Effect of Nanofillers on Adhesive Toughness Measurement

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Abstract: Aluminum is used widely in automobile because of its light weight and fuel economy compared to steel. Joining is one of the most crucial part in manufacturing decision of aluminum and therefore significant in design. The aim of this research is to produce nanofiller from graphite materials for toughening adhesive and determining its mechanical properties. In other word, creating a physical joining which consists the mixture of epoxy and modified nanographite for aluminum panel. The weight percentage of the modified nanographite used is 1%, 1.75% and 2.5%. Two type of analysis were made which are mechanical properties and morphological structure. The analysis of mechanical properties consists of tensile test, porosity density and double cantilever beam test. Result from tensile test showed that 1wt% of modified nanographite produces the highest maximum strength of 2.305 MPa. For porosity density test, it shows that 1 wt% of modified nanographite indicated the lowest value of 1.10%, in which affects the mechanical properties of composite significantly. For double cantilever beam test, the results of 1wt% modified nanographite obtained were 6265.32 J/m² and 9397.98 J/m² for the respective crack lengths 37.5 mm and 25mm. The method used for pre-crack was a non-sticky thin film in adhesives. From both results, it showed that 2.5 wt% modified nanographite produces the lowest value of adhesive strength which mean that adding too much modified nanographite will reduce the brittleness of epoxy thus the strength of adhesive will reduce. For the morphological structure, Scanning Electron Microscopic (SEM) was used in order to observe the dispersion of nanographite inside the composite. Overall, the research reveals that the adhesive towards aluminum metal is sucessfull. However, an in-depth study still need to be carried out in order to improve the composite's mechanical properties.

Keywords: Aluminium, Adhesive Toughness and Nanocomposites

1. Introduction

Joining can be defined as a process to bond two or more parts together. In engineering, joining types are one of the most crucial part in manufacturing decision and therefore significant in design. There are a lot to be considered by engineers for the methods in assembling parts into product where it is related with the manufacturing cost, performance of product and the impact of the end product’s weight. Few things related with the decision making is by making sure the availability of the equipment, skilled labor and also the energy and cost of materials [1-3].

Basically there are three classifications of joining for assembly and joining of engineering components which are by mechanical, chemical and physical. Mechanical joining methods are usually based on localized, point-attachment process where the joint is provided by a rivet, nail, bolt or screw [4]. The joints are depending on the tensile stresses in the attachment where the components are being hold in compression.

For chemical joining method, it is related to the chemical reaction for the material mixed to be bonded with each other. There would be significant residual stresses happened when the components are chemically bonded, which can damage in the reaction of material that will reduce the strength of the bonded joint. The reaction between a liquid precursor and a hardener will determine the strength of the adhesive before it is applied to the joint [5]. Meanwhile, for the use of solvent-based adhesives, welding, soldering and brazing are the examples of physical methods of joining. In can be classified
as all the processes base on a phase transition from liquid to solid state.

In automobile industry, metal is one of the main materials used to make parts of the vehicle. The metal preferred by most automakers is steel. However, in recent years, the regulation in recycling has intensified in which attempts of weight reduction and fuel economy have become a priority. In this case, changing the material from steel to aluminum can be the ideal engineering solution because its density is one-third of steel and also satisfies the stiffness and torsion requirement in material used in automotive product making [6,7].

In joining metal together, there are few different techniques that can be used, such as welding, bolting, riveting, brazing, soldering and adhesive joining. These techniques are depending on the parts to be joined, material used and the strength needed by the product. For aluminum in automobile industry, the suitable techniques are by using bolting and adhesive joining. Bolting is usually a lot stronger than adhesive joining, however, encounter few problems such as vibration could lead to the bolt loosening. Subsequently, with the continuous high stress at the loosen bolt joining can induce fatigue and weakening the material [4]. To overcome this problem, adhesive joining is proposed to be the solution of this aluminum joining problem.

In this paper, adhesive joining was prepared from advanced composite materials. The word root of composites can be defined as the combination of two or more material that results in better properties. The study includes the selection of appropriate reinforcement of the composites which is graphite to be used in the aluminum joining. The adhesive composites were analyzed in term of its microstructure and the mechanical properties.

2. Materials and Preparation Method

Adhesive are to be made for joining aluminium parts in automobile industry. The adhesive are made using epoxy as the matrix while the fillers are graphite. The graphite fillers are to be expanded in the furnace to reduce the size becoming nano-dimension and sonication process to disperse it well. The sonication machine was adjusted for one variable to investigate the materials strength when undergoing different weight percentage of filler. The samples were undergoing tensile test, porosity density and double cantilever test to know its mechanical properties and adhesive strength. The samples also were evaluated using scanning electron microscope (SEM) in order to check the size and dispersion of particles and for the chemical bonding will be tested using Fourier Transform Infrared Spectroscopy (FTIR)

2.1 Raw Material Preparation

Proper methods in preparing raw materials are very important to obtain and produce a good sample. The material used in this study is epoxy as the matrix and graphene which will be reacts as the filler. The weight percentage of the filler is 1%, 1.75% and 2.5% to be used as the reinforcement in the composites

Thermal expansion process is being made by using furnace to expand graphene material before adding into epoxy. The purpose is to gain nano-sized filler to be absorbed in epoxy later. The temperature of the furnace is 1000°C. By using silica crucible, it is pre-heated in the furnace for about 10 minutes. 0.5 gram of graphite is put inside the silica crucible and closed it using its lid. Let the graphite expand for 60 seconds in the furnace and take it out. Let it cool for 2 minutes before transferring the expanded graphite inside a container. Fig. 1 shows the graphite after expand.

Fig. 1 – The expanded graphite

Sonication process is made to disperse the material before mixing with epoxy by using ultrasonic bath machine. The expanded graphene will be set through this process. The frequency of the sonication machine is 50 to 60Hz. There will be one set time limit for this process which is 1 hour. This process is to make sure that the filler are equalized quantity in every part inside the epoxy matrix. 1.5 gram of expanded graphite is put inside a metal container with additional 100 gram of acetone. The metal container is sealed using plastic wrap and rubber band to avoid the acetone from vaporized. The metal container is placed inside the sonication bath and water is pour inside the machine. Make sure that the water content is above the quantity inside the metal container. The sonication process is set for one hour at 10°C. Water flow for the machine is very useful to make sure that the water is in the temperature needed.

2.2 Preparation of Composites

2.2.1 Mixing

Two methods used in the fabrication are mechanical stirring and magnetic stirring. Mechanical stirring is used for a large quantity of liquid that is relatively have a high viscosity, while magnetic stirring is suitable for a low quantity of thin liquid. In this research magnetic stirring with hot plate is used to mix expanded graphite, acetone and Jeffamine (J230) for modification interface process while for mechanical stirrer is used to mix the mixture after added with epoxy.

Fig. 2 – Modified expanded graphite
Expanded graphite and acetone is stirred using magnetic stirrer for 10 minutes with 600 rpm. After that, sonicate the mixture for 30 minutes to make sure that the expanded graphite float in the acetone. The mixture is then modified using J230 to get better interface for the graphite. The ratio of expanded graphite to J230 is 1:1. It will undergo stirring process again using magnetic stirrer at 100°C for one hour using 600 rpm. Make sure the container is sealed properly to avoid acetone from evaporate. Fig. 2 shows the modified expanded graphite (M-EG).

The next process is to add 396 gram of epoxy in the mixture of 1% modified expanded graphite. The calculation of epoxy is shown in Table 1. Stir it manually around 5 minutes before sonication process for one hour at 10°C. After sonication process, the mixture is stir using mechanical stirrer for two and a half hours with temperature and speed value is 120°C and 300 rpm respectively. Make sure the acetone vaporized at this stage. Put the mixture inside the oven with temperature 120°C of necessary. Finish the stirring process; let the mixture cool down in room temperature for few hours before adding 198 gram of hardener inside it. The shape of mixture must be in high viscosity such in Fig. 3.

**Table 1 - Calculation of Epoxy for 1% M-EG**

<table>
<thead>
<tr>
<th>Description</th>
<th>Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mold = 104.72 gram for 8 samples</td>
<td></td>
</tr>
<tr>
<td>Each beaker contains 6g of expanded graphite</td>
<td>(104.72/1.0472) X 6g of graphite in beaker = 600g of total weight</td>
</tr>
<tr>
<td>So for 1% of expanded graphite = 1% X 104.72 = 1.0472g</td>
<td></td>
</tr>
<tr>
<td>600g – 6g of graphite in beaker = 594g of epoxy with hardener</td>
<td></td>
</tr>
<tr>
<td>The ratio of epoxy and hardener is 2:1</td>
<td></td>
</tr>
<tr>
<td>So, 594/3 = 198g</td>
<td></td>
</tr>
<tr>
<td>Therefore, Epoxy = 198 X 2 = 396g</td>
<td></td>
</tr>
<tr>
<td>Hardener = 198 X 1 = 198g</td>
<td></td>
</tr>
</tbody>
</table>

Before adding the mixture, make sure that the mold is spray using silicone spray which is to make it easier to get the samples after it cures. After the mixture is pour inside the mold, it was cured at room temperature. This epoxy mixture will cure for 12 hours and fully solidify in 24 hours.

3. Results and Discussion

3.1 Analysis of Mechanical Properties

This analysis is to determine the mechanical properties of composites such as its tensile strength and shear, elasticity, yield strength, Modulus Young and other properties. There are two parts to be analysis which is for the composite testing and also adhesive testing.

There are three types of testing to be done for composite testing which is tensile test, density porosity and double cantilever beam test. These testing are important in order to make sure the adhesive made have good mechanical properties which is suitable to bond aluminum parts together.

3.1.1 Tensile Test

A tensile test is the fundamental mechanical test where the specimen was loaded while measuring the applied load and the elongation of specimen over the distance. Tensile testing was performed on dumbbell samples at a strain rate of 0.5 mm/min. Three samples are taken for the test. The result is shown in Table 2.
Table 2 - Result of tensile test

<table>
<thead>
<tr>
<th>Material</th>
<th>Yield Strength, MPa</th>
<th>Max Stress, MPa</th>
<th>Young's Modulus, MPa</th>
<th>Elongation Break, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% of M-EG</td>
<td>1.249</td>
<td>2.305</td>
<td>17.76</td>
<td>24.99</td>
</tr>
<tr>
<td>1.75% of M-EG</td>
<td>0.981</td>
<td>1.745</td>
<td>14.14</td>
<td>20.03</td>
</tr>
<tr>
<td>2.5% of M-EG</td>
<td>0.712</td>
<td>1.185</td>
<td>10.52</td>
<td>15.07</td>
</tr>
</tbody>
</table>

From the result, it shows that when adding nanofillers with the epoxy, it will decrease the brittleness thus maximum stress will decrease. The more weight percentage of modified expanded graphite added, the lower the maximum stress, Young's modulus and yield stress value. It shows that the characteristic of modified expanded graphite will change the pure mechanical properties of epoxy [8]. Adding it will increase the ductility of the composite and lower its brittleness. It will become more elastic than epoxy itself. However, the value of mechanical properties is too obvious before and after adding the modified expanded graphite, this is due to the bubbles at the specimen which will reduce the actual mechanical properties of a material.

3.1.2 Porosity Density

Porosity testing is conducted to measure the void empty spaces in a material which is calculated in percentage. Increasing area fractions of porosity in the cross-section will reduce strength. Fine porosity - when present in sufficient quantity to contribute a total area comparable to that of large pores - also causes a loss in strength [9]. To calculate the porosity, Guerot Efford Ferry equation is used which is:

$$\varepsilon = \left(\frac{W_{w} - W_{d}}{W_{w} - W_{s}}\right) \times 100$$

Where:

- $\varepsilon$ = Porosity, %
- $W_{w}$ = Wet Weight, gram
- $W_{d}$ = Dry Weight, gram
- $W_{s}$ = Immersed Weight, gram

The results of porosity for all three weight percentage of modified expanded graphite are shown in Table 3.

Table 3 - Result of porosity density test

<table>
<thead>
<tr>
<th>Material</th>
<th>Dry Weight, Wd</th>
<th>Immersed Weight, Ws</th>
<th>Wet Weight, Ww</th>
<th>Mean Density (g/cm³)</th>
<th>Porosity (%)</th>
<th>Mean Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% MEG</td>
<td>710.6</td>
<td>660.2</td>
<td>695.6</td>
<td>1.1501</td>
<td>0.71</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>621.5</td>
<td>683.4</td>
<td>673.9</td>
<td>0.773</td>
<td>0.74</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>620.8</td>
<td>695.6</td>
<td>674.9</td>
<td>0.792</td>
<td>0.74</td>
<td>1.19</td>
</tr>
</tbody>
</table>

The results of this study indicates that the porosity content increase when the weight percentage of M-EG increases. Furthermore, an increase in porosity was shown the decrease value of mechanical properties as shown in the tensile test result. This means that the porosity of a material relates with the mechanical strength of a material. Few factors should be considered are the temperature of expanding graphite, the sonication time of dispersion and also the ratio and type of modification material used.

3.1.3 Double Cantilever Beam Test

Adhesive testing is the test to be done to determine the strength of bonded part of material which in this study is aluminum. This test consists of two variables which is adhesive itself and also adherends. There are one adhesive used for this test which is the composites of epoxy with modified expanded graphite. While for the adherends used in this study is Aluminum. According to ASTM 3433-99, the adherends dimension is 25.4 x 9.5 x 150 mm of aluminum 6061 which has Young’s modulus of 68.9 Gpa and yield strength of 276 MPa.

The width and thickness of adherends were measured before bonding using a Vernier caliper. The substrate was rubbed using electrical sender to remove metal oxide and dirt. Acetone and tissue were used to clean and remove particles produced by polish. The substrates were put inside a container contain 20 wt% sodium hydroxide solutions and sat for 15 min. The substrates were removed from solution and cleaned again using acetone and distilled water.

Pre-crack is been made by using a 40μm in thickness which is put in between the adherends. Aluminium shim of 0.6mm thickness is put in front and back of the adherends to make sure that the mixture of composite will be the same. Remember to put some silicone grease at the shim so that it is easy to take it out from the adherends after the epoxy mixture solidifies. Fig. 5 shows the double cantilever beam condition and how it reacts.

$$G_{IC} = \frac{3P\delta}{2B\alpha}$$
highest peak of load while δ value is taken for the highest elongation peak. Two calculation has been made which is the differences in the crack length.

Table 4 - Result of P and δ from the DCB test with crack length 25 mm

<table>
<thead>
<tr>
<th>Material</th>
<th>P(N)</th>
<th>δ(mm)</th>
<th>B(mm)</th>
<th>α(mm)</th>
<th>GIC (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>355</td>
<td>3.199</td>
<td>25.4</td>
<td>25</td>
<td>2682.63</td>
</tr>
<tr>
<td>1%-MEG</td>
<td>721</td>
<td>5.518</td>
<td>25.4</td>
<td>25</td>
<td>9397.98</td>
</tr>
<tr>
<td>1.75%-MEG</td>
<td>675.5</td>
<td>4.838</td>
<td>25.4</td>
<td>25</td>
<td>7719.85</td>
</tr>
<tr>
<td>2.5%-MEG</td>
<td>630</td>
<td>4.158</td>
<td>25.4</td>
<td>25</td>
<td>6187.89</td>
</tr>
</tbody>
</table>

Table 5 - Result of P and δ from the DCB test with crack length 37.5 mm

<table>
<thead>
<tr>
<th>Material</th>
<th>P(N)</th>
<th>δ(mm)</th>
<th>B(mm)</th>
<th>α(mm)</th>
<th>GIC (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>355</td>
<td>3.199</td>
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<td>25</td>
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</tr>
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<td>25.4</td>
<td>25</td>
<td>6187.89</td>
</tr>
</tbody>
</table>

From the results, it shows that the adhesive toughness depends on the highest peak load which indicates the highest elongation peak value. The epoxy itself give the lowest value of adhesive toughness which is 2682.63 J/m² for crack length of 25 mm and 1788.42 J/m² for crack length 37.5 mm. The data show the highest value of adhesive toughness for 1% weight percentage of modified expanded graphite which is 9397.98 J/m² and 6265.32 J/m² for crack length of 25 mm and 37.5 mm respectively. However from the data gain, it shows that when the value of weight percentage of modified expanded graphite increases, the adhesive toughness reduce such in Table 4 and Table 5. This is because, adding too much M-EG will change the brittleness of epoxy becoming too ductile which mean the strength of adhesive will reduce.

Other than that, failure at the adhesive joint maybe can be the factor of the result. Based upon the distribution of adhesive on the fracture surface of adherends, adhesive fracture is recognized in this experiment. Based on Fig. 6, the adhesive fractures occurs exactly at the interface on adhesive and adherend which mean there is no adhesive at the adherend surface after fractured. This is due to the surface treatment of adherend is not good enough with the adhesive. Human errors are also concluded where maybe not enough adhesive are put at the adherend on the sample preparation.

3.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a tool to identify the types of chemical bonds in a molecule by produce infrared absorption spectrum that is looks like a molecular “fingerprint”. This machine also can identified unknown materials, the quality or consistency of a sample and the amount of components in the mixture. Specimen is prepared by cutting the sample into small pieces. The surface of sample is examined by FTIR to investigate the chemical bonding in sample structure.

From Fig. 7, it shows the differences between epoxy before and after adding modified expanded graphite. The chemical bonding for all graph is almost the same just slightly difference in the percentage of T. The chemical bonding depends on the epoxy, hardener, modifying agent and graphite itself. When bonding with the elements, it will produce different chemical bonding comparing with epoxy and just hardener itself.

3.3 Analysis Morphological Structure

Morphological structure can be defined as the study of shape where microstructure of a material can be determined. By doing a morphological structure test, the microstructure of material can be seen whether it has been dispersed well or to see the actual size of the microstructure. Each material has different microstructure so it is easy to see which material does not follow the requirement needed. The analysis of morphological structure can be done using a Scanning Electron Microscopic (SEM) machine or Transmission Electron Microscopy (TEM). In this study, SEM machine is used to determine the microstructure of modified expanded graphite whether it is dispersed well or not.

Scanning Electron Microscopic (SEM) is used to see the morphological structure of a material. The existence of other particle other than the matrix or epoxy can be seen by using this testing. On top of that, the dispersion of graphite can also be seen through this method. The morphological structure of epoxy, 1 wt%, 1.75 wt% and 2.5 wt% of graphite is shown in Figs. 8, 9, 10 and 11 respectively. The microstructure is zoomed at 2000 of 10μm.
Fig. 8 – Morphological Structure of Epoxy

From Fig. 8, it shows that there is no existent of graphite while for Figs. 9–11 there is the existent of filler. The dispersion of the micron-sized particles of filler can be seen which is relatively uniform and in randomly condition. Some large particle maybe aggregates small particle. The micro composites was fabricate by dispersing expanded graphite in acetone, modifying it with Jeaffamine (J230) and mixing it with epoxy, followed by evaporation of the acetone. Due to lack of particle surface modification, this aggregation may happen. This is the important of interface modification which is to uniformly dispersed particles in polymers. Without modifying the interface, the particles may merely aggregate in polymer matrix owing to their high specific surface area [7,8].

4. Conclusion

In conclusion, the two main objectives of this paper which is to produce the nanofillers from graphite materials for toughening adhesive and determining its mechanical properties and adhesive strength has been successfully achieved. The nanofillers are produce by expanding graphite using furnace at 1000OC. Then the expanded graphite is modified by adding Jeaffamine (J230) to get better interface and being sonicate for well dispersion before mixing it with epoxy using mechanical stirrer at uniform speed and temperature which is 300rpm and 1200C respectively. The weight percentage of modified expanded graphite used in this study is 1%, 1.75% and 2.5%. This difference of weight percentage is used to see the effects of expanded graphite towards the mechanical properties and morphological structure.

The mechanical properties of nanocomposites are calculated using tensile test by producing dumbbell size specimen according to ASTM D-638 where the yield strength and maximum stress is being considered. Other than that, physical testing which is porosity density test is done to give the see the effects of porosity in a material towards the mechanical properties.

Furthermore, for adhesive strength, double cantilever beam test is done where the specimen is according to ASTM 3433-99. The results show the adhesive toughness, GIC where which mixture of weight percentage of expanded graphite will give the best result and compared it with pure epoxy itself.

The characterization of nanocomposites has been study using Fourier Transform Infrared Spectroscopy (FTIR). It is used to analyze the functional group of the sample composition. Other than that, Scanning Electron Microscope (SEM) is used to analyze the morphological structure of the composites. It shows the dispersion of expanded graphite and the microstructure. The dispersion of expanded graphite is best related to the sonication method and modifying process. Other problem occur is maybe due to the human error when conducting the experiment and also not compatible mixing for the epoxy, hardener, graphite and modifying agent.

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