The polymer/clay nanocomposite has unique morphologies which help to improve the properties of the nanocomposite material itself. The morphologies are the intercalation and also the exfoliation. Intercalation is happen when the clay layers is penetrated by epoxy resin and the epoxy resin continue to expand inside the clay layers and with several help from other process the clay layers being separated and disperse throughout the epoxy resin. The separation of the clay layers is called exfoliation. There is a lot method being studied by the researchers all over the world to control these morphologies. Some of them are shearing and pre-conditioning. The objective of this study is to check the relationship between the effects of the homopolymerize state of the sample after pre-conditioning for various times/temperatures and then the sample being sheared by using the roll mill machine to see the dispersion of the clay particle. Several nanocomposite samples are pre-conditioned at a certain temperature and time, and then the sample is being sheared using the 2-roll mill machine. In this report also studies the effect of using different epoxy resin on the homopolymerize state of the samples.
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INTRODUCTION

Nanocomposites are widely used especially in automotive, marine, coating, and aerospace industries due to its advantage in having improved properties such as barrier, flame-retardance, thermal stability, and mechanical properties. These nanocomposite materials were first discovered by Toyota research group in early 90’s.

Nanocomposite is basically consisting of two basic materials which are silicate clay layers and a polymer matrix. The silicate clay layers are known as Montmorillonite (MMT) is composed of two tetrahedral sheet of alumina with a thickness of about 1nm and a length approximately 100 to several hundred nanometres. Plus, this MMT needed to be modified to make sure that compatibility between the silicate layers and the polymer matrix is improved. As for the polymer matrix, epoxy resin is one of the best materials to be mixed with MMT to create nanocomposites. Epoxy resins are created by transforming liquid polyether into infusible solids through a special curing process[1]. Epoxy resins are normally used as adhesive but also can be used in electronics industries to make insulators, transformers, etc. Plus, it is also widely used in other industries as well.

When Nanocomposite materials are mentioned, there are two typical types of morphologies has been always being studied. The morphologies are called intercalated and exfoliated. These morphologies can be obtained depending on the layered silicate charge density, the nature of the interlayer-exchanged ion, the cure conditions and the curing agent[2]. The intercalation can be achieved when a single or a few polymer chains enter the gallery of the silicate and the basal planes expand (basically from 10Å to 40Å which means around 1nm to 4 nm) while exfoliation is further process from intercalation where silicate layers become highly separated from each other (from 100Å and more) and they are well dispersed within polymer matrix. As the epoxy resin and the MMT were mixed together, the clay particles tend to stack together and later on being penetrated by the polymer chain but the penetration degree depends on the modification of the clay
layers which modify the clay interlayer from hydrophilic to hydrophobic to reduce the physical or electrostatic bonding force. This electrostatic force within the clay interlayer will prevent the penetration of the polymer chain into the clay interlayer causing the clay to be separated from the polymer chain. The stage for the morphologies formation is shown in **figure 1** to give better view towards how the morphologies can be formed. From these morphologies, the exfoliated nanocomposite is the most favourable because it gives the maximum enhancement towards the properties of the nanocomposites material as the clay loading increase[2][3][4][5][6]. Moreover, these nanocomposites would give the same reinforcement as the conventional composites, the good part of the nanocomposite is that its only use significantly lower amount of clay loading.

![Layered silicate and Polymer](image)

**Figure 1:** The morphologies of nanocomposite materials.

There is a lot of processing method being studied by the researchers all over the world to find the great ways to control the intercalation/exfoliation of the
nanocomposites. Some of the ways are by pre-conditioning the nanocomposite mixture before continuing with other processing method[7][8]. Before the pre-conditioning can be done, the clay and the epoxy resin needed to be mixed together and then the pre-conditioning take place by placing the nanocomposite mixture inside a thermostatic bath set with certain temperature and left it for certain amount of time. During pre-conditioning process, a reaction between the clay and the epoxy resin happens. This reaction is known as the homopolymerization process. During homopolymerization process, the d-spacing between the clay layers increase and the glass transition temperature, $T_g$ also increase as the time for the pre-conditioning increases. Tolle et al.[7] has made a study about the effect of pre-conditioning process by comparing (1) different weight fraction and (2) mixture age. They found that the glass transition temperature, $T_g$ of the nanocomposite and the d-spacing of the clay layers increase when the pre-conditioning temperature set increases. The high amount of clay loading would result the higher glass transition temperature when compared with the same pre-conditioning temperature and time. Moreover, they have found that pre-conditioning process also improve the mechanical properties of the nanocomposite through the mechanical analysis especially in the fracture toughness of the nanocomposite. They compared the toughness of the mixture-age nanocomposite with the baseline and they found that mixture-aged nanocomposite is tougher than the baseline. Later on, Pustkova et al.[8] made the same studies as Tolle’s but this time they are using different mixing method in the process of mixing the clay and the epoxy resin to study the effect of it. They also made an extra study by pre-conditioning a mixture in room temperature to study whether the homopolymerization process could take place when the pre-conditioning temperature is reduced to room temperature. The result that they got is just the same as Tolle’s which are the glass transition temperature, $T_g$ increase when the pre-conditioning temperature and time increases. As for the pre-conditioning at room temperature, they realized that there is almost no homopolymerization reaction take place when pre-conditioning at room temperature because there is no increment in glass transition temperature, $T_g$ although the sample has been pre-conditioned for about 3 years. Although there is no
homopolymerization happens when pre-conditioning at room temperature, Pustkova et al[8] has found that homopolymerization reaction can take place when pre-conditioning at room temperature but in condition the sample needed to be pre-conditioned at high temperature first. This happens due to the momentum from pre-conditioning at high temperature which gives effect towards the mixture to continue homopolymerize when continue pre-conditioning at room temperature. As for the mixing method, it will be discuss on the next part.

Other processing method to obtain intercalation/exfoliation of the nanocomposite is the mixing method. Mixing method is one of the crucial methods because in order to obtain the intercalation, the epoxy resin and clay have to be mixed together. As mentioned before, the pre-condition would give effect differently according to the mixing method used for example mechanical mixing and solvent mixing[8]. There are a lot of mixing method has been studied to control the intercalation/exfoliation of the nanocomposite materials. Although we know that the intercalation would occur whenever or whatever mixing method is used, but there is always some agglomeration that remains. Besides that, the fully exfoliation of the cured nanocomposite would never be achieved. Therefore, some approaches have been made to attempt to improve the situation and one of them are pre-conditioning and solvent mixing but it is still not good enough to improve the dispersion of the clay and the degree of exfoliation. Of course, shear is already occurring when ordinary mechanical mixing method is applied, but the combination of shear with other approaches seems to offer some advantages[2][5][3][9][10][11]. For example, Chen et al[9] combine high shear mixing with the ultra-sonication to improve the exfoliation while Lu et al[3] combine high shear mixing with ketone as a solvent to make the shear mixing possible. In our case, we have an idea to combine pre-conditioning with shear of the sample when it already has a rather higher viscosity, which permits greater degrees of shear to occur. In figure 2 shows the schematic mechanisms of clay platelets intercalation/exfoliation in the epoxy matrix by shear mixing to provide better understanding on how shear works. Ngo et al[10] has found that intercalated state is easy to achieve since it is the effect from thermodynamics of the
mixture and shear does not affecting the intercalation while Oh et al[2] has found that curing process did not affect the exfoliation due to the homopolymerization reaction on extragallery is faster than the extragallery during the curing process. As the shear force is one of the important features to make sure that the exfoliation to occur, some of the researcher studied the effect of different shear force towards the morphologies of the nanocomposite. Lu et al[3] has compared the shear mixing method by using ball milling and study the effect of it, while Yasmin et al[5] using the three roll mill machine to produce high shear force towards the nanocomposite. Chen et al[9] has studied the different type of shear force which are magnetic bar, high-shear mixer, combination of high shear and ultra-sonication, and one pot ultra-sonication. They have discovered types of morphologies which are the effect of shear force in mixing method. The morphologies are:

a) Intercalated nanocomposite with the silicate with 150Å interplanar spacing and relatively large-size aggregates (>10µm).

b) An intercalated nanocomposite with 150Å interplanar spacing and relatively small agglomeration (0.5-3µm, 30 to 200 nanolayers per agglomeration).

c) A well-dispersed nanocomposite with random and homogenous dispersion of several nanolayered agglomerations (2 to 8 nanolayers).

d) An exfoliated nanocomposite, in which the individual silicate nanolayers were randomly and continuously dispersed in the polymer.

According to all studies mentioned above, the small aggregate produce by the shear mixing has given improvement towards the mechanical properties of the nanocomposite. This mechanical property includes the tensile strength, Young’s modulus, flexural modulus and the impact strength of the nanocomposite material. In some cases, void space could happen due to high shear force. The void space would affect the nanocomposite by lowering its mechanical properties.
The other mixing method is ultra-sonication or sonication mixing as mention before. Ultra-sonication is the act of applying sound energy to agitate particles in a sample and it is called ultrasonic when the frequency applied is 20 kHz. Figure 3 is shown to demonstrate the setup for sonication mixing. In nanocomposite study, this sonication mixing is always being compared with shear mixing[9][12][6]. Dean et al[6] has studied about the different effect of sonication and shear mixing towards the nanocomposite morphologies. It is can be seen that the dispersion by using sonication is much better than the shear mixing. Moreover, the void space that can be produced in shear mixing cannot be seen in sonication mixing. Dean also studies the effect of sonication and shear mixing towards the increment of Tg for the nanocomposite and the she found that sonication and shear mixing did not give any effect towards it but the amount of clay loading is the factor for the Tg increment. Kahraman et al[12] has found that the clay agglomeration can be controlled by adjusting the time of the sonication as the time for sonication increase, the size of the clay agglomeration decrease which means that the dispersion of the clay agglomeration is getting better. In additional, Kahraman found that the sonication mixing is better than shear mixing just the same as Dean’s result.
The objective of this study is to check the relationship between the effects of the homopolymerize state of the sample after pre-conditioning for various times/temperatures and then the sample being sheared by using the roll mill machine to see the dispersion of the clay particle. There are two types of epoxy resin used for this study the DGEBA and the TGAP, the reason for using two different types of epoxy resin is to check the Tg effect of the nanocomposite with different mixture. As we know that pre-conditioning the nanocomposite would have effect on the intercalation/exfoliation of the nanoclay layers, so with the help of the roll mill machine the dispersion of the clay will be observed by using the micrograph from Leica DME microscope. From the help of the roll mill machine, the dispersion for the nanocomposite will be expected to be well dispersed throughout the epoxy matrix.
MATERIALS

For this experiment, there are several materials used. The materials consist of two main components which are epoxy resins and also montmorillonite clay. These two materials will be mixed together to produce the nanocomposite.

Epoxy Resins

In case of the epoxy resin, we are using two types of epoxy resin which is DGEBA resin and also TGAP resin. Each type of epoxy resin will react differently when mixed with the MMT clay.

1. DGEBA

This type of epoxy resin also known as BADGE resin which stands for Bisphenol A diglycidyl ether. DGEBA is a chemical compound used as constituent of epoxy resins which is a derivative of Bisphenol A and glycidol that is used in epoxy resins for its cross-linking properties. The chemical structure of Bisphenol A diglycidyl ether is shown in figure 4.

![Figure 4: Chemical Structure of Bisphenol A diglycidyl ether.](image)

In our case, we use DGEBA epoxy resin from DOW Company which is DER 331 which is a liquid reaction product of epichlorohydrin and Bisphenol A. In addition, the dependence of the viscosity on temperature is shown in figure 5 down below.
2. TGAP

This type of epoxy resin is a trifunctional epoxy resin. For this type of epoxy resins, the **Araldite My0510** is used. The epoxy resin is produced by the HUNTSMAN Company. According to the datasheet, it is said that this epoxy resin is a very low viscosity and high functionality amine-based. Moreover, it is also cures very rapidly during curing process which will be expected during the experiment. The figure 6 below will show the chemical structure of this epoxy resin.

![Chemical structure of Araldite My0510](image)

**Figure 6: the chemical structure of Araldite My0510.**
Montmorillonite Clay

Montmorillonite clay is a very soft phyllosilicate group of minerals that typically form microscopic crystals, forming clay. It is a member of the smectite group which means that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. For the project, the MMT used is the Nanomer I30E from the Nanocor Company. According to the technical datasheet, this type of clay is a surface modified montmorillonite mineral which disperse to nanoscale in epoxy resin systems thus producing the nanocomposite material. Moreover, the nanocomposite produced will have an increasing of Tg for about 30-45% indicating the thermal stability of the nanocomposite.

EXPERIMENTAL PROCEDURES

1. Manual Mixing

For this part, a 250ml beaker is used and more or less 100g of epoxy resin is poured into the beaker. After that, the amount of the MMT clay needed is 10% from the weight of the epoxy resin. The two materials were mixed together by using a glass rod to stir the materials. All this measurement was measured by using the balance.

There are 4 nanocomposite samples were made by using the materials mention above in the material section. The 4 samples are being preconditioned inside the silicon bath with certain temperature. They are:

a) DER 331 + 10%MMT at 100ºC.
b) DER 331 + 10%MMT at 80ºC.
c) TGAP + 10%MMT at 80ºC.
d) TGAP + 10% MMT at 60ºC.

2. Shearing Process

This process is done by using the 2 roll mill machine and also using the cone and plate. The cone and plate is used at the early stage of the curing process due to the low viscosity of the nanocomposite material. It is done by put a bit of the nanocomposite sample on the plate and then being compressed by the cone. The shearing happened when the cone is spinning using the mechanical stirrer. To show the idea how the cone and plate works the work schematic is shown in figure 7.

![Figure 7: the illustration of the working system for cone and plate.](image)

For the roll mill, in early stage one of the roll mills is covered by plastic layer in order to reduce the gap between the roll mills to promote the maximum shear. Later, the plastic layer is no longer used because the viscosity of the nanocomposite samples increases. The roll mill machine used is the W 100 T roll mill machine build especially
for laboratory works by a company named Dr. Collins. In figure 8 the model of the roll mill machine is shown to give the idea how the machine looks like.

![Roll mill machine](image)

*Figure 8: 2-roll mill machine used for shearing process of the sample.*

Before the shearing process can be done, all the equipment needed to be clean with acetone in order to make sure that the equipment is free from any dirt or contamination. After that, the shearing process can be done. The parameters for the shearing process for both cases are:

a) Roll speed = 10 rpm.

b) Temperature = room temperature.

c) Time for shear = 30 minutes.
3. Dispersion viewing using microscope

In this experimental part, before the dispersion of the nanocomposite sample can be seen in the microscope it needs to undergo a process of removing the air bubbles inside of the nanocomposite. This process is known as Degassing process.

In Degassing process, a small drop of the sample is placed on a glass slide, and the glass slide is then placed inside the vacuum oven. The temperature inside the vacuum oven is set to 80ºC to reduce the viscosity of the sample in order to remove the air bubble inside. The glass slide is left for about 5 minutes inside the vacuum oven.

After the Degassing process, we can continue with the viewing the dispersion using the microscope from Leica Company but first, the sample needed to be compress by putting a cover slip on top of the sample. Then, the dispersion of the sample can be seen in the microscope and some picture can be taken using a computer.

4. Glass Transition temperature measurement using DSC Machine

For this experimental part, the machine used is the DSC 821 from the Mettler Toledo Company. The method used for the samples are:

a) For DGEBA nanocomposites: -50/20ºC @ 10ºC/min + N₂.

b) For TGAP nanocomposites: -70/0ºC @ 10ºC/min + N₂.

At first, the DSC machine needed to be start and undergo preliminaries process to make sure that the machine is working perfectly. Then, all the samples needed to be prepared by using the aluminium pan and lid. Small drop of the sample more or less
about 10mg of weight is introduced into the aluminium pan and the lid is used to close the pan. After that, the process for the Tg measurement can be done.

The Tg measurement is done by the DSC measures the heat flow when sample is subjected to the programmed heating rate, as given above. The glass transition is an endothermic process, and for reasons associated with the kinetics of the change from a glassy state below the glass transition temperature, Tg to liquid-like state above Tg, the glass transition temperature appears as a small peak superimposed on a step change. The glass transition temperature can be determined in a number of ways, all of which are available in the software of DSC 821. The so called “Richardson” temperature will be used here to quantify the glass transition temperature.
RESULT AND DISCUSSION

Glass Transition Temperature (Tg).

The glass transition temperature being analysed by using the DSC 821 Mettler Toledo, the graph produce by the machine is shown in figure 9. In the graph, the x-axis represents the reference temperature and the y-axis represents the heat flow, on a relative rather than an absolute scale, and hence there is just a scale bar instead of an absolute scale. The glass transition is determined as the midpoint Richardson which can be measured by using the DSC 821 software. The value is then being plotted in a graph to show the evolution of the glass transition according to the material used.

![Figure 9: Graph produce by DSC machine to measure the Tg for the nanocomposite.](image-url)
For the TGAP nanocomposite, the evolution of the Tg cannot be seen clearly because the reaction for the TGAP nanocomposite to turn into solid is very rapid due to the functionality of the TGAP material itself. In figure 10 shows that the TGAP nanocomposite pre-conditioned at 80ºC transform into solid in just 2 weeks while the TGAP nanocomposite pre-conditioned at 60ºC takes about 5 weeks to transform into solid but the Tg in solid state cannot be measured due to the difficulty to take the sample to be measured. The Tg evolution for both pre-conditioned TGAP did not show the same pattern as the 80ºC shows high slope while the 60ºC shows a more horizontal with less slope. The high slope pattern for the pre-conditioning at 80ºC is because the sample has become solid thus the difference in Tg change is high. While for the sample pre-conditioning at 60ºC shows that the final Tg measured is about -29ºC if the solid state sample’s Tg can be measured it will surely has a Tg the same as the previous sample. This happens because the initiation period for the lower pre-conditioning temperature is longer compared with the higher pre-conditioning temperature.

Figure 10: The evolution of Tg for TGAP nanocomposite.
With DGEBA epoxy resin, the nanocomposite shows a much slower reaction than the TGAP epoxy resin. The DGEBA nanocomposite pre-conditioned at 100°C has the evolution of the Tg higher than the DGEBA nanocomposite pre-conditioned at 80°C as shown in figure 11. The DGEBA nanocomposite pre-conditioned at 100°C takes about 12 weeks to become solid while 13 weeks for pre-conditioned at 80°C. The pattern for both of the pre-conditioned nanocomposite is more or less the same. The only difference between them is that the higher pre-conditioning temperature shows a higher glass transition temperature of the nanocomposite. With this we can agree with Tolle and Anderson[7] and Pustkova et al[8] as they said that the higher the pre-conditioning temperature produce higher Tg for the nanocomposite. This can be applied in both cases for TGAP and DGEBA since higher pre-conditioning temperature produce higher Tg although for TGAP the graph pattern is not the same. As the Tg increase, it signifies that the homopolymerization in the nanocomposite has taken place. Homopolymerization ensures that reduction of epoxy group and as time goes on the number of epoxy group keeps on decreasing until the nanocomposite become solid.
In **Figure 11**, the graph shows a no change in Tg from week 6 until week 8 for both of the sample pre-conditioned at 80ºC and 100ºC. The reason for switching off the silicon bath is because it was Easter Holidays on week 7 where the laboratory was closed and no one was allowed to enter it. This closure was made use of in the sense that it allowed us to look at the effect of “stopping” the pre-conditioning. Because of this idea, the bath was closed for 3 weeks from week 7 until week 9 and continues with the normal pre-conditioning on week 10. So, from week 6 until week 8 the Tg value is about the same and then in week 9 it started to go up once again. If the nanocomposite were pre-conditioned at room temperature there will be very small change in Tg or no change at all. So when the nanocomposite were pre-conditioned at high temperature and then left at room temperature there will be quite noticeable change in Tg because the pre-condition at high temperature somehow create an inertia towards the reaction in the nanocomposite[8] which means that the homopolymerization still continue although it became slower than pre-conditioning at high temperature. The silicon bath was switched off on week 6 and

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**Figure 11**: The evolution of Tg for DGEBA nanocomposite.
the sample be left at room temperature from week 7 until week 9. As we can see on the graph, there is no change in Tg from week 6 until week 8 and there is slight change in week 9. The sample in week 9 is still left at room temperature but there is still a change in Tg. With this, it shows that the homopolymerization is still occur but the reaction is very slow because it takes about 3 weeks to start the change in Tg and the change is very small.

In **figure 12** shows the graph of TGAP pre-conditioned at 80ºC and also DGEBA pre-conditioned at 80ºC to compare the increment of Tg between different epoxy resin used. Between the initial stage of pre-conditioned until the 2nd week of pre-condition where the TGAP nanocomposite has become solid, the Tg has increase for about 17ºC while the DGEBA nanocomposite has an increment of Tg for about 2ºC. From this, we can say that different epoxy resin used for nanocomposite can affect the Tg value of the nanocomposite itself. The increment of Tg for TGAP is higher than DGEBA is because of the functionality of the TGAP is higher than the DGEBA so it is expected for TGAP nanocomposite to have higher Tg increment than the DGEBA nanocomposite.

![Comparison of DGEBA and TGAP](image)

**Figure 12**: The graph comparison between TGAP and DGEBA nanocomposite.
The Dispersion of Clay Particles.

The dispersion can be achieved in any number of ways, but the one that needed is a good dispersion. This good dispersion can be obtained by introducing shear force to the nanocomposite. The nanocomposite sample after being sheared is then analysing by using microscope to check the dispersion produce by shearing and also by pre-conditioning. Figure 13 shows the dispersion of TGAP pre-conditioned at 80ºC from the initial stage of pre-conditioning until the last stage before the sample become solid. At the initial stage we can see clearly the clay particle and some of them are quite large in size and when the nanocomposite age 1 week the clay particle seems to change a bit. The particles have become to expand a bit compared with the one before preconditioning and some of the clay particle is blurred. This is because the some of the clay layers has been dispersed but the dispersion is somehow bad because the large clay particle can be clearly seen. As we know, the morphologies of the nanocomposite consist of intercalation and also exfoliation. In order for exfoliation to happen, the epoxy resin needed to penetrate the clay galleries which known as the intercalation. But in some cases, there is some clay particles are highly agglomerated, and then the access of the resin to the clay galleries is restricted which resulting many particles will be not intercalated, let alone exfoliated. To improve this situation, the dispersion of the clay particle needed to be improved so the purpose of the shear applied is to improve the clay dispersion. When shearing a large agglomeration, the large agglomeration has changed in shape from a sphere to a flatter disc. This is what has shown in the optical micrograph which has made the particles seem to be expanding and blurred.
The dispersion for TGAP pre-conditioned at 60°C is shown in figure 14. It takes about 4 weeks for the sample to turn into solid. The dispersion for the first 3 weeks for the sample seems to be just the same as the initial stage of pre-conditioning. But in the 4th week the dispersion seems to be better because the dispersion is more or less the same as the sample pre-conditioned at 80°C on week 1. The dispersion for both samples seems to be better but it is not enough to get the dispersion desired because the clay particle is still large and it is still can be seen clearly as nothing happen to them. From these, it is easier to conclude that the dispersion for TGAP in both cases is bad.
The study continues with the dispersion for DGEBA nanocomposite sample pre-conditioned at 100°C. The evolution for this sample’s dispersion is shown in figure 15. The shear force can be applied to the sample at the 3rd week of the pre-conditioning due to the sample’s low viscosity which made the shearing process impossible. The sample was able to be sheared until the 6th week because in that time the sample’s viscosity already high with Tg of more or less -2°C. The initial stage of the pre-conditioning shows clearly the bad dispersion of the clay particle when after the mixing process without shearing. As pre-conditioning process continues and after shearing, the clay particle especially the big clay particle seems to be blurred. In week 4, week 5 and week 6, the large clay particle which can be clearly seen in the initial stage are now cannot be seen clearly. From these, there are several hypothesis can be made. First, the clay layers may have been separated which is equivalent to partial exfoliation. Second, the clay agglomeration may have been broken up into smaller clay agglomeration. Both of these hypotheses cannot be confirmed due to TEM or SAXS is not done for this experiments.
For DGEBA nanocomposite sample pre-conditioned at 80°C, it contains 11 evolution of dispersion of the clay particles. The dispersion for this sample at early stage which is from the initial pre-conditioning until 8 weeks of pre-conditioning did not show any significant changes. There are still presences of large clay particles plus the clay particles can be seen very clearly from week 3 to week 6 as shown in figure 16 and the small clay particles are getting blurry. In week 8 the dispersion is more or less better than before. It is because the large particles which can be clearly seen are less plus some of the large particles are blurry.

Figure 15: The dispersion of DGEBA sample pre-conditioned at 100°C. Scale bar 100µm.
The study of the dispersion for the sample pre-conditioned at 80°C continues with the dispersion shown in figure 17. From week 9 until week 13 the dispersion is more or less the same with the sample in week 8. There are still a lot of large clay particles can be seen and it seems that the dispersion did not become any better. Plus, the clay particles seem to increase and because of that the dispersion cannot be seen clearly. When the sample compared with the sample pre-conditioned at 100°C, it seems that the dispersion has gone worse. This is a possible reason for the clay particle becoming a lot is because of the sedimentation of the clay during pre-conditioning making the clay particle sediment at lower part or the nanocomposite and leave the upper part with epoxy resin with small
amount of clay particle which are not sediment. Due to that reason another method to check the dispersion without using microscope was used and the method is curing experiment. In the epoxy/clay mixtures with a poor dispersion and cured with Jeffamine, there is a shoulder after the main reaction peak in the non-isothermal cure curve. This shoulder has been attributed to a homopolymerization reaction in the clay galleries, and the fact that it occurs after the main peak means that the nanocomposite is not exfoliated because the bulk resin outside the clay galleries has transformed by the main reaction into a rigid solid, which does not permit any further nanostructural development in the clay particles. If the procedure for shearing the pre-conditioned mixtures has had the desired effect, then there will be a reduced amount of this homopolymerization reaction, and hence a reduced shoulder. The data analysis for curing experiment is shown in figure 18 and figure 20.

Figure 17: The continuation of DGEBA sample pre-conditioned at 80ºC dispersion. Scale bar 100µm.
The stoichiometry for the epoxy/clay mixture is calculated by the calculation of the epoxy equivalent (EE) for the epoxy resin used and also the molecular weight for the Jeffamine D-230. After that, the weight for the clay is added according to the weight percentage of the epoxy resin and then the stoichiometry is calculated. In case the mixture is being pre-conditioned, the epoxy equivalent for the epoxy resin is increased. So, to know the new epoxy equivalent for the pre-conditioned sample the graph of the relationship between the Tg and EE from Pustkova et al[8] is used. The calculation for the stoichiometry amount of Jeffamine is subjected to some uncertainty, for several reasons: the epoxy equivalent is not actually calculated because the epoxy equivalent is obtained by using the relationship between Tg and epoxy equivalent given by Pustkova et al. The sedimentation also gives effect towards the stoichiometry as the value of the clay content is now uncertain. These all calculation step is shown in annex. With these uncertainties, three different amount of curing agent is used: the stoichiometric amount calculated by making some assumptions (21% Jeffamine), and two other amounts which are 11% greater than (32% Jeffamine) and 7% less than the stoichiometry (14% Jeffamine). In figure 18 shows the curing process of the nanocomposite with the 3 different amount of Jeffamine D-230 used as mention before to cure the sample. If there is less Jeffamine than stoichiometric, then there are epoxy groups which do not have any amines with which to react, and so there will be considerable homopolymerization, which is exactly what is seen in the graph for the 14% amount of Jeffamine used. On the other hand, if there is more Jeffamine than stoichiometric, then there are plenty of amine groups to react with the epoxide groups, and because of that homopolymerization would not be expected, provided that the amines can get access to the epoxy groups within the clay galleries, and a shoulder on the high temperature side of the main peak would not be expected; all these explanation are exactly what the graph for 32% amount of Jeffamine shows. Finally, the stoichiometric ratio appears to have a small shoulder on the high temperature side of the main peak, which suggests that some epoxy groups are still not able to react with amines, and accordingly homopolymerize. This is shown in the graph for the 21% amount
Jeffamine used. The result obtained here is just the same as the one done by Montserrat et al.[13]. Montserrat et al has done the study about the epoxy curing using the same method as we did but they used different heating rates to see the effect of it and they did not applied any shear force towards the sample. The graph that they obtained is shown in figure 19 and we compared the graph with the heating rates at 10K/min which the same heating rates that we used. By comparing the graph, we can say that shearing did not improve the exfoliation of the clay layers as the graph show the same size of shoulder.

To check whether the calculation of the stoichiometry is correct or not can be done by comparing the value of energy for the process as shown in figure 18. The higher the energy value for the green lined graph shows that the calculation is correct because all the nanocomposite has been cured while for the black and the red graph shows much smaller value of the energy which shows that the curing is not completed and also the excess amount of the Jeffamine did not react with the nanocomposite. The same goes with the Tg measurement of the cured sample in figure 20. As we can see, in figure 20 the highest Tg value belongs to the amount of Jeffamine used is the same as the stoichiometry and the other two values of Tg is more or less the same. With these, it is enough to say that the stoichiometry calculation is correct and the data from the curing analysis is reliable.
Figure 18: curing process of the nanocomposite sample.

Figure 19: Fit of the autocatalytic model (dashed lines) to the non-isothermal data (points) obtained for NEPAJ10 at heating rate of 2.5, 5, 10, 15, and 20K/min (in order, from bottom to top).
The comparison of the dispersion between the DGEBA nanocomposite and the TGAP nanocomposite shows that the dispersion for the DGEBA nanocomposite is better than TGAP nanocomposite. The degree of dispersion for DGEBA is far higher than the TGAP nanocomposite. This is because the reaction for TGAP is very fast making the epoxy chain difficult to enter the clay layers resulting the epoxy resin become solid before it can enters the clay layers and then expand inside of the clay layers producing the intercalation/exfoliation morphologies. As for the DGEBA nanocomposite, the slow reaction of its epoxy resin ensures that the epoxy chain can enter the clay layers and expand inside it making the intercalation/exfoliation morphologies possible and even better than the TGAP nanocomposite. The slow reaction of epoxy resin like DGEBA could produce sedimentation which resulting the distribution of the clay particle not even as the clay sediment at bottom of the epoxy resin. Thus making the dispersion looks worse but the analysis of curing experiment shows otherwise.
CONCLUSION

The nanocomposite reacts differently because it depends on the type of epoxy resin and type of modified clay used. This can be proved by comparing the DGEBA nanocomposite with the TGAP nanocomposite. For example, the Tg changes for TGAP nanocomposite is faster than DGEBA nanocomposite because of the functionality of TGAP epoxy resin making it react faster than DGEBA.

The pre-conditioning of the nanocomposite helps by promoting the homopolymerization to occur before continuing with any reaction. As the pre-conditioning temperature increase, the Tg changes also increase due to promotion of homopolymerization reaction to occur is higher in high temperature[8], [7]. When the pre-conditioning temperature is reduce to room temperature and left for about 3 weeks, the homopolymerization reaction seems to stop. But it is only happens for the first 2 weeks and on the 3rd week the homopolymerization reaction seems to occur. The homopolymerization reaction can be seen as the very small increment of Tg from week 8 to week 9 which shows that the homopolymerization reaction that occur is very slow. This shows that there is still some momentum in the reaction itself because of the pre-conditioning at high temperature. This result agrees with Pustkova et al with their study about the homopolymerization reaction when the sample is left at room temperature after pre-conditioning at high temperature[8].

When it comes to shear force applied to the nanocomposite, the shear force indeed helps to increase the dispersion of the clay particles as mentioned by others [9][12][11][2][10]. As in our case, dispersion of the clay particle especially for the DGEBA nanocomposite pre-conditioned at 100ºC is good as the large clay particles which can be clearly seen in initial stage are now blurred and their presence is less than the initial stage. But at certain shear force has its limit of dispersion it would get due to the amount of shear force applied itself[3][5]. As in our cases the roll mill cannot give high shear force to
the nanocomposite because it has a very large gap between the rolls so because of that it can be sure that the shear for applied by the roll mill is low.

Finally, it can be said that the nanocomposite studies is very wide and it is very important to find the exact solution to control the dispersion of the clay particle and also to control the intercalation/exfoliation morphologies of the nanocomposite as it helps the nanocomposite to improve its mechanical and also its chemical properties. There are a lot of method can be used to control the morphologies of the nanocomposite has been studied by the researchers all over the world because this material is widely used in a lot of field especially in aerospace.
REFERENCES


CALCULATION OF THE JEFFAMINE STOICHIOMETRY

1. The calculation of the epoxy equivalent for the epoxy resin.

From the molecular formula of the epoxy resin, the epoxy’s molecular weight can be calculated.

\[ M_w = 57 + [284]_n + 226 + 57 \]

Where \( n \) is the repetition for epoxy group. With the number of \( n \) known we can know the epoxy equivalent for the epoxy resin.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( M_w )</th>
<th>g/eq</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>340</td>
<td>170</td>
</tr>
<tr>
<td>0.1</td>
<td>368.4</td>
<td>184.2</td>
</tr>
<tr>
<td>0.15</td>
<td>382.6</td>
<td>191.3</td>
</tr>
</tbody>
</table>

But, the DER 331 has the epoxy equivalent in range of 182-192g/eq given the provider. So, we assume the epoxy equivalent for our sample is 190g/eq.

2. The calculation of the molecular weight for the Jeffamine D-230.
As shown in the **figure 21**, the x value is 2.6 so the molecular weight for the Jeffamine is 60g/eq.

3. **Stoichiometric calculation.**

From the data before, we have the epoxy equivalent for the epoxy resin and also the molecular weight for the Jeffamine.

**Stoichiometric for DER331 + Jeffamine**

\[
M_w = 190g \text{ DER331} + 60g \text{ Jeffamine} = 250g \text{ total}
\]

**Stoichiometric for DER331 + Jeffamine + 10%MMT (weight epoxy)**

\[
M_w = 190g \text{ DER331} + 60g \text{ Jeffamine} + 19g \text{ MMT} = 269 \text{ total}
\]

[70.6%] [22.3%] [7.1%] = 100%

If the epoxy has been preconditioned, the epoxy equivalent is increased. Because of that, the relationship between Tg and EE from Pustkova et al is used. We use the for preconditioning at 80ºC and the Tg of our sample is around -2ºC and the epoxy equivalent is about 265g/eq.
4. The new stoichiometry.

From before we have the new value of epoxy equivalent which is 265g/eq.

With this we can calculate the new stoichiometry for the Jeffamine.

\[
M_w = 265g \text{ DER331} + 60g \text{ Jeffamine} + 26.5g \text{ MMT} = 351.5 \text{ total}
\]

So, if I have 82.9g of epoxy/clay mixture, I need 17.1g of Jeffamine which is equal to 21% amount of Jeffamine from the epoxy/clay mixture.