y, Goh B M, Mondinos N, Amri A and Dlugogorski B Z 2016 Double-sided F and Cl adsorptions on graphene at various atomic ratios: Geometric, orientation and electronic structure aspects *Appl. Surf. Sci.* **373** 65-72
- [13] Putri S L 2016. *Pembuatan bioplastik dari pati singkong (Manihot Escullenta Crantz) dengan menggunakan gliserol dan polivinil alkohol (PVA)*. Skripsi Universitas Andalas.
- [14] Syakir 2015 Kajian pembuatan oksida grafit untuk produksi oksida grafena dalam jumlah besar *Jurnal Fisika Indonesia* **55** Vol XIX, Edisi November 2015
- [15] Shao et al. 2012 Graphene oxide: The mechanisms of oxidation and exfoliation *J. Mater. Sci.* **47** (10) 4400-4409
- [16] Huang N et al. 2011 Simple room-temperature preparation of high-yield large-area graphene oxide *Intl. J. Nanomed.* **6** 3443-3448
- [18] Bayhaki M 2015 Kristalinitas graphene oxide (GO) dari karbon aktif menggunakan metode difraktometer sinar-X UNESA *J. Chem.* **4** 3
- [20] Naebe M et al. 2014 Mechanical property and structure of covalent functionalised Graphene/Epoxy nanocomposites *Scientific Reports* **4** (3) 4375
- [21] Chen et al. 2013 An improved hummers method for eco-friendly synthesis of graphene oxide *journal homepage www.elsevier.com/locate/carbon*
- [23] Tiannan et al. 2011 A simple and efficient methode to prepare graphene by reduced of graphite oxide withh sodium hydrosulfite *Nanotechno.* **22** 045704
- [24] Indrayati L, Indrarti and Rahmi E 2006 Pengaruh carboxymethyl cellulose (CMC) dan gliserol terhadap sifat mekanik lapisan tipis komposit bakterial selulosa *Journal Sains Material Indonesia* **8** (1) 40-44
- [25] Amni C et al. 2015 Pembuatan bioplastik dari pati ubi kayu berpenguat nano serat jerami dan ZNO *Journal Universitas Syiah Kuala*
- [26] Darni Y and Utami H 2010 Studi pembuatan dan karakteristik sifat mekanik dan hidrofobisitas bioplastik dari pati sorgum *Jurnal Rekayasa Kimia Dan Lingkungan* **7** (4) 88-93

- [27] Wypich G 2003 *Plasticizer Use and Selection for Specific Polymers* (Toronto: ChemTec Laboratories)