

# Characterization of Graphene Filled with Sustainable epoxidized Oil resin for Conductive Polymer Coating Applications

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**Abstract**— This study was aimed to characterise polymer conductive coatings by employing conductive additive such as graphene which is incorporated onto epoxidised oil resin. Solutions of polymer substrate of graphene with different percentages between 0.1 to 0.5% were incorporated with epoxidised oil as resin and cured with photoinitiator for the development of UV curable conductive coating. Resins are spin coated onto glass substrate through spin coating technique with spin rate between 250 and 500 rpm/min before undergoing UV light exposure. Characterization of cured coating via Fourier Transform Infrared (FTIR) showed the existence of carboxyl group of oil and graphene. Differential Scanning Analysis (DSC) exhibited cured resin with T<sub>g</sub> between 129°C to 137°C. Small changes of cured resin T<sub>g</sub> were observed upon increasing graphene percentages. Adhesion pull off test were highest for 5% graphene. For conductivity, all samples were found to have conductivity within  $10^{-8} \text{ Scm}^{-1}$ .

**Index Terms**— Characterization, Coating, Conductive polymer, Conductivity, DSC, Epoxidised oil, FTIR, Graphene

## 1 INTRODUCTION

**I**NTRINSICALLY conducting polymers (ICPs) or conductive polymers are an organic compound that can conduct electricity. ICPs general properties are that, it can have high electrical conductivity but with different mechanical properties when comparing to other commercial available polymers. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques. ICPs have conductivity levels between those semiconductors and metals. The biggest advantage of conductive polymers is their processability and they are mainly applied by dispersion.

The introduction of conductive polymer to the world had opens completely new opportunities in numerous applications, particularly in the electronics industry, which is were previously thought as impossible to happen. Polyacetylene or polypyrrole are well known for the first generation of conductive polymers. They are not suitable for practical applications due to low long-term stability of the conductivity and/or low processability. Polyanilines (PANi), polypyrroles and polythiophenes are other examples of conductive polymers which become conductive by removing an electron from their conjugated  $\pi$ -orbitals via doping. Some polymers such as polyacetylene, polythiophene and polyphenylenevinylene are also examples of conductive polymers that possess significant level of electrical conductivity, and versatile promising applications in field of energy storage, sensors, electrical and optical applications [1].

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Solar cell energy is alternative green energy compared to fossil energy that had been used for centuries. Those fossil energy causes very serious environmental problems as they are non-renewable sources [2]. In the application of solar cell, layered, laminate or coating were used on rigid silicon crystal or flexible substrate with conductive material as thin layer in the cell construction. Highly purified crystalline silicon (Si) in solar cells were used dominantly but then other cell types are developed as either to reduce cost of production or improved efficiencies such as solar cells based on the use multicrystalline-Si or Si- ribbon and the thin film cells based on the use of amorphous Si, CdTe or CIGS.

The conductive polymer (CP) brings huge advantage in electrical application. Due to its light weight, easily adherence and low manufacturing cost, manufacturer tend to prefer polymer rather than other materials. The synthesis of polymer conductive from conductive fillers and in fact from recycle polymer [3] can help to reduce cost and dependency for expensive conducting polymer such as polythiophene, polypyrrole (PPy) and polystyrenesulfonate (PEDOT). Additives are normally dispersed in suitable resin to be applied in fluid form and cast or spin as thin film. Normally epoxy or acrylate based resin from fossil resources are used. In this study, sustainable oil which can cure and act as the resin matrix, can reduce dependency on fossil fuel. Thus, it can replace the existing normal epoxy acrylate resin. Other than from sustainable

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ble oil, it can reduce the cost and bring economic and environmental benefit to human.

### 1.1 Conductive Polymer

Conductive polymer is an organic polymer that can conduct electricity. It is also known as intrinsically conducting polymer (ICPs). The ICPs application in electronic material/devices are very few because of misconception that all carbon-based polymer are insulators [4]. A conductivity of an electrical devices is measured by its ability to pass current through them or deliver the electrical charge to another targeted sample. According to Chen and Xue, (2005) [5] conducting polymer possess properties of both organic polymers and inorganic conductors. As organic polymers are defined as monomeric units that are covalently linked and this material will be conjugated and born with ability to become conducting polymer

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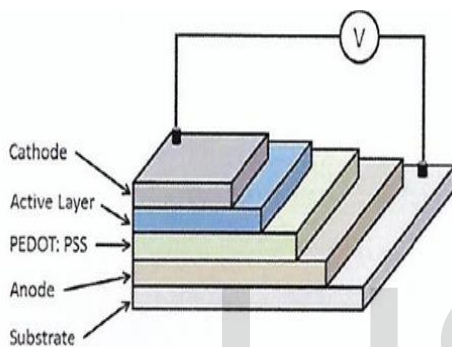
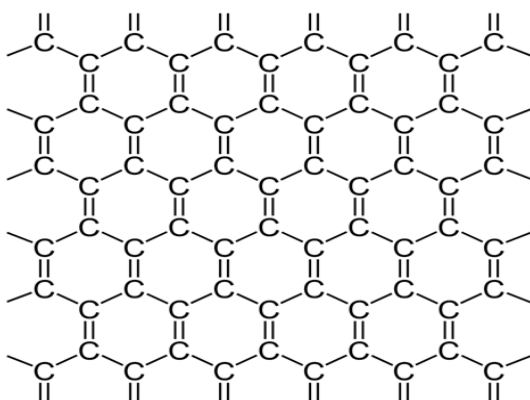


Fig. 1. Schematic layer of polymer solar cell.

### 1.2 Graphene

Graphene is a new material that discovered in the 21<sup>st</sup> century. It is made from honeycomb sheets of carbon just one atom thick [6]. Crystal lattice or known as crystalline structure of a structure for the grapheme is 3-dimensional structure as in Figure 2. Although diamond have 3- dimensional structure like graphene too, but both have completely different structure. In graphite, atoms are bonded tightly in two dimensional layers. These layers are held by up and down layers around them with a relatively weak force [6]. Amazingly, graphene is better at carrying heat with high thermal conductivity and can conduct electricity very well. Graphene flat, hexagonal lattice of graphene made it low resistance to electrons and easy to transport electricity [6].



### 1.3 Epoxidized Oil (EO) Resin as Coating

Epoxidised oil is a type of vegetable oil is a raw material that can be synthesized into environmental friendly polymers. This type of soil is apparently available in bulk where triglycerides molecules are main element that derived from unsaturated acid such as oleic acid (22%), Linoleic acid (55%) and linolenic acid (7%). Even this oil had unsaturated acid that are processed as double bond, a reactive site for coating or paints to take place, it is still need to be functionalized with adding with epoxy, hydroxyl and carbonyl groups in order to achieve its full characterize in polymeric coating applications. Double bond that present in soybean oils act to chemically alter their structure to improve some of properties since they it is possess natural oxidants where they do not oxidize naturally [7].

## 2 METHODOLOGY AND MATERIALS

There are several materials used in this study which include Diethyl Ether, Epoxidised Oil, Graphene, and Photoinitiator supplied by Merck Sdn. Bhd, Suka Chemical Sdn Bhd. Gra-

TABLE 1  
FORMULATION FOR GRAPHENE SOLUTION PREPARATION

Samples, %	Mass of graphene (g)	Diethyl ether (ml)	Modified epoxidized soybean oil (MESO) (ml)	Initiator
Samples 1	0.1	1.5	3	0.2
Samples 3	0.3	1.5	4	0.2
Samples 5	0.5	1.5	5	0.2

phene from Angstrom Material.

### 2.1 Preparation of Graphene Solution

Mass of Graphene was weighed before mixing with modified epoxidized soybean oil. The mixture is then in ultrasonic bath for 10 minutes and with temperature set is 38°C to make its particle more disperse and mixed well. The formulation is shown in the Table 1 shown below.

### 2.2 Coating and Curing Polymer Solution Preparation

Each of the sample is then coated onto glass substrate to undergo few tests to determine its characterization. For this liq-

uid substrate type sample, it will coat by using spin coat technique. Spin coater (Model LAURELL WS-400A- 6TFM-LITE) is used to obtain the thin film. The glass substrate to be coated is placed on rotating chuck and will hold onto it by vacuum applied. The glass substrate will spin and the polymer to be coated is then drop by dropper through the hole on the lid. In this experiment, rotating speed were maintained at 500 rpm for 2 minutes to obtain thickness about 40  $\mu\text{m}$  to 50  $\mu\text{m}$  for FTIR testing. For pull off adhesion test, sample having rotation at 250 rpm for 2 minutes to obtain higher thickness. The thicknesses of each sample were measured by using thickness gauge.

Next, each sample were cured under UV radiation machine. The coated glass substrate is passed thru UV radiation by placing them on conveyer belt. For all sample, it is passed three times with adjusted speed of conveyor belt. Those sample are left for 24 hours before it can run test analysis.

## 2.3 Characterization of Polymer Conductive Coated with EO

Testing were conducted for film sample prepared via spin coater and UV curing. The testing performed include Fourier Transform Infrared Spectroscopy (FTIR), *Electrical Conductivity Analysis and Pull Off Adhesion Test*.

FTIR was used to obtain infrared spectrum of absorption and vibrational changes of bonded structure in organic and inorganic specimens. In this study, it is used to analyze the qualitative value of disappearance peak of main polymer and structural bonding shifts if any. Perkin Elmer Spectrum One A instrument were used in the analysis of polymer structural features. The conductivity of polyene coated with modified EO is measured by two probe d.c technique with HIOKI 3532-50 machine. The electrical conductivity of material is measured in unit of  $\text{Scm}^{-1}$ , which S stand for Siemens. This machine will measure conductivity and impedance measurement of sample. The conductivity is calculated from formula

$$C = \frac{t}{RbA} \quad (1)$$

where 't' is a thickness of the film, 'A' the area of electrode and Rb the bulk resistance of the material which is determined from the intercept on the axis of semicircle.

Pull Off Adhesion Test were performed to determine adherence of the sample on glass substrate. The adhesion between coatings on the various substrates ere measured by using a PosiTest Adhesion Tester (DeFelko, USA) with ASTM 4541 as reference.

## 3 RESULTS AND DISCUSSION

### 3.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Figure 3 showed the spectra of modified EO (MEO) that mixed with 0.1 g of graphene, diethyl ether and Irgacure 1173. The wave number from Table 2 showed that broad peak for this spectrum is 3426.57  $\text{cm}^{-1}$  that is assigned to O-H. The wave numbers that appear to be broad peak for this spectrum is

3546.81  $\text{cm}^{-1}$  that assigned to O-H functional group. For graphene value, the peak where shows at value of 1726.26  $\text{cm}^{-1}$  and 1405.25  $\text{cm}^{-1}$  with each of them representing carbonyl (C=O) and carboxyl functional group (COOH). This can be seen in the other spectrum of graphene. Figure 4 and 5 showed the spectra of remaining graphene 3% and 5% mix with MEO. The optical absorption of graphene arises from two distinct types of contributions, those from intraband and those from interband optical transitions [8][9]. The relative importance of the two contributions depends largely on the spectral range of interest. In the far-infrared region, the optical response is dominated by the free-carrier (or intraband) response. In the mid- to near-infrared region, the optical absorbance is attributable primarily to interband transitions [9] Graphene conjugate alkene were not significant between 1405 and 1600. The C=C which arise from C=C existence around 1600 is obscured probably due to high oxidation of the graphene C=C to C=O. According to K.H Chudek et al [10] absorption bands: D (1348  $\text{cm}^{-1}$ ), G (1588  $\text{cm}^{-1}$ ) and 2D (2680  $\text{cm}^{-1}$ ) are characteristic for graphene materials ..Graphene is easily oxidised and the transmittance depends on the amount of graphene powder used in the process of fabrication. The more graphene is added to the composite, the less light is transmitted through the material. [11] Absorption spectra is mostly determined by the transmittance and thus, it is directly related to graphene loading. Blocking of light by graphene flakes dispersions can originate from two main mechanisms – absorption or multiple reflection (internal scattering). [12]

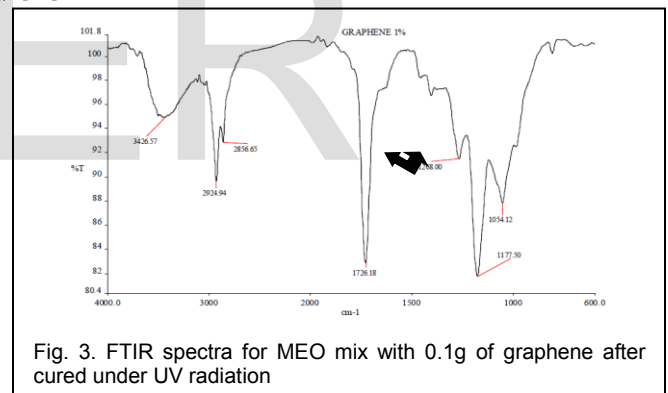


Fig. 3. FTIR spectra for MEO mix with 0.1g of graphene after cured under UV radiation

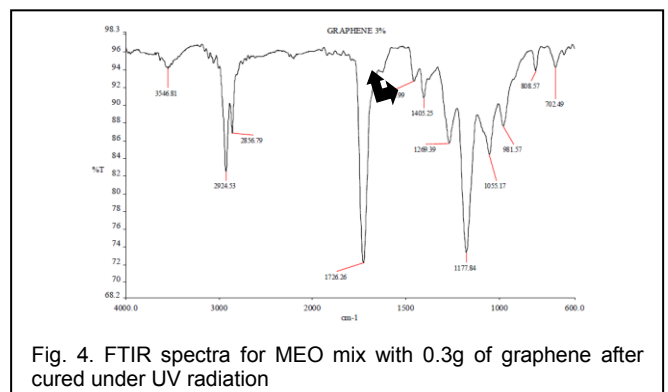


Fig. 4. FTIR spectra for MEO mix with 0.3g of graphene after cured under UV radiation

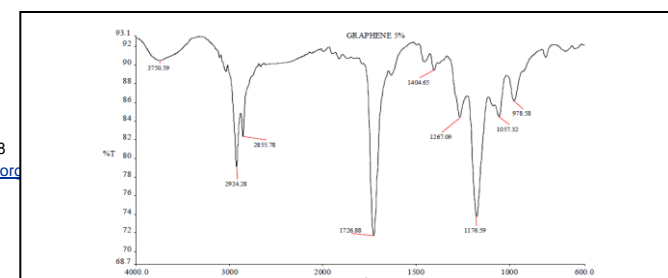


TABLE 2  
ASSIGNATION OF EACH BOND IN SPECTRUM OF GRAPHENE

Bond	Spectra Graphene		
	1%	3%	5%
O-H (alcohol)	/	/	/
C-H (alkane)	/	/	/
C-C (alkane)	/	/	/
C=O (carbonyl)	/	/	/
C-O (alkyl aryl ether)	/	/	/
C-O (vinyl ether)	/	/	/
C=C (alkene)		/	/
O-H (carboxyl)		/	/
O-H (alcohol)	/	/	/

ples are exhibited as in Figure 6 followed:

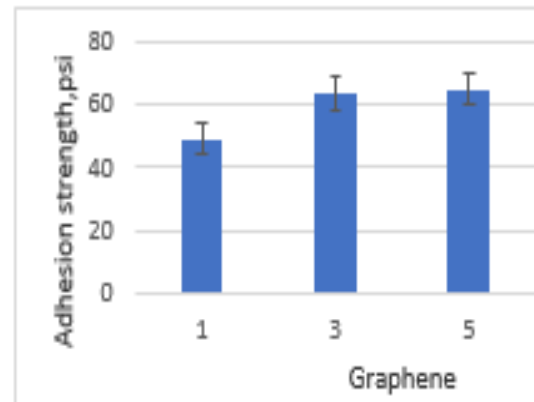


Fig. 6. Pull off adhesion strength of graphene

### 3.1 Electrical Conductivity analysis

Electrical conductivity of cured MEO after passing through UV machine with 0.1,0.3 and 0.5g of graphene measured by using HIOKI 3532-50 machine

Formation of parallel combination of bulk resistance which is due to migrations of ions and bulk capacitance that occurs due to immobile polymer chains built the semicircle. The conductivity of coating at room temperature is recorded as in Table 3. From the result, it shows that both polymer has almost very low conductivity value. The lower conductivity value is probably due to lesser amount of conjugated structure available. The materials that have conductivities value of below than  $10^{-8}$  Scm<sup>-1</sup> are categorized as insulators, for value between  $10^{-8}$  Scm<sup>-1</sup>

TABLE 3  
VALUES IMPENDENCE AND CONDUCTIVITY FOR GRAPHENE

Samples, %	Area, cm <sup>2</sup>	Thickness, cm	Impedance	Conductivity, Scm <sup>-1</sup>
1	48.4	0.210	5.40X 10 <sup>5</sup>	80.349X 10 <sup>-8</sup>
3	48.4	0.224	2.32X 10 <sup>5</sup>	1.9949X 10 <sup>-8</sup>
5	48.4	0.229	0.812X 10 <sup>5</sup>	5.8269X 10 <sup>-8</sup>

to  $10^{-3}$  Scm<sup>-1</sup> are considered as semiconductor and for materials with more  $10^{-3}$  Scm<sup>-1</sup> are considered as conductor materials. Conductivity will increase mainly due to an increase in the number density of mobile ion [3].

### 3.2 Pull Off Adhesion

Pull off adhesion test were performed on sample containing MEO and graphene. Each samples are adhere on a glass substrate with thickness about 50 µm. There are three samples of MEO with graphene. Data of adhesion strength of each sam-

Based on Fig 6, the adhesion strength is increased with increase in graphene composition. Graphene had interacted well with modified EO on glass substrate. Matrix filler adhesion are enhanced with higher graphene. This make coating easier and strong adherence to glass substrate.

## 4 CONCLUSIONS

Based on this research, there are few conclusion that can be determined. From the FTiR spectrum analysis, the peak for modified EO was found around 3584 cm<sup>-1</sup> until 3700 cm<sup>-1</sup> and peak of graphene that have several functional group which is carbon, hydroxyl, epoxide, carbonyl and carboxyl are spotted for each sample spectrum. As for the adhesion pull off test, it can be concluded that graphene has good adhesion properties and it shows increasing adhesion value when increasing mass are applied. Next, for conductivity test, found 5% of Graphene which has  $5.8269 \times 10^{-8}$  Scm<sup>-1</sup> conductivity value.

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