

## Thermal Conductivity Properties of Graphene Based Epoxy Nanocomposite (Sifat Kekonduksian Termal Nanokomposit Epoksi Berasaskan Grafina)

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### ABSTRACT

*Thermally conductive polymer composites offer new potentials for replacing metal parts in numerous applications, including power electronics, electric motors and generators, heat exchangers, and so on. Current interest to enhance the thermal conductivity of polymers is focused on the selective addition of nanofillers with high thermal conductivity. Therefore, graphene is the best choice material for thermally conductive composite. This study focuses on conducting the experiment to measure the thermal conductivity of graphene based epoxy nanocomposites with various variables and preparation conditions. Along this project, a series of experiment is done by manipulating the graphene loading ratio, the stirring rate, and the stirring time. 34 samples were prepared, tested, and analysed in order to determine the composite samples with the optimum variables. At the end of the experiment, the highest thermal conductivity of graphene based epoxy nanocomposites is identified at 0.204 W/mK. The optimum variables and conditions that came out with the best result are 0.3 wt% of graphene loading and 500 rpm of stirring rate at 30 minutes of stirring time. The enhancement of the thermal conductivity is 19.53% higher than that of the neat epoxy alone which is 0.17067 W/mK. This project is expected to serve as a good reference for future studies.*

*Keywords: Graphene; thermal conductivity; epoxy nanocomposites; rules of mixture; series model*

### ABSTRAK

*Komposit polimer konduktif haba menawarkan potensi baru bagi menggantikan bahan logam dalam pelbagai aplikasi, termasuklah elektronik kuasa, motor dan penjana elektrik, penukar haba dan sebagainya. Perhatian utama ketika ini adalah untuk meningkatkan kekonduksian haba polimer terhadap penambahan nanofiller tertentu dengan kekonduksian haba yang tinggi. Oleh demikian, graphene adalah pilihan terbaik untuk bahan komposit konduktif haba. Projek tahun akhir ini tertumpu kepada menjalankan eksperimen untuk mengukur kekonduksian haba graphene berasaskan epoksi nanokomposit dengan pelbagai pembolehubah dan keadaan penyediaan. Bersama-sama projek ini, beberapa siri eksperimen dilakukan dengan memanipulasi nisbah graphene, kadar kacau, dan masa kacau. 34 sampel disediakan, diuji dan dianalisis untuk menentukan sampel komposit dengan pembolehubah optima. Pada akhir eksperimen, kekonduksian haba tertinggi nanokomposit epoksi grafena dikenalpasti pada nilai 0.204 W/mK. Pembolehubah dan keadaan penyediaan optima dengan hasil yang terbaik adalah 0.3 wt% nisbah graphene dan 500 rpm kadar kacau pada 30 minit masa kacau. Peningkatan kekonduksian haba adalah sebanyak 19.53% lebih tinggi daripada sampel epoksi semata-mata iaitu 0.17067 W/mK. Semoga projek ini menjadi rujukan yang baik untuk kajian pada masa hadapan.*

*Kata kunci: Grafena; kekonduksian terma; nanokomposit epoksi; peraturan campuran; model siri*

## INTRODUCTION

Epoxy resins are a significant class of polymeric materials and one of the most versatile classes of polymers. Epoxy resins are used widely in industrial use such as electrical insulation materials, aerospace composites, and automotive primer (Pham & Marks 2005). This epoxy resins are formed by transforming liquid polyether into infusible solids through a specific curing process.

Graphene is the allotrope of carbon in the structure of a plane of sp<sup>2</sup> which are arranged in a hexagonal honeycomb structure (Ghaemi et al. 2018). The bonded atoms are separated by a distance of 1.4 angstroms and the bonding energy is approximately 5.9 eV (Pop, Varshney & Roy 2012). Graphene is the best alternative to substitute carbon nanotubes as filler materials (Jones et al. 2010) for enhancement of the thermal stability and the thermal conductivity of polymer (Yang et al. 2020). The most common method to synthesis graphene is the liquid phase exfoliation and chemical vapor deposition (Ghaemi et al. 2018). It was reported by (Shahil & Balandin 2012) that the graphene has an extremely high intrinsic,  $K_i$  which exceeds carbon nanotubes. The first study of graphene thermal conductivity was carried out by using an original non-contact Raman - optothermal technique. It was found that the thermal conductivity can exceed ~3000 W/mK near room temperature which is above the thermal conductivity (TC) of bulk graphite limit (Shahil & Balandin 2012).

Due to this, graphene is often added into various polymers as an attempt to increase the TC of the composite. The polymers or matrix include epoxy resin, paraffin, PA 66, natural rubber; just to name a few. The values of thermal conductivity of the composites were seen to increase, depending on the graphene loading as well as the matrix/polymer used. For example, incorporating 25 wt.% graphene nanoplatelet (GNP) into epoxy resulted in the TC values of 2.67 W/m.K, by using ball milling technique (Guo & Chen 2014). This is an increment of about 10 times compared to the TC value of neat epoxy. GNP has also found to increase the TC values of polytetrafluoroethylene (PTFE) up to 4.02 W/m.K, at a loading of 20 wt.% (Cai et al. 2018). This value is an increment of about 1 300% compared with pure PTFE. A complete review on enhanced thermal conductivity values of various polymer matrix is available in the literature such as (Huang et al. 2020) and many more.

Although there are many papers that reported the enhancement of epoxy composites by incorporating GNP, there are still relatively few that focuses on the effects of composites processing in influencing the values of TC. As such the objectives of this paper is to analyse the effects

of graphene loading, stirring rate, and stirring time. The results will also be compared with rules of mixture and series model.

## EXPERIMENTAL

Diglycidyl ether of bisphenol-A (epoxy) CP 812P were used in this experiment with the corresponding hardener CP 812P, as supplied by local manufacturer. Graphene Nanoplatetes (GNP) were purchased from TOB Group (China), specialised for thermal conductivity enhancement.

The experiment was designed to study the effects of three important parameters such as graphene loading, stirring rate, and stirring time. Due to this, the values of stirring rate and stirring time were kept constant to 100 rpm and 30 minutes, respectively for the first stage. Graphene were first added to the epoxy at various loadings of wt.% set to 0.1%, 0.3%, 0.5%, and 1.0%. Next, hardener will be added to the mixture, accordingly, at weight ratio of 2:1. The mixture was further stirred at 200 rpm for 10 minutes. Next, the mixture was poured into the 12 cm plastic mold with 1 cm diameter. The samples were left in the fume chamber for 24 hours to ensure the samples were cured properly. After the samples were cured, they were taken for drilling with 2.4 mm in the centre of the cross section to fit the TR-1 sensor of KD2 Pro Analyzer. The samples were then tested with KD2 Pro Thermal Analyzer in order to determine the TC of the graphene based epoxy nanocomposites. The sample that contains graphene loading with highest value of TC was then recorded for the next experiment.

The purpose of the next stage is to access the effects of stirring rate on the values of TC, by keeping other parameters constant. As such, the next experiment was conducted by varying the stirring rate to 200 rpm, 500 rpm, 750 rpm, and 1000 rpm, while keeping the stirring time at 30 minutes. The graphene loading was set to 0.3 wt.% as this was the loading that yielded the highest TC, as obtained from previous experiments. The TC of the cured sample was then measured using KD2 Pro Thermal Analyser in order to determine the sample that highest TC.

For the final stage of the experiment, the stirring time was varied at 15 minutes, 30 minutes, 60 minutes, and 90 minutes. The graphene loading and the stirring rate were set to 0.3 wt.% and 500 rpm, respectively; which was decided based on the highest TC of the samples obtained from the previous two experiments.

All of the samples were measured using KD2 Pro Thermal Analyser. The specifications of the sensor used is as shown in Table 1.

TABLE 1. Specification of the sensor used for KD2 Pro Thermal Analyser

Type	TR-1 (100 mm – large single needle)
Size	2.4 mm diameter
Length	100 mm
Range	0.10 to 4.00 W/mK

The experimental result obtained in this experiment will be compared to the theoretical results. The equations involved were the rule of mixture and the series model (Han & Fina 2011) which represents the theoretical values of the thermal conductivity of graphene epoxy nanocomposites. The rule of mixture was assumed to have perfect contact between particles in a fully percolating network which maximizes the contribution of the conductive phase. Otherwise, the basic series model was assumed to have no contact between particles and thus the contribution of particles is confined to the region of matrix embedding the particle (Han & Fina 2011). The equation for rule of mixture is

$$k_c = k_p \phi_p + k_m \phi_m \quad (1)$$

where  $k_c$  = thermal conductivity of composites (W/mK),  $k_p$  = thermal conductivity of particle (W/mK),  $k_m$  = thermal conductivity of matrix (W/mK),  $\phi_p$  = volume fraction of particle,  $\phi_m$  = volume fraction of matrix. The equation for series model is

$$k_c = \frac{1}{\left(\frac{\phi_m}{k_m} + \frac{\phi_p}{k_p}\right)} \quad (2)$$

where  $k_c$  = thermal conductivity of composites (W/mK),  $k_p$  = thermal conductivity of particle (W/mK),  $k_m$  = thermal conductivity of matrix (W/mK),  $\phi_p$  = volume fraction of particle,  $\phi_m$  = volume fraction of matrix. Both Equation (1) and Equation (2) are representing the upper bound and the lower bound for thermal conductivity of composites. Most of the experimental results were found to fall in between the two equations (Han & Fina, 2011). Both of these equations representing the upper bound and the lower bound for thermal conductivity of composites. Most of the experimental results should fall in between the two equations (Han & Fina 2011).

## RESULTS AND DISCUSSION

### EFFECTS OF GRAPHENE LOADING

In this stage, the stirring rate is fixed at 500 rpm for 30 minutes stirring time. The result from this experiment is as shown in Figure 1, together with values plotted

according to Rules of Mixture and Series Model. The experimental values of TC of the composites are seen to slowly increase from neat epoxy up to graphene loading 0.1 wt.% and 0.3 wt.% before dropping at higher graphene loading. The graph shows that the highest thermal conductivity of graphene is 0.204 W/mK which is at 0.3 wt.% of graphene and the lowest value of thermal conductivity is 0.1725 W/mK at 1.0 wt.%. The highest value of thermal conductivity is verified as the value lies between the upper and lower boundaries. Then, the graph shows the increment of thermal conductivity as the loading ratio increase until 0.3 wt% loading ratio which gives the highest reading of thermal conductivity. After that highest point, the graph starts to decrease.

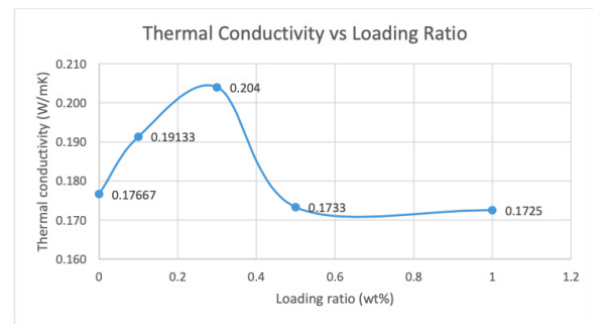


FIGURE 1. Thermal conductivity of the epoxy composites as a function of weight loading

Looking into Figure 1, 0.1 wt% graphene loading shows the lowest thermal conductivity of sample. At low filler loading, graphene sheets are covered by polymer chains which is not enough to reach a percolation limit in the mixture (Li et al. 2014) that result in low conductivity. By adding more filler, the conductivity of composite begins to increase slowly.

According to (Du & Cheng 2012), the distribution of graphene dispersed in the polymer affect the properties of polymer based composites. As the graphene added reaches a critical loading, the flat graphene sheets restacked and cause difficulties to get the uniform dispersion (Du & Cheng 2012). In addition, referring to (Mirjalili, Chuah & Salahi 2014), at higher filler loading, the dispersion of filler into the polymer matrix is irregular and tend to agglomerate. Hence, large voids or holes occur between nanoparticles and matrix cross link (Mirjalili et al. 2014). Therefore, we can say that 0.3 wt% loading ratio is the optimum graphene loading for the graphene to disperse uniformly in the epoxy matrix before it restacked and agglomerated. Higher than 0.3 wt% loading ratio, the dispersion of graphene in the epoxy resin is irregular and forming many voids which cause the thermal conductivity to decrease. Furthermore, graphene is suitable to wrinkle and wrinkling will decrease the intrinsic properties of the mixture (Du & Cheng 2012).

Therefore, the possibilities of graphene to wrinkle is higher when the large amount of graphene is added into the epoxy resin which will decrease the electrical and thermal properties.

As shown in Figure 1, only 0.3 wt% of graphene loading sample falls between the upper bound and the lower bound. The other three experimental value which are 0.1933 W/mK, 0.1733 W/mK, and 0.1725 W/mK with graphene loading of 0.1 wt%, 0.5 wt%, and 1.0 wt% are out of range and falls lower than the lower bound value. Therefore, 0.204 W/mK at 0.3 wt% of graphene loading is more in favour to be promoted to the next stage, thus accepted and verified the data.

#### EFFECTS OF STIRRING RATE

This set of experiment is performed to discover the maximum thermal conductivity of graphene based epoxy nanocomposites from several stirring rate of the mixer. At this stage, 0.3 wt% of graphene loading from the and 30 minutes stirring time is kept constant throughout the experiment. The results are shown in Figure 2 where four levels of stirring rate are set. As can be seen, the samples that show the lowest thermal conductivity is at 200 rpm, which is 0.182 W/mK. Then, the graph increased to 0.204 W/mK which is the highest thermal conductivity as the stirring rate increase. The stirring rate at this point is 500 rpm and it is the optimum point of thermal conductivity of the sample. The value lies in the range of the boundaries and it is verified. Just after the optimum point, the thermal conductivity started to decrease as the stirring rate increase.

The higher shear forces are needed to achieve a fine dispersion in the polymer matrix to avoid agglomeration of graphene (Ma et al. 2010). However, vigorous mixing with external stirring may wrinkle or tear the large flakes of the graphene derivatives, which can be very unfavourable to achieving the ultimate mechanical, optoelectronic, electrical, and thermal properties of the resulting nanocomposites (Hu et al. 2014). Therefore, the best stirring rate for 0.3 wt% of graphene loading is 500 rpm and the stirring rate higher than 500 rpm is assumed as a vigorous mixing.

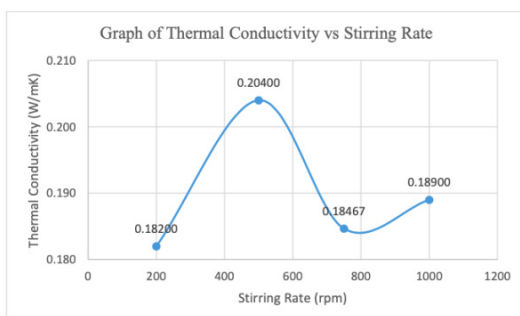


FIGURE 2. Thermal conductivity of the epoxy composites as a function of stirring rate

#### EFFECTS OF STIRRING TIME

This set of experiment is performed to evaluate the effects of stirring time on the values of TC of the composites, at constant 0.3 wt% of graphene loading and 500 rpm stirring rate, obtained from the previous experiments. As shown in Figure 3, the best stirring time is 30 minutes where the value of TC recorded in 0.204 W/m.K, with the values of graphene loading and stirring rate are 0.3 wt.% and 500 rpm, respectively. This reflects a 19.53 % increment as compared to the TC of neat epoxy, which is almost reach the value of percentage increment of 23.8%, as reported by (Dilini Galpaya, 2012). The lowest value of TC is 0.189 W/mK, at stirring time of 90 minutes. Therefore, we can see clearly that 30 minutes is the most suitable time to mix the graphene filler with the epoxy to gain the best dispersion of graphene. The thermal conductivity value at this point is accepted as it lies between the boundaries of rule of mixture. However, long exposure to stirring induce defects in graphene sheets which cause damage to the nanocomposite properties (Irene S. Fahim, 2013).

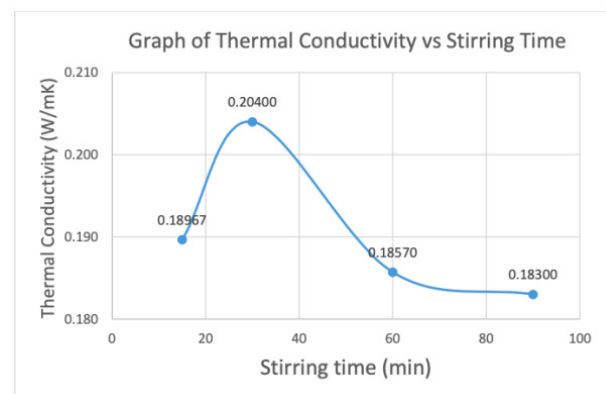


FIGURE 3. Thermal conductivity of the epoxy composites as a function of stirring time

There are other several parameters that affect the thermal conductivity of graphene based epoxy nanocomposites. These factors including the aspect ratio, the sizes and thickness, and the interfacial thermal resistance.

The first factor is the aspect ratio. The length or aspect ratio (length to diameter ratio) of filler was predicted by using the outcomes of the agglomerate size measurement. The maximum value of the aspect ratio decreases, if the mean size of the agglomerate decreases. Extreme decrease of the aspect ratio will result in destruction on physical properties of polymer composites (Park & Youn 2012).

Besides that, the sizes and thickness of graphene also cause significant effect to the thermal conductivity of graphene based epoxy nanocomposites. The larger and thicker graphene nanofillers caused much greater thermal conductivity improvement. This occurred due to the increased thermal interface resistance as a result of



enhanced phonon scattering at the interfaces of the smaller graphene nanofillers (Fan et al. 2013).

The interfacial thermal resistance represents a barrier to the heat flow and weak contact at the interface result in the thermal resistance to be increasing. As the contact resistance is low the thermal conductivity will be increasing. This shows that the graphene epoxy nanocomposites have better thermal conductivity in low concentration. Van der Waals interactions between graphene result in entangled bundles or rope-like aggregates (Han & Fina 2011). Separation of agglomerated by means of atom functionalization will give higher thermal conductivity, and this can be achieved by treating the graphene under ultrasonication (Han & Fina 2011).

## CONCLUSIONS

In this work, the experiment is divided into three chronological stages according to the variables and preparation condition. Each phase is set to certain variables that need to be tested. Overall, there were 39 specimens prepared for the experiment. The objective is achieved as the obtained results from the experiment is analyzed and compared to the theoretical value. Every experimental data was compared and analysed to the theoretical data which is calculated from the rule of mixture as the upper boundary limit and the series model as the lower boundary limit. The experimental data that lies between the ranges of boundary limits is verified and accepted.

According to the experiment, each sample that was verified from every stage were continuously brought to the next stages. The final variables obtained is the optimum variables that produced the highest and the best thermal conductivity of graphene based epoxy nanocomposites which are 0.3 wt% of graphene loading, 500 rpm of stirring rate and 30 minutes of stirring time. The final thermal conductivity of graphene based epoxy nanocomposites that is verified in this experiment was compared to the thermal conductivity of neat epoxy. From the calculation in Chapter 4, there is 19.53% increment of thermal conductivity. The increase in thermal conductivity of the samples conclude that the addition of graphene to the epoxy resin makes graphene potentially favourable for improving the thermal conductivity properties of polymer matrices in certain variables and conditions.

## ACKNOWLEDGEMENT

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## DECLARATION OF COMPETING INTEREST

None

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