

CHAPTER III

EXPERIMENTAL WORK

The following experimental work concentrates on how to improve the mechanical properties of epoxy resin especially the toughness. The concept is to make composite polymers by adding some types of rubber into the epoxy resin.

3.1 MATERIALS

3.1.1 Epoxy Resin

Epoxy resin used as a matrix in the present work is diglycidyl ether of bisphenol-A (DGEBA). It is manufactured by Shell Chemical Company Limited under the tradename of "EPIKOTE 828". Its viscosity is about 12-14 Pa.sec at 25 °C. At room temperature, DGEBA is viscous liquid with a density of 1.16 g/cc. The epoxy content is about 5,260-5,420 millimol/kg. The structure of DGEBA is shown in Figure 3.1.

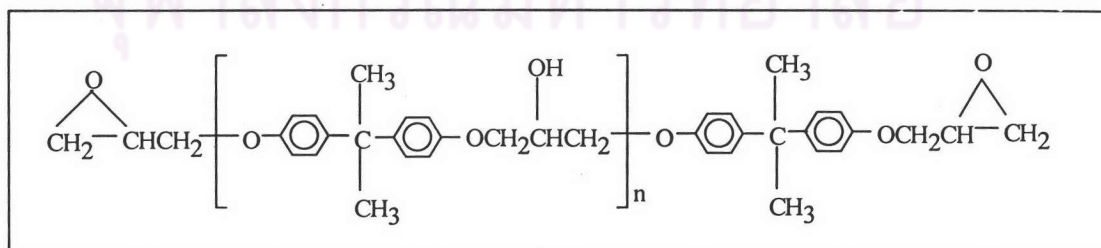


Figure 3.1: The structure of Diglycidyl ether of bisphenol-A (DGEBA).

The reasons of choosing DGEBA type of epoxy resin as the matrix are because they are most widely used in many industries and they can easily react with most of the curing agents.

3.1.2 Curing Agents

Diethylene triamine (DETA) from Shell Chemical Company Limited was used as the curing agent in the present work. DETA is an aliphatic amine type of curing agent. It has a long chain structure. As depicted in the structure of DETA in Figure 3.2, DETA has five amine groups in one single chain. Each amine group can easily react with the epoxide group in the epoxy resin.

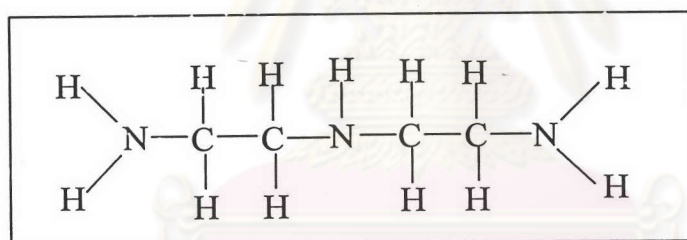


Figure 3.2: The structure of Diethylene triamine (DETA).

The DETA used as the curing agent in the present study has an amine content of 98%. It is a light, colorless liquid with a density of 0.95 g/cc. Its molecular weight is 103. One of the most significant property of DETA is that it can react with epoxy resin to form crosslinkages at room temperature. The reaction is exothermic; the heat generated during the crosslinking reaction may enhance the temperature of the epoxy system to about 100 °C. The rate of the reaction of DETA with epoxy resin depends on the temperature of cure too. a higher cure

temperature can increase the reaction rate and leads to a more brittle epoxy.

3.1.3 Additives

The additives used individually in this experiment are four types of synthetic rubber. The first two rubbers are solid rubber particles whose surface was treated and untreated with a coupling agent. The other two rubbers are of liquid stage. All four types of rubbers were applied separately with the aim to improve the toughness of the epoxy resin.

For particle rubber, the nitrile-butadiene rubber (NBR) under the tradename of “CHEMIGUM P83” was used. It was manufactured by Good Year Company Limited. The NBR is a copolymer of acrylonitrile and butadiene with the acrylonitrile content of 33%. The NBR used has a particle size range from 0.25-0.5 mm. It is light with a density of 1 g/cc. NBR is considered a non-reactive rubber. Its chemical structure is shown in Figure 3.3.

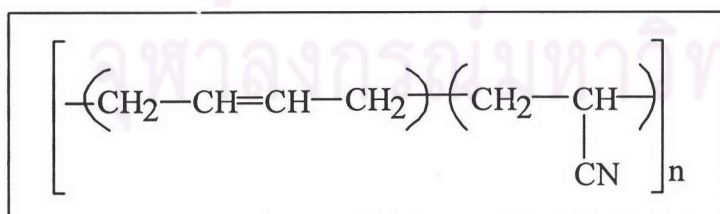


Figure 3.3: The structure of Acrylonitrile-co-butadiene rubber (NBR).

Another type of rubber used was a liquid rubber. It is also copolymerised from acrylonitrile and butadiene but both ends of the chain are terminated with carboxy groups. It is known as “ *carboxy terminated butadiene-co-acrylonitrile rubber* ” or CTBN. In this experiment, two types of CTBN’s are used namely the “PERBUNAN N LATEX 1590” which has an acrylonitrile content of 15% and the “PERBUNAN N LATEX VT” which has an acrylonitrile content of 30%. Both CTBN’s are supplied by Bayer Company Limited.

PERBUNAN N LATEX 1590 has an approximate viscosity of 13 milliPa.sec. Its density ranges from 0.98-1.00 g/cc. The acrylonitrile content is 15% and it is capable of self-crosslinking. PERBUNAN N LATEX VT has an approximate viscosity of 50 milliPa.sec. Its density range from 0.99-1.01 g/cc. The acrylonitrile content is 30%. Both types of liquid CTBN rubbers are reactive and they can react with the epoxide group in the epoxy resin. The structure of CTBN is shown in Figure 3.4.

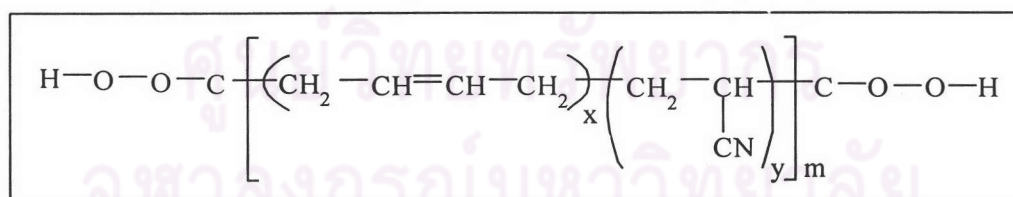


Figure 3.4: The structure of liquid CTBN rubber.

3.1.4 Coupling Agent

In this experiment, a titanate coupling agent under the tradename of "LICA38" was used. It was supplied from Kenrich Petrochemical Incorporation. LICA38 is green brown. It has a viscosity range of 1200-9000 cps at 25 °C. The density of LICA38 is 1.13 g/cc at 16 °C. Its initial boiling point tested according to ASTM-D86 is 71.1 °C or 160 °F. Its pH range is 3.0 ±0.5. LICA38 can be soluted in aromatic plasticizers such as DOP, DIDP, MEK and xylene. The structure of LICA38 is shown in Figure 3.5.

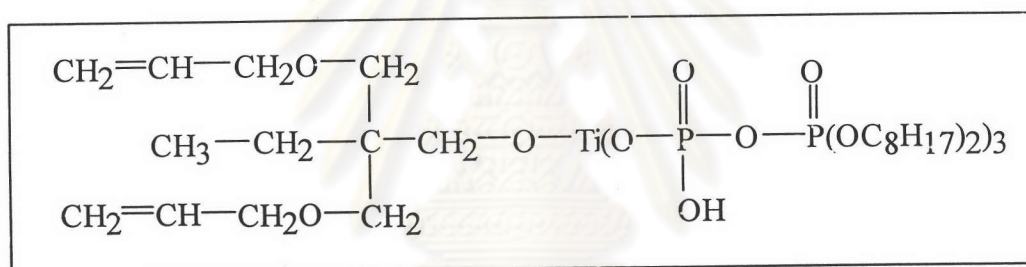


Figure 3.5: The structure of LICA38 titanate coupling agent.

3.2 NBR SURFACE TREATMENTS

About 0.5 % by weight of LICA38 was used as titanate coupling agent. The surface treatment of NBR was conducted by dissolving LICA38 in a small quantity of ethyl alcohol solvent. The compound was then poured into a mixing chamber where more solvent was added. NBR particles were added while continuously stirring the system for 1 hour. The slurry was later dried in an oven at 70 °C for

approximately 48 hours for complete elimination of the solvent. The product received was titanate-treated NBR which was more yellow in colour than the untreated NBR.

3.3 CURING PROCEDURE

3.3.1. Curing of Pure Epoxy Resin

To curing epoxy resin, a stoichiometric amount of the epoxy resin and the diethylene triamine was used. This was calculated to be about 100 part by weight of the epoxy resin to 10.9 part by weight of the DETA. Both the epoxy resin and the DETA were mixed by mechanically stirring thoroughly for about 10-15 minutes. Then they were transferred into an opened mould that has already been coated with a silicone mould releasing agent. The compound was left to cure at room temperature for about 2 hours. Curing was conducted by heating the system at 40 °C for 30 days. Post cure was finally carried out in an oven at 120 °C for 2 hours. Then, the system was slow cooled to room temperature to minimize the residual stress. The rate of cooling must not exceed 10 °C/min. Figure 3.6 shows the crosslinking network of epoxy resin cured with diethylene triamine.

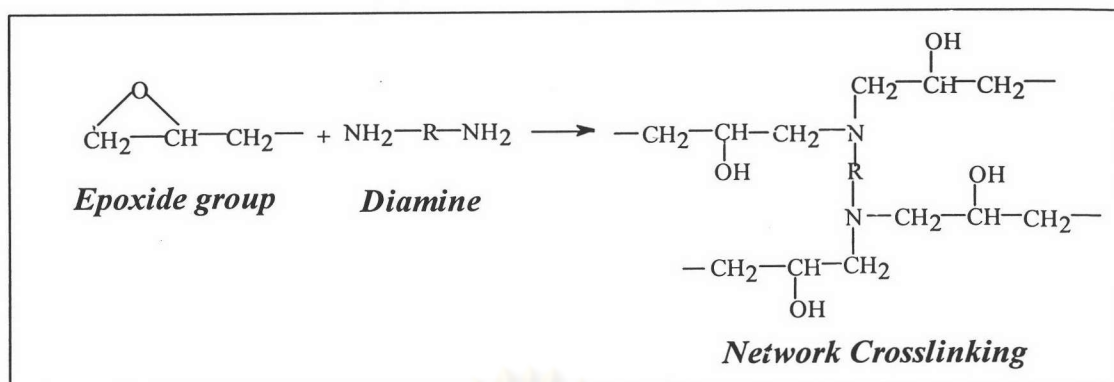


Figure 3.6: Network crosslinking of epoxy resin and amine curing agent.

3.3.2 Curing Epoxy-Rubber Composites

For rubber-modified epoxy composites, the epoxy resin and the DETA were prepared at a stoichiometric ratio of 100 to 10.9 parts by weight respectively. NBR was weighted to 5.14 g and it is used as the modified additive for the epoxy resin. The aforementioned amount of NBR is equivalent to the 5% by volume of NBR in the epoxy composite. The system was stirred thoroughly to ensure good dispersion of the NBR in the epoxy resin. The prepared DETA was then added. Stirring is conducted for another 10 to 15 minutes. The liquid composite was then transferred into an opened mould that has already been coated with a silicone mould releasing agent. The system was left to cure at room temperature for 2 hours. Then it was left to cure in an oven at 40 °C for 30 days. Finally, the system was post cured for 2 hours at 120 °C. Then, it was slow cooled to room temperature. Other composite systems with greater amount of NBR were prepared. The amount of NBR in each system was increased to 10, 15, 20, 25 and 30 % by volume respectively.

The additives used were NBR, treated NBR, and two types of CTBN. They could be done by the same procedure as adding the NBR in the epoxy resin. However, the CTBN which have acrylonitrile content of 15% can be filled in the epoxy resin to only 25 vol% and the CTBN which have acrylonitrile content of 30% can be filled in the epoxy resin to only 10 vol%. This is because the viscosity of the epoxy resin when filled more than the aforementioned amount of CTBN is so high that it does not flow.

3.4. MECHANICAL TESTING

3.4.1. Compression Test

The compression test of polymers is not as widely used as the tensile or the flexural tests although it is a fast test that yields several useful information. Quite often during their service life, plastic products are subjected to compressive load for a long period of time. Their deformation is hence induced or caused by the compressive stress.

Test specimens in a square shape of 12 x12 mm with a thickness of 4 mm were individually compressed between two parallel plates. The compression testing was conducted by using a mechanical testing machine (LLOYD model 200R). The crosshead speed was set constant at 1.3 mm/min. The test was conducted at a standard condition of 23 °C. Ten specimens were tested for each composition. Only average values were reported. Figure 3.7 shows schematically the compression tool and the test specimen.

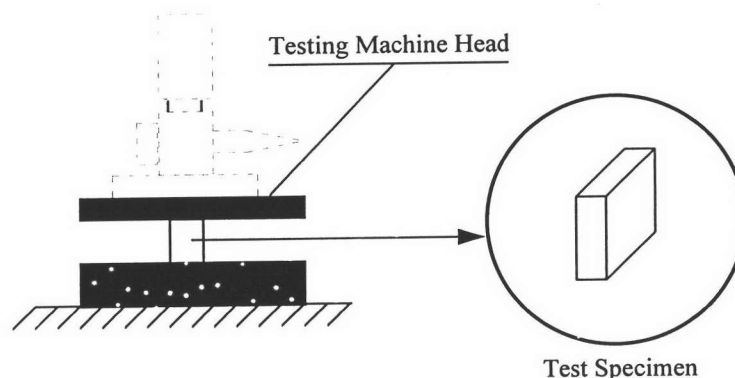


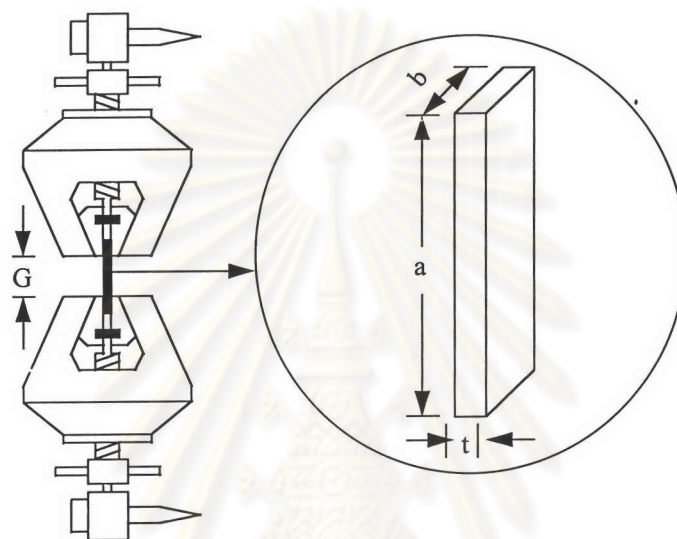
Figure 3.7: The compression tool and the test specimen.

3.4.2 Tensile Test

A tensile test was conducted to determine the tensile properties of pure epoxy and the rubber modified ones. The test conditions such as the pre-treatment, temperature of test, humidity and testing machine speed are identical for all specimens.

ASTM D638-91 is used as a reference for the tensile test. Tensile properties may vary depending upon the specimen preparation, the crosshead speed and the environment of testing. The specimen shape and dimension is conformed to that specified in the ASTM D638-91 as shown in Figure 3.8. The gauge length is fixed at 50 mm. All surfaces of the specimen is free of visible flaws, scratches, or imperfections. Any marks left by coarse machining operations must be carefully removed with a fine file or an abrasive; and the filed surfaces shall then be smoothed with an abrasive paper number 00 or finer. The finishing sanding strokes must be made in a direction parallel to the long axis of the test specimen. The test specimen was held in such a way that slippage relative to the grips was prevented insofar as possible. The

specimens were conditioned at 23 ± 2 °C and 50 ± 5 % relative humidity for not less than 40 hours prior to the test and between the test, too. Testing machine speed is kept constant at 1 mm/min. Eight specimens were tested and only the means of these results were used to analyse and compare with other specimen formulations.



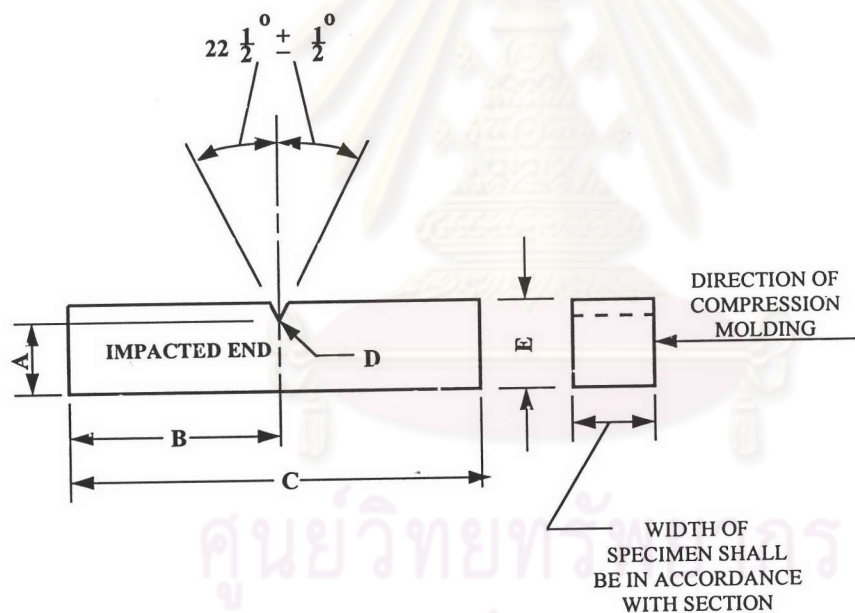
($a = 80$ mm, $b = 12$ mm, $t = 3$ mm, $G = 50$ mm)

Figure 3.8: Schematic representation of the tensile test and the specimen dimension.

3.4.3. Izod Impact Test

The Izod impact test was applied to measure the energy to break a notched specimen upon application of a sudden load by using a pendulum. The notch was made by using a revolving multitooth cutter disc. Both the feed speed and the cutter speed were constant throughout the notching operation. In general, a combination of a high cutter speed and a slow feed rate will result in greater thermal damage than a slow

cutter speed and a fast feed rate. Using a high feed rate or a high cutter speed ratio can induce crack in the specimen. Impact specimens were notched (45°) by using a Toyoseiki notch cutting apparatus. The shape and dimensions of the test specimen are shown in Figure 3.9. The notched specimens were tested according to the ASTM D-256 procedure by using the Izod Toyoseiki Tokyo tester. The Izod tester, the notched specimen and the specimen support are shown in Figure 3.10 . The test was carried out at a standard testing condition of $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity. Eight specimens were tested for each composition. Only average values were reported.



	mm	in.
A	10.16 ± 0.05	0.400 ± 0.002
B	32.00 max 31.50 min	1.260 max 1.240 min
C	63.50 max 60.30 min	2.500 max 2.375 min
D	$0.25R \pm 0.05$	$0.010R \pm 0.002$
E	12.70 ± 0.15	0.500 ± 0.006

Figure 3.9: The dimensions of an Izod impact test specimen.

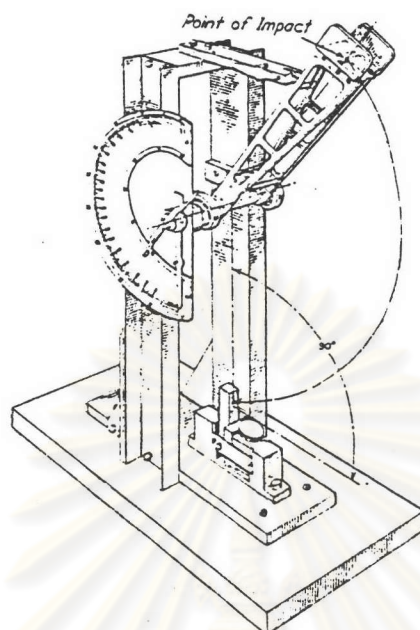


Figure 3.10: Cantilever beam (Izod-Type) impact machine.

3.4.4 Falling Weight Test

The falling weight test enables the impact resistance to be measured. This is indicated by the energy to break or crack the epoxy systems at a high and variable weight. Compression molded plate with 2 mm in thickness was tested according to the procedure set in the ASTM D-3029. The test was done by using an Energy Absorption tester (model D-4092). The falling weight machine is shown schematically in Figure 3.11. The test was performed at room temperature of 25 °C. The energy absorbed versus the sample deformation and the dart velocity were obtained for each sample. Three specimens were tested for each composition. Only average values were reported.

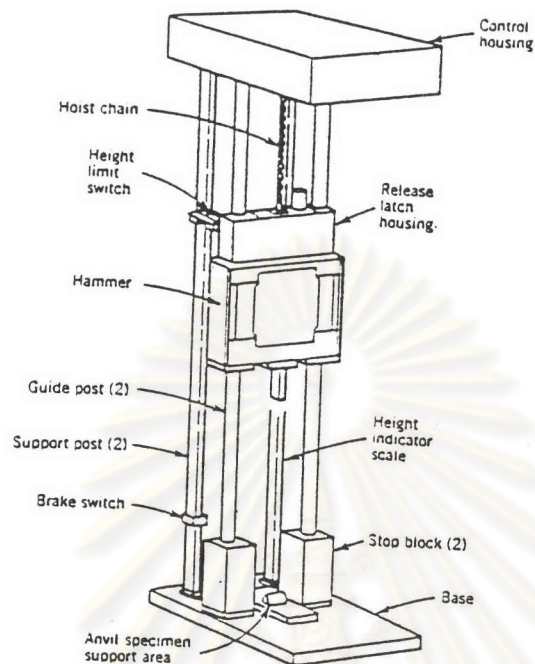
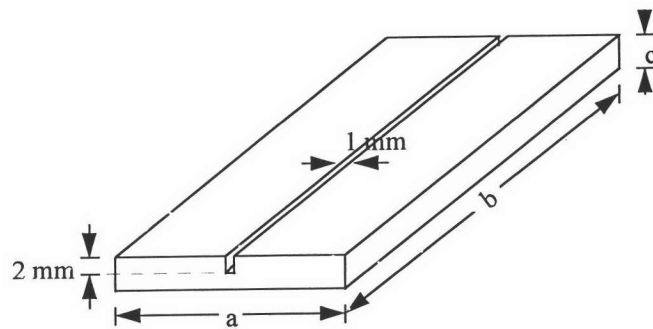


Figure 3.11: The falling weight testing machine.

3.4.5 Double Torsion Test

Double torsion test is performed to find the energy required to break the specimen under Mode I. The sample is cut to a rectangular piece with the dimensions as shown in Figure 3.12. The specimen is 110 mm in length, 52 mm in width and 4 mm in thickness. The specimen is eroded to a ditch which looks like a U-shape with 1 mm in width and 2 mm in depth.



$$(a = 52 \text{ mm}, b = 110 \text{ mm}, c = 4 \text{ mm})$$

Figure 3.12: The shape and dimension of the double torsion specimen.

Test was made by placing the test specimen on a double torsion fixture. The design of which is shown schematically in Figure 3.13. A fixture was made from stainless steel. The fixture and the specimen were placed on the LLOYD testing machine. Compression mode is used with a crosshead rate of 0.05 mm/min. All test specimens were conditioned at 23 ± 2 °C and 50 ± 5 % relative humidity for not less than 40 hours prior to the double torsion test. All specimens were tested and the analysis will be performed in Chapter IV.

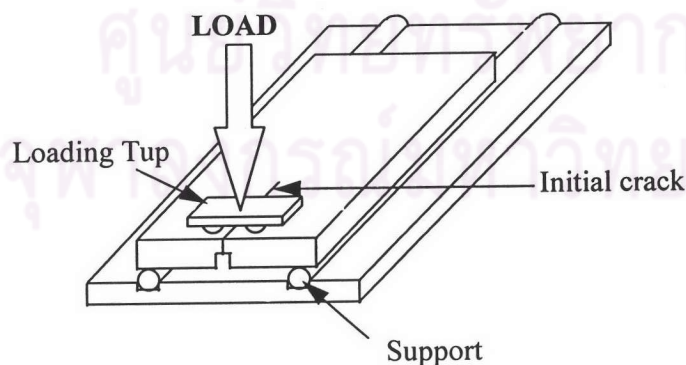


Figure 3.13: Double torsion fixture arrangement and specimen.

3.5 SAMPLE CHARACTERIZATION

3.5.1 Density Test

The density of a solid is a conveniently measurable property. Frequently it is a useful property related to some physical changes in a sample. In this study the density of the sample is determined by using density gradient technique. ASTM D1505-85 is applied in the density measurement. It covers the determination of density of solid particles. The test specimen was allowed to sink in a liquid column exhibiting a density gradient.

The test specimens were cut to any convenient shape for easy identification but it should have the dimensions that permit the most accurate position measurement of the center of volume when the specimen was suspended in the liquid. The specimen must be free of any foreign matter and voids. It should have no cavities or surface characteristics that will cause entrapment of bubbles. Moreover, care should be taken in cutting specimens to avoid changes in density resulting from compressive stress. The density of liquid layers in the gradient column increases from top to bottom. The level which the sample sinks in the column shows its density.

Density-gradient column can be made by filling the solution of two liquids into a tall cylinder immersed in a controlled water bath. The temperature of the water bath is kept constant at 23 ± 0.1 °C. The

liquid system chosen must have a range of density cover the density of the test specimens. Table 3.1 shows the liquid systems for density-gradient columns.

System	Density Range, g/cm ³
Methanol-benzyl alcohol	0.80 to 0.92
Isopropanol-water	0.79 to 1.00
Isopropanol-diethylene glycol	0.79 to 1.11
Ethanol-carbon tetrachloride	0.79 to 1.59
Toluene-carbon tetrachloride	0.87 to 1.59
Water-sodium bromide	1.00 to 1.41
Water-calcium nitrate	1.00 to 1.60
Carbon tetrachloride-trimethylene dibromide	1.60 to 1.99
Trimethylene dibromide-ethylene bromide	1.99 to 2.18
Ethylene bromide-bromoform	2.18 to 2.89

Table 3.1: The liquid systems for density-gradient columns.

In this experimental work, toluene-carbon tetrachloride (CCl₄) system was chosen because its density range appropriately covered the density range of pure epoxy and the rubber modified epoxy composites. Toluene and carbon tetrachloride were mixed at eleven different ratios as shown in Table 3.2. Each amount of the liquid at the predetermined ratio was poured into the column as shown in Figure 3.14. The column was left untouched to settle for 24 hours. The density gradient column is achieved when the liquid system had settled.

Level	Carbon tetrachloride (cc)	Toluene (cc)	Total amount (cc)
1 (bottom)	40	0	40
2	36	4	40
3	32	8	40
4	28	12	40
5	24	16	40
6	20	20	40
7	16	24	40
8	12	28	40
9	8	32	40
10	4	36	40
11 (top)	0	40	40

Table 3.2: The eleven ratios of the toluene- CCl_4 system for density gradient column.

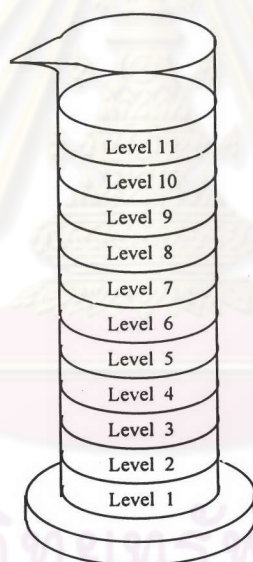


Figure 3.14: The column shows each level of the liquid-liquid solution system.

3.5.2. Differential Scanning Calorimeter (DSC)

The glass transition point of the pure epoxy resin was tested according to ASTM D-2117. The equipment used was a Differential Scanning Calorimeter model 2110 TA Instrument tester.

The DSC heater and the sample cells are shown schematically in Figure 3.15. Each composition of the pure epoxy resin and the rubber-modified ones was weighed to as close to 10 mg as possible. It was then placed in the DSC aluminium pan. The sample was heated from 50 °C to 200 °C at a heating rate of 10 °C/ min. A DSC scan of the specific energy against the temperature was obtained. It also showed the glass transition temperature of the rubber-modified epoxy composites.

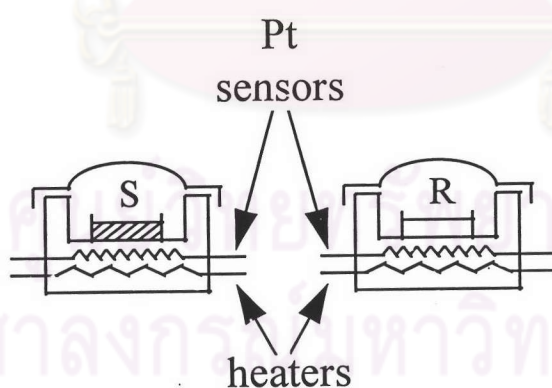


Figure 3.15: The DSC sample cell consists of a sample pan (S) and a reference pan (R).

3.5.3. Dynamic Mechanical Thermal Analysis (DMTA)

The technique of DMTA was used to determine the glass transition temperature (T_g) of epoxy resin and the rubber-modified ones via their state of chain motion. In this method, the sample was deformed cyclically under a sinusoidal stress amplitude which was usually applied as a function of a sine wave while the temperature was raised. The results indicated the sinusoidal stress-strain relationship. Many modes of vibration are possible. The specimen can be loaded under tension, torsion, compression, bending and shear. But the most popular mode of loading is the bending mode, e.g. the single or double cantilever as shown in Figure 3.16. The usual range of frequencies for DMTA test are 0.1 to 110 Hz. In the present study, a frequency of 1 Hz is selected.

The T_g of each HDPE formulation was measured by using a dynamic mechanical thermal analyser (model DMTA *Mk III* ; Polymer Laboratory). The single cantilever mode was used. Specimens were prepared by cutting rectangular bars of 5 mm in width, 25 mm in length and 1.5 mm in thickness. The test was conducted at a frequency of 1 Hz. The heating rate was 3 °C/min. The specimen was tested over a broad temperature span from -100 °C to 200 °C. The T_g of the epoxy was seen at the peak of $\tan \delta$.

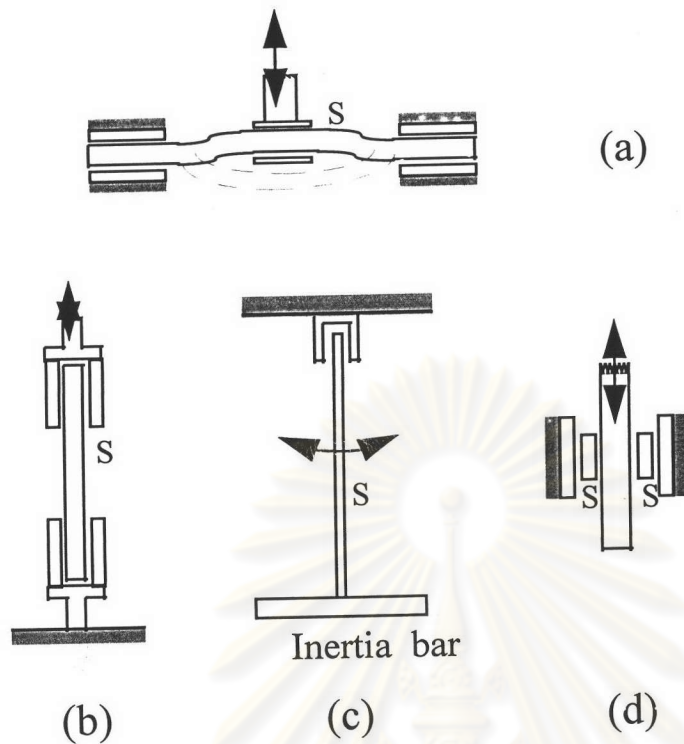


Figure 3.16: Available modes of loading in the Dynamic Mechanical Thermal Analyser (DMTA):

- (a) single or double cantilever
- (b) tension or compression mode
- (c) torsion mode and
- (d) shear mode.

3.5.4 Scanning Electron Microscope (SEM)

In scanning electron microscopy, electron can be reflected from the surface of an object which are often used for display. The incident electrons from the electron source acted as a beam, which is then scanned over the entire area of fracture surfaces. The morphology of the

fractured epoxy and the rubber-modified epoxy composites was studied by using a scanning electron microscope (JOEL JSM 840A). The fracture surfaces were sputtered with 300 Å in thickness of gold. The accelerating voltage for the SEM was 10 kV.



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