CERTIFICATION OF APPROVAL

Thermal Characterization of Carbonaceous Pitches from Residue of PETRONAS Refinery

by

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A project dissertation submitted to the
Mechanical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(MECHANICAL ENGINEERING)

Approved by,

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UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January 2008

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

Residue often not treated well and being disposed as waste. It is formed from heavier fractions of crude oil that fail to vaporize. The main objective of the project is to study the thermal characterization of carbonaceous mesophase pitches from the residue of PETRONAS refinery. From the result the mesophase forming ability and graphitizability can be established and recommendations can be made on how to make use of the residue pertaining to fabrication of carbon and graphite materials. Properties of pitch materials derived from the residue of distillation of hydrocarbons might vary depending upon the source of the crude oil. Mesophase pitch which has a high graphitizability is highly favoured due to its value as a precursor to expensive or exotic carbonaceous or graphite materials. So far studies on the petroleum residue from PETRONAS refineries were not well reported. Since it might have a high economic values, the petroleum residue of PETRONAS refineries need to be studied in its ability to be used as precursor to carbonaceous materials. Throughout the project, several experiments have been conducted to achieve the objectives. The experiments performed were XRD, DSC, SEM, optical microscopy, FTIR and TGA. In the end of the project, all the outcome results are positive and indicate the sample which is residue that obtained from PETRONAS refinery is mesophase.

ACKNOWLEDGEMENT

First and foremost I would like to express my gratitude to all those who gave me the possibility to complete this thesis. I want to thank the Department of Mechanical Engineering of Universiti Teknologi PETRONAS for giving me the opportunity to commence this thesis in the first instance, to do the necessary research work and to use facilities provided. I am deeply indebted to my supervisor AP Dr. Bambang Ariwahjoedi for continuous help, inspiring suggestions and support in all the time of research for and writing of this thesis. The technicians, examiners and lecturers especially Mr. Anuar and Mr. Faisal for their assistance and time to ensure my experiments can be conducted smoothly.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

The project title is thermal characterization of carbonaceous mesophase pitches from residue of Petronas refinery. Typical oil refinery is a process plant where crude oil is processed and refined. From the processes products such as diesel fuel, gasoline, kerosene and asphalt base are produced. Refinery processes can be split into 3 categories which are separation, conversion and purification processes. During separation process, crude oil is heated and fed into a high tower or fractioning column which contains a number of floors and trays. The tower or column is cooler at the top than at the bottom. The light parts of crude oil will be first to be evaporated and then rise to the top. Since top is the coolest part of the tower, they become liquid again and trapped. Those parts with higher boiling points form liquid on the halfway up of the trays where the temperature is higher. Those with the highest boiling points become liquid on the lowest trays where the temperature is highest of all. The all the liquid is then piped off from the tower or column. This process is called distillation. During the process, residue can not be avoided. Residue is heavier fractions of crude oil that fail to vaporize. Residue often not treated well and considered as waste. For the project, residue samples will be analyzed and it's potential to be used as precursor to carbonaceous material will be studied.

1.2 Problem Statement

Properties of pitch materials derived from the residue of distillation of hydrocarbons might vary depending upon the source of the crude oil. Mesophase pitch which has a high graphitizability is highly favoured due to its value as a precursor to expensive / exotic carbonaceous / graphite materials. So far studies on the petroleum residue from Petronas refineries were not well reported. Since it might have a high economic values, the petroleum residue of Petronas refineries need to be studied in its ability to be used as precursor to carbonaceous materials.

1.3 Objectives and Scope of Study

This Final Year Project course plays a very important role in achieving UTP's vision which is to produce a well rounded graduate. The course also gives very great opportunity for students to relate the theoretical knowledge from class, exploring new knowledge and applying it in the project. Despite that, students will develop skills in work ethics, communication, management and interpersonal skills. The objectives of this Final Year Project are:

1. To characterize the thermal behaviour of pitches resulted from Petronas refinery.
2. To establish the pitches mesophase forming ability and graphitizability.
3. Make some recommendations to fabrication of carbon and graphite materials from the pitches after its thermal behaviour are understood.

The project concern is to study on the thermal characterization of carbonaceous mesophase pitches that obtain from residue samples of Petronas refinery.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Residue and Mesophase Pitch

Residue from the refinery can be used to produce high quality of mesophase pitch. Carbon fiber is one of the high technology products that can be made by mesophase pitch. The conventional method to produce mesophase pitch involves the removal of low molecular weight species from petroleum residue. It is also can be transformed into a mesophase pitch through polymerization process. Petroleum pitch contains complex aromatic molecules with an average molecular weight of 200 to 800. The other hand, mesophase pitch has molecular weight range of 1200 – 1300.

2.1.1 Nature of Mesophase Pitch

Mesophase pitch has potential to become inexpensive material for producing high performance carbon fiber economically. Petroleum pitches contain high molecular weight carbonaceous materials and are residues from crude oil distillation. The complex molecules are classified into four groups which are saturates, naphthene aromatics, polar aromatics and asphaltenes. Saturates made of low molecular weight aliphatic compounds. While naphthene aromatics are low molecular weight aromatics. Polar aromatics consist of higher molecular weights and have more heterocyclic rings. The highest average molecular weight among the groups is asphaltenes.

2.1.2 Mesophase as the Precursor to Graphitizable Carbon

Most of the organic materials carbonize in which they thermally decompose in an inert atmosphere to provide volatile compounds and black carbonaceous residues. They are known variously as chars, charcoals, soots, carbon, semi-cokes or cokes. Carbonization systems occur in two processes either by pass through a fluid phase as with petroleum and coal-tar pitch and some coals or remains entirely in the solid phase as with cellulose and coconut shell. Carbons that formed in latter process are regularly non-graphitizing because on heating to 3300 K they do not develop to any significance degree, an extensive, crystalline, three-dimensional, graphite lattice. However, carbons formed in the former process with few exceptions such as from sugar, are graphitizing because on heating to 3300K, they develop extensive crystalline structure and are essentially graphitic.

The non-graphitizing carbons are described as hard carbons, isotropic in bulk properties and possess appreciable surface area and pore volume within a microporous network. The graphitizing carbons are described as soft carbons, anisotropic in properties and possess low surface areas and little porosity. There exist important differences between the structures of these two classes of carbons which will explain these major differences in properties. All soft graphitizing carbons are not identical but exhibit significant differences in the extent of development of their graphitic properties which for example in the size and relative orientations of the crystal (lite) components. These differences are intimately associated with the chemical properties of the parent material being carbonized and are dependent on the conditions of carbonization.

In the studies of both classes of the carbon, the optical microscope has played a major role. Optical microscopy, using polarized light and preferably a phase sensitive plate can distinguish these two classes of carbon. The anisotropic structures rotate the plane of the polarized light and exhibit extinction contours, bands, nodes etc. with “tinted polarized light” which obtained by using a gypsum phase-sensitive plate, the anisotropic carbon exhibits from its polished surface, yellow, blue and red areas which interchange colour on rotation of the specimen. Each colour represents a section of a volume element of a given crystal orientation. If the similarly orientated areas are small of small diameter (< $5\,\mu\text{m}$) and appear with a sensitive-tint as a multi coloured mosaic which they are termed "mosaics". For larger areas (5 to $100\,\mu\text{m}$) are termed as "domains" and appear as large isochromatic areas. The isotropic carbons exhibit a purple colour at all orientations of the specimen. It is the shape, size and structure of these anisotropic areas which essentially control the properties of the heat-treated carbons. These shapes, sizes and structure are themselves functions of the chemical and physical properties of the carbonization system.

2.2 Liquid Crystals

The anisotropic properties exhibited by carbons that graphitize imply that the lamellar structure of graphite is already established in low temperature carbons (800 K), albeit in a highly imperfect form. To understand the imperfection, lamellar structure form from an isotropic, fluid phase of carbonization (pyrolysate), it is necessary to first consider the properties of (nematic) liquid crystals. Brooks and Taylor of CSIRO, Australia who examined anisotropic development of cokes in coal seams metamorphosed by igneous intrusions, suggested an explanation of the growth of anisotropy in terms of liquid crystals.

Liquid crystal systems have been accepted since 1888. The term was originally used to describe system obtained by melting such substances as cholesteryl benzoate which had unusual fluid properties and which were anisotropic when viewed in thin sections between the crossed-polarizers of an optical microscope. Such systems possessed more structural order than found in normal (isotropic) liquids but were not genuinely crystalline. For the purpose of nomenclature, Friedel suggested that the term "mesophase" (intermediate state) would obviate the apparent inconsistency of a "crystalline liquid". However, mesophase is rather too imprecise a term itself. On the other hand, its use as a description of an intermediate phase in carbon formation is now established and this current usage will be discussed below.

From several categories into which liquid crystal may be placed, it is the nematic (thread-like) rather than the smectic (soap-like) or cholesteric system which has relevance to carbonanization. We can determine the nematic liquid crystal from others in the way it separates from the isotropic liquid as spherical droplets which eventually coalesce to give a nematic domain. The resulting droplets are anisotropic. The materials form domains of preferred orientation of molecules in the optical microscope. The domains are being illustrated by boundaries which appear as black lines (threads) in the filed of view of the microscope. Change of direction of molecule alignment and such structural discontinuities can be demonstrated by the reticular net of extinction contours which termed "disinclinations" are considerable relevance to discussions of carbon formation.

The arrangement of molecules, for example 6-methoxy-2-naphtoic acid, in the nematic liquid crystal is usually envisaged as one in which the molecules lie parallel to one another but with no order in the stacking sequence. Containing surfaces exert a considerable influence with constituent molecules near to the surface or interface lying parallel to the surface as in Figure 1. Molecules which form nematic liquid crystals usually possess elongated or rectilinear. Flat segments such as benzene rings enhance liquid crystallinity thus the molecules are rigid along the long axis and the existence of strong dipoles and easily polarizable groups are important.

2.3 Mesophase

The nematic liquid crystal could be formed from the liquid phase of certain carbonization system was suggested by Brooks and Taylor. The immediate implication is that the stacking sequences of molecules in such liquid crystals correspond to the parallel imperfect stacking of molecules or lamellae in pregraphitic carbons. Therefore, the nematic liquid crystal formed during carbonization processes termed as mesophase. It was Taylor who made the relevant initial observations in the Wongawilli coal seam of New South Wales. An igneous dyke, a tongue of molten magma had penetrated the coal seam and established a positive thermal gradient through the coal seam towards the dyke. The effect over some hundreds of meters was to establish a very gradual thermal gradient reaching maximum temperatures which passed through and exceeded the temperatures of formation of anisotropic coke from coal. It was the slow rates of heating and the identification of a very narrow temperature zone of formation of anisotropic carbon which provided the first clues of the dependence of anisotropic carbon formation upon a liquid crystal type precursor. Previous laboratory experiments had all used too rapid a heating rate and the detail for the formation of the anisotropic carbon was missed.

Taylor observed that on approaching the dyke, small spheres which initially micrometer sizes were observed in the vitrinite. Figure 2 shows similar sphere growing in laboratory carbonized acenaphthylene. The spheres in polished section exhibited rather unusual optical properties which were consistent with anisotropic stacking of the constituent lamellae parallel to an equatorial plane. An alternative possibility of circumferential stacking as in onion was discounted. These spheres when under more heating grew at the expense of the vitrinite and coalesced to form the mosaic structures. Taylor recognized that this anisotropic sphere was providing the clue to the formation of graphitizing carbons. The molecular arrangement within the sphere can be deduced from optical properties and confirmed electron diffraction. From the result it closely resembled the mechanism of formation of graphitizable carbons (via the mesophase) came to be associated with properties of liquid crystals.

2.4 Relationship between Liquid Crystals and Mesophase

Brooks and Taylor originally suggested of the possibility of close similarity in growth processes and properties between the mesophase and nematic liquid crystals. At present it is generally accepted that *the mesophase is a plastic, anisotropic phase which grows from the fluid pyrolysate and solidifies to give the anisotropic coke*. The plastic properties of the mesophase such as

- Its high degree of anisotropy.

- The effect of magnetic fields which can align the constituent molecules of mesophase.
- The orientation of molecules parallel to contained or confining surface.
- Eutectic effects

All the characteristics above fit in well with the known properties of liquid crystals.

However, there exists evidence that indicate this intermediate phase between the isotropic pyrolysate (e.g. plastic coal or coal-tar pitch) and anisotropic coke is *NOT* nematic liquid crystals. For example, for almost all systems the mesophase is formed irreversibly. It is relatively insoluble in benzene and in pyridine. Activation energies of formation between 140 to 180 KJ mol^{-1} correspond to chemical rather than to physical processes. Observation showed increment in molecular weight, C/H ratios and indicated the chemical nature of the processes leading to mesophase formation. The spacing between constituent lamellae of the mesophase is known to decrease with time at constant temperature which also being indicative of continuing chemical processes occurring within the mesophase after its formation.

Similarities with nematic liquid crystals mainly concern the ordering or stacking process of mesophase growth while the dissimilarities properties are indicative of chemical processes of mesophase formation and change within the mesophase. There is argument that although mesophase has structural similarities to nematic liquid crystals, its formation and maturation is a chemical process. Thus, it is suggested as definitions of the two terms, that mesophase is a transient, nematic liquid crystals phase in which only Van der Waals and dipole interactions orientate the molecules. Therefore, a ‘model process’ can be described as follow.

During the carbonization process of a parent substance (e.g. coal, coal-tar pitch, petroleum pitch etc.), the various pyrolytic reactions of the carbonization result in an increase in the average molecular weight of the fluid, carbonization system. This is illustrated in the carbonization of anthracene in a closed system which leads to the formation of dianthryl and trianthryl which further co-condense to produce large, planar molecules containing nice to about thirty hexagonal rings, with increasing carbonization temperature, increasing fluidity of the system increases the diffusivity of the constituent molecules leading to an enhance probability of molecule-molecule interactions. An anisotropic structure subsequently develops suggests that surface-to-surface interactions come first, with the edge-to-edge coming later. This surface-to-surface interaction could resemble a physical adsorption process. The larger is the adsorbed molecule the higher is the molar enthalpy of adsorption. Associated with these higher enthalpies of adsorption are the longer residence times or duration of stay of the adsorbed molecule on the adsorbent surface. In the carbonizations systems, this physical interaction results in the formation of the nematic liquid crystal from the planar (aromatic) molecules. If such attractive forces can withstand the disruptive force of molecular collisions then a relatively stable, stacked, molecular structure can be exist within the pyrolysate. Additional molecules can be adsorbed, increasing the thickness and length of what is now an ‘embryonic’ nematic liquid crystal. At this stage, the liquid crystal may be reversibly dissociated. But, if the duration of its existence is sufficiently long, perhaps milliseconds as distinct from nanoseconds (the duration of molecular collisions), then chemical bonding may occur between the constituent molecules of the ‘embryonic’ liquid crystal which now loses its ability to dissociate reversibly into its constituent molecules. The nematic liquid crystal then becomes a polymeric, anisotropic stable phase with a structure base upon that of the transitory liquid crystal. This polymeric phase is the *mesophase* which with few exceptions is detected and studied in the optical microscope.

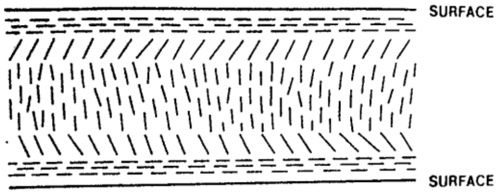


Figure 2.1: Diagram of molecular arrangements within Nematic Liquid Crystals

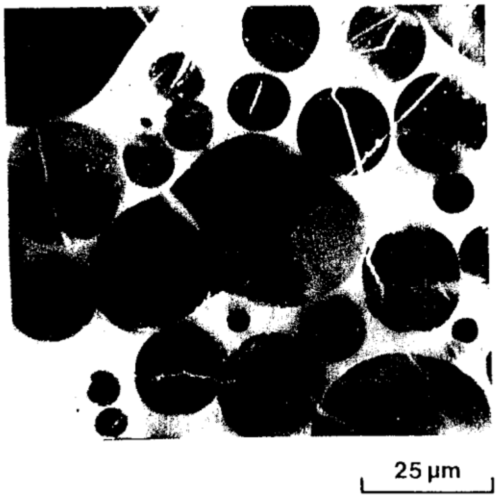


Figure 2.2: Optical micrograph showing mesophase growth and coalescence from acenaphthylene

2.5 Carbon Fiber

Carbon fiber is a polymer which is a form of graphite. Graphite is a form of pure carbon. In graphite, carbon atoms are arranged into big sheets of hexagonal aromatic rings.

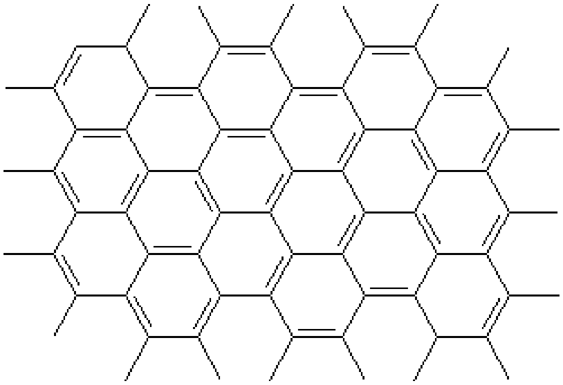


Figure 2.3: A section of a sheet of graphite

Carbon fiber is a form of graphite in which these sheets are long and thin. They can be illustrated as ribbons of graphite. Bunches of the ribbons pack together to form fibers, therefore the name is carbon fibers.

Graphite is fairly soft and flaky (easily break), whereas carbon fiber is strong and requires larger forces to fracture. They are both brittle, chemically inert hence unreactive. The major difference between the graphite and carbon fibers can be observed from their structure, not at atomic scale but at how the individual strands/ sheets are arranged. In graphite, large layers of the structure above lay one on top of the other with weak interactions between the layers. On the other hand, carbon fiber still lays one on top of the other but is less ordered.

Carbon fibers aren't used by themselves. Instead, they are used to reinforce materials like epoxy resins and other thermosetting materials. These reinforced materials are called composites because they have more than one component. Carbon fiber reinforced composites are very strong for equivalent weight with other materials. They are stronger than steel but a whole lot lighter. That is why they can be used to replace metals, from parts for airplanes, space shuttle, tennis racquet, golf clubs etc.

Other desirable physical properties of carbon fibers include its resistance to corrosion, fire and high stress tolerance level as well as its chemical inertness.

To give an idea of some of the properties of carbon fibers, a table below shows comparison between carbon fibers and steel.

Table 2.1: Comparison between carbon fiber and steel

	TENSILE STRENGH (GPa)	DENSITY (g/ccm)	TENSILE MODULUS (GPa)
CARBON FIBER	3.50	1.75	230.0
STEEL	1.30	7.90	210.0

Source: http://www.chm.bris.ac.uk/webprojects2002/mjames/chemistry.html

From the table above, carbon fiber has a tensile strength almost 3 times greater than steel yet 4.5 times less dense.

There are many different grades of carbon fibers available which have different properties and can be used for specific applications. Table 2 below shows details on some of the properties of various grades of carbon fibers.

Table 2.2: Details on some of the properties of various grades of carbon fibers

	TENSILE STRENGTH (GPa)	TENSILE MODULUS (GPa)
HIGH TENACITY	4.00	240
ULTRA HIGH TENACITY	4.80	240
INTERMEDIATE	6.00	290
HIGH MODULUS	3.50	375
ULTRA HIGH MODULUS	3.40	425

Source: http://www.chm.bris.ac.uk/webprojects2002/mjames/chemistry.html

2.5.1 Production of Carbon Fiber

Carbon fiber can be either **PITCH** or **PAN** based. **PITCH** based fibers do not have as great strength, lightness or mechanical properties as PAN based fibers. The raw material for **PAN** based fibers is polyacrylonitrile which is commonly prepared using Sohio process. In the early manufacturing processes acetylene and hydrogen cyanide (HCN) were used as raw material. HCN is incredibly toxic to humans but only yield 60%-65% of production. Thus, the Sohio process was invented by the Standard Oil Company, Ohio supported by concern for energy conservation, lessening environmental loading and improvement in technology. The process involves an amonoxidation (single stage) reaction between propylene and ammonia.

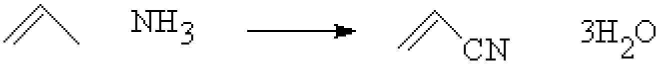


Figure 2.4: Sohio process

The Sohio process improved from the earlier process in several aspects , namely it dramatically increased yield, produced less waste gases and water, generally more economically and environmentally efficient. Polymerization of the product gives polyacrylonitrile which is a long chain polymer.

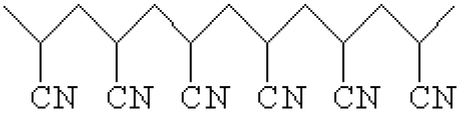


Figure 2.5: Oxidation of polyacrylonitrile

Once this type of polymer has been produced, the manufacture of carbon fiber can be produced. The first step of the process is to stretch the polymer so that it is parallel to what will eventually become the axis of the fiber. Once this has been done, the polymer is then oxidised at 200^{o}C-300 ^{o}C in air. This process removes hydrogen and adds oxygen to the molecule and forms the basis of the hexagonal structure as shown above.

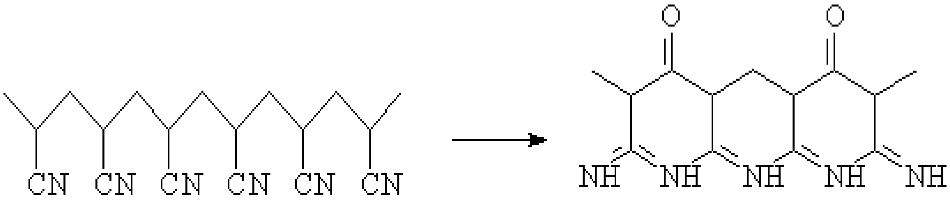


Figure 2.6: Carbonization process

During this process, there is a colour change from white chain polymer to the ring black ring polymer. The polymer produced has very high melting point and now has to be purified. A process called Carbonisation for the purpose that involves heating the polymer in a nitrogen rich environment which expels impurities in the chain as volatile by products. The impurities removed until the polymer contains 92%-100% carbon depending on the quality required for the fiber. Temperature ranging from 1000^{o}C - 2500^{o}C is used during the process depending on the desired properties needed in the fiber.

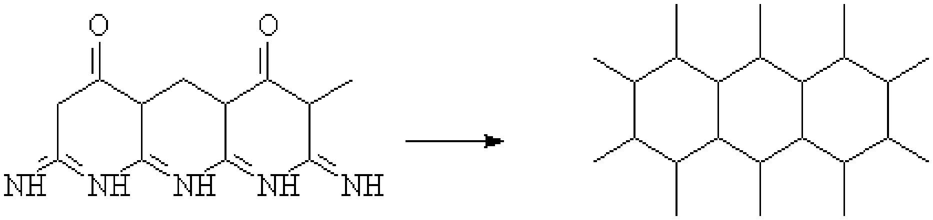


Figure 2.7: Final stage of carbon fiber after carbonization process

Each of the fibers produced is about the fifth of the width of a human hair. The final stage in the production of carbon fibers involves weaving the fibers into sheets or tubes and then embedding them in an epoxy resin. There are several different patterns of weave, including plain, satin, twill or basket weave that gives the fiber customizable properties. The final stage of embedding in a resin is known as sizing and forms the final composite that ready for further processing to form a variety of products.

2.5.2 Carbon Fibers from Mesophase Pitch

Carbon fibers derived from mesophase pitch have high modulus, moderate strength type but different from the other types of precursors as they are significantly higher in density and are graphitizable and develop three dimensional crystalline orders at high temperature. Recent advancement in technology has led to the elimination of structural flaws in both yarns and components filaments thus resulting in improvement levels of strength for the fibers which possess a Young modulus of 380 GPa. Strand strength of 2.4 GPa have been achieved and researches continue to achieve higher level.

Carbon fibers from mesophase pitch are capable of reaching a high Young modulus with economical processing techniques and therefore are suitable for all modulus-critical applications. They also may possess the capability of achieving extremely high tensile strengths.

2.5.3 Process to Form Carbon Fibers from Pitch

Below indicates the process to prepare carbon fibers from a mesophase pitch precursor:

Commercial pitch → polymerize to mesophase → melt spin → thermoset → carbonize (1500-13000 ^{o}C)

Petroleum or coal tar pitch is thermally treated to temperature above 350^{o}C to convert it to a mesophase pitch that contains both isotropic and anisotropic (liquid crystal phase) material. The mesophase pitch is melt spun through a multiple-hole spinneret to produce green yarn. Then, the yarn is made infusible by oxidation at temperature below its softening point to avoid fusing filaments together. After that, it is carbonized to temperature around 2000^{o}C.

2.6 Application of Carbon Fiber

Carbon fibers are used primarily in reinforced composites. These are structures containing two or more components. In the case of reinforced composites it contains the fiber and a resin. A composite contains two types of fiber which are carbon and glass that known as a hybrid composite structure. The origins of textile reinforced composites are linked to the development of glass fibers, which commenced in 1938 by the Owens Corning Fiberglass Corporation (USA). Original large scale applications included air filtration, thermal and electrical insulation and the reinforcement of plastics. As the technology of textile reinforced composites expanded, a growing demand from the aerospace industry for composite materials with superior properties emerged. In particular, materials with higher specific strength, higher specific modulus and low density were required. Other desirable properties are good fatigue resistance, and dimensional stability. Carbon fibers were developed to meet this demand. Below are some of the applications of carbon fibers.

2.6.1 Airplane

Figure 2.8 shows Boeing 787 which is the most advance passenger aircraft ever. It is quieter, environmentally and passenger friendly, longer travel distance and more fuel efficient.

(Source: www.boeing.com)

Figure 2.8: Boeing 787 that made from carbon fiber technologies.

2.6.2 Tennis Racquet

Figure 2.9 show the tennis which is another sport where the same technology is being used to create light, strong rackets. The basic racket is constantly being tweaked by manufacturers in the search for maneuverability and power.

(Source:http://www.dkimages.com/discover/Home/Sports-Games-Recreation/Ball-Games/Tennis/Equipment/Equipment-12.html)

Figure 2.9: Application of carbon fiber in tennis racquet manufacturing

2.7 Equipments for Testing

There are 6 main equipments that been used to test the samples. Their functions are briefly explained as below.

2.7.1 X-Ray Diffraction (XRD)

X- ray diffraction is a useful technique for qualitative analysis and for the determination of major and minor phases. In X-ray diffraction analysis, X-rays are used to determine crystalline compound in a given sample. The analysis is based on that X-ray will be diffracted by crystal planed and minerals can be identified by measuring this diffraction at different angles. The diffraction pattern of unknown material is compared with that of the reference database in order to identify its chemical compound. Each crystalline compound has its unique characteristic X-ray pattern which may be used as a fingerprint for its identification.

Figure 2.10: Example of x-ray diffraction instrument

2.7.2 Scanning Electron Microscopy (SEM)

The scanning electron microscope is a type of electron microscope capable of producing high-resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample.

Figure 2.11: Example of scanning electron microscopy

2.7.3 Differential Scanning Calorimetry (DSC)

Differential scanning Calorimetry is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, heat will need to flow to it than the reference to maintain both at the same temperature.

Figure 2.12: Example of differential scanning calorimetry instrument

2.7.4 Optical Microscopy

The optical microscope is a type of microscope which uses visible light and a system of lenses to magnify images of small samples

Figure 2.13: Example of optical microscope

2.7.5 Fourier Transformed Infrared Spectroscopy (FTIR)

Fourier transformed infrared spectroscopy is a measurement technique whereby spectra are collected based on measurements of the temporal coherence of a radiative source which use time-domain measurements of the electromagnetic radiation or the other type of radiation.

2.7.6 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can be used to tell the point at which weight loss is most apparent. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

Figure 2.14: Example of thermogravimetric analysis instrument

CHAPTER 3

METHODOLOGY/ PROJECT WORK

3.1 Research

Before starting the project, knowledge related mesophase pitch must be understood. The knowledge about it can be obtained from internet, UTP's Information Resource Center or consulting supervisor.

3.2 Samples Collections

To begin the project, samples of residue should first be obtained from Petronas refinery. Permission has to be obtained and arrangement of time schedule has to be made to collect the samples by following the proper procedures. The samples were obtained after arrangements made with the respective person who is Pn. Nurul Asni Bt. Mohamed from PETRONAS Penapisan (Melaka) Sdn. Bhd.

Figure 3.1: sample of residue obtained from PETRONAS Penapisan Melaka

3.3 Experiments and Data Collections

3.3.1 X-Ray Diffraction (XRD)

Before the experiment conducted, the samples were heated in an oven to ensure the conditions of the samples are dry as humidity present in the samples can alter the accuracy of the results. After about 2 hours in oven, the samples were taken out carefully and let it cooled down to room temperature. Then, the samples were grinded to fine powder with a grinder before the XRD experiment conducted. With the assistance of lab's technician, the experiment was conducted smoothly and successfully. The data observed was recorded.

Figure 3.2: The sample that grinded to fine powder

3.3.2 Scanning Electron Microscopy (SEM)

Same as the XRD, the sample must be in fine powder condition before SEM experiment can be conducted. Lab's technician prepared the sample and performed the experiment. The samples then observed with initial 3000 times, 5000 times and 8000 times magnifications. Some of the samples also coated with gold palladium to enhance the visibility of the samples. The data observed was recorded.

3.3.3 Differential Scanning Calorimetry (DSC)

The experiment conducted with Pyris 1 machine built by PerkinElmer. The sample was inserted in an aluminum capsule. Then the aluminum capsule that filled with the sample weighted carefully before put into the machine. The sample was heated with initial of 25^0C up to 300^0C with the temperature increment of 5^0C per minute in pure nitrogen condition. The data observed was recorded.

3.3.4 Optical Microscopy

For optical microscopy experiment the sample used was in the size of adult thumb which was different from using fine powder for the sample in DSC, XRD and SEM. The sample was polished by the Lab's technician until the desired surface finish was achieved before the experiment was performed. Then, the sample is pressed with plasticine to ensure the surface that will be observed by the optical microscope is flat. With the assistance of lab technician and supervisor, the experiment was performed smoothly. The sample was observed under the microscope with initial magnification of five times, 100 times and 200 times. Polarization light also applies to further show the structures of the sample's surface. The image observed then captured and recorded.

3.3.5 Fourier Transformed Infrared Spectroscopy (FTIR)

It is important to produce a good optical contact between the prism and material to obtain reliable result. The sample is carbon in black colour thus obtain a good optical contact becomes difficult as it has high porous structure and high light absorbing property. Therefore, potassium bromide (KBr) layer was introduced to enhance the optical contact between the sample and the prism. KBr was mixed carefully with the sample and stirred until the mixing of both was even and in fine powder. Then, the sample that has been mixed together was placed inside a disk shape container and pressed by hydraulic press until 8000 psi. The outcome product was a tablet form sample. Finally, the tablet form sample was put inside the FTIR device for analysis. During the process, preparations of the samples have to be repeated several times as FTIR device failed to analyze the samples due to its properties as stated above.

3.3.6 Thermogravimetric Analysis (TGA)

The experiment is to determine the relationship of weight change to temperature change. The sample was put under the TGA device in pure nitrogen atmosphere from 25^0C to 900^0C with increment of 5^0C per minute. The result recorded.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 X-Ray Diffraction (XRD)

Figure 4.1 shows the XRD spectrum that obtained from the sample. 002 peak shown from the Figure 4.1 is comparable with 002 graphite peak from Figure 4.2 which is approximately at 25 Degree. It is proved that the sample which is residue from PETRONAS refinery has high graphitizing characteristics and possible as precursor to carbonaceous material.

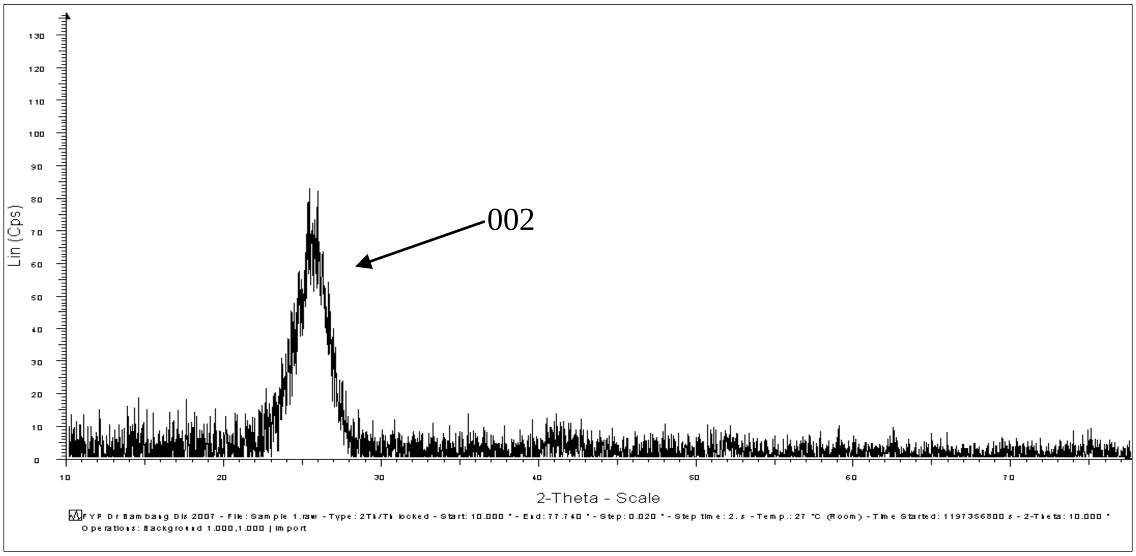
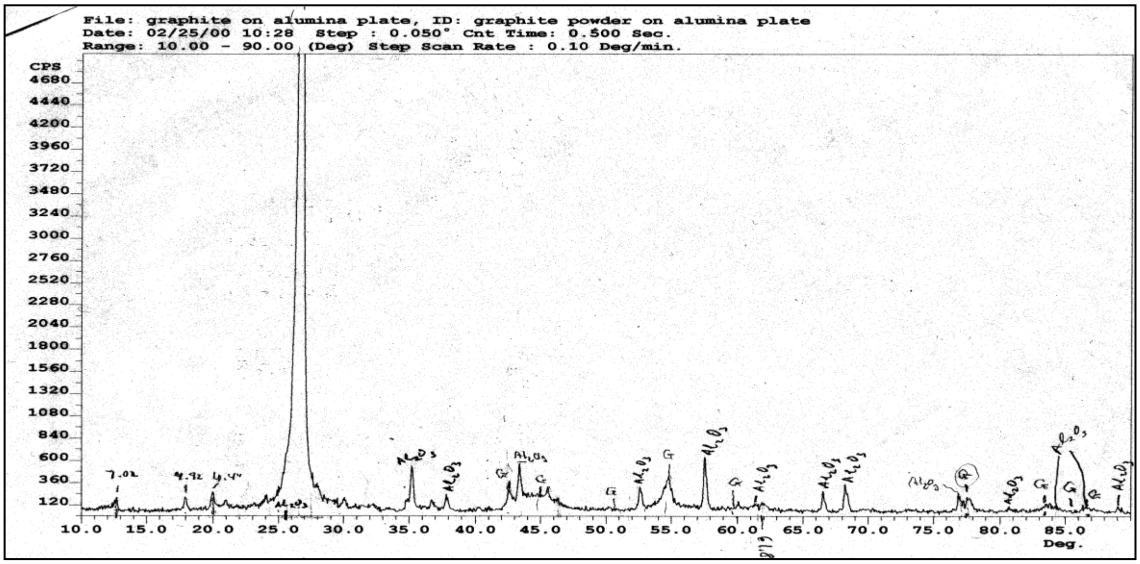


Figure 4.1: The profile of 002 peak from XRD spectrum of turbostratic sample



(Source: M. Balasubramanian, X. Sun, X. Q. Yang and J. McBreen. *In situ X-ray diffraction and X-ray absorption studies of high-rate lithium-ion batteries*)

Figure 4.2: Profile of 002 graphite peak from XRD spectrum of graphite

4.2 Scanning Electron Microscopy (SEM)

Figure 4.3 shows the image under the magnification of Scanning Electron Microscopy (SEM). For Figure 4.4, the image shows image of the sample that coated with gold palladium to further enhance the quality of the image. The sample is residue (coke) from Petronas refinery. From all the images shown, we can conclude that the morphology of the sample is in hexagonal form.

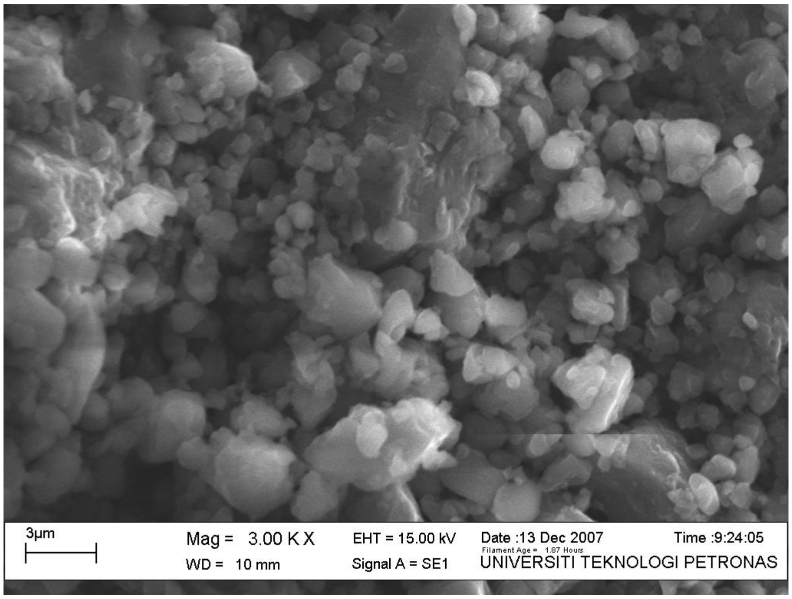


Figure 4.3: The image of the sample after magnification with SEM

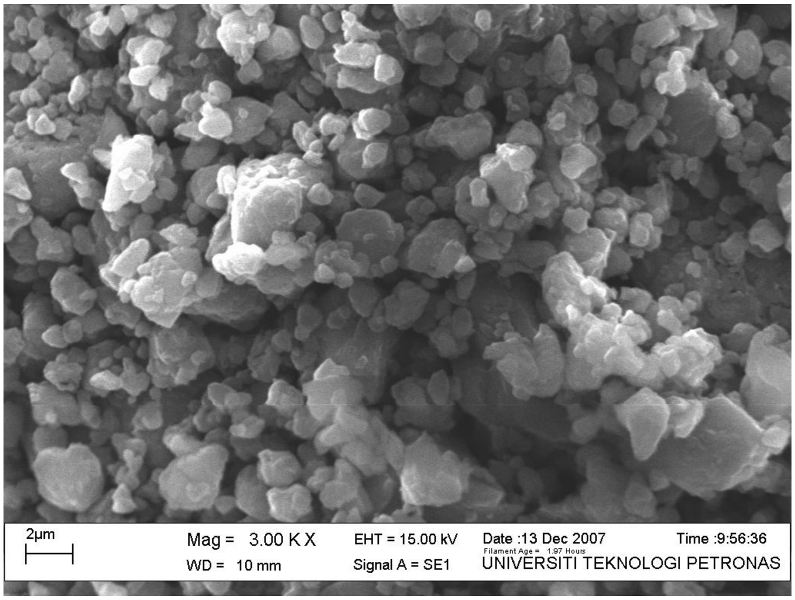


Figure 4.4: The image of the sample coated with gold palladium

4.3 Differential Scanning Calorimetry (DSC)

The figure 4.5 shows the relationship of Heat Flow versus Temperature when the sample was heated from 25^0C to 300^0C with the increment of 5^0C per minute in a pure nitrogen atmosphere. There is an indentation at approximately 120^0C as shown by red circle and line in the graph. That point determines the glass transition temperature for the sample and marks the difference of two properties in the sample. Between 25.8^0C to about 120^0C the sample is having glassy property where the sample is easily break if force is applied to it. Between about 120^0C to 300^0C the sample has opposite property by having rubber like property where the sample will act elastically and not easily break. Instead it expands as rubber band like. It is proved that when the sample is heated further, it shows characteristics of mesophase that has rubber like property.

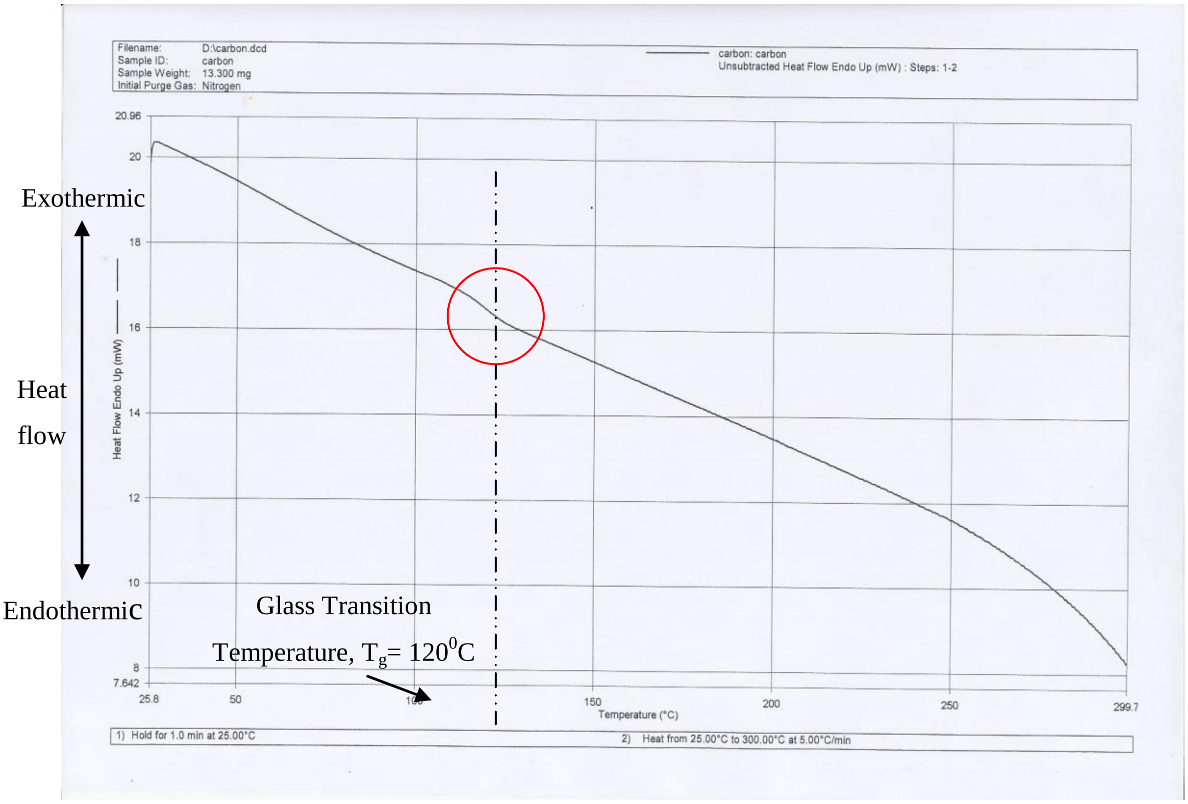


Figure 4.5: The graph of Heat Flow (mW) versus Temperature (^{0}C) in experiment of DSC

4.4 Optical Microscopy

Figure 4.6 and Figure 4.7 show the texture of the sample which is residue (coke) from PETRONAS Refinery.

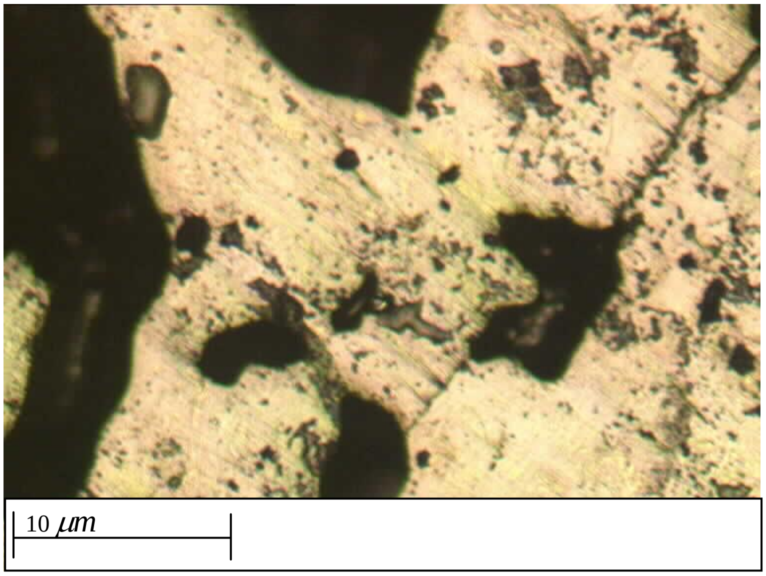


Figure 4.6: The image of sample under optical microscopy

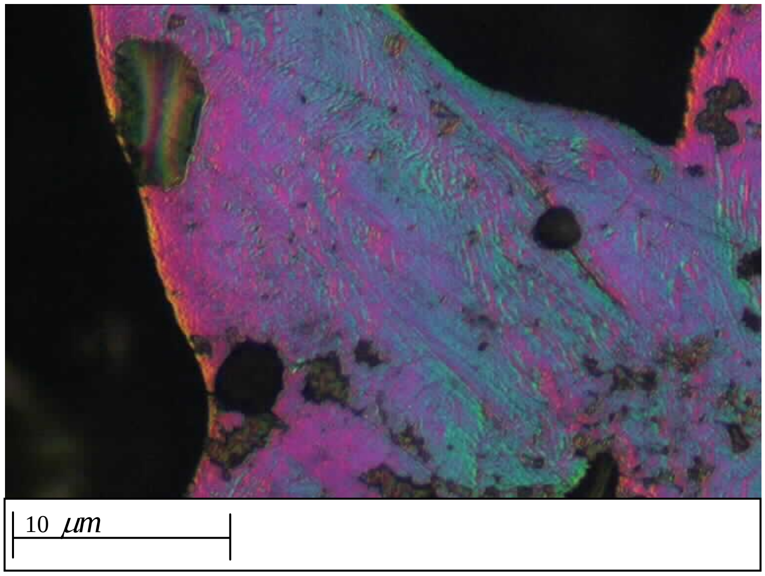


Figure 4.7: The image of sample under optical microscopy with polarized light

Former observed with normal light and latter with polarized light to enhance the visibility of the texture. From the latter image, it shows that the texture under the effect of polarized light exhibits colour contours around the observed areas with colours such as purple, blue and red. From this observation, it is proved that the sample has anisotropic structure which made it possible to be mesophase thus precursor of carbonaceous material.

4.5 Fourier Transformed Infrared Spectroscopy (FTIR)

Figure 4.8 shows the graph of the sample from Fourier Transformed Infrared Spectroscopy (FTIR) experiment.

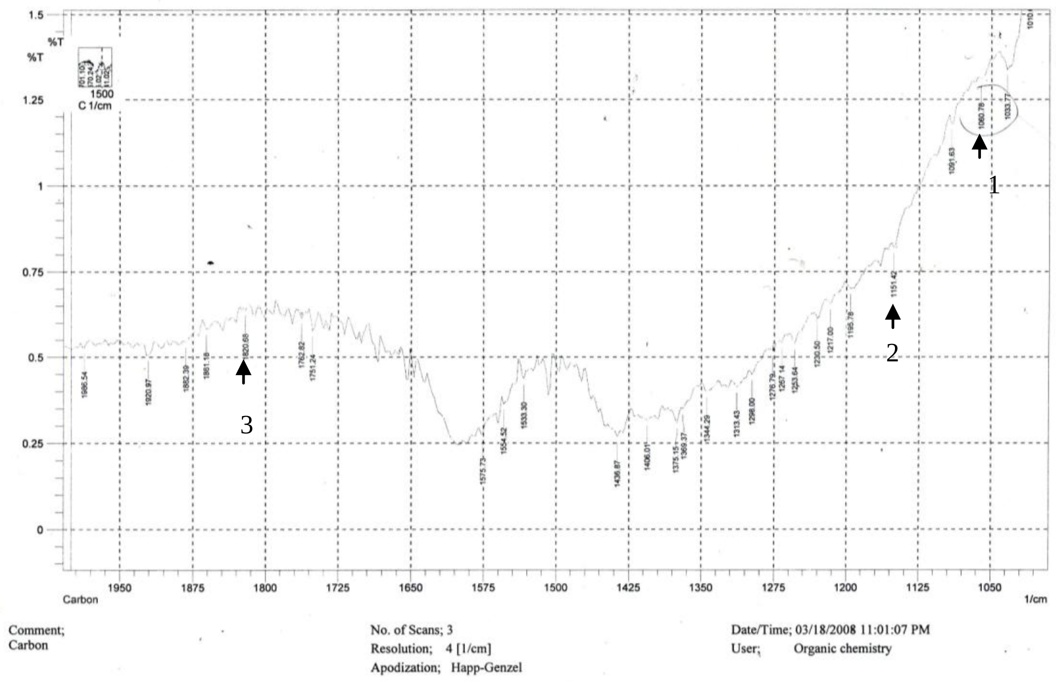


Figure 4.8: graph of the sample from FTIR experiment

From the graph, the functional groups of the sample can be determined by comparison with the table 4.1. By comparing between the two tables, the functional groups of the sample can be investigated as shown in table 4.2.

Table 4.1: Functional groups on active carbon and their corresponding infrared assignment

Wave number (cm^{-1})	Functional Group
1850-1786	Anhydrides
1740,1724	Lactones (C=O)
1264	Lactones(C-O-C)
1710-1680	Carboxylic(C=O)
1440	Carboxylic(O-H)
1670-1660	Quinone or conjugate ketone
1076-1014	Alcohol(C-O)
1162-1114	Phenol (C-O) and (O-H bend/stretching)
1250-1235	Either bridges between rings

(Source: S. Shin, J. Jang, S.H Yoon, Mochida. *A Study of The Effect of Heat Treatment on Functional Groups of Pitch Based Activated Carbon Fiber using FTIR*)

Table 4.2: Functional groups from the sample in comparison with table 4.1

Wave number (cm^{-1})	Functional Group	References
1033.77-1060.78	Alcohol(C-O)	1
1151.42	Phenol (C-O) and (O-H bend/stretching)	2
1820.68	Anhydrides	3

4.6 Thermogravimetric Analysis (TGA)

Figure 4.9 shows that the sample started to decompose at temperature of 420^{0}C. Isotropic pitch decomposes at the temperature range between 300^{0}C to 350^{0}C.

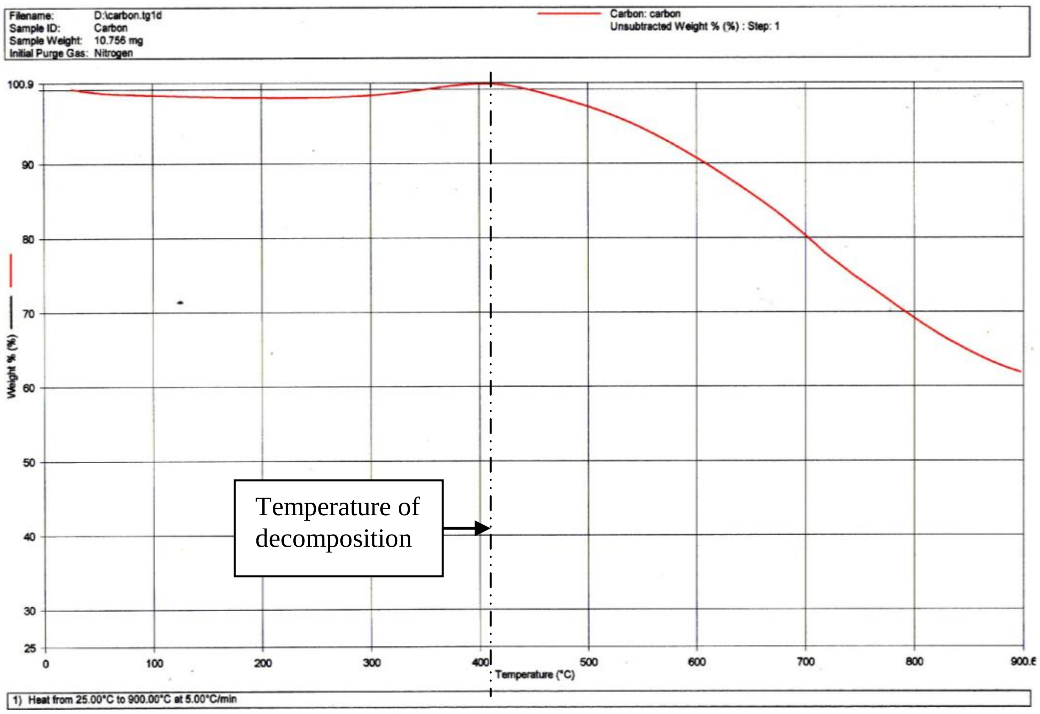


Figure 4.9: Graph of TGA obtained from the sample

In the other hand, anisotropic pitch decomposes at the temperature range between 400^{0}C to 450^{0}C. From the result it shows that the sample is anisotropic pitch thus has high possibility to be used as precursor to carbonaceous material.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

For the conclusion, the samples obtained from PETRONAS refinery which is residue (coke) proved to have possibility to be precursor to carbonaceous material such as graphite and carbon fibers. This is based from the experiments performed. Mesophase is generally accepted as material that has rubber property, anisotropic phase and towards graphite that can be precursor to carbonaceous materials. It is also known that the molecule structure of the mesophase can be in hexagonal form. From the experiment of XRD, It indicates the sample has profile of 002 graphite which proves it that has high graphitizing characteristics. From the experiment of SEM, the sample shows morphology of the sample is in hexagonal form which also proves the sample is mesophase. The next experiment performed which was DSC indicates the sample glass transition temperature is 120^0C and when heated further it shows similarity characteristic with mesophase that inhibit rubber like property in which it is not easily break when force is applied on it. Observation from the optical microscopy also indicates that the sample exhibits colour contours. Colour contours on the sample's surface provide hint that the sample has anisotropic structure which similar as mesophase. TGA experiments further strengthen that the sample obtained from Petronas refinery is mesophase. It shows that the sample started to decompose at temperature of 420^0C. Mesophase start to decompose at temperature between 400^0C to 500^0C. It shows that the sample has characteristic of mesophase. From the experiments performed, all the objectives are achieved. The thermal behaviour of pitches obtained from PETRONAS refinery are successfully characterized, the sample forming ability and graphitizability established indicates similarity with mesophase and it is positive that the residue I obtained from PETRONAS refinery is mesophase and suitable to be precursor to carbonaceous material such as carbon fiber which very valuable and return high profit.

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APPENDICES

PROGRESS SCHEDULE (FIRST SEMESTER)

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Selection of Project Topic	🟪	🟪													
2	Preliminary Research Work		🟪	🟪	🟪											
3	Submission of Preliminary Report				x											
4	Seminar 1 (optional)					🟪	🟪	🟪								
5	Project Work					🟪	🟪	🟪								
6	Submission of Progress Report									x						
7	Seminar 2 (compulsory)										🟪	🟪	🟪	🟪		
8	Project work continues									🟪	🟪	🟪	🟪	🟪		
9	Submission of Interim Report Final Draft														x	
10	Oral Presentation															x

x	Suggested milestone
🟪	Process

PROGRESS SCHEDULE (SECOND SEMESTER)

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Project Work Continue	🟪	🟪	🟪												
2	Submission of Progress Report 1				x											
3	Project Work Continue				🟪	🟪	🟪	🟪								
4	Submission of Progress Report 2									x						
5	Seminar (compulsory)										🟪	🟪	🟪			
5	Project work continue									🟪	🟪	🟪	🟪			
6	Poster Exhibition											x				
7	Submission of Dissertation (soft bound)													x		
8	Oral Presentation														x	
9	Submission of Project Dissertation (Hard															x

x Suggested milestone

🟪 Process