

Preparation of GNPs Thermally Conductive Adhesive at Different Epoxy Resin/Curing Agent Ratio and Mixing Method

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ABSTRACT

Reinforcement of GNPs fillers to polymer composite show remarkable improvement in thermal conductivity. However, high aspect ratio of GNPs attributes to agglomerate during the preparation process, which limits its performance. A proper step methodology is in urgent need to improve the interfacial reaction between the polymer matrix and fillers. The factors that play a significant role during preparation are controlling the epoxy resin/curing agent ratio (stoichiometry ratio) to ensure complete curing reaction and an appropriate mixing and processing method to improve dispersion and distribution of fillers. This study focuses on the effect of varying the ratio of polymer/curing agent to its curing reaction and combining the mixing method with solvent-free approach on the performance of the polymer composite. The results show that a complete curing reaction was observed at its stoichiometry ratio, which is ratio 3:1. The GNPs fillers also founded distribute and disperse well, especially when using BS+PCTM at the ratio of 3:1. This mixing method can avoid agglomeration of fillers and improve the interfacial reaction with good contact between filler-filler interface. As a result, the thermal conductivity of BS+PCTM was enhanced compared to BS+UH. The results presented perhaps facilitated improvement in the preparation of high performance of TCA.

Keywords: Agglomeration, dispersion, distribution, exothermic reaction, mixing method, thermal conductivity

1. INTRODUCTION

The use of Graphene Nanoplatelets (GNPs) as fillers in the recent development of die-attach materials with high thermal conductivity or also known as Thermally Conductive Adhesive (TCA), has attracted both academicians and industrial interest [1–3]. GNPs are known to have a high intrinsic thermal conductivity, electrical conductivity, and mechanical strength owing to their sp² hybridized carbon atom arrangement in a 2-dimensional (2D) lattice. However, GNPs tend to agglomerate/aggregate or stack in the polymer matrix, especially during mixing. The agglomeration/aggregate and stacking usually occur due to the strong Van Der Waals force and the π - π bonding-between the fillers [4,5]. On account of that, graphene was mentioned cannot be dispersed well in a polymer matrix just by a simple mixing method [6]. Hence, a proper methodology is needed to induce a good distribution and dispersion of GNPs fillers in the polymer matrix when preparing the composite formulation.

Multitudinous exploration has been put forward to achieve homogenous and thorough dispersion of GNPs during the TCA preparation by using different mixing and processing

methods [7–9]. Obviously, different mixing and processing methods would result in different dispersion of GNPs in the polymer matrix. The examples of mixing methods used are direct and indirect mixing. Ball-milling, ultrasonic homogenizer, mechanical stirring, and shear mixing [10] are examples of direct mixing. The mixer rotor/ probe and a stator produce a shear force that has direct contact with the composite. In comparison, indirect mixing like bath sonication [6] and planetary centrifugal mixing [11,12] are using ultrasonic energy or centrifugal force, which gives less damage to the fillers when dispersing the fillers.

Previous studies have shown that direct mixing can prevent the agglomeration of GNPs and help to exfoliate the graphene layers, which provides a good interface between the GNPs and polymer [13]. Unfortunately, it also may cause fragmentation of fillers, which is reduce the size of GNPs fillers. This occurrence basically may increase the number of defects in fillers and distorted the properties of fillers.

In fact, the use of small filler size in polymer composite is also not encouraging since it can create a high interfacial area between the fillers and polymer matrix, which increases the interface thermal resistance and simultaneously slanted its thermal conductivity [14–17]. It has been proven by a study conducted by Zhou *et al.* where smaller filler sizes exhibit low thermal conductivity compared to larger filler sizes due to the small contact area between filler-filler and larger interfacial with the polymer matrix [18]. It could be seen that direct mixing is not the best option for high distribution and dispersion with good thermal conductivity performance than indirect mixing since this method gives less damage to the fillers [19].

Other than the mixing method, the processing method also greatly influences the dispersion of GNPs. The processing method is essential to enhance the dispersion of the composite during mixing to improve its properties. Using a surface modifier during the mixing is one of the common processing methods used during mixing. This method is also known as an acid treatment, which involves a surface modification using a solvent solution to functionalize the conductive fillers such as KH-560 [20] and KH-550 [21,22]. The modification might reduce the interface thermal resistance between the filler and polymer, which helps to improve TCA performance. However, this method tends to create a defect and voids to the fillers and requires high-power energy for a uniform stirring [23].

The use of solvents, especially from alcohol-based like ethanol and acetone [24], are also commonly used during the mixing process as some mixing methods required a low viscosity solution to mix, for example, is solution mixing method [25]. However, it should be noted that the solvent needs to be removed entirely before mixed with the polymer matrix as it may influence the conductivity of the composite. Hence, a lot of published researches indicates that using a solvent-free processing method is preferable as it can shorten the processing duration and complexity [12,26–28].

With the fact mentioned earlier, combining two types of mixing method with solvent-free processing can be a solution to enhance the GNPs homogeneity in the polymer matrix. Gupta and his co-worker investigate the effect of filler dispersion by combining the mixing method over a single mixing method only. The mixing methods used in their study are microfluidizer, planetary shear mixer, and ultrasonication. The results demonstrated a better dispersion with only a small aggregation when combined mixing method [ultrasonic and planetary shear mixing; microfluidizer and planetary shear mixer] was used compared to the single mixing method used. The tensile properties were observed to increase when the combination method of ultrasonic and planetary shear mixer methods was used [27].

A similar observation was demonstrated by Wang *et al.*, where the combination mixing method used shows a significant improvement in dispersion homogeneity without the help of solvent. However, to the best of the author's knowledge, there are still limited sources in reports study

on combined mixing methods with a solvent-free method that initiated the motivation for this study. The contribution of this study is prominent, as the resulting outcome can be capitalized as a guideline to combine two mixing methods with a solvent-free method and able to achieve good performance.

Table 1 is the summary of the mixing method used in past studies with the advantages and disadvantages to provide a general guideline in choosing the right mixing and processing method.

Table 1 Summary of the mixing method

Mixing Method	Medium of Mixing	Solvent	Advantages	Disadvantages	Ref
Probe sonicate [UH]	Ultrasonic energy	Need a solvent to be low viscosity for mixing	<ul style="list-style-type: none"> • Break-down the agglomeration 	<ul style="list-style-type: none"> • Direct mixing may cause fillers fragmentation • Increase the number of defects • Longer process 	[19,25,29]
Bath sonication	Ultrasonic energy	Optional to use solvent	<ul style="list-style-type: none"> • Inexpensive equipment • Simple processing 	<ul style="list-style-type: none"> • Not suitable for high viscosity 	[19]
High-shear mixer	High shear force and centrifugal force from rotor blade and stator	Need solvent to minimize the shear energy	<ul style="list-style-type: none"> • It can be scaled up for large-quantity production • Break-down the agglomeration 	<ul style="list-style-type: none"> • Fragmentation of fillers • Improve distribution 	[10]
Ball milling	High shear force and compressive force	Not required	<ul style="list-style-type: none"> • Can achieve in situ exfoliation, dispersion • Not damage the crystal structure of the filler 	<ul style="list-style-type: none"> • Reduce the filler size 	[30]
Melt Mixing	Melted with the presence of inert gas	Not required	<ul style="list-style-type: none"> • In-situ polymerization • Compatible with current industrial processes 	<ul style="list-style-type: none"> • High cost • Time-consuming 	[31-32]
Solution Mixing	-	Required	<ul style="list-style-type: none"> • Low viscosity solution and easy to disperse during mixing 	<ul style="list-style-type: none"> • Used copious of solvent 	[19]

Though, it is essential to note that choosing the right mixing and processing method is not the only factor that should be emphasized during TCA preparation. Understanding the polymer matrix properties to be used, such as its curing temperature properties and curing time, is also vital as different polymer matrix types exhibit different properties. The most common polymer matrix used in TCA preparation is the thermoset epoxy resin. Epoxy resin, also known as polyepoxides, has been widely used in many applications due to its most flexible and universal high-performance polymer that offers low-cost [33–36]. Nowadays, the combination of conductive fillers, especially GNPs with epoxy resin, has led to a new nanocomposite class for advanced engineering applications such as in electronic packaging, solar-cell, and stretchable conductive ink [15].

Nevertheless, the epoxy resin must be cured for the cross-linking process before it can be used as a product. The curing can be achieved by reacting the epoxy with itself [homo-polymerization] or forming copolymerization by mixing the epoxy resin with a curing agent. The common classes of curing agents are including amines, acid, anhydride, phenol, and thiols. However, it should be noted that the amount of curing agent added into the epoxy resin will affect the cross-linked between both materials as well as its mechanical properties. The addition of a curing agent into the epoxy resin will cause heat release or an exothermic reaction, which results from polymerization. The polymerization process also can speed up by initiating with catalysts such as UV light or ambient temperature, but it has very low and limited reactivity. Thus, the most typical curing reaction method is by exposure to the heat as this approach is faster to achieve complete cross-linked and convenience.

It should be noted that the amount of heat should be sufficient to ensure a complete exothermic curing reaction. Insufficient heat during the curing will result in a network with incomplete polymerization or cross-link, thus may reduce the mechanical, chemical, and heat resistance of the composite performance. On the other hand, some researchers mentioned that the curing procedure depends on the precise combination of resin with a curing agent or catalyst [35]. If the heat is sufficient but incorrect combination of epoxy resin and curing agent or catalyst, the curing process will be incomplete. It cannot form a cured thermoset epoxy resin. Therefore, the right combination of epoxy resin and curing agent is significant to ensure a complete cross-linked thermoset epoxy resin during curing reaction.

Theoretically, most researchers are using a stoichiometric ratio to predict the optimum amount of epoxy resin to the curing agent, as expressed in Eq.1 [37,38]. The stoichiometric ratio is the ratio between epoxy equivalent weight (EEW) to the amine equivalent weight (AEW) ratio, where EEW and AEW were calculated when the average molecular mass of epoxy and curing agent is divided by the number of epoxy groups and active hydrogen, respectively.

$$\text{Stoichiometric Ratio} = \text{EEW} / \text{AEW} \quad (1)$$

This paper attempts to provide a more detailed investigation of the effect of different epoxy resin/curing agent ratios using two different mixing methods. There is no solvent involved during the preparation of GNPs TCA. The present study is motivated by the need to consider the correct methodology before prepared a highly thermal conductivity TCA. The thermal properties of epoxy resin/ curing at different ratios were analyzed before cured at different curing times. Besides, the cross-linked thermoset epoxy resin by hardness testing, the thermal conductivity of GNPs TCA, and the dispersion of GNPs in the polymer matrix when using different mixing methods also have been extensively explored.

2. METHODOLOGY

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2.1 Raw Materials

Graphene Nanoplatelets (GNPs) with a particle size of 5 μm (M5), a surface area of 120-150 m^2/g (Grade M) and a layer thickness of 6-8 nm was used as a conductive filler. Meanwhile, an epoxy resin (ER) Araldite 506 with a density of 1.168 g/cm^3 was used as a binder with 178.5 epoxy equivalent molar mass. Both GNPs and epoxy resin were purchased from Sigma Aldrich,

while the curing agent JEFFAMINE D-230 polyester amine with a density of 0.948 g/cm³ was obtained from Huntsman Singapore Pte Ltd. The curing agent has an amine hydrogen equivalent molar mass of 60 g/ mol.

2.2 Mixing Preparation

The study of GNPs TCA involved two formula preparations; epoxy/curing agent at a different ratio and GNPs filled epoxy/curing agent at a different ratio. The sample preparation of the epoxy/curing agent was done at the following ratios; 1:1, 2:1 and 3:1. The mixture was weighed by using an analytical balance Mettler Toledo and mixed slowly using a hand to prevent air bubbles until the mixture from cloudy turned into a crystal clear mixture, as shown in Figure 1. Next, the mixture was poured into the silicon mold and left at elevated temperature for at least 12 hours for air bubble removal. This step is crucial to ensure that the air bubble was removed entirely. The samples were then placed into the Memmert UF55 Oven with various curing times (30 min, 1 hour, 2 hours, and 3 hours) before undergoing hardness testing.

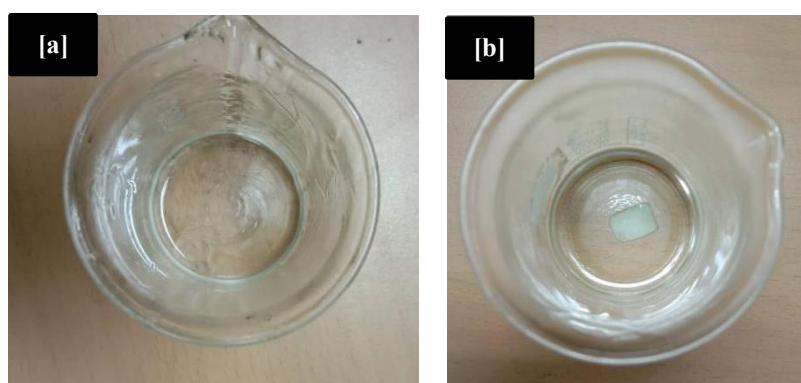


Figure 1. Epoxy resin/ curing agent mixture, (a) cloudy and (b) clear

The mixing method's effect was studied by adding 3 wt.% of GNPs filler into the polymer matrix containing different epoxy resin and curing agent ratios, as shown in Table 2. The epoxy resin, curing agent, and GNPs filler were precisely measured before added accordingly. Throughout this study, the double mixing method was used. Epoxy resin was initially mixed with GNPs filler using GT SONIC bath sonication (BS) as pre-mixing for 1 hour before mixing with curing agent by using either LABSONIC® P Ultrasonic Homogenizer (UH) or Planetary Centrifugal Thinky Mixer ARE-310 (PCTM) for another 15 minutes. Then, the GNPs TCA paste was poured into the silicone mold for thermal conductivity testing, while for electrical testing, the paste was printed on the glass slide by using Mr. Blade method.

Table 2 Formulation for GNPs TCA

Sample Name	GNPs		Polymer matrix (wt%.)				Ratio	Mixing method
	(wt%.)	(g)	Epoxy Resin		curing agent			
			(wt%.)	(g)	(wt%.)	(g)		
1	3	0.15	48.50	2.43	48.50	2.43	1:1	BS+ PCTM
2	3	0.15	64.67	3.23	32.33	1.62	2:1	
3	3	0.15	72.74	3.637	24.25	1.21	3:1	
4	3	0.15	48.50	2.43	48.50	2.43	1:1	BS+PCTM
5	3	0.15	64.67	3.23	32.33	1.62	2:1	
6	3	0.15	72.74	3.637	24.25	1.21	3:1	

2.3 Characterization Methods

2.3.1 Thermal Properties

Differential Scanning Calorimetry (DSC) was done as a preliminary characterization to investigate the curing reaction [exothermic reaction] of epoxy resin and curing agents at different ratios. The exothermic curing peaks of the epoxy and curing agent composition at different ratios will be a guideline for the heating process of GNPs TCA. The DSC used in this study is a DSC Q20 brand TA instrument with a sample weight of ~10mg in an Al open pan. The analysis was performed with the heating rate of 10°C/min in a nitrogen atmosphere. Table 3 shows the description of five samples prepared for DSC testing at different ratios (epoxy resin: curing agent).

Table 3 Description of samples for DSC testing

Sample 1	Pure epoxy resin (ER)
Sample 2	Pure curing agent (CA)
Sample 3	1:1
Sample 4	2:1
Sample 5	3:1

2.3.2 Mechanical Properties

Shimadzu Micro Hardness Tester HMV-G21 with Vickers indenter was used to test the hardness of the epoxy resin/curing agent mixture without filler. This test was done to indicate the cross-link of GNPs TCA when cured at different curing times. The Vickers hardness was obtained using Eq. 2, where the test force is $F = HV \cdot 0.5$ [1.96N] when the indentation is formed in the surface, and the average length of the diagonal lines in the indentation denoted as d . The indentation was measured using the digital image obtained by the CCD camera. The captured image was displayed on the PC for manual reading using cursor bars. The reading was repeated three times for each sample. Figure 2 shows the indentation of Vickers Indenter of Shimadzu Micro Hardness Tester HMV-G21.

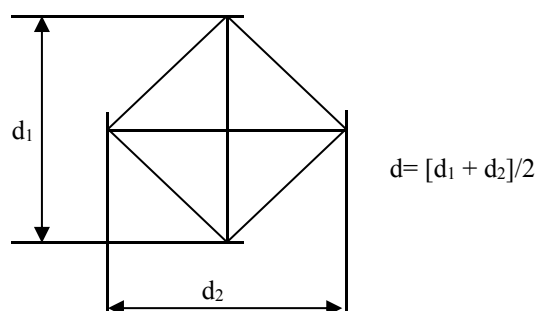


Figure 2. The indentation of Vickers indenter.

$$HV = 0.1891 \frac{F}{d^2} \quad (2)$$

2.3.3 Surface Morphology

Scanning Electron Microscopy (SEM, JEOL) was done to understand GNPs fillers' distribution and dispersion in the epoxy matrix at different mixing methods and ratios. The findings were correlated with its thermal properties.

2.3.4 Thermal Conductivity

This test was measured using KD2 Pro Thermal Properties Analyzer. It consists of a handheld controller and sensor that inserted into the sample. The sensor used for this measurement is the TR-1 thermal conductivity/ resistivity sensor, which is for solid material. The temperature range during the measurement is in between 27°C to 29 °C. The KD2 Pro measures the thermal conductivity using the transient line heat source method during measurement that complies with IEEE Standard 442-1981 and ASTM Standard D5334-08.

3. RESULTS AND DISCUSSION

3.1 Thermal analysis of polymer curing reaction

Figure 3 shows the differential scanning calorimetry (DSC) curve to explain the thermal properties of pure epoxy resin, pure curing agent, and epoxy resin/curing agent at different ratios. Curve 1 for pure epoxy resin shows the glass transition (T_g) of 27.60°C and for pure curing agent (Curve 2) is at -47.3 °C. Neither of the measurements indicated an exothermic curing peak, which means no curing reaction occurs [39].

Meanwhile, as the curing agent was added to the epoxy resin, the resin eventually starts to cure as an exothermic curing peak can be observed in curves 3, 4, and 5. The exothermic curing peak indicates the maximum rate to cure the epoxy resin. For the ratio of 1:1, the exothermic curing peak was observed at the temperature of 119.8°C (Curve 3). The curing reaction also was noticed started even at room temperature. The same occurrence can be seen for curve 4 (2:1) and curve 5 (3:1), with the exothermic curing peak at 129.0°C and 129.1°C, respectively. Thus, from the DSC analysis result, it is essential to add a curing agent to cure the epoxy resin. Besides, this analysis also provides insightful information about curing temperature. In order to ensure a complete curing process, it is essential to cure solutions according to their exothermic curing peak as a different ratio of polymer and curing agent provides a different temperature of exothermic curing peak.

The results in Figure 3 also show that increasing the epoxy/curing agent ratio will increase exothermic heat to cure the composition. The area under the exothermic peak represents the exothermic heat required to cure the composition [40], and the ratio 3:1 shows the largest needed exothermic heat. This is because increasing the polymer amount will require more energy, leading to a complete polymerization reaction [41].

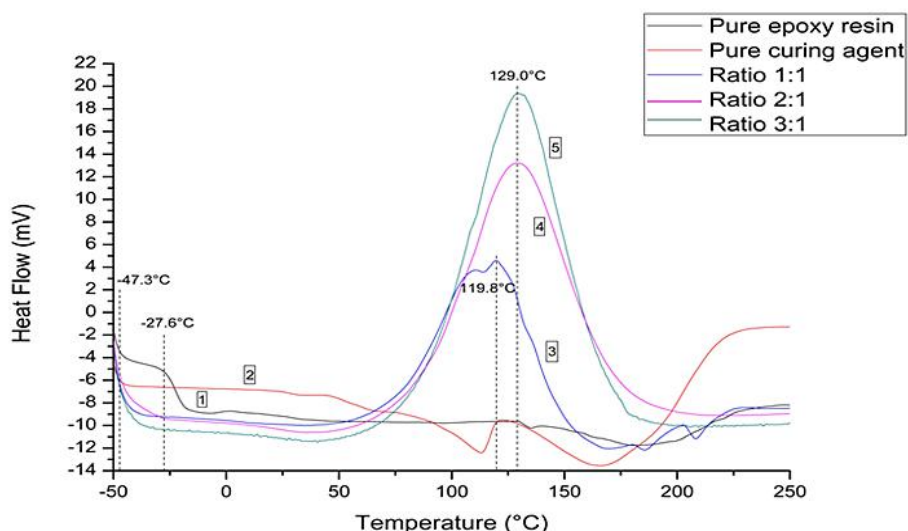


Figure 3. DSC curve of epoxy resin and curing agent at the pure condition and different epoxy resin/ curing agent ratio.

3.2 Vickers Hardness

The Vickers hardness test was done to measure the hardness of the epoxy resin/curing agent mixture at different ratio and curing time. However, at the ratio of 1:1, the epoxy resin/curing agent mixture is still in the liquid phase despite the samples was heated to its maximum heating temperature at 119 °C for 30 minutes, 1hour, 2 hours, and 3 hours. Figure 4 [a] shows the uncured epoxy resin and curing agent mixture at the ratio of 1:1. The uncured mixture was believed due to the excess amount of curing agent that was not cross-linked with epoxy resin.

This is closely related to the stoichiometry ratio between epoxy and curing agent. Curing agent Jeffamine D-230 is a diamine hardener with four active hydrogens atoms, while the epoxy resin has two epoxy groups. Alhabil *et al.* stated that one amine group should react with two epoxy groups for a complete polymerization to occur. That means the amount of epoxy resin used should be higher than the curing agent. Table 4 shows the stoichiometric ratio calculated for this study. It was found that the optimum amount of epoxy resin to the curing agent for maximum polymerization rate is at the ratio of 3:1, where 30 parts of curing agents are needed to cure 100 parts of epoxy resin. Thus, ratio 1:1, which is under stoichiometry ratio, shows that there is not enough epoxy resin to react with the curing agent, leading to a large amount of unreacted curing agent. It was expected that there is an excess in curing agents and almost half of the amine group left unreacted, which causes incomplete cross-linking between the epoxy resin and curing agent. Hence, the composition is not hardened, and no hardness measurement can be reported.

Table 4 Stoichiometric Ratio

Stoichiometric Ratio of Epoxy Resin 506/ Curing agent JEFFAMINE D-230	$\text{phr} = \frac{178.5 \text{ (g/eq.)}}{60 \text{ (g/eq.)}} \times 100$ $= 30.0$
$\text{phr} = \frac{\text{AHEW of Curing Agent} \times 100}{\text{EEW of Epoxy Resin}}$	Therefore, 30 parts of curing agents are needed to cure 100 parts of epoxy resin
Ratio 1:1	Under Stoichiometry
Ratio 2:1	Under Stoichiometry
Ratio 3:1	Stoichiometry

The same occurrence can be seen for ratio 2:1, where the composition was observed not fully cured and at an elastic phase. This phenomenon has been confirmed when undergoing hardness testing. After a few seconds of indentation, the indentation marks gradually disappear and return to their original state, as shown in Figure 4 (b) and (c). No hardness value had reported and obviously showed that the 2:1 sample is in an elastic and rubbery state.

This is due to the fact that ratio 2:1 is under stoichiometry ratio, which causes small amounts of uncured epoxy and unreacted amine groups present in the sample that leads the sample to be partially complete. It is agreed by Alhail and his co-workers, where it is likely due to some of the amine group only being reacted with only one of their active hydrogen atom. Therefore, it relatively produces a flexible linear cross-link node, which causes the 2:1 composition in the rubbery state [42]. This phenomenon has caused the increased rotational and conformation motion of the sample. The research study by Altuna et al. also reveals similar results as excess in amine groups form pendent chains and lead to a plasticizing effect [43]. Thus, it is explained how the indentation returned to its original state after a few seconds of indentation, and no hardness was reported.

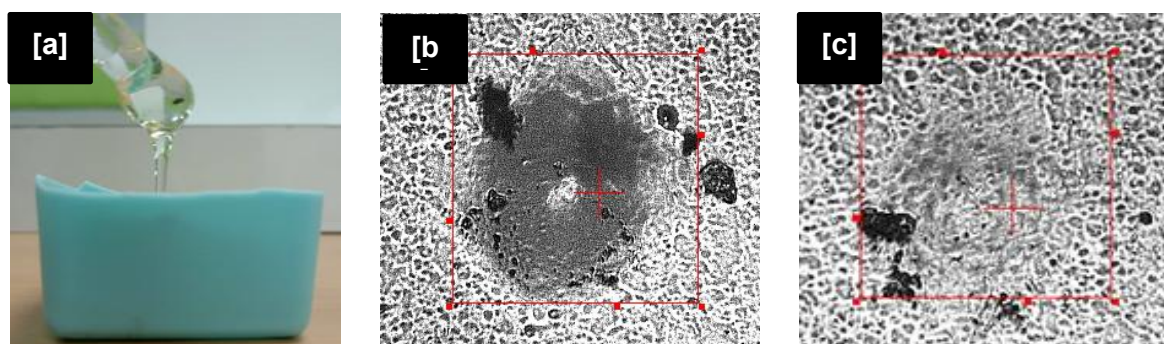


Figure 4. (a) uncured mixture of 1:1 ratio; indentation marks of 2:1 ratio after and (b) 1s (c) 3s.

Meanwhile, the sample 3:1 ratio shows fully cured samples after curing at the exothermic curing temperature of 129 °C at varying curing time. Since ratio 3:1 is at stoichiometry ratio, a complete polymerization and curing reaction could be achieved. All epoxy and amine groups are expected to react fully to each other and form a fully cross-linked network for all 3:1 samples.

The cross-linked reaction also occurs between the hydroxyl group bonding with another epoxy group and forming an ester bond. The hydroxyl group is formed through the reaction between the epoxy and amine groups. In addition, the epoxy group also bonded with themselves to form a complete polymer chain. The complete cross-linked reaction between the epoxy resin and curing agent is illustrated in Figure 5, where each terminal of the amine group was attached with two epoxy groups and formed the hydroxyl group.

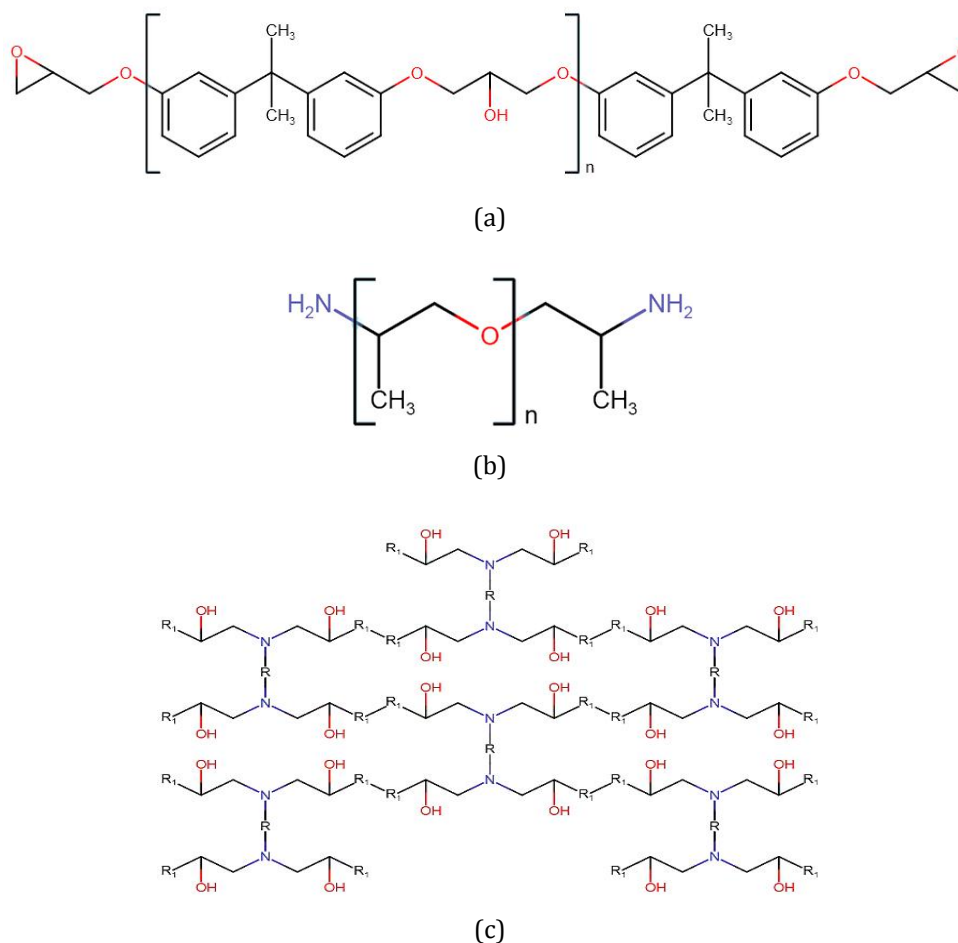


Figure 5. Chemical structure of (a) Epoxy resin 506 (b) JEFFAMINE D-230 and (c) Cross-linked of epoxy resin and JEFFAMINE D-230.

To further confirm this hypothesis, a hardness test was done to evaluate the degree of polymerization known as the cure level for ratio 3:1 [44,45]. The graph in Figure 6 shows that the hardness value is directly proportional to the curing time. The hardness was observed to increase from HV=3 to HV=7 after curing the sample for 30 minutes and 3 hours. The increase of the hardness was believed due to the increase of conversion and cross-linking between the epoxy resin and curing agent over time [46]. A higher degree of conversion allows more carbon with a double bond change to a single bond in the polymer chain, allowing more bonded between epoxy and amine groups, especially with temperature. It will cause a packed cross-link density of composition and a high level of cure [network] formed, restricting molecules' movement in the polymer system. Consequently, the hardness of the surface increases over time, which also enhanced the mechanical properties of the composition.

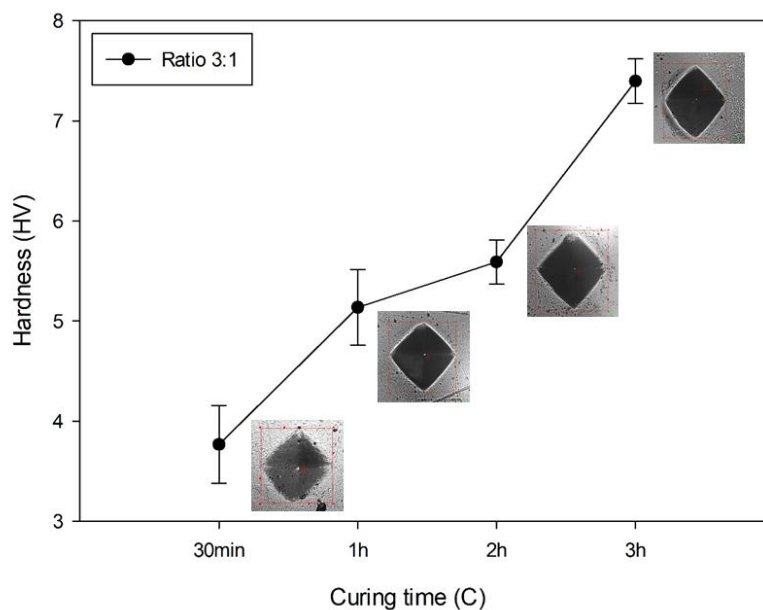


Figure 6. Vickers hardness and indentation marks for 3:1 ratio.

3.3 Distribution and Dispersion of GNPs Filler in Polymer Matrix

The study on the effect of different ratios between the epoxy resin and curing agent was further explored with the inclusion of conductive filler GNPs into the polymer matrix at 3 wt% using two different mixing methods. The mixing method is one of the factors that should be considered during the preparation of homogenous TCA. This study focused on the use of 2:1 and 3:1 only as at the ratio of 1:1; the sample is not cured (liquid phase).

Figures 7 and 8 show the surface morphology of GNPs dispersion in the polymer matrix at different ratios and mixing methods at x700 (a and c) and x2000 (b and d) magnification. In general, the results indicate that using the combining method of BS+PCTM gives a higher dispersion of GNPs in the polymer matrix than BS+UH. The apparent finding can be observed, especially when the ratio of epoxy resin and curing agents used is 3:1, as shown in Figure 7 (c and d). This observation is in agreement with Shtein, where GNPs are distributed well when using a planetary centrifugal mixer as this method lacks mechanical blades and mixed the composite through the centrifugal force due to the revolution. It is believed as an effective method to enhance filler dispersion homogeneity through the elimination of air trapped in the composite [11].

Interestingly, a contrary finding was obtained when mixed the GNPs into epoxy resin/agents using a BS+PCTM at the ratio of 2:1. The GNPs were observed agglomerates as shown in Figure 7 (a and b), and the main factor was believed due to fast curing reaction, giving a difficult to mix the composition using BS+PCTM. Both BS + PCTM are bladeless, which cause requiring a sufficient amount of time to achieve homogenous dispersion. However, as the curing agent was added to the epoxy resin, the exothermic reaction started to eventuate even at room temperature. The molecular chain of epoxy resin is started to fix in a short time, which causes the epoxy resin to be cured and hinder the GNPs filler from further disperse for ratio 2:1. This can be proved by the result obtained in DSC analysis where the amount of heat required for exothermic reaction to take place is less than 3:1, which indicates faster reaction occur for ratio 2:1.

Consequently, the fast curing process will limit the time for dispersion of GNPs to occur in 2:1 composition that significantly causes the agglomeration. It is also agreed by Patel et al. as the

fast curing will result in non-homogenous distribution of filler in the composite. In addition, it also leaves the composition to be partially cured and in a soft phase, as can be observed in ratio 2:1. This observation coincides with the previous results obtained in hardness testing for ratio 2:1, where it is found in a rubbery state.

Even so, the agglomeration of ratio 2:1 when using BS+ PCTM can obviously observe as the level of roughness is too high compared to ratio 3:1. It should be noted that the white region corresponds to GNPs fillers.

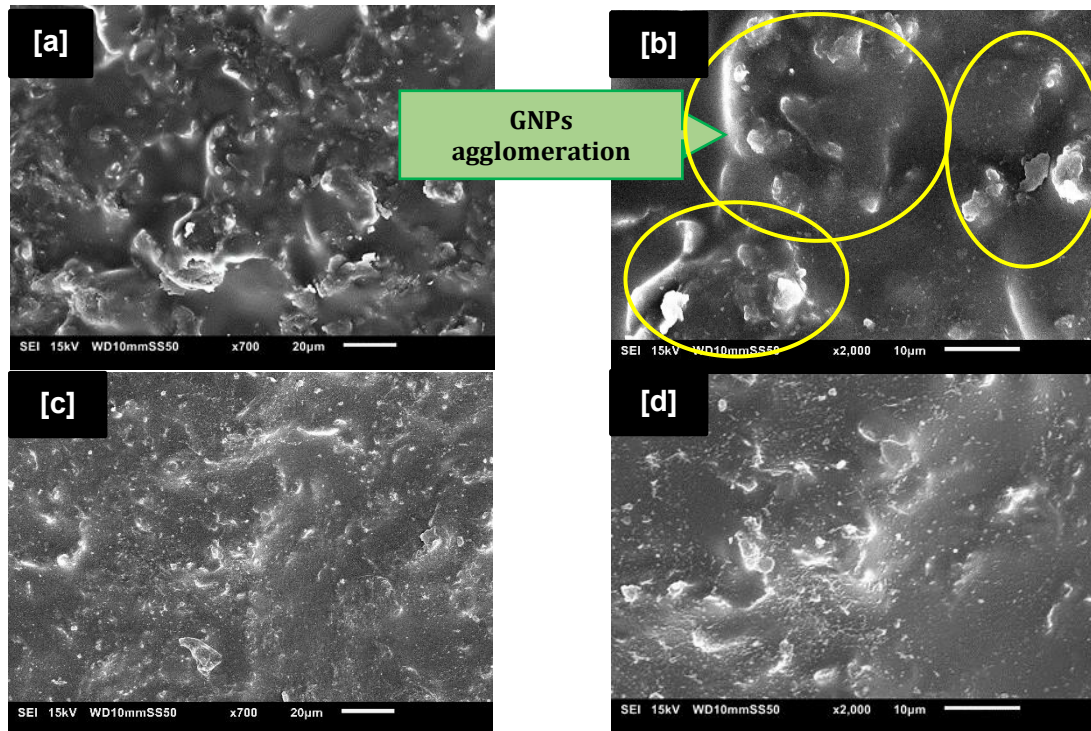


Figure 7. Mixing of GNPs and polymer matrix by using Planetary Centrifugal Thinky Mixer at the ratio of (a) 2:1 (x700), (b) 2:1(x2000), (c) 3:1 (x700) and (d) 3:1 (x2000).

Figure 8 present the surface morphology of GNPs when mixed by using BS+UH at the ratio of 2:1 and 3:1. It appears at the ratio of 2:1, the GNPs were observed agglomerate as shown in Figure 8 (a and b), but the size of agglomeration is smaller than when mixed by using BS+PCTM (Figure 7 (a and b)). It was believed due to the direct mixing process of the UH method. UH generates an ultrasonic energy wave from its probe sonicator that directly passes through the agglomeration of GNPs. Therefore, it is started to cause agitation during the mixing process and simultaneously causes agglomeration to break down into a smaller size. Even so, since the ratio 2:1 is a fast curing, the facilitation of ultrasonic energy from the UH probe to break the agglomeration entirely is limited, leading to poor distribution and poor dispersion of GNPs in the polymer matrix.

However, Figure 8 [c and d] shows that mixed GNPs in the ratio of 3:1 of polymer and curing agent using BS+UH attributes to a good distribution of filler but poorly dispersed. As similar in the ratio of 2:1, the wave energy produced agitated the agglomeration of GNPs into a smaller size. However, since the ratio 3:1 is not fast curing as the ratio 2:1, the probability of the wave energy to break the GNPs agglomeration is high. It also can be seen that the GNPs agglomeration can even turn into a monodispersed state where individual GNPs fillers are completely separated from each other and distribute evenly in the polymer matrix.

Unfortunately, the individual GNPs was observed break-off into smaller size or also known as fragmentation. This is because GNPs layers were held weakly by van der wall force. As the ultrasonic energy produced passes through the fillers, it eventually causes the Van der wall force between the GNPs interlayer to break easily. As a result, it reduces the aspect ratio of GNPs fillers and may increase the number of defects in GNPs filler due to the fragmentation. The present finding also supports Zhang et al. study, which concludes that fragmentation tends to destroy the structural integrity of GNPs during the ultrasonic mixing as it may increase the dangling bond [C-atom] in the honeycomb structure of GNPs, which decrease the GNPs performance [29]. Basically, sonication power produce by the probe sonicator is known to damage the GNPs as the mechanical vibration amplitude generates, resulting in shear force and shockwave and directly in contact with the fillers. Theoretically, reduce in size may help to increase the homogeneity of GNPs in the polymer matrix. It is also not encouraging as this may distort the properties of the filler and simultaneously affect its performance, including its thermal, electrical, and mechanical performance. The reduction of size is not even for every filler, which causes it to have poor dispersion.

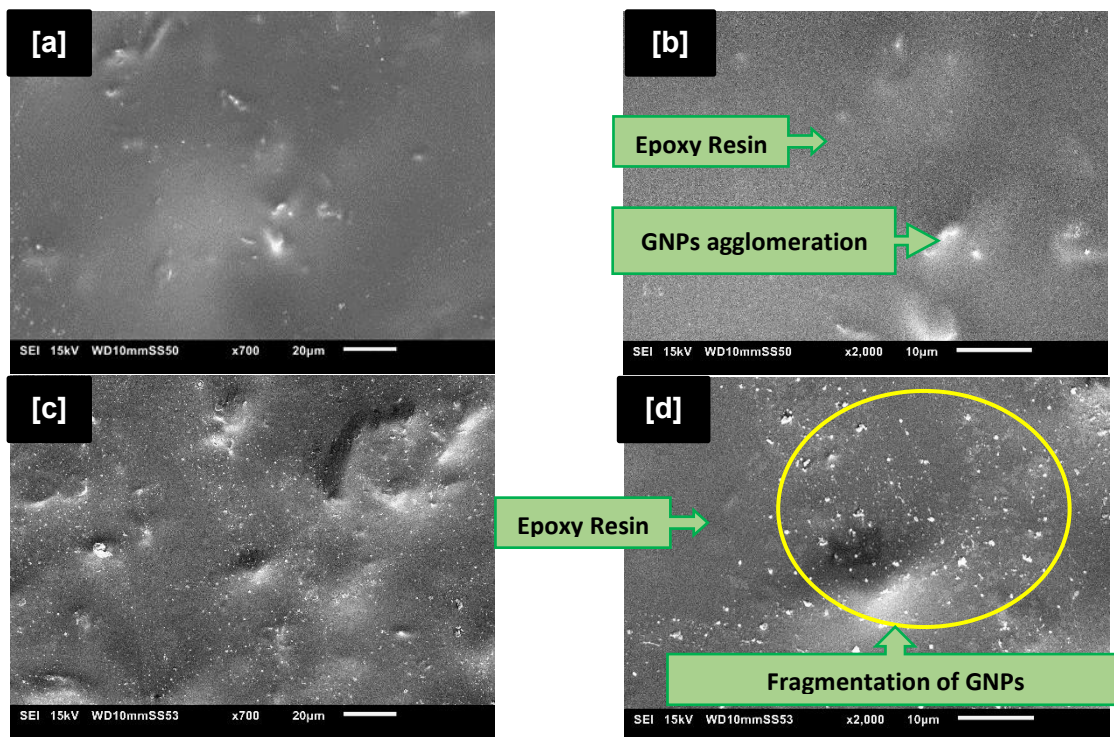


Figure 8. Mixing of GNPs and polymer matrix by using Ultrasonic homogenizer at the ratio of (a) 2:1 (x700), (b) 2:1(x2000) and (c) 3:1 (x700), (d) 3:1 (x2000).

In order to achieve maximum enhancement of polymer composite properties, the fillers should be dispersed and distributed well. Otherwise, it may lead to agglomeration of particles at which will deteriorate the composite properties. This study indicates that using different stoichiometry ratios and mixing methods significantly affects the distribution and dispersion of GNPs filler in the polymer matrix.

The most apparent finding that emerged from this study is that the GNPs fillers can distribute well in polymer binder and curing agent at the ratio of 3:1. Meanwhile, using BS+PCTM as a mixing method can enhance the dispersion of GNPs in polymer composite compared to the BS+UH method. However, at the ratio of 2:1, it should be noted that the GNPs tend to agglomeration either using BS+ PCTM or BS+UH.

Figure 9 shows the illustration of distribution and dispersion of GNPs fillers in the polymer matrix at different ratio and mixing method of this study, (a) good distribution, poor dispersion (b) good distribution, good dispersion (c) poor distribution, poor dispersion (d) good distribution, poor dispersion. The evidence from this study makes a noteworthy suggestion that the distribution and dispersion of GNPs fillers can be improved by mixing it with polymer and curing agent at the ratio of 3:1 by using BS+PCTM.

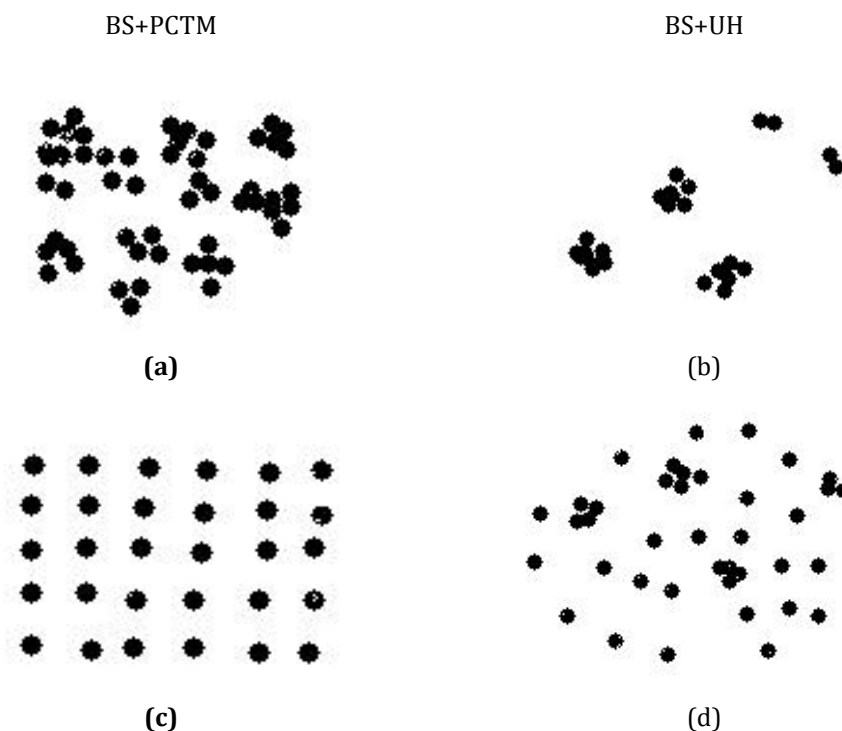


Figure 9. Illustration of distribution and dispersion of GNPs fillers at stoichiometry ratio (a)(b) 2:1 and (c)(d) 3:1.

3.4 Thermal Conductivity of GNPs Polymer Composite

Figure 10 shows the thermal conductivity of GNPs TCA. It was observed that the thermal conductivity of BS+PCTM and BS+UH increase with the increase of epoxy resin and curing agent fraction. However, BS+PCTM indicates the highest thermal conductivity reported significantly at the ratio of 3:1, where the thermal conductivity was increased from 0.733 W/mK to 1.662 W/mK. For BS+UH, the thermal conductivity was increased from 0.253 W/mK to 0.336 W/mK at the ratio of 2:1 and 3:1, respectively.

The difference in the thermal conductivity reported for each composition is in conjunction with the distribution and dispersion level of GNPs fillers in the polymer matrix, as shown in Figures 7 and 8. The higher the level of distribution and dispersion, the higher the thermal conductivity. Such observation is indicated by the ratio of 3:1 when using BS+PCTM as shown in Figure 7 (c-d), where the GNPs are evenly distributed and dispersed, which increases the thermal conductivity of GNPs TCA composite. This is because good distribution and dispersion of fillers will create more contact areas or conducting network between fillers.

Apart from that, the larger GNPs (macroscale) size was also believed to contribute to the increase of thermal conductivity in the composite as the heat can be transferred smoothly. It is agreed by Liu *et al.* [47] and Rad *et al.* [48] that increasing the filler size increases the heat to be transferred. The PCTM method used during mixing will prevent any damage or defect to the

fillers during the mixing process as this method only uses centrifugal force to mix the composite. Hence, it was expected that the size of GNPs is preserved during mixing, which amplifies the thermal conductivity value compared to other ratios or method.

Meanwhile, the use of the BS+UH method at the ratio of 3:1 shows a good distribution but poor dispersion of GNPs in the composite. By considering this factor, the thermal conductivity obtained is lower than the value obtained during mixing with BS+PCTM at the same ratio. As mention earlier, the GNPs were fragmented during the mixing process, which significantly distorted the performance of GNPs. Consequently, the GNPs have a poor filler-filler contact, which contributes to high thermal contact resistance due to the break-off of GNPs into small pieces. The smaller in filler size also creates a high interfacial area with a polymer matrix, leading to thermal boundary resistance. These factors were believed to be responsible for low thermal conductivity.

The finding is consistent with the study by Li et al., in which small filler size attributed to high thermal contact resistance and thermal boundary resistance. Both phenomena are known as interface thermal resistance, at which these occurrences limited the heat transfer. Phonon, which is the primary heat carrier in the polymer composite, started to scatter due to mismatch between the bodies and differences in polymer and filler density when the interface thermal resistance is high [49]. By default, an increase in phonon scattering may reduce the thermal conductivity as experience by BS+UH at 3:1.

In solid materials, the heat was transported by lattice vibration waves, known as phonon, or by free electrons predominant by one of these mechanisms. For GNPs polymer composite, the heat transfer is dominant by phonons and relatively few free-electron present. The sum of these two contributions determines the thermal conductivity value (k), as shown in eq. 3;

$$k = k_l + k_e \quad (3)$$

Where k_l represents the lattice vibration [phonon] and k_e is electron thermal conductivities.

The phonon transfers the thermal energy when the first layer forms vibration and continuously transfers to the neighbouring atoms. That is why a good distribution and dispersion of GNPs is significant to allow phonon to pass more easily.

At the ratio of 2:1, the distribution and dispersion level of GNPs in the composite is poor, leading to agglomeration for both mixing methods. It reflects the thermal conductivity obtained, which is much lower than in 3:1 in the magnitude of 0.08 and 0.9 for BS+UH and BS+PCTM. During the preparation of polymer composite, researchers always put an arduous work to avoid the agglomeration as it always leads to a decrease in thermal conductivity. Agglomeration of GNPs is formed due to its large aspect ratio. Besides, the strong van der Waals force and electrostatic interaction between the nanofillers also mention causing the agglomeration. Even though the van der Waals force is considered a weak intermolecular force, it has become significant at the nanoscale as it depends on its surface area per unit mass of fillers [7].

It is worth noting that the agglomeration causes the weak contact area between filler-fillers interface or define as high in thermal contact resistance, which leads to the phonon scattering and simultaneously discontinued the conduction network path. However, there is a case where heat can be transfer through the agglomeration of fillers. This implies only when the agglomeration forms clusters and creates a heat transfer pathway through contact between these clusters [50].

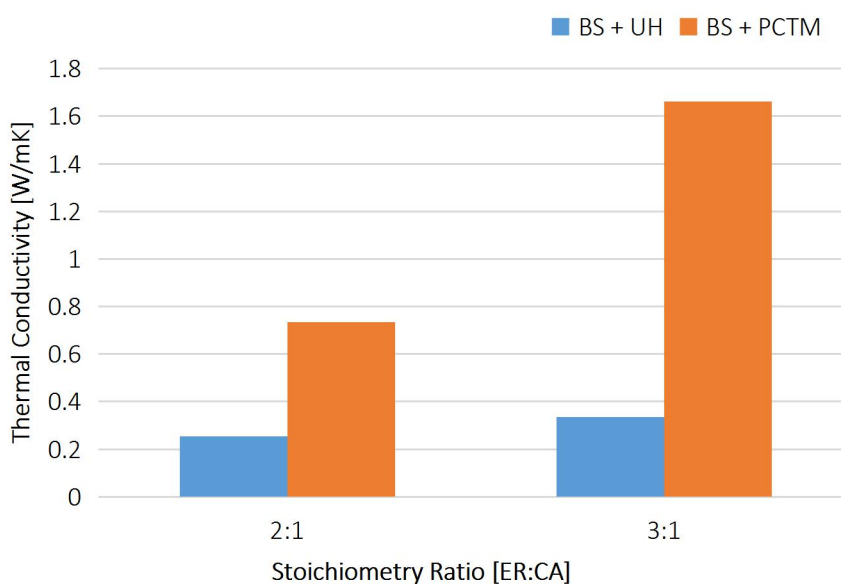


Figure 10. Thermal conductivity of GNPs TCA.

4 CONCLUSION

This paper is an effort to contribute to the current literature to enhance thermal conductivity by improved its interfacial interaction with the right preparation methodology. The study was set out to determine the effect of different epoxy resin/curing agent ratios with different mixing methods on the curing reaction and the distribution and dispersion of GNPs. In summary, the critical conclusion drawn from this study is that the different ratio of epoxy resin/curing agent significantly influenced the curing process where it will exhibit different exothermic curing peak. Even so, for a polymer to be cured entirely, it is vital to mix the polymer and curing agent at the stoichiometry ratio. In this study, it was founded that the mixture is completely cured at the ratio of 3:1, which corresponds to the stoichiometry ratio.

Epoxy resin is already known as a thermoset polymer matrix. The curing agent was used as an additive in formulating TCA to help the epoxy resin polymer cure with the presence of temperature. However, if the fraction ratio used between the epoxy resin and curing agent during the formulation is not enough, the composition is not fully cross-linked even though it was exposed beyond its curing temperature.

Besides, it also found that at stoichiometry ratio, the GNPs fillers can distribute and disperse well. The use of the combining method US+ PCTM is one of the factors that helps the distribution and dispersion. The thermal conductivity reported for this method is high as compared to other methods and ratios. The evidence from this study indicates that using different mixing methods definitely influences the distribution and dispersion. It is vital to avoid agglomeration as it may prevent heat conduction in the polymer.

ACKNOWLEDGEMENTS

The authors would like to thank the Ministry of Education and Universiti Teknikal Malaysia Melaka [UTeM] for providing laboratory facilities and financial assistance under project no. FRGS/2018/FKM-CARE/F00366.

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