The effects of graphene oxide functionalization on the properties of sago starch-based bioplastics

To cite this article: Amun Amri et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 420 012061

View the article online for updates and enhancements.
The effects of graphene oxide functionalization on the properties of sago starch-based bioplastics

Amun Amri\textsuperscript{1,*}, Rifati Hanifa\textsuperscript{1}, Evelyn\textsuperscript{1}, Ella Awaltanova\textsuperscript{1,2}

\textsuperscript{1}Department of Chemical Engineering, University of Riau, Pekanbaru, Indonesia
\textsuperscript{2}Surface Analysis & Materials Engineering Research Group, School of Engineering and Information Technology, Murdoch University, Perth, WA 6150, Australia

* amun.amri@eng.unri.ac.id

Abstract. This study aims to determine the effects of graphene oxide (GO) addition to the properties of sago starch-based bioplastic. Bioplastics were prepared via the solution intercalation method while the GO was synthesized using Hummers method. The mechanical properties (tensile strength, elongation and Young’s modulus), morphology and functional groups involved were studied. The interaction mechanism between the GO and the matrix composites was also proposed. From the mechanical properties analysis, the more GO addition and the longer mixing time, the more tensile strength and Young’s modulus and the less elongation would be. The best tensile strength (4.018 MPa) was exhibited by bioplastic synthesized using 15% graphene oxide and 50 minutes mixing time. The micrograph analysis probed using Scanning Electron Microscopy (SEM) revealed that the GO filler in bioplastic synthesized with 50 minutes mixing time has been distributed evenly. The Fourier Transform (FTIR) analysis showed that a good inter-components interaction has been established due to the secondary O-H bonds between the GO and the bioplastic matrix components.

1. Introduction

The use of plastic has expanded into various sides of life because it is considered economical, flexible, light and not easily broken. The consumption of plastic products consumption in the world is still very large [1]. The use of plastics in everyday leads to problems with the environment. The widely used plastics come from petroleum, natural gas and coal which begin to experience a reduction in nature and can not be renewed. In addition, the use of plastics derived from petroleum, natural gas and coal will increase environmental pollution such as soil contamination [2]. Bioplastic or often called biodegradable plastic is one type of plastic that is almost entirely made from renewable materials, such as starch, vegetable oil, and microbiota. The availability of basic materials in nature is overwhelming with the diversity of non-toxic structures. This renewable material has a high biodegradability that is potentially for bioplastic material [3]. One of the bioplastic feedstocks that easily biodegradable by microorganisms is starch. Besides its biodegradable, starch comes from renewable, available and affordable natural resources so that starch can be a promising material to be combined with matrix and fillers to form polymer biocomposites [4]. Sago (Metroxylon spp) is one type of plant with starch as the largest component therein. Sago starch consists of 27\% amylose and 73\% amylpectin [5]. Based on the amylose content and high starch productivity, sago has the potential to be used as the basic material of starch-based bioplastics. Bioplastics as biodegradable plastics still have deficiencies compared to...
conventional plastics especially in terms of mechanical properties that are easily torn and not as strong as conventional plastics. One strategy for improving the bioplastic mechanical properties is by addition of fillers in a bioplastic mixture.

One of the fillers potentially added to bioplastics is graphene oxide (GO). Graphene oxide (GO) is an oxidized form of graphene laced with oxygen-containing group such as hydroxyl, carboxyl and epoxy. It is easy to dissolve in water or in other solvents. The synthesis of graphene oxide includes easy to synthesis, easily soluble, adjustable conductivity, high surface area, biocompatibility, abundant and cheap material resources [6]. Based on the degradable nature of sago starch and the advantage of graphene oxide, it is estimated that the composite of these materials can produce bioplastic with better properties. The aim of this study is to determine the effects of graphene oxide (GO) addition and stirring time to the properties of sago starch-based bioplastics.

2. Experimental

2.1 Synthesis of graphene oxide

Graphene Oxide (GO) was synthesized using Hummer’s method. 1 gram of graphite powder was oxidized using 23 ml of H$_2$SO$_4$, 0.5 gram NaNO$_3$ and 3 gram KMnO$_4$. The process of mixing the material was carried out inside the ice bath and the temperature was kept below 20°C. Then the solution was stirred at 40°C in the heat bath. After 14 hours of stirring the solution was transferred to ice bath and as much as 50 ml of H$_2$O was added gradually into the solution with a temperature maintained below 90°C. The solution was heated to 50°C in a heat bath and stirred for 1 hour. Subsequently the solution was removed from the heat bath and 150 ml of H$_2$O was added in solution. Then, 5 ml of H$_2$O$_2$ was added to the solution and stirred for 30 minutes. These procedures have been reported elsewhere.

The separation step of Graphite oxide with solution was used filter paper and washed with H$_2$O repeatedly until the pH was near neutral. The precipitated of graphite oxide was heated at 800°C using an oven for 4 hours and its result was as a graphite oxide solid. Then graphite oxide was mixed with H$_2$O and dispersed using ultrasonic vibrations to strip out the layers that make up graphite oxide to obtain the dispersed graphene oxide in solution [7].

2.2 Synthesis of bioplastics

Preparation of bioplastic was using intercalation method of solution. A 10 grams of tapioca starch was dissolved into 100 ml aquadest and heated over the water bath with a temperature of 720°C while stirring. Thereafter, glycerol and graphene oxide plasticizers were added according to the variables (0%, 5%, 10%, 15%) and stirred until homogeneous with stirring variation (15 minutes and 50 minutes). The homogeneous solution was poured into a glass mold and dried for 1 day at room temperature [8]. Then bioplastic was separated from the mold and tested for bioplastic characterizations.

2.3 Characterizations

The mechanical properties of bioplastics (tensile strength, elongation, and elasticity modulus) were tested using universal testing machine (UTM) via ASTM D822-02 using RG 3010 tensile test equipment with specimen size of 100 mm x 15 mm. The surface morphology was observed using JSM-6390A SEM. FTIR was used for functional group analysis.
3. Results and discussions

3.1. The Effects of graphene oxide and stirring time to the mechanical properties (tensile strength, elongation and young modulus) of bioplastics

Table.1 shows the mechanical test results of bioplastics. It can be seen that the tensile strength increases with the addition of graphene oxide and the stirring time. The increase of tensile strength is due to the addition of graphene oxide interact with starch via the formation of hydrogen bond so that the tensile strength is bigger than sample without the addition of graphene oxide. There is an increasing interaction of tensile force between the starch molecules and the graphene oxide along the increasing of graphene oxide composition [9].

The stirring time also affect the mixing between the matrix and filler in the bioplastic. This is related to the distribution of graphene oxide particles as fillers in the matrix cavity. The more agitation time, the better distribution of graphene oxide within the matrix and it will improve the mechanical properties of bioplastics.

**Table 1. The Results of Bioplastic Mechanical Properties**

| Addition of Graphene Oxide (%) | Stirring Time (minutes) | Tensile Strength (Mpa) | Elongation (%) | Modulus Young (Mpa) |
|-------------------------------|-------------------------|------------------------|----------------|---------------------|
| 0%                            | 15                      | 1,960                  | 22,476         | 8,720               |
|                               | 50                      | 2,352                  | 21,499         | 10,940              |
| 5%                            | 15                      | 2,940                  | 19,515         | 15,066              |
|                               | 50                      | 3,332                  | 19,007         | 17,531              |
| 10%                           | 15                      | 3,430                  | 18,612         | 18,429              |
|                               | 50                      | 3,626                  | 18,195         | 19,929              |
| 15%                           | 15                      | 3,724                  | 17,231         | 21,613              |
|                               | 50                      | 4,018                  | 16,128         | 24,913              |

Fig. 1 shows the influence of graphene oxide addition and the mixing time to the tensile strength of bioplastics.

![Figure 1](image.png)

**Figure 1.** Effects of graphene oxide addition and stirring time on the bioplastic tensile strength

Fig. 2 show the effect of graphene oxide addition to the bioplastic elongation. The chart shows that the elongation values tend to decrease along with the increase of graphene oxide.
composition and stirring time. The average percentage of elongation decline resulted in this research is relatively small namely at 8.5% when it is compared with the research from Putri (2016) which had an average elongation decline of 43.8%. The higher elongation value of a plastic does not guarantee the quality of the plastic [10]. The decrease of elongation is due to the strong interaction between the starch molecules and the graphene oxide. This strong interaction inhibits the elongation in the bioplastic by decreasing the bond spacing and it can reduce the internal hydrogen bonds and weaken the tensile forces on the polymer chains [9].

Fig. 3 show the effect of graphene oxide addition to the bioplastic Yong’s modulus. The chart shows that the values of Young’s modulus increase with increasing the number of graphene oxide addition and stirring time. Young’s modulus is obtained from the comparison between the values of tensile strength to the values of elongation. The value of Young’s modulus is directly proportional to the value of tensile strength and inversely proportional to elongation [11].

![Figure 2. Effects of Graphene Oxide Addition and Stirring Time on Bioplastic Elongation](image2)

![Figure 3. Effects of graphene oxide addition and stirring time on bioplastic modulus young](image3)

3.2. **Morphology Analysis**

Fig. 4(a-c) show the morphology comparison of between the bioplastic with and without the addition of graphene oxide. Fig. 4 (a) is bioplastic morphology without GO addition which has a relatively smooth surface and good degree of homogeneity. However, when GO
is added, the samples show the presence of white patches on the bioplastic surface (Fig. 4 (b,c)). The patches are probably air trapped by the gelatination process due to the lack of time spent on evaporation.

**Figure 4.** Bioplastics morphology of: (a) 0% graphene oxide, mixing time (t) =50 min, (b) 5% graphene oxide t=50 minutes, (c) 15% graphene oxide t=50 min.

The effect of stirring time on bioplastic morphology can be seen in Fig. 5 (a, b). From the figure it can be seen that the sample with 50 minutes stirring time has a smoother surface and better homogeneity compared to the bioplastic with a stirring time of 15 minutes. This indicates that stirring time affects the homogeneity of the resulting bioplastic. Perfect stirring is required to obtain a homogeneous distribution.

**Figure 5.** Bioplastics morphology with variation in mixing time: (a) 15% graphene oxide, mixing time =15 min, (b) 15% graphene oxide t=50 min

3.3. **FTIR analysis**

Fig. 6 shows the FTIR spectra of bioplastic with and without addition of graphene oxide. The FTIR spectrum of graphene oxide itself is also inserted as comparison. The figure shows the existence of some functional groups formed on the produced graphene oxide. The oxygen functional groups appear at the transmittance peak in range of 3200-3600 cm\(^{-1}\) wavenumbers indicating the presence of O-H bond. Then there is a vibration at the 2850 cm\(^{-1}\) wavenumber corresponding to the presence of the C-H bond. The presence of vibrations around the wavenumber of 1540-1640 cm\(^{-1}\) corresponds to the C=O bond which is associated with the presence of carboxyl groups at the edges of the graphene oxide layer. In addition, there is a vibration around the 1200 cm\(^{-1}\) corresponding to the presence of the C-O bond.
The FTIR spectrum of bioplastics without the addition of graphene oxide has shown the presence of oxygen bonds such as O-H and C-O with low values. The oxygen bond is probably derived from the bond between the starch component, glycerol plasticizer and water. Each of these components has an O-H group so that it is hydrophilic. The FTIR of bioplastic with the addition of graphene oxide show the oxygen functional groups at range of 3200-3600 cm\(^{-1}\) which indicates the presence of an O-H bond with a higher value than bioplastic without the addition of graphene oxide. This indicates that the addition of graphene oxide can increase the number of water molecules and hydroxy functional groups thereby increasing the hydrophilic properties of bioplastics.

There is a change in the bioplastic structure at wavelength range of 2853-2962 cm\(^{-1}\), where there is an increase in the value of the C-H group on the bioplastic with the addition of graphene oxide. The vibrations in the 1540-1640 cm\(^{-1}\) wavenumber is associated with the presence of the C=O bond. Furthermore, the vibrations around the 1200 cm\(^{-1}\) corresponds to the presence of a C-O bond with a high enough value.

3.4. Estimated interaction mechanism of bioplastic graphene oxide composites

The composite consists of matrix and constituent filler. The starch which is the matrix of composite consists of amylose and amylopectin. Basically, the heated starch granules will break when reaching the gelatination temperature (75°C). The heat energy will cause the hydrogen bonds to break and the water molecules come into the starch granules. The process will cause the granules to expand and eventually break. The broken starch granules will open the cavities in the starch crystalline structure and also cause the amylose and amlopectin parts to diffuse out of the granules. The composite formation begins by mixing the starchy starch with filler and plasticizer. Fig. 7 is the estimated mechanism scheme of bioplastic and graphene oxide composites formation.
The glycerol as plasticizer will open the cavities formed from the breaking of starch granules into the larger ones so that the matrix becomes more elastic which affects the elongation value. To strengthen the mechanical properties of bioplastics, the addition of filler in the form of graphene oxide will fill the cavities formed to form a solid and strong structure.

4. Conclusions
The addition of graphene oxide increased the values of tensile strength and Young’s modulus as well as decreasing the elongation. The highest value of tensile strength (4.018 MPa) was shown by the bioplastic synthesized using 15% graphene oxide with 50 minutes stirring time, with an elongation of 16.128% and Young’s modulus of 24.913 MPa. Analysis of bioplastic micrographs showed that a longer mixing time would enhance the filler distribution in the composite matrix. The Fourier Transform (FTIR) analysis showed that a good inter-components interaction has been established due to the secondary O-H bonds between the GO and the bioplastic matrix components.

5. Acknowledgement
We gratefully acknowledge Dikti for funding via Hibah Penelitian Unggulan Perguruan Tinggi 2017.

6. References
[1] Gu F, Guo J, Zhang W, Summers P A, Hall P 2017 Science of The Total Environment. 601 1192-1207.
[2] Darni, Y. and H. Utami 2009 Jurnal Rekayasa Kimia & Lingkungan. 7(2)
[3] Stevens E S 2002 Green plastics: an introduction to the new science of biodegradable plastics (Princeton University Press)
[4] Ma X, Chang P R, Yu J, Stumborg, M 2009 Carbohydrate Polymers. 75(1) 1-8
[5] Flach M 1997 Sago palm.Metroxylon sagu Rottb (International Plant Genetic Resources Institute)
[6] Chen D, Feng H, Li J 2012 Chemical Reviews. 112(11) 6027-6053
[7] Rafitasari Y, Suhendar H, Imani N, Luciana F, Radean H, Santoso I 2016 Sintesis graphene oxide dan reduced graphene oxide. in prosiding seminar nasional fisika (e-journal) pp SNF2016-MPS-95-98.
[8] Sri L P 2016 Pembuatan bioplastik dari pati singkong (manihot esculenta crantz) dengan menggunakan gliserol dan polivinil alkohol (pva) (Universitas Andalas)
[9] Razak A, Humairah N, Ahmad Z, Sarifuddin N, A WN I 2014 Advances in Environmental Biology. 8(3) 765-769.
[10] Amni C, Marwan M, Mariana M 2015 Jurnal Litbang Industri. 5(2) 91-99.
[11] Rifaldi A, Hs H,Bahruddin B 2017 Jurnal Online Mahasiswa (JOM) Bidang Teknik dan Sains. 4(1)1-7