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Conductive composites of tapioca based bioplastic and electrochemical-mechanical liquid exfoliation (emle) graphene

A Amri^{1,2}, H Rahmana¹, S P Utami¹, R S Iriyanti¹, Z T Jiang² and M M Rahman^{2,3}

¹Department of Chemical Engineering, Universitas Riau, Pekanbaru, Indonesia

²School of Engineering and Information Technology, Murdoch University, Australia

³Department of Physics, Jahangirnagar University, Bangladesh.

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

Abstract. The conductive composites of tapioca based bioplastic and the electrochemical-mechanical liquid exfoliation (EMLE) graphene have been successfully synthesized via the solution intercalation method for conductive bioplastic applications. The synthesized EMLE graphene quality, the mechanical properties, the functional group interactions and the conductivity of bioplastic composites, respectively, were analyzed using Raman spectroscopy, Universal Testing Machine (UTM) via ASTM D882-92, Fourier Transform Infrared (FTIR) spectroscopy, Multitester via Four Probe Method. Raman spectroscopy analyses revealed that the graphene used is multi layer graphene (~ 3-10 layer) with defects and minor impurity of graphene oxide (EMLE graphene). The tensile strength and the Young's modulus increased with the increasing of the EMLE graphene content in the composites, while the elongation decreased. The bioplastic synthesized using the 9% EMLE graphene content and the mixing time of 50 minutes exhibited the best mechanical properties with the tensile strength of 4.116 Mpa, the Young's modulus of 75.476 Mpa, and the elongation of 5.453%. The FTIR spectra indicated that there was a good interactions of EMLE graphene in the bioplastic matrix due to the hydrophylic properties and the secondary bonds between the EMLE graphene and the starch and glycerol plasticizer. The higher amount of graphene added, the higher conductivity of bioplastic would be, and vice versa for the resistivity. The best electrical properties of 1.57×10^{-1} /ohm.cm (conductivity) and 6.34 ohm.cm (resistivity) was reached by the bioplastic synthesized with addition of 9% EMLE graphene and 50 minutes stirring time. EMLE Graphene is the promising filler for further development of Tapioca based conductive bioplastics.

1. Introduction

Plastics play an important role in human life, ranging from simple needs to complex and sophisticated needs. The need for plastic from time to time increases continuously [1]. Conventional plastics that are still used today are derived from synthetic polymeric materials made from petroleum or natural gas whose feedstocks are increasingly limited and non-renewable as well as difficult to recycle and non-degradable. This can lead to the environmental pollution [2]. Different from the conventional plastic, the bioplastics is a biodegradable plastic, which is in turn, it will break down by microorganisms enzymatically in soil and produce water and carbon dioxide gas. Bioplastic is a solution to reduce the environmentally problem due to of the non-degradable plastic wastes.



Bioplastics can be synthesized from renewable natural materials such as starch [3,4], protein [5], and bacteria [6]. Generally, among the polysaccharides and biopolymers, starch is considered the most potential and promising natural ingredient for use in biodegradable plastics [7]. Because it is easy to obtain and the amount is abundant as well as it is easy processing so it is very promising to be developed. One source of starch is tapioca flour from cassava plants which has the highest starch content reaching 90% [8]. Generally, the bioplastics from cassava starch have good tensile strength and transparency properties [3].

The lack of bioplastic applications in the electronics sector is due to the isolator properties of bioplastic. Whereas the biodegradable properties of bioplastics are very useful in electronic devices. The strategy of converting the non-conductive to conductive properties of bioplastic is the brilliant thought. One of the most suitable alternatives and up to date is by the integration graphene into the bioplastic matrix. Graphene is the thinnest, strongest and most powerful material in the world today formed from the arrangement of two-dimensional carbon monolayer atoms that make up the hexagonal crystal structure resembling a honeycomb [9]. Graphene has electronic properties with high electrical conductivity and good flexibility. Graphene has unique and superior properties compared to other materials such as high electron mobility reaching 200,000 cm²/Vs, high electrical conductivity ($0.96 \times 10^6 \Omega^{-1} \text{ cm}^{-1}$), high thermal conductivity (5000 W/mK), good optical transparency (97.7%), and has a tensile strength of 1 TPa or 200 times harder than steel and 20 times harder than diamond and 130 GPa stiffness [10]. The electronic structures of graphene is also affected by the relative orientation of the adsorbed sites (zigzag or armchair) and possibly the relative size / mass of the adatoms and carbon [11,12].

This work investigates the properties of tapioca based bioplastic with the addition of graphene and study their interactions. The discussed variables are the effects of graphene content and mixing time in the synthesis process of composite against the mechanical and electrical properties of bioplastic composites. In this work, Graphene is obtained from combination of electrochemical and mechanical liquid exfoliation (EMLE) method. The identity of graphene used (EMLE graphene) and its interactions in the composite are also discussed. The tensile strength, Young's modulus and the conductivity of biocomposite increase around 2.8 times, 10.5 times and 14.4 times, respectively, after the addition of 9% v/v multi layers (~3-10 layers) graphene. The remarkable improvement of mechanical and electrical properties accompanied by the low cost and environmentally friendly in the synthesis process, make this bioplastic-graphene conductive composite is very promising to be explored further for industrial scale.

2. Experimental

2.1 Synthesis of electrochemical-mechanical liquid exfoliation (EMLE) graphene

The electrochemical-mechanical liquid exfoliated (EMLE) Graphene made via electrochemical process of graphite rod of 2B pencil continued by the mechanical liquid turbulence shear exfoliation. In the electrochemical process, the graphite was applied as working electrode, while the stainless steel was as counter electrode. Both electrodes were then dipped in Na₂SO₄ solution. Electrochemical peeling was started by applying a positive voltage of 10 V in the system. When the exfoliation process was complete, the produced graphite flakes were filtered and washed using aquadest repeatedly until neutral pH was reached [14]. Then, it was dried forming the graphite flakes powder. Mechanical liquid exfoliation process was applied to the 10 of grams graphite flakes powder in rotor blade household blender with addition of 5 ml FL (fairy liquid) surfactant and addition of aquadest until total volume of 500 ml. Blender was operated at maximum speed for 60 minutes and keep the process in the blender cold [12]. The product of this electrochemical and mechanical exfoliation process was called as EMLE graphene.

2.2 Synthesis of conductive bioplastics composite

Preparation of bioplastic was carried out using solution intercalation method. 10 grams of tapioca flour were dissolved into 100 ml aquadest and heated over with water bath with temperature of 60°C while stirring. Thereafter, glycerol plasticizer and EMLE graphene were added according to the variables (0%, 3%, 6%, 9% v/v) of EMLE graphene, then stirred until homogen with stirring time variation (30 minutes and 50 minutes). The homogeneous solution was then poured into the flexi glass mold and dried for 1 day at room temperature. The bioplastic was separated from the mold and ready for characterizations.

2.3 Characterization

The produced graphene was analyzed using Raman spectroscopy identified using excitation energy at wavelength 532 nm. The mechanical properties (tensile strength, elongation and Young's modulus) were tested based on the ASTM D882-92 standard using Universal Testing Machine (UTM). The qualitative interactions of graphene with the organic/functional groups in bioplastics were investigated using FTIR spectrophotometer. The electrical conductivity of bioplastic was probed based on the four probe method by using multimeter.

3. Results and discussion

3.1 Raman spectroscopy analysis

Raman spectroscopy is used to study the quality and the number of graphene layers produced. Fig. 1 shown the Raman spectrum of sample generated from the process of electrochemical and mechanical liquid exfoliation graphite. From the spectrum looks there are three major peaks, namely peak of G band at the wavenumber of 1583.64 cm⁻¹, peak of 2D band at 2690.88 cm⁻¹ and peak of D band at 1353.46 cm⁻¹. Normally, for a single-layer graphene, the G band appears at wavenumber around of 1580 cm⁻¹ [15]. This vibrational involves sp² of carbonized carbon hybridization consisting of graphene sheets. While the 2D and D bands appear at around wavenumber of 2680 cm⁻¹ and 1350 cm⁻¹, respectively [15].

The size and shape of G and 2D band peaks can be analyzed for identification purposes. The single-layer Graphene has higher 2D band spectrum with a symmetrical and sharp compared to the G band [17], and it is vice versa exhibited in Fig. 1. Another analysis, from Fig. 1, the peaks intensity ratio of 2D and G bands (I_{2D}/I_G) is 0.48 which is far from the pristine (without defects) and single layer graphene where the I_{2D}/I_G value of 2 [15,16, 17]. The wider and the higher peak of the 2D band indicate the higher multi layer of graphene and vice versa. The thicker the layer, the 2D band form is more asymmetric [15,18]. These elucidations indicate that the produced graphene in this work is not a single layer.

Quantitatively, the number of layers in graphene can be counted via the analyses of G and 2D bands, while the presence of D band indicates the existence of defects in the graphene [15]. The position of G band will shift to a lower wavenumber if the number of graphene layer increase. It can be predicted through the following equation [15, 16]:

$$\omega_G = 1581,6 + 11 / (1 + n^{1,6}) \quad (1)$$

where the ω_G is the G band wavenumber detected on the sample. From this equation, it is found the number of layers in the EMLE graphene is ~ 3 layer. The 2D band can also be used to determine the graphene layer qualitatively. However, the position and shape of the 2D bands can differ significantly depend on the excitation energy applied. Therefore, it is important to use the same excitation laser frequency when the comparisons are carried out (532 nm or 633 nm) [15]. [19] have The identification of graphene layers based on the G and 2D band shapes has been elucidated [19]. Based on this view, the G and 2D bands in this work have a high similarity with the G and 2D bands of ~5-10 layers of graphene [19].

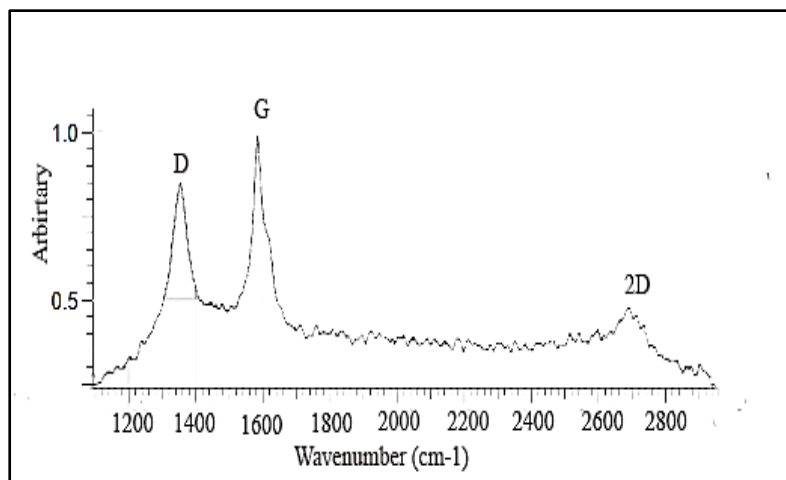


Figure 1. Raman spectrum of sample obtained from EMLE graphite.

The appearance of band D in this study indicates the presence of defects in graphene produced and the addition of sp^3 hybridization by covalent bonds. This peak is very weak in graphite or in high quality graphene. If the value of band D is high or significant, it can be interpreted that a lot of damages or impurities exist in the sample [15,16]. If the defect level in graphene is very high, indicated by the very high D band peak, then there will be the D' band at around 1620 cm^{-1} and the D+G band at around 2940 cm^{-1} as reported in [16]. However there is no these extra bands in the graphene produced in this work.

The graphene oxide could be exist in the sample even though the synthesis process did not involve the oxidation reactions directly. It is possibly due to the C^+ from the graphene sheet edge (when defects occurred) captures the electron from hydroxyl (OH) forming the graphene oxide. The shoulder at the higher wavenumber of G band peak as seen in Fig. 1, it indicated that the presence of graphene oxide (C-OH) bonds in the EMLE graphene produced [20]. However the C-OH bonds are minority in the sample as indicated by the lower intensity of D band peaks than G band peak and the absence of D' and D+G extra bands [20]. From the analyses either from band position, band shapes, comparisons or from the calculations performed, it can be concluded that the graphene produced in this research has defects with the number of layers are ~ 3 -10 layer (multi-layer) and with minor impurity of graphene oxide. We call this product as electrochemical and mechanical liquid exfoliation (EMLE) graphene or EMLE graphene.

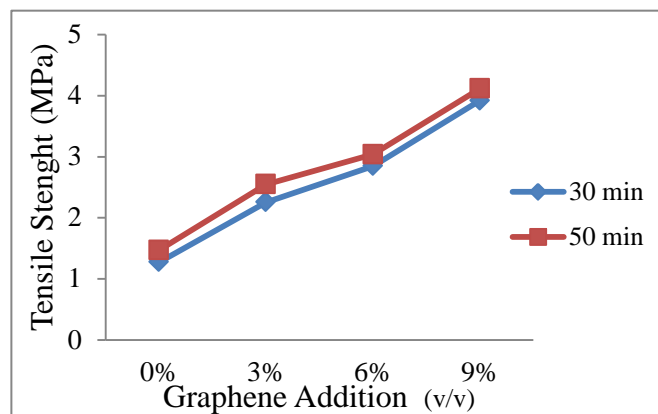
3.2 Mechanical properties

The mechanical properties of bioplastic with several of EMLE graphene content and mixing time are presented in Table 1 and Fig. 2-4. From Figure 2, it can be seen that the tensile strength increase with the increasing of the EMLE graphene content, and the increasing of the mixing time. This phenomenon may be elucidated as follow: the graphene will fill the cavities formed when the galatinization of starch (in the synthesis process) occurred. This composite forms a solid and compact structure due to the interaction of graphene with the matrix physically or chemically via the secondary bonding especially the adjacent oxygen and hydrogen atoms between the graphene oxide and the matrix as elucidated in FTIR analysis section. Indriyanti et al. [21] reported that the higher filler content in bioplastics will increase the stiffness and tensile strength values of bioplastics. The increase in tensile strength is due to the tensile forces interactions between thin-film molecules. The stirring time will affect the distribution of graphene filler within the matrix cavity, the longer the agitation (50 minutes) the graphene particles will spread evenly within the bioplastic matrix, and the mechanical properties of bioplastic tensile strength will increase.

Table 1. Testing results of bioplastic mechanical properties

Sample (v/v)	Tensile Strength (Mpa)		Elongation (%)		Young Modulus (Mpa)	
	30 min	50 min	30 min	50 min	30 min	50 min
0%	1.274	1.47	27.58	20.617	4.619	7.129
3%	2.254	2.548	18.684	18.613	12.063	13.689
6%	2.848	3.038	16.12	11.782	17.63	25.783
9%	3.92	4.116	8.516	5.453	46.031	75.476

The addition of larger quantity of graphene in this work (9%) results the larger tensile strength values compared with no graphene addition (0%) and fewer graphene additions (3%). A longer mixing time (50 minutes) has the higher tensile strength than a shorter mixing time (30 minutes). The largest value of tensile strength is 4.116 MPa showed by sample synthesized using graphene addition of 9% and stirring time of 50 minutes.

**Figure 2.** Effects of graphene addition and mixing time to the bioplastic tensile strength.

The effect of graphene filler and mixing time to the elongation properties of bioplastic produced can be seen in Figure 3. It can be seen that the elongation value greatly decreases as the increase of graphene content and the length of stirring time. Elongation is a maximum change in length of the bioplastic before it is broken. The higher the elongation value the less of quality of the plastic [22]. In this work, the lowest elongation value showed by sample at 9% graphene content and 50 minutes agitation time namely 5.453%. The addition of graphene filler will decrease the bonding distance between molecules and reduces the internal hydrogen bonds to weaken the tensile force on the polymer chain before breaking up [23]. The same thing was also reported by Sriprachubwong et al., [24] which obtained good flexibility results along with the increase in the amount of graphene in their polymer [24].

The Young's modulus is obtained from the comparison between the tensile strength to percent of elongation (elongation at break). Young modulus can also be regarded as a measure of the strength of a material [25]. Fig. 4 shows the effect of graphene filler and stirring time to the Young's modulus. It can be seen that the Young's modulus increases with the increase of graphene content and stirring time. The greatest Young's modulus (75.476 Mpa) is exhibited by sample synthesized at addition of 9% graphene and 50 minutes of stirring time. The similar trend was also reported by Susanti et al., [26] who conducted research to synthesize tapioca starch bioplastic with bamboo fiber reinforcement. This trend is due to the value of the Young's modulus is directly proportional to the value of tensile

strength and inversely proportional to the value of elongation. Thus, the addition of graphene and the duration of mixing time will affect the value of tensile strength and Young's modulus.

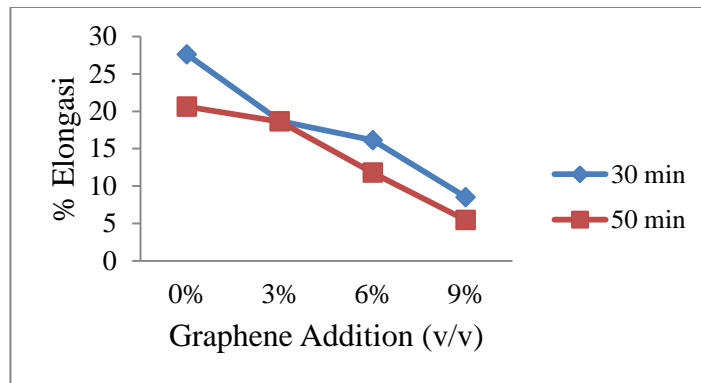


Figure 3. Effect of graphene addition and stirring time against the bioplastic elongation.

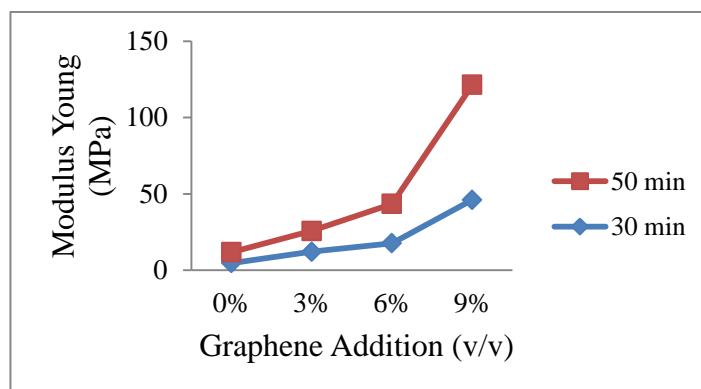


Figure 4. Effect of graphene addition and mixing time to young's modulus of bioplastic.

3.3. FTIR analyses and interactions mechanism

Figure 5 is the FTIR spectra of bioplastic without and with graphene content, respectively. It can be seen that the FTIR spectrum of bioplastic without the addition of graphene shown the presence of O-H bonds at 3321.56 cm^{-1} , C-H bonds at 2917.46 cm^{-1} and C-O bonds at 1057.75 cm^{-1} (Fig. 5.a). They are from the starch (glucose) and glycerol plasticizer. The bonds from O-H group indicated the hydrophilic property of bioplastic. Plasticizers in bioplastic make hydrogen bridges with starch molecules that weaken the strength of both the intra and intermolecular bonds of hydrogen, thereby reducing the interaction between amylose and amylopectin and making the film flexible. Fig. 5b shows the wavenumber shifting of bioplastics after the addition of graphene. It can be seen the significant change occurs at spectra around 1057 cm^{-1} (C-O bonds) and the bonds at around 2400 cm^{-1} which could be associated with the C=C bonds in graphene. These indicate a good interaction between the bioplastic matrix and graphene filler.

The interactions in the biocomposites are elucidated as the following. Basically the heated starch granules will be broken when the gelatination temperature (60°C) is reached and water comes into the starch granules [27]. This will cause the granules to expand and eventually break. The cracked starch granules will open the cavities in the starch crystalline structure and also cause the amylose and amylopectin as the component of the starch to diffuse out of the granules [27,28]. The amylose and the

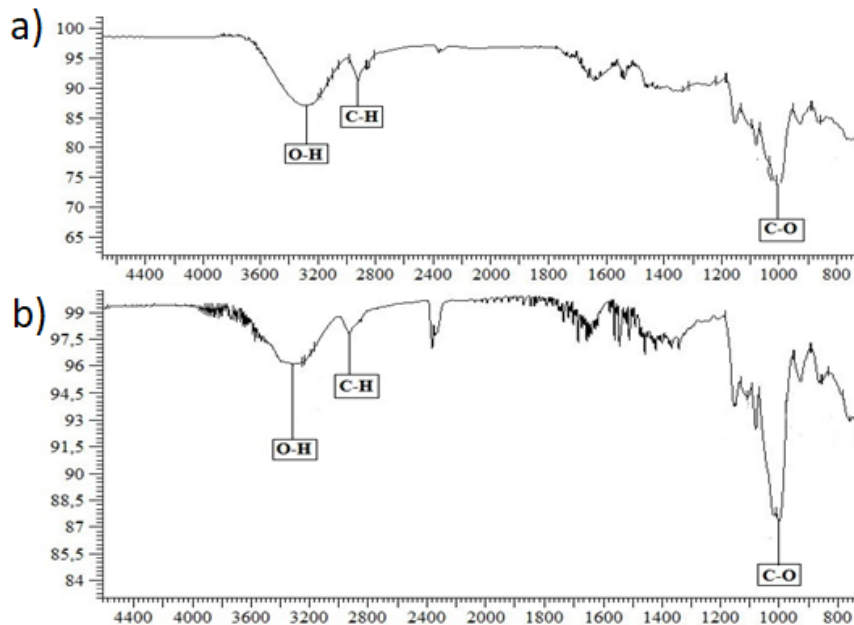


Figure 5. FTIR spectra for bioplastic: a). without graphene and, b) with 9% of graphene.

amylopectin then have a good interaction with the glycerol structure and the graphene filler due the hydrophylic properties among them and due to the secondary bonds (hydrogen bonds, O--H) between the oxygen from the graphene and the hydrogen from the matrix, and vice versa. The interactions mechanism among the starch, glycerol and the graphene in the biocomposite can be estimated as seen in Figure 6.

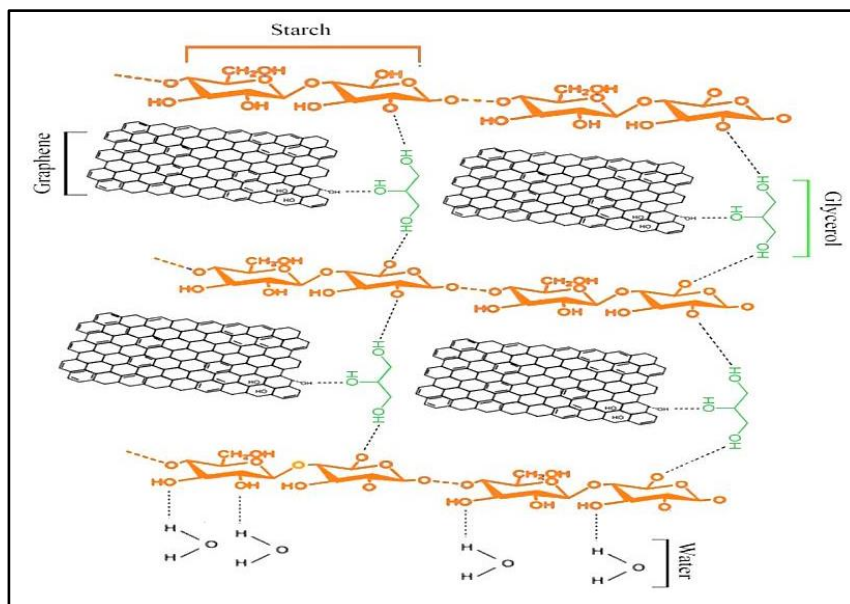


Figure 6. Estimation of starch-glycerol-graphene interactions mechanism.

3.4 Resistivity and conductivity of bioplastic composite

Bioplastic electrical properties were measured using the Four Probe Method. Electrical resistance (resistivity, R_s) and conductivity (σ) are calculated by the following equation:

$$R_s = \frac{\pi t}{\ln 2} \times R \quad (2)$$

$$\sigma = \frac{1}{R_s} \quad (3)$$

The results of the experiment are listed in Table 2 and Fig. 7. Generally, it can be seen that when the

Table 2. Resistivity and conductivity of bioplastic composite

Sample (v/v)	0%		3%		6%		9%	
	30 min	50 min	30 min	50 min	30 min	50 min	30 min	50 min
R (ohm)	200	202	38	34	30	28	19	14
t (cm)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Resistivity/ R_s (ohm.cm)	90.60	91.51	17.21	15.40	13.59	12.68	8.61	6.34
Conductivity (/ohm.cm)	0.011	0.011	0.058	0.065	0.074	0.079	0.111	0.158

EMLE graphene content increase, then the resistivity decrease or conductivity increase. Likewise the mixing time, where the longer mixing time, the resistivity decrease or the conductivity increase.

The best conductivity value was found in sample with graphene content of 9% v/v and mixing time of 50 minutes namely $1.57 \times 10^{-1} / \Omega \text{cm}$ or resistivity of $6.34 \Omega \text{cm}$. As a comparison, Arrieta et al., [3] reported the best conductivity value for their bioplastic-lithium perchlorate system is $8.1 \times 10^{-3} / \Omega \text{cm}$. For their bioplastics, the similar trend was also found where the conductivity increased when the lithium perchlorate filler was increased [3]. Even though the filler added was quite high, but the conductivity was still very low [3]. The type of fillers will affect the properties of the resulting bioplastic composites including the electrical property. Therefore, the structure and functional properties of the composite can be prepared in accordance with the desire by selecting the filler materials [2]. In this case, graphene has unique and superior properties compared to other materials, i.e. high electrical conductivity of $0.96 \times 10^6 / \Omega \text{cm}$ [10].

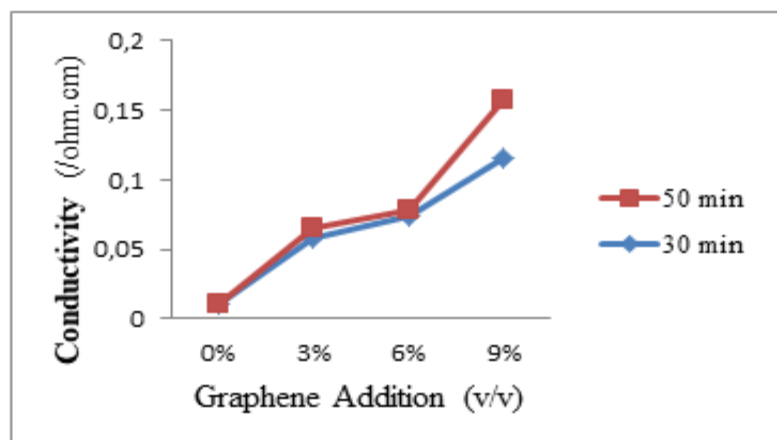


Figure 7. Effect of graphene content and mixing time on electrical conductivity of bioplastic composite.

4. Conclusions

The conductive composites of tapioca based bioplastic and the electrochemical-mechanical liquid exfoliation (EMLE) graphene have been successfully synthesized via the solution intercalation method. Raman spectroscopy analyses showed that the graphene used is multi layer graphene (~ 3-10 layer) with defects and minor impurity of graphene oxide (EMLE graphene). The tensile strength and the Young's modulus increased with the increase of the EMLE graphene content in the composites, while the elongation decreased. The bioplastic synthesized using the 9% EMLE graphene content and the mixing time of 50 minutes exhibited the best mechanical properties with the tensile strength of 4.116 Mpa, the Young's modulus of 75.476 Mpa, and the elongation of 5.453%. The FTIR spectra indicated that there was a good interactions of EMLE graphene in the bioplastic matrix due to the hydrophylic properties and the secondary bonds between the EMLE graphene and the starch and plasticizer. The higher amount of graphene added, the higher conductivity of bioplastic would be, and vice versa for the resistivity. The best electrical properties of 1.57×10^{-1} /ohm.cm (conductivity) and 6.34 ohm.cm (resistivity) was reached by the bioplastic synthesized with addition of 9% EMLE graphene and 50 minutes stirring time.

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